REMOVAL OF HEAVY METALS ON A CARBON SORBENT PREPARED FROM FLAX SHIVE

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ABSTRACT

Carbon is prepared from flax shive by treatment with sulphuric acid. The optimised conditions of preparation were based on metal sorption (Cd^{2+}, Hg^{2+}), carbon yield, and acid and energy consumption. The carbon product retains its fibrous woody texture and XRD indicates an amorphous structure which has a very low surface area determined by nitrogen adsorption. Elemental analysis of the sorbent shows a very low amount of sulphur (~1%), while FTIR shows the presence of carboxyl, carbonyl and hydroxyl (or phenolic) groups.

Cadmium shows fast kinetics of sorption for this material reaching equilibrium within 3 hours and having a sorption capacity similar to the cation exchange capacity (CEC) and base neutralisation capacity data. On the other hand mercury shows slow kinetics with 120 hours equilibrium time. Sorption capacity for mercury was high compared to that of cadmium or the cation exchange capacity. Base neutralisation capacity shows that the sorbent prepared at 200°C (C200) possesses more carboxylic and hydroxyl groups than that prepared at 160°C (C160) and agrees with the cation exchange capacity data and cadmium sorption.

A comprehensive study for cadmium on C200 sorbent found that sorption increases with pH and decreases with the presence of other metal ions in the aqueous solution. Mechanism of sorption investigated by the ratio of $[H^+]/[Cd^{2+}]$ on a molar basis gave a value ~ 2 indicating an ion exchange mechanism. Other metals such as Co^{2+}, Cr^{3+}, Cu^{2+}, Ni^{2+}, Pb^{2+} and Zn^{2+} were found to behave in a similar way to cadmium. These metals show fast kinetics with C200 reaching equilibrium within 3 hours. The ratio of metal sorbed on C160 to that on C200 is similar to that of cadmium and also to the ratio of CEC C160/CEC C200. Such results suggest that these metal ions are sorbed via an ion exchange mechanism onto sites such as carboxylic and hydroxyl groups. Sorption was found to fit the Langmuir equation with an insignificant increase with temperature. Column studies proved that C200 can be used several times to sorb Cd^{2+} from aqueous solution and using 0.5 mol/dm^3 sulphuric acid as a stripping solution.

On the other hand, mercury behaves differently showing, in addition to slow kinetics, a much higher uptake. This suggests that mercury sorption is not only an ion exchange mechanism. Such slow kinetics were found to follow a first order rate equation and the sorption data also fits the Langmuir equation. Wet samples showed a higher sorption than one that had been previously dried. Other metals such as Au (III), Cr (VI), Pd (II), Ag (I), Pt (II) and Pt (IV) were found to behave similarly to Hg (II) following the Langmuir equation with higher uptake with increasing temperature and also showing slow kinetics. The kinetics of uptake of these metals follows the first order rate equation and during the sorption process these metals were reduced. In addition, MnO_4^- was converted to MnO_2 and Mn^{2+}; Fe^{3+} to $Fe^{2+}$and Cr^{6+} reduced to Cr^{3+} which was then sorbed via an ion exchange process. Also, and depending on the initial pH, the kinetics of sorption of Cr^{6+} was found to follow a second order rate equation at pH 4.5, while starting at pH 1.5, chromium reduction follows a first order rate equation. Sorption of this group of metals depends on the pH of the aqueous solution. Hg^{2+} sorption shows maximum uptake in the pH range 6-7 while Cr^{6+} shows maximum sorption within pH range 2.2-2.6 depending on the sorbent state (wet, dry) and the concentration of Cr^{6+}. Reduction of Hg^{2+} to Hg_2Cl_2 and elemental mercury was confirmed with the observation of deposits on the carbon surface from SEM photographs. X-ray powder diffraction (XRD) showed that the crystals formed on the carbon surface are mercury (I) chloride. Some other metal species such as $AuCl_4^-$, $PdCl_2$, $AgNO_3$ and $PtCl_4^{2-}$showed reduction on the carbon surface to their elemental forms as observed on the SEM photographs and confirmed by XRD. Reduction of the metals was followed by the formation of new carbon-oxygen groups on the surface and also evolution of carbon dioxide. $PtCl_6^{2-}$ does not show any reduction on the carbon surface suggesting the possibility that the carbon reduction potential is perhaps very close to +0.7V.

This material seems to be an efficient alternative for activated carbon sorbents to remove and recover heavy metals from waters, with added advantages for those metals which can be reduced to the elemental form.

Nomenclature

b	dm^3g^{-1}	A constant related to the heat of adsorption (Langmuir equation).
Ce	$mg\ dm^{-3}$, $mmol\ dm^{-3}$	Equilibrium metal ion concentration.
C_o	$mg\ dm^{-3}$, $mmol\ dm^{-3}$	Initial metal ion concentration.
C_t	$mg\ dm^{-3}$, $mmol\ dm^{-3}$	Concentration of metal ions at anytime t.
E^o	volt	Standard reduction potential.
i	dimensionless	Valency of active sorbent ligand.
j	dimensionless	Valency of metal cations.
k_1	hr^{-1}	Rate constant of a first order reaction.
k_2	$dm^3\ mmol^{-1}hr^{-1}$	Rate constant of a second order reaction.
k_d	$mmolg^{-1}hour^{-0.5}$	Rate constant of pore diffusion.
k_f	$dm^3\ mmol^{-1}$	Stability constant (formation constant).
L	dimensionless	Ligand.
m	g	Mass of sorbent.
M	dimensionless	Metal.
R	dimensionless	Correlation coefficient.
R_s	dimensionless	Separation factor or equilibrium parameter.
S_{BET}	$m^2\ g^{-1}$	BET surface area of sorbents.
T	%	Transmittance.
V	$cm^3\ g^{-1}$	Volume of nitrogen adsorbed on the solid surface.
V_m	$cm^3\ g^{-1}$	Monolayer capacity of the solid.
X	$mg\ g^{-1}$, $mmol\ g^{-1}$	Metal ion concentration on sorbent.
X_m	$mg\ g^{-1}$, $mmol\ g^{-1}$	Metal ion concentration on sorbent at monolayer coverage.

C160 a carbon material prepared as follows: sulphuric acid (12 mol/dm^3) was added to flax shive in a weight: volume ratio of flax: acid of 1:9 for 25-30 minutes at 160°C.

C200 a carbon material prepared as follows: sulphuric acid (12 mol/dm^3) was added to flax shive in a weight: volume ratio of flax: acid of 1:9 for 25-30 minutes at 200°C.

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CHAPTER 1. INTRODUCTION

1.1. Aims of the Work

Flax shive is produced in the UK in huge quantities as a waste product through the processing of flax. Such material has little or no value and indeed causes a problem for disposal.

Aims of this research include:

1) production of an inexpensive sorbent material from flax shive by chemical treatment and optimising the process parameters for the preparation, and characterisation of some selected sorbents. Results, which cover this point, are presented in Chapter 4;

2) the application of selected sorbents for the removal of heavy metals from aqueous solution; application for different metal ions in different oxidation states. The mechanism of the sorption process is investigated and related to different models. Results including column studies and discussions are reported in Chapters 5 and 6.

1.2. Heavy Metals in the Environment

1.2.1 Introduction

During the past few years, there has been an increasing interest in the determination of concentrations, sources and fluxes of heavy metals in the environment (1-3). There is a widespread concern with the effects of technological advances on the chemical composition of the total environment including streams, lakes, oceans, atmosphere and soil systems.

"Heavy metals" is a general collective term which refers to the group of metals with an atomic density greater than 6 g/cm^3 (4). Since they belong to the group of elements which collectively do not exceed 1% of the total element content in the earth's crust, they are geochemically described as "trace elements"(5).

The primary production of some heavy metals in 1930 and 1985 is shown in table 1.1 which indicates that the mine production of all the metals has increased over this 55 year period (6). The point that needs to be emphasised is that these metals will finally enter the environment as wastes on a cumulative basis.

Metal	Production in	
	1930	1985
Cd	1.3	19
Cr	560	9940
Cu	1611	8114
Hg	3.8	6.8
Ni	22	778
Pb	1696	3077
Zn	1394	6042

Table 1.1. Primary production of metals (1000 metric tonnes yr.$^{-1}$) (6)

Some heavy metals (8) are essential to living organisms and deficiencies can lead to disease or even death of the plant or animal. These include Co (for bacteria and animals), Cr, Mn and Zn (animals and plants), Ni and Mo (plants), Se and Cr (animals). Although these elements are essential to life, at certain concentration above these levels they can become toxic. Other heavy metals including Cd, Pb, As, Ag and Hg have no known essential function and like the essential metals cause toxicity above the tolerance level.

1.2.2. Geochemical origin of heavy metals

The earth's crust consists mainly of soil and rocks (2). The latter can be subdivided into two main groups, igneous and sedimentary. In igneous rocks (4,5) the heavy metals occur as trace constituents in primary minerals which are those originally crystallised from the molten magma. At the time of crystallisation, the heavy metals isomorphously substituted various major elements that comprise the primary elements in the minerals.

Sedimentary rocks are formed of secondary minerals, such as clays and sandstones formed as a result of weathering of the primary minerals in igneous rocks. The secondary minerals provide the sites for concentration of the heavy metals because of their ability to adsorb metal ions (4). In general, clays and shales tend to have high concentrations of many metals whereas sandstones have low concentrations of most elements because they mainly consist of quartz grains which have low ability to adsorb heavy metals (5). The final product of weathering are soils and here, heavy metals are found as a result of weathering of the parent material (rocks) and from external contaminating sources (2).

Typical ranges of values for heavy metal concentrations in the earth's crust and various major rock types are given in table 1.2, and table 1.3 indicates the concentrations of some heavy metals in the atmosphere in various locations and ranges in fresh and sea water.

In areas near volcanoes, such as Etna and Hawaii, the concentrations of heavy metals in the atmosphere are high because the lavas contain high concentrations of these metals (4). The concentrations of heavy metals in an area remote from human activities like the South Pole are low whereas the concentrations ranges in Europe are high. This reflects the anthropogenic effects as a main source of the heavy metal pollution in the environment. In fresh water and sea water, different ranges of concentrations of heavy metals are found and this probably reflects the different sources of contamination.

1.2.3. Sources of heavy metals in the environment

1.2.3.1. Natural sources (2)

i) Atmosphere: The natural sources of heavy metals into the atmosphere are desert wind blown particulates, sea spray and point sources like volcanoes and forest fires.

Metal	Earth's crust	Igneous rocks			Sedimentary rocks		
		Ultramafic	Mafic	Granitic	Limestone	Sandstone	Clays / Shales
Cr	100	2980	200	4	11	35	39
Cu	50	42	90	13	5.5	30	39
Hg	0.005	0.004	0.01	0.08	0.16	0.29	0.18
Ni	80	2000	150	0.5	7	9	68
Pb	14	14	3	24	5.7	10	23
Zn	75	58	100	52	20	30	120

Table 1.2. Typical concentrations (mg/kg) of some heavy metals in the earth's crust and major types of igneous and sedimentary rocks (4).

Metal	Atmosphere ($\mu g/dm^3$)			Hydrosphere ($\mu g/dm^3$)	
	near volcano	Europe	South pole	Fresh water	Sea water
Cd	8-92	0.5-620	<0.015	0.01-3	0.01-9.4
Cr	45-67	1-140	0.005	0.1-6	0.2-50
Cu	200-3000	8-4900	0.036	0.2-30	0.05-12
Hg	18-250	<0.009-2.8	—	0.0001-2.8	0.01-0.22
Ni	330	4-120	—	0.02-27	0.13-43
Pb	28-1200	55-340	0.63	0.06-120	0.03-13
Zn	10000	13000-16000	0.03	0.2-100	0.2-48

Table 1.3. Metals in the atmosphere and hydrosphere (7).

ii) Hydrosphere: Here are two main natural sources of heavy metals; the atmosphere and water run-off. Atmospheric sources as noted above are dust, volcanic emissions, and sea spray and combustion emissions which enter the hydrosphere as a result of scrubbing the air by rain. The material that enters by water run-off comes from the weathering of geological materials which ultimately gets into the rivers, lakes and oceans.

ii) Soils: Weathering of the geological materials is considered as the main natural source of heavy metals in the soils. Variation in the heavy metal content of soil is related to the small particle sizes and the possibility that chemical reactions, e.g. oxidation / reduction, and solubilisation / precipitation can occur depending on soil type. Thus metals can be retained in the soil depending on their basic chemistry and nature of the soil.

1.2.3.2. Anthropogenic sources

As a result of the industrial revolution, heavy metal pollution has increased because of heavy metal additives in many technological products. Typical important anthropogenic sources are:

1.2.3.2.1. *Metalliferous mining* (4,5)

Ores are naturally occurring concentrations of minerals with a high proportion of metals. With increasing demand for metals, ore bodies with lower concentrations are being mined requiring a high proportion of rock to be mined per tonne of metal extracted and as a result much greater quantities of waste are produced. Modern techniques of metal extraction are efficient and so the tailings produced from such ores have small concentrations of metals. However ore separation techniques were not always so efficient and for historic mine bodies and their tailings, high concentrations of metals are found. The tailing particles can be transported by either wind or water thus constituting a significant source of contamination in soils and rivers. Accidental flooding resulting from the failure of dams in tailings lagoons has been responsible for many severe pollution events in several countries. Table 1.4 gives some of the most common ore minerals of non-ferrous metals.

Mining activities (4) provide a wide range of opportunities for pollution of the air by fumes, fine tailings and ore dusts; waters through aqueous effluents and tailings; soils with waste tips, deposited dust and fumes.

Metal	Ore minerals	Associated heavy metals
Ag	Ag_2S, PbS	Au, Cu, Sb, Zn, Pb, Se, Te
Ba	$BaSO_4$	Pb, Zn
Pb	PbS	Ag, Zn, Cu, Cd, Sb, Tl, Se, Te
Zn	ZnS	Cd, Cu, Pb, As, Se, Sb, Ag, Au, In

Table 1.4. Some ore minerals of non-ferrous metals (4).

1.2.3.2.2. *Agricultural materials*

Agriculture is considered as a very important non-point source of metal contaminants into the environment. The main sources with associated pollutants are (4,5):

- impurities in fertilisers: Cd, Cr, Mo, Zn and V;
- manure from animal production, especially pigs and poultry: Cu, As and Zn;
- pesticides: Cu, Hg, As, Pb, Mn and Zn;
- sewage sludge: especially Cd, Ni, Cu, Pb and Zn (and many other elements);
- wood preservatives: As, Cu and Cr;
- desiccants: As;
- corrosion of metal objects: (e.g. galvanised metal roofs and wire fences: Zn, Cd).

All of these will affect mainly the soil but can also contaminate the air with dust, fungicide droplets and water with fungicide spillages and wash-off of solid particles.

1.2.3.2.3. *Fossil fuel combustion* (4)

There is a wide range of heavy metals in fossil fuels which can be emitted into the environment as particles during combustion or accumulate in residual ash which may be transported and dumped thus contaminating soils and waters. Some of the metals emitted from fossil fuel combustion are: Cd, Zn, As, Pb, Se, Sb, Ba, Cu, V and Mn. Petrol containing lead additives gives rise to large amounts of lead particulates. These pollutants contaminate the air with aerosol particles from combustion, water with ash-pollutants leached into water and soils with deposited aerosol particles, ash disposal and leaching.

1.2.3.2.4. *Metallurgical industries* (4)

Many heavy metals such as: V, Mn, Pb, Cr, Co, Ni, W, Zn, Sn, Cd, Ag and As are used in alloys and steels. Hence the manufacture, disposal or recycling of such materials can lead to environmental pollution from a wide range of metals. Non-ferrous metal production causes environmental pollution not only of the metal being manufactured but also of other minor associated metals (as shown in Table 1.4). Such contamination can affect the air with aerosol particles from furnaces and dusts from re-suspension of deposited larger particles; waters with effluents and wash-off of particles and soils with deposited aerosols and larger particles, metal-rich sewage disposal and waste dumps.

1.2.3.2.5. *Electronics* (4)

Semiconductor manufacture and other electrical components include a large number of heavy metals such as Cu, Zn, Au, Ag, Pb, Sn, W, Mo, Hg, and As. The manufacture of such components and their disposal in waste both from manufacture and consumers are sources of environmental pollution.

These contaminants can affect the air with aerosol from manufacturing processes; waters with effluents and corrosion of electrical components and soils with wastes and corrosion of electrical components.

1.2.3.2.6. *Waste disposal* (4)

Some metals such as Cd, Cu, Pb, Sn and Zn are dispersed into the environment in leachates from landfills, which pollute soils and ground waters, and in fumes from incinerators. Sewage sludge contains many metals like Pb, Zn, Cu, Cd, Cr, and As which again can pollute both soils and water. Such pollutants can affect air with aerosols from incinerators of metal containing wastes; water with leachates from landfill, run-off, and corrosion of waste dumps in wet pits and soils with disposal of wastes such as sewage and fallout from incinerators.

1.2.3.2.7. *Other sources* (4)

- pigments and paints: Pb, Ba, Cd, Mo, As and Cr;
- polymer stabilisers: Cd, Zn, Sn and Pb;
- batteries: Pb, Sb, Hg, Ni, Cd and Zn;
- catalysts: Pt, Ru, Co, Ni, Re, Mo and Pb;
- additives in fuels and lubricants: Se, Pb, Mo and Te;
- medical uses: e.g. heavy metals such as Ag, Sn, Hg, Cu and Zn used in dental alloy manufacture while As, Se, Bi, Ba, Ta and Pt are used in drug/medicinal preparations;

- printing and graphics: Se, Pd, Cd, Zn, Cr and Ba.

The media affected by these sources include air, waters and soils through manufacturing, disposal and weathering.

1.3. Water Quality

The European Economic Community (EEC) issued in May 1976 a Directive (76/464/EEC) on pollution caused by certain dangerous substances discharged into the environment of the community and stated that ".. there is an urgent need for general and simultaneous action by the Member States to protect the aquatic environment of the community from pollution, particularly that caused by certain persistent toxic and bioaccumulatable substances". The directive classifies the dangerous substances into two lists (9):

> List (I) includes "certain individual substances selected mainly on the basis of their toxicity, persistence and bioaccumulation." Substances included in this list are considered to be most harmful and pollution by these must be eliminated. List (I) is called the "black list", and includes the heavy metals mercury and cadmium and their compounds;
>
> List (II) contains "substances which have a deleterious effect on the aquatic environment which can be confined to a given area and which depends on the characteristics and location of the water into which they are discharged". Substances within list II are less harmful and pollution by these must be reduced. This list is called the "grey list". The other heavy metals are included in this list.

Methods of control include (9):

> limit value (LV) which expresses the maximum amount of substance (in grams) which may be discharged per unit of production capacity (in tonnes). Limit value or maximum admissible amount is usually expressed as concentration in effluent;
>
> environmental quality standards (EQS) which give the concentration limits not to be exceeded at particular locations in receiving water. EQS's are chosen scientifically to achieve the environmental quality objective. There may be several EQS's depending on the nature of the receiving water. It is recognized that the

EQS may be exceeded in an area of water in the vicinity of the outfall, referred to as a mixing zone, where the effluent mixes with the receiving water. If the EQS cannot be met then the limit value or maximum admissible concentration may be used instead. Table 1.5 indicates the permitted levels for some selected metals in various environments.

Metal	Standards ($\mu g/dm^3$)	
	Drinking water MAC	Fresh water EQS
Cu	3000	1-28
Zn	5000	8-125
Pb	50	4-20
Hg	1	1
Cd	5	5
Cr	50	5-50
As	50	50

MAC; Maximum Admissible Concentration - absolute - total.
EQS; Environmental Quality Standard - annual average - dissolved/ total; EC/UK EQS values.

Table 1.5. Limits for metals (10)

1.4. Removal Processes of Heavy Metals from Aqueous Solution

As noted above, heavy metals can occur in wastes in different forms, ranging from large particles to metal ions and complexes in solution. There are two main reasons for the removal of heavy metals from aqueous solutions: first, toxicity removal as an environmental requirement; and secondly, recovery of metals of value as an economic asset. The most common methods of heavy metals removal from waste-waters are:

1.4.1. Precipitation

Chemical precipitation is the most widely used process for the removal of heavy metals from industrial waste-waters (13) with approximately 75% of the electroplating facilities employing a precipitation treatment (12). The precipitation methods include:

1.4.1.1. Hydroxide precipitation

Hydroxide precipitation by pH adjustment is confirmed as an effective method for removing heavy metals from electroplating rinse waters (13). It is the most commonly used precipitation technique due to its relative simplicity, low cost of precipitant (lime or caustic soda) and ease of automatic control (14,15). Although it has a wide application there are some shortcomings:

some metal hydroxides have relatively high solubilities in water and others possess amphoteric properties resulting in re-dissolution if the pH is changed (11, 15);

the presence of complexing agents can reduce the effectiveness of the precipitation (11);

certain metals like chromium (VI) are not removed directly by hydroxide precipitation but require pre-treatment e.g. reduction, prior to the precipitation process (14,15);

hydroxide precipitation may not be effective for mixed metal wastes because the minimum solubilities for different metals occur under different pH conditions (15);

the quantities of hydroxide sludge produced are substantial and difficult to dewater (15) and also present difficulties over disposal.

1.4.1.2. Carbonate precipitation

The feasibility of carbonate precipitation for the removal of lead and cadmium has been studied by Patterson *et al* (16). Carbonate precipitation has several advantages over hydroxide precipitation for these metals:

carbonate sludges have better filtration characteristics than hydroxides;

metal carbonate precipitates are also denser than hydroxide precipitates leading to improved solid separations;

carbonate precipitation for lead occurs at lower pH conditions than that for optimum hydroxide treatment while for cadmium approximately equivalent pH conditions were found.

1.4.1.3. Sulphide precipitation

There are two main processes for sulphide precipitation (17), the first, soluble sulphide precipitation (SSP), uses water soluble sulphides such as sodium sulphide, ammonium sulphide; whereas the second, insoluble sulphide precipitation (ISP), uses a slightly soluble ferrous sulphide (FeS). These are added to the waste-water to give the sulphide ions needed to precipitate the heavy metals. Advantages of the ISP process include the absence of any detectable H_2S gas and reduction of chromium (VI) to (III) by the iron(II). However the disadvantages include the need for an amount of the reagent larger than stoichiometric and the large volumes of sludge which result from ferrous hydroxide precipitation in addition to the metal sulphides.

The use of sulphides for the precipitation of heavy metals has even more advantages thus:

metal sulphides have a lower solubility and higher stability than the hydroxides and therefore a high degree of metal removal can be obtained even from dilute metal solutions (11, 13);

most metals can be precipitated as sulphides even in the presence of chelating agents (11);

the removal is effective over a broad pH range (11);

the resulting sludges have better dewatering characteristics than those of the corresponding metal hydroxides (11, 15);

However there is a major disadvantage caused by the possible evolution of hydrogen sulphide gas and sulphide toxicity in water (15).

1.4.2. Ion exchange

Ion exchange is a reversible chemical reaction where the heavy metals to be removed from waste-waters are exchanged with the ions held by solid ion exchange materials. These ion exchange materials "ion exchangers" are normally insoluble high molecular weight polyelectrolytes with fixed ionic groups attached to a solid matrix. However ion exchange properties can be displayed by any solid substances which possess labile cations or anions. These include natural materials like clays (18), synthetic inorganic materials like zirconium phosphate (26) and derivatives of cellulose (19). These all have their particular areas of application with the inorganic ion exchangers capable of operating under harsh conditions such as high temperatures and high levels of radiation (20,26). Cellulose derivatives are particularly useful for recovery of proteins from fermentation baths. However the most widely used compounds are the materials based on an organic polymer such as polystyrene or polyacrylamide derivatised by acidic or basic groups, as the wide range of available synthetic methods allows the designing of resins for particular applications.

When the ion exchangers become saturated or fully loaded they must be regenerated with a concentrated solution of another ion to remove the heavy metal ions from the ion exchanger bed (15) transferring them into an aqueous solution as shown in the equations 1.1 and 1.2.

$$2Na^+R^-_{(s)} + M^{2+}_{(aq)} \longrightarrow MR_{2\,(s)} + 2Na^+_{(aq)} \qquad \text{loading} \qquad (1.1)$$

$$MR_{2\,(s)} + 2Na^+_{(aq)} \longrightarrow 2Na^+R^-_{(s)} + M^{2+}_{(aq)} \qquad \text{regeneration} \qquad (1.2)$$

Thus the process of ion exchange results in a separation and concentration of the heavy metals which then must undergo additional treatment for recovery. Ion exchangers cannot only recover uncomplexed metal ions but also some complexed species (21).

Ion exchangers have advantages when compared with conventional precipitation methods:

precipitation and clarification equipment require a lot of space whereas ion exchange equipment is very compact (15);

sludges generated from the precipitation processes can be difficult requiring transport to a landfill licensed to accept them while ion exchange avoids sludge generation;

ion exchange allows the direct concentration and recovery of metals for further use.

Disadvantages include (15):

non-selective behaviour in the presence of a mixture of metal ions;

fouling of the resin beads by organic materials;

the presence of free acids can reduce the operation efficiency;

fairly high operational costs, caused by disposal of spent regenerant solutions.

1.4.3. Solvent extraction

Solvent extraction is a separation process used for the removal of heavy metals from industrial waste-waters. The process basically involves a two phase system consisting of an organic liquid which contains a dissolved, water-insoluble active compound "the extractant" and a second phase, the aqueous phase containing the heavy metals to be removed. The extractant reacts with the metal ions forming a metal complex which is soluble in the solvent phase (22). Following extraction, the two phases are separated and the "loaded" organic phase containing the metal is then treated with an aqueous regenerating solution to recover the metal and regenerate the extractant for recycle as represented in figure 1.1.

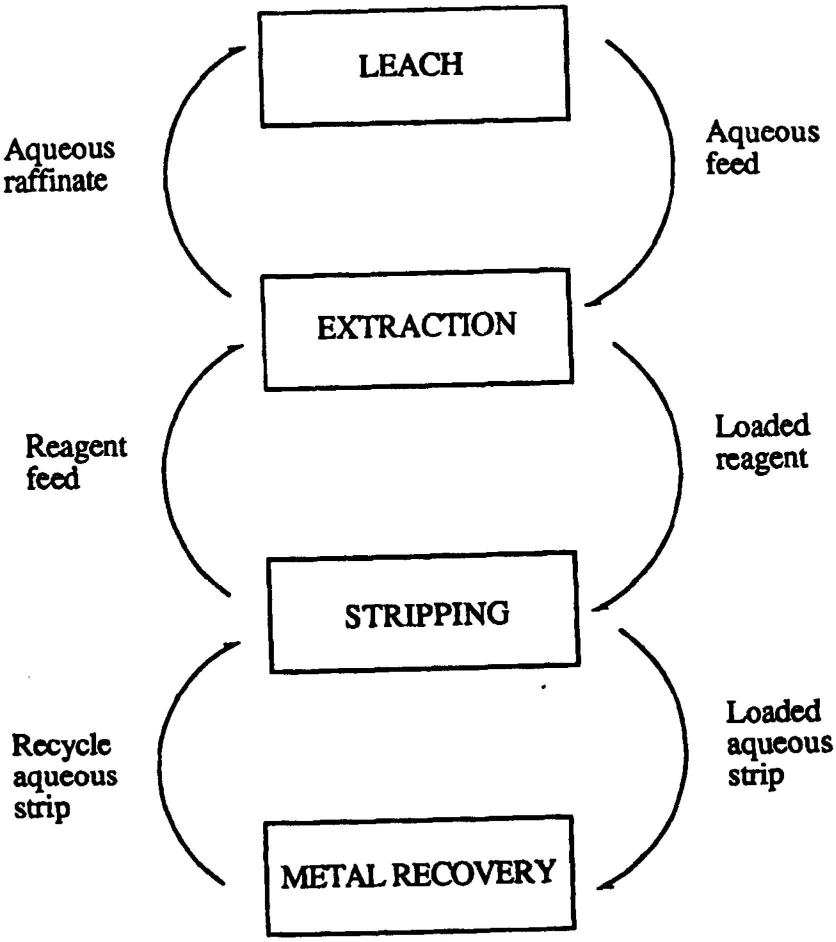

Figure 1.1. Representative diagram of a leach-solvent extraction- metal circuit.

The common extractants are acid, basic or neutral organic compounds with molecular mass 200-450 (22) which form a complex metal-containing species soluble in the organic phase (23). They are generally used in the form of 20-50% solution in industrial hydrocarbon solvents (22). Among the most widely used acid extractants is di-2-ethylhexylphosphoric acid (DEHPA). Among the basic extractants the most important are primary, secondary and tertiary amines with high molecular mass e.g. tri-n-octylamine. Tri-n-butylphosphate (TBP) is a representative of the neutral compounds suitable for heavy metal extraction. In addition there is an increasing number of chelating acid extractants designed for the selective extraction of heavy metals based on particular donor atom preferences and stereochemistry of the chosen metal (27).

Advantages of solvent extraction process include (15,22):

the selective extraction of the desired metallic cation from a solution containing a significant concentration of other metal ions;

the concentration of the desired metal in the final aqueous solution allowing recovery by methods inappropriate to the metal in the initial dilute solution;

low energy consumption;

complete regeneration of the extractant and the possibility of obtaining individual metal compounds in the purity required;

the feasibility of an efficient, large automated process for metal recovery.

Disadvantages:

the requirement of the feed solution to be free of particulate matters and surfactants to minimise problems with phase separation;

losses of the organic compounds in the aqueous phase by solubility and entrainment;

limitations in the degree of concentration which can be efficiently achieved from dilute solutions.

1.4.4. Cementation

Cementation is a process based on replacement of the metals in the waste-waters by another less harmful solid metal such as iron. The process relies on a spontaneous electrochemical reaction (15) between the metal ion to be recovered which is reduced to the metallic state with simultaneous oxidation of the sacrificial metal as shown in the following reaction:

$$Cu^{++} + Fe^{o} = Cu^{o} + Fe^{++} \qquad (1.3)$$

Typical metal cementation agents, which are used in several hydrometallurgical applications, are iron and zinc (28). The feasibility of a cementation process can be predicted from the electrode potentials of the various metals involved. Treatment of copper from waste-water by cementation using metallic iron has been studied by Patterson and Jancuk (24). Advantages of the process include:

recovery of valuable metals , such as copper but in a relatively impure form;

control requirements are simple and the reagents used such as iron are relatively cheap (28).

Disadvantages:

cementation process is not technologically clean and the final metal ion concentrations in the treated solution are not low enough for the process to be used for effluent treatment (28);

the increased concentration of the sacrificial metal can cause difficulties. Thus in the case of iron, atmospheric oxidation to ferric iron and hydrolysis can cause coloration and staining problems.

1.4.5. Coagulation and flocculation

Coagulation refers to the addition of a chemical compound to a colloidal dispersion that leads to particle destabilisation by the reduction of the repulsive forces among the particles. Flocculation refers to the process of promotion of the agglomerization of the destabilised particles to form larger particles (flocs). These processes are normally used to clarify water from colloidal particles from solution. Heavy metals previously insolubilized by precipitation or pH adjustment can be captured and removed during coagulation/flocculation process (13, 25).

In the coagulation process (14) the addition of a strong cationic electrolyte such as aluminium sulphate reduces the repulsive forces among the particles and allows van der Waals forces to be effective, resulting in agglomerization. By the addition of a cationic electrolyte and an alkali, charged hydrated metal oxides are formed and these particles become adsorbed on the colloid. The addition of a polyelectrolyte promotes the agglomerization process and thus floc formation. The most common coagulants are alum, lime and iron salts such as ferric chloride and sulphate. Synthetic organic polymers such as polyacrylic acid and polystyrene sulphonate are some of the most common flocculants (29). An excellent review is provided by Daniels (25) on the removal of heavy metals by iron salts and polyelectrolyte flocculants.

1.4.6. Flotation

Foam flotation depends on producing a stable foam by adding a surfactant (to the solution) and bubbling air through the bulk solution. This foam then attracts the heavy metal species present and concentrates them in the foam phase. Foam floatation (30) includes the following types:

ion flotation, where the metal ions are precipitated by surfactant either in the bulk solution or on the gas bubble interfaces and then are concentrated in the foam phase;

precipitate flotation, the metal ions are precipitated first by a non- surface-active ion and then are floated and carried into the foam phase;

adsorbing colloid flotation, here the metal ions are adsorbed on the surface of colloidal particles which are then floated and carried in the foam phase.

The removal of heavy metals from waste-waters using foam flotation technique has been well studied (30). For dilute waste-waters containing heavy metals in trace amounts, foam flotation has the following advantages (15):

simplicity;

limited space requirement for rapid reactions;

small volumes of concentrated sludge are produced;

moderate costs comparable to lime precipitation and low costs in terms of energy chemicals , equipments and labour;

applicable on small, moderate and large scale;

capability of reducing the contaminant concentration to below the required standard levels.

Disadvantages include:

addition of surfactants to effluent introduces another contaminant which requires a further process for removal of residual concentrations, e.g. activated carbon sorption (31).

1.4.7. Evaporation

Evaporation is one of the most common methods used in industry for the concentration of aqueous solutions. But the use of this method for effluent treatment is rare and occurs only under certain conditions where the effluent contains a high concentration of a valuable material. One of the few applications for this process is the concentration of static rinses from electroplating operations (8), such as chromium plating. In such applications the rinse liquor is evaporated until the concentration becomes suitable for reuse in the plating bath. Commercial units have been built to handle Zn, Cu, Ni , Cr and other metal plating baths.

Disadvantages of this process include:

relatively high costs;
high energy consumption.

1.4.8. Electrochemical operations

1.4.8.1. Electrodeposition

Electrolysis is capable of removing metals from waste waters and has been applied for recovery of metals from plating tanks. In such recovery (13), a direct current is passed through an aqueous solution containing metal ions between cathode plates and insoluble anodes. Under the electric current the metal ions move to the negatively charged cathodes and are reduced leaving a metal deposit that can be stripped off and recovered. Heavy metals (e.g. copper, cadmium) can be recovered by electrodeposition (28).

Electrodeposition has some shortcomings (28) including:

loss of efficiency at low concentrations of metal ions;
presence of a mixture of metal ions can lead to interference and a non-selective behaviour which require some other separation processes.

1.4.8.2. Electrodialysis

Electrodialysis involves the separation and concentration of inorganic ions from water by applying electrical potential between electrodes separated by ion exchange membranes. Ion exchange membranes consist of intertwined polymer chains attached to each other at points of contact by crosslinking (32). These polymers can be derivatized to produce cation or anion exchange membranes similar in structure to resin ion exchangers.

Cation exchange membranes which possess negative fixed charges on the polymer chains are permeable only to cations and the negative fixed charges on the chains repel negative ions preventing them from passing through the membrane. Anion exchange membranes which possess positive fixed charges on the polymer chains are permeable only to anions and the positive fixed charges on the chains repel positive ions preventing them from entering through the membrane.

In electrodialysis (32), cation exchange membranes and anion exchange membranes are arranged alternatively in a parallel array forming a series of thin solution compartments. This stack of membranes is held between two electrodes. The solution to be treated is circulated through the compartments. A d. c. electrical potential is applied to the electrodes, all cations transfer towards cathode (negative electrode) and anions towards anode (positive electrode). Presence of these membranes leads to the formation of a series of clarified compartments (which withdrawn together to give a purified effluent) and concentrated compartments (which withdrawn together to give a concentrated effluent solution which can be treated in a further process).

Advantages: (28)

allows direct concentration and recovery of metals for further use;
high selectivity for charged components;
low energy and investment cost;
continuous operation.

Disadvantages (14):

large organic ions and colloids which are attracted to the membranes result in fouling, which leads to an increase in electric resistance and decrease in the demineralisation capacity;
turbidity in the feed also leads to membrane fouling.

1.4.9. Membrane processes

1.4.9.1. Ultrafiltration

In ultrafiltration (UF), solutes of molecular weight greater than 500 and less than 500,000 can be separated from a solution. Solutes above the upper limit can be separated by conventional filtration (33). The pressure applied in ultrafiltration ranges from 138-690 kPa (15). UF is applied to aqueous solutions which may contain soluble macromolecules, colloids, salt, sugar, etc. (32). Ultrafiltration has been used for the separation of heavy metals (e.g. chromium, zinc, copper and nickel) after precipitation and flocculation from electroplating rinse water (13).

Ultrafiltration (13) has an advantage over conventional clarification and sand filtration providing a more complete solid separation as a result of the small pore size, e.g. 0.1 µm, of the membrane filters.

1.4.9.2. Reverse osmosis

Reverse osmosis (RO) or hyperfiltration, is used to remove much smaller molecular weight solutes than ultrafiltration. Reverse osmosis can be classified into two categories (15): High pressure reverse osmosis (3450 -10350 kPa) and low pressure reverse osmosis (1380 -3450 kPa). For reverse osmosis, the applied pressure must be greater than the osmotic pressure of the rejected solutes.

The process allows the solution to flow under pressure through a suitable porous membrane and withdraws the product water under atmospheric pressure. Reverse osmosis has been used for the treating of plating waste waters for the removal of cadmium, copper, nickel and chromium at pressures from 1380- 2070 kPa. The concentrated stream is returned to the plating bath and the treated water is returned to the last rinse tank (14).

Major limitations associated with the use of membrane processes include (14,15) :

membrane fouling which can be minimised by pre-treatment to remove suspended matter , bacteria and precipitable ions;

limited life of the membrane, although active life-times are increasing;

destruction of the membrane by strong oxidising agents, solvents and other organic compounds.

1.4.10. Biosorption (Biological treatment)

Biosorption is a potential method for the removal of heavy metals from waste-waters and refers to the metal uptake from solution by biological material (34) including bacteria, algae, fungi and yeast (35).

Biosorption is generally used for binding and accumulating metallic species even when the cell is no longer metabolically active (34) while bioaccumulation refers to the metal accumulation by living cells. Bioaccumulation and biosorption have often been combined into the single heading of metal uptake because the predominant mechanism is not known (34).

Due to the complexity of the structure of the micro-organism there are many ways for the metal to be captured by the cell. Therefore biosorption mechanisms are various and in some cases are still not well understood (35). Biosorption mechanism can be classified in two different ways:

i) depending on the cell metabolism the mechanism can be either metabolism dependent, which include precipitation process and transportation across cell membranes, or non-metabolism dependent, which include the processes of ion exchange, complexation and physical adsorption.

ii) according to the location where the removed metal was found thus: extracellular accumulation (precipitation), or intracellular accumulation (transport across cell membranes), or cell surface sorption/ precipitation which includes ion exchange, complexation, physical adsorption and precipitation.

Biosorption mechanisms involve:

physical adsorption (35) on the cell wall;

ion exchange (36) on the cell walls through the interaction with polysaccharides which are well known for their ion exchange properties;

complexation between the metal ions and active groups such as carboxylic acids on the surface of the cell walls (37);

precipitation which may occur as a result of an active defence system of the micro-organism reacting in the presence of toxic metal to produce compounds which favour the precipitation process (38). However precipitation can also be independent of cellular metabolism and can occur as a consequence of chemical interactions between the metal and the cell surface (35);

transport across the cell membrane where heavy metal ions may be transported by the same mechanisms used to convey metabolically essential ions such as potassium, sodium and magnesium (35). In this situation the heavy metals are retained with the active biomass and may be removed by harvesting.

1.4.11. Adsorption

Adsorption of heavy metals on substances such as charcoal has proved to be an efficient method for the removal of heavy metals from waste-waters and as it forms the basis of the current project it will be discussed in detail in the following Chapter.

CHAPTER 2. ADSORPTION OF HEAVY METALS (LITERATURE SURVEY)

2.1. Introduction

The first use of adsorption is lost in antiquity and carbon is the oldest and most widely used sorbent. The early Egyptians used carbon around 1500 B. C. as an adsorbent for medical and purification purposes (39,40). Ancient Hindus in India filtered their drinking water through charcoal (40,41). In the 15th century, the ability of certain materials to remove colours from solution was known and bone chars were used for decolourising sugar solutions in the late 18th century (42). In England in the mid 19th century, treatment of drinking waters for the removal of odours and tastes was carried out using carbon filters (41).

Currently, adsorption is an important chemical engineering process (39) in water treatment and has very wide application in the efficient removal of various pollutants including both organic compounds (dyes, phenols, etc.) and heavy metals.

Adsorption is a surface phenomenon that is defined as the selective collection and concentration of particular components from a liquid or a gas onto solid surfaces. Generally, in any solid, atoms at the surface are subject to unbalanced forces and these forces are responsible for the phenomenon of adsorption. The interaction between the surface and the adsorbed species may be either physical or chemical. In physical adsorption, the adsorbates are attached to the surface of an adsorbent without any chemical reaction and thus, as there is no sharing or transfer of electrons between the adsorbate and the adsorbent surface, the interactions are reversible. The process of physical adsorption is not site specific so the adsorbed molecules can cover the whole surface and thus the adsorption capacity is related to the surface area of the solid.

In chemical adsorption, chemical bonding between the adsorbate and the adsorbent surface is involved. The process is irreversible and site specific and the chemisorbed molecules are fixed at specific sites on the surface. One of the most important differences between physical adsorption and chemical adsorption is the heat of adsorption thus while it is low for physical adsorption, it is very high in chemical adsorption. The mechanism of adsorption can change according to the experimental conditions thus the heat of adsorption of hydrogen on zinc oxide at 0 °C (physical adsorption) is 7.9 kJ mol^{-1} while at 300-444 °C (chemical adsorption) is 83.6 kJ mol^{-1} (43).

2.2. Forces of Adsorption

Several types of interactions are found between the solid surface and the adsorbed species including van der Waals forces, electrostatic forces, chemical adsorption, hydrogen bonding and hydrophobic bonding.

2.2.1. Van der Waals forces (44)

These are weak forces and responsible for the physical adsorption of the adsorbates on the surface. Three contributions are known which lead to van der Waals attraction and are introduced below in order of their relative strengths of attraction.

i- Electrostatic contributions (dipole -dipole interactions):

An electrostatic interaction arises between molecules having permanent dipoles which leads to a special orientation of the adsorbate molecules and the dipole sites on the adsorbent to maximize their attraction.

ii- Induction contribution (dipole- induced dipole interactions):

This is caused by an induced polarization of non-polar molecules as a result of their proximity to a permanent dipole. The electric field of the dipole distorts the electron charge distribution of the other species producing an induced dipole, again causing an attractive force.

iii- Dispersion contributions (London dispersion forces):

London dispersion forces provide a major contribution to van der Waals attraction forces among non-polar molecules. These forces exist for all types of matter and they always act as an attractive force between adjacent atoms and molecules (45).

Electronic motion in an atom or a molecule is continuous and thus electron density fluctuates in time and space. At any instant there is a lack of symmetry of electrons about the nuclei and so an instantaneous electric dipole is formed. This dipole will oscillate with the variation in electron density. When in proximity to a solid surface, each instantaneous dipole of an approaching molecule will induce an instantaneous dipole in a surface molecule. These two dipoles interact to produce an instantaneous attraction (45).

In addition to these forces of attraction there is also a repulsion force which arises when an adsorbate molecule approaches very close to a solid surface molecule due to a degree of interpenetration of their repulsive electron clouds.

2.2.2. Electrostatic (Coulombic) forces

Electrostatic attraction between charged ions to charged sites on the adsorbent leads to a phenomenon referred to as exchange adsorption (29). In this case incoming cations, for example, approach the negatively charged sites on the surface and exchange with those cations already held by these negative charged entities. The phenomenon is termed as ion exchange and because the exchanging ions must undergo a phase transfer from solution phase to surface phase, ion exchange is classified as a sorption process (29).

2.2.3. Chemical adsorption (41)

In this kind of adsorption, electrons are transferred or shared between the adsorbate and the solid surface so that a chemical reaction occurs forming a strong chemical bond, for example, oxygen (46) is chemisorbed on carbon forming lactone groups at 250 °C and carbonyl groups at 300 °C on the adsorbent.

2.2.4. Hydrogen bonding

A hydrogen bond occurs between a proton donor group AH and a proton acceptor group B, where B is an electronegative atom such as O, N or F, such that a weak chemical bond is formed through the binding hydrogen atom as shown in the equation (2.1).

$$\mathrm{A}\text{——}\mathrm{H} + \mathrm{B} \quad = \quad \mathrm{A}\text{—}\mathrm{H}\cdots\cdots\mathrm{B} \qquad (2.1)$$

Proton acceptor groups can be the lone pair of electrons of an electronegative atom or a π-electron orbital of an unsaturated system. Adsorption of water vapour onto modified activated carbon by oxidation with different oxidising agents has been studied by Youssef *et al* (47). Oxidation changes the chemistry of the surface by forming carbon-oxygen groups which provides the sites upon which the initial adsorption of water vapour takes place through hydrogen bonding.

2.2.5. Hydrophobic bonding

It is known that hydrocarbons are sparingly soluble in water but easily soluble in non-polar solvents. When such compounds are added to a mixture of polar and non-polar solvents, by mechanical shaking, they tend to migrate from polar to the non-polar solvent demonstrating their hydrophobic character. Many organic compounds such as soaps, detergents and long chain alcohols exhibit both a hydrophobic nature through the hydrocarbon chains, and also a hydrophilic nature from the ionic parts of the molecule. When such compounds are added to water the polar hydrophilic groups hydrogen bond to the water molecules while the hydrophobic carbon chains try to migrate away from the aqueous phase. This causes the molecules to congregate at the air-water interface, or, once this is saturated, they aggregate in the aqueous solution as micelles, where the hydrophobic chains associate together away from the water molecules. This phenomenon of self association through the hydrophobic chains of the molecules is called hydrophobic bonding.

2.3. Adsorption of Heavy Metals

Adsorption on solid surfaces has been shown to be an efficient process for the removal of heavy metals from waste-waters. Many adsorbents have been investigated for this purpose ranging from natural adsorbents (such as agricultural products and by-products, clays, etc.) and man-made adsorbents (such as activated carbons).

2.3.1. Carbon sorbents

2.3.1.1. Activated carbons

Carbon is mainly manufactured by the action of heat at higher temperatures, e.g. 700 - 1200 °C, and removal of volatile matter and tarry compounds which are formed as by-products. The carbon then can be activated physically or it can be activated chemically prior to the carbonisation process. Carbonaceous raw materials include various types of coals, peat, lignite, coconut husks, peach and apricot stones, bones, various types of wood and polymers such as polyvinylchloride. Carbonization involves the pyrolysis of the feed material in the absence of air without addition of any chemical reagents. The carbon thus produced is virtually inactive and its surface area is quite low. Activation, which increases the surface area, can be achieved in one of two ways: chemical or physical activation. Chemical activation occurs by the addition of chemical activating agents, e.g. zinc chloride, potassium sulphide, phosphoric acid, sulphuric acid and sometimes alkali metal hydroxides, prior to the carbonization process. While physical activation can be carried out by allowing the carbonized inactive material to react at higher temperature with suitable substances, usually gaseous, such as steam, oxygen, or carbon dioxide (44).

2.3.1.2. Carbon by dehydration

Sulphuric acid is a strong acid and if concentrated, can also behave as a dehydrating agent and oxidant (48). It decomposes carbohydrates by the removal of water, thus in contact with sugar, sulphuric acid reacts to leave a charred mass of carbon (48). Carbonisation of agricultural materials can be performed by dehydration with sulphuric acid and phosphoric acid at low temperature resulting in a colloidal and porous active charcoal (49, 50). Few studies have been reported on this type of carbon which has been variously named as collactivit (52,53), colloidal carbon (54) and activated carbon (55). Some other names for such carbon have been used by some researchers in Japan. As reported by Hanzawa and Satonaka (49), Mizuno and Kato first called this carbon “shitsujun kasseitan” (moistened active charcoal) and later “suika kasseitan” (hydrated active charcoal) which was also used by Hanzawa and Satonaka in their studies (49,51). Komoto named this carbon by dehydration with sulphuric acid as sulphuric acid-activated carbon and ion exchange activated carbon (56) and finally the name used by Pichugin *et al* (57) was "sorbent" which was prepared from flax shive (58).

Mizuno and Kato prepared the carbons from raw materials such as filter papers, saw-dust and mandarin orange peel as reported by Hanzawa and Satonaka (49), Dehydration is performed with 70% sulphuric acid at 150 ^{o}C and the carbon obtained a good decolorizing activity. The carbonised product which was prepared by the removal of the structural water from raw materials has highest activity in the moistened state which is decreased by drying.

Hanzawa and Satonaka (49,51) prepared carbon from saw-dust using sulphuric acid. The carbons prepared under different conditions from different raw woody materials were tested for their decolourization potential by methylene blue and caramel.

Komoto (56) studied the conditions of the preparation and properties of sulphuric acid carbon from saw-dust with a view to using it in sugar refining by varying activation time, temperature, concentration and amount of sulphuric acid. The optimum activation recommended from this work was as follows: 1 part saw-dust was added to 3 parts 85 % sulphuric acid at about 90 °C for 2-3 minutes with stirring. The temperature of the mixture rose to 155-160 °C and was maintained for 10 minutes as the activation time. The resulting carbon containing 72% moisture has both decolourising and ion exchange properties. This preparation was mainly based on the decolourising property of the carbon for use in sugar refining. The yield of the carbon decreased at lower acid concentrations but in the range 80 - 95 % it remained virtually constant. Variation of activation time showed no significant change in the yield except at lower value. A slight increase in the yield was obtained by increasing the amount of sulphuric acid while increasing the temperature of the acid decreased the yield. The product was named ion exchange active carbon (I. A. C.) and the ion exchange property was related to the presence of carboxylic, sulphonic and hydroxyl groups found on the surface. The ion exchange capacity increased as the concentration, activation time, and amount of sulphuric acid increased while the effect of temperature seemed to have no effect. During storage, or on drying, the carbon did not decrease its cation exchange capacity at all, but lost its decolourising power.

2.3.2. Heavy metals adsorption (literature survey)

Activated carbon can remove both uncomplexed and complexed metals from aqueous solutions (59) and it has an added advantage which is the absence of any sludge formation. It is one of the most widely investigated adsorbents for heavy metals removal from aqueous solutions (60-69), as shown in table 2.1.

Various processes are available for the modification of the surface chemistry of activated carbon to increase its capacity for heavy metal adsorption. Thus surface oxidation by nitric acid (70) increases the capacity for copper adsorption. The oxidation process increases the concentration of carbon-oxygen groups on the surface which act as ion exchange groups for copper. Other methods of modification include: sulfur impregnation (71) which increases the adsorption capacity for the mercuric ion; treating the activated carbon with hydrogen sulphide at high temperature increases the adsorption of lead (II)

(72) and impregnation of active carbon with phosphates and nitrogen containing compounds also exhibits advantages for the adsorption of heavy metals (73).

Adsorbent	Metal(s)*	Reference
Activated Carbon	Pb , Cu, Ni, Zn	60
	Cr (VI)	61,66,67
	Hg	62,63,68
	Zn , Cd	65
	Pb	64
	Cu , Ni, Cu-Ni, Cu-Cd, Cu-Zn	69
	Cr (III)	92
Modified activated carbons	Cu,	70
	Hg	71,73, 93
	Pb	72,93
	Cd	93
Peat and Lignite	Cu, Cd , Zn	39, 74
Chitin and Chitosan	Cr (III), Cr (VI)	39, 75
Lignin	Pb, Zn	76
Peanut Skins	Cu	77
Cotton fibres, bamboo pulp, jute fibres , saw-dust	Cu	78
Cottonseed hulls, rice straw, soybean hulls, sugarcane bagasse	Cr (III), Co, Cu, Ni, Zn	79
Melon seed husks	Pb, Cd, Cu , Ni	80
Straw	Cd, Cu, Ni, Pb, Zn	82
Onion skins	Cd, Cu, Pb, Hg, Cr (VI), Cr (III), Ni, Zn	84
	Hg	85
Corncobs	Cu	86
Bark	Hg	87
Maize cob meal	Cd, Cu	88
Tea leaves	Pb, Cd, Zn	90,76
Waste rubber	Hg	89
Ground-nut husks	Cd, Cu, Pb	81
Linseed fibre	Cu, Cd, Ni	83

*Metals without notified oxidation states mean the oxidation state (II).

Table 2.1. Removal of metal(s) from aqueous systems using various adsorbents.

Peat and lignite, in general, have a good affinity for metals and have been widely studied for this purpose. Peat, the first stage in the coalification process of plant materials, is a rather complex material. It contains as its major constituents, lignin, cellulose and humic acids which possess polar functional groups such as alcohols, aldehydes, carboxylic acids, ketones and phenolic hydroxides (39,74). When peat becomes buried beneath the earth's surface and in the presence of increasing pressure and temperature, it transforms to lignite which tends to retain the functional groups found on peat. The adsorption of heavy metals on these materials has been widely studied and adsorption was found to occur mainly by ion exchange via these functional groups on peat and lignite (74).

Chitin and its deacetylated derivative chitosan have been used for the adsorption of heavy metals from aqueous solution (39). Maruca *et al* (75) studied the adsorption of chromium (III) and (VI) by chitin and chitosan. The uptake of chromium (III) on chitosan was significantly greater than on chitin. This was related to the nitrogen moiety of the two polymers, thus both the N-acetylated amine groups in chitin and the free amine groups in chitosan could act as specific chemical binding sites for ions capable of forming complexes, with the free amine groups on chitosan being much better ligands for metal ions. Chromium (VI) adsorption was found to be minimal on both chitin and chitosan.

Studies on the adsorption of heavy metals on lignin obtained from the black liquor from paper industry showed that in comparison to the low cost adsorbents such as tea leaves, humic acid and china clay, the capacity is high for zinc and lead ions on lignin (76).

Since it has been realized that an effective and economic removal of heavy metals from waste-waters is required, research has been carried out on the use of agricultural products and by-products of cellulosic origin which are readily available at little or no cost. Such research for the adsorption of heavy metals onto such materials, either modified or in their natural state, has intensified in the last two decades, table 2.1. Randall *et al* (77) studied the adsorption of cupric ions from aqueous solution using peanut skin which behaves as an efficient ion exchange material for cupric ion removal. Cotton fibres, bamboo pulp, jute fibres and saw-dust containing reactive dyes have been studied as adsorbents for cupric ion (78) from aqueous solution. It was found that although the adsorption of cupric ion is significant onto the undyed substrates, their capacity increases after treatment with reactive dyes. e.g. the adsorption capacity for saw-dust undyed and then dyed with Reactive Red, Orange and Yellow is 45.25, 59.25, 61.3 and 52.75 mg/g respectively from copper nitrate solution. The other fibers mentioned exhibit similar behaviour. These results suggests that when the undyed substrates are used, the metal cations are adsorbed on various groups present in the substrates, e.g. hydroxyl groups, either from cellulose or lignin. In the case of dyed substrates, only few hydroxyl groups are used in forming dye-cellulose bonds which are not then available for metal cation adsorption. However, on the dyed substrate a greater number of groups of varied nature from the dyestuff molecule became available to combine with the metal cation (78).

Soybean hulls, cottonseed hulls, rice straw and sugarcane bagasse have been used as adsorbents for heavy metals (79). Okieimen *et al* (80) studied the adsorption of heavy metals onto melon seed husks and showed that adsorption increased following modification with EDTA. Similar results were found using other cellulosic materials such as ground-nut husks (81). Larsen *et al* (82) studied the adsorption of heavy metals by barley straw. It was found that 1g of straw was able to adsorb amounts of zinc, copper, lead, nickel and cadmium ranging between 4.3 - 15.2 mg while with activated carbon and pine saw-dust adsorption varied 6.2 - 19.5 and 1.3 - 5.0 mg respectively.

Adsorption of cadmium, copper and nickel by waste linseed fibre has been studied by Williams *et al* (83). The fibre is obtained by desiccation and retting in the field. Using a semi-continuous batch adsorption system, the total uptake capacity of copper, nickel and cadmium by linseed fibre after the seventh adsorption cycle (where total metal ion removal was maximal) was 8.01 mg/g.

Onion skins (84, 85), corncobs (86), bark (87) and maize cob meal (88), waste rubber tyres (89) and even waste tea leaves (90) have been all used as adsorbents for heavy metals from aqueous solutions.

Pichugin *et al* (57) prepared carbon from flax fibre waste which was actually flax shive (58) using 10-12 mol/dm^3 sulphuric acid at a ratio of 1: 5-6 by weight flax shive: acid at 150-155 °C for 15-20 min. The carbon adsorbent thus obtained has a good adsorption affinity for heavy metals from water. The capacity for mercury and sodium was 0.98 and 4.35 mmol/g respectively (58).

2.3.2 Factors affecting heavy metal ions sorption from aqueous solution

In general, it is very important to know the physical and chemical conditions of waste-water prior to its treatment. For water containing heavy metals, it is essential to have information about the solution to be treated.

2.3.2.1. Effect of pH

The pH of the aqueous solution is an important variable which controls the adsorption of metals at carbon-water interface (60-62, 64). The adsorption percentage of lead (II) increased sharply between pH 1 and 3 attaining a maximum value (98%) around pH 3 on olive stone-activated carbon (64). Marzal *et al* found that cadmium (II) and zinc (II) removal from aqueous solution on activated carbon increased from zero to 100% in a narrow pH range (approximately 4.5-8), with the greatest adsorption occurring the highest pH values (65). Chromium (VI) removal on activated carbon was found to be very dependent on the pH showing an increase of its removal in acidic pH values reaching a maximum at pH 3 and decreasing sharply at pH values higher than 3 (67). Similar behaviour was found by Huang and Wu (66) with a maximum chromium (VI) sorption at pH 5-6.

2.3.2.2. Presence of other metal ions

Adsorption of a particular metal ion is affected by the presence of other metal ions in solution as well as their concentration. The effect of sodium chloride on the adsorption of lead was studied by Rivera-Utrilla *et al* (64). It was observed that the presence of sodium chloride, in the range of 10-50 mg/dm^3, decreased the adsorption percentage to 80%. Increasing sodium chloride concentration led to a sharp decrease down to 1% lead adsorption at 100 mg/dm^3 of sodium chloride (64). This was related to the competition between both sodium and lead ions for the active centres on the surface of the carbon. Modified bark has been used for mercury (II) removal in another study (87) where it was found that the presence of sodium, potassium, magnesium and calcium decreased mercury uptake due to their competition for adsorption sites.

The presence of calcium (II) or magnesium (II) over 50 mg/dm^3 in an aqueous mercury (II) solution decreased the uptake of mercury on granular activated carbon (68). In the same study, iron (III) and aluminium (III) in concentrations up to 10 mg/dm^3 at pH 7 showed an increase in mercury (II) removal, being higher in case of iron than that of aluminum which seemed insignificant for mercury (II) removal. This was explained by added sorption sites for mercury on the precipitate of aluminum (III) and iron (III) hydrous oxides which precipitated at the experimental conditions (pH 7), either free in solution or coating the carbon particles, being larger with iron (III) oxide than that of aluminum (III).

2.3.2.3. Surface area

Numerous attempts have been made to correlate the adsorption capacity of activated carbons to their surface areas and textural properties but this relationship seems to be limited to pure physical adsorption (70, 91).

In case of chemical adsorption or specific sorption, surface area is not the controlling factor in determining the adsorption capacity. Treating activated carbon, with surface area 862 m^2/g, with an oxidizing agent such as nitric acid, led to a decrease in the surface area to 758 m^2/g but in spite of this the acid treated activated carbon showed about a four fold increase in water vapour sorption capacity compared to that before treatment. This was related to the concentration of carbon-oxygen functional groups on carbon surface (47). Youssef and Mostafa (70) found that although steam activated carbon had a high surface area it showed no adsorption of copper while zinc chloride activated carbon showed a significant copper sorption reaching 0.88 meq/g. Although both have relatively high surface areas the former has a reasonable surface basicity while the latter has a significant surface acidity. This shows that method of preparation of activated carbons is an important factor affecting heavy metal removal. When both carbons were treated with nitric acid, copper sorption increased reaching a copper adsorption capacity 1.26 meq/g for HNO_3-steam activated carbon and a value of 2.83 meq/g for HNO_3-zinc chloride activated carbons. The copper sorption was related to surface acidity which was lower in the former (0.36 mmol/g) and higher in the latter (0.91 mmol/g). This study shows that acidic sites on carbon surface may be considered as the active surface area for the uptake of copper ions.

In another study (92), activated carbon was treated with nitric acid to produce a high carbon - oxygen content on the carbon surface. The surface area decreased from 1089 to

164 m^2/g and chromium (III) sorption was increased from 2.7 to 25.3 mg/g and this was attributed to the increase in carbon oxygen functional groups (ion exchange sites) (92). Thermal treatment of the carbon at 600 °C for two hours under a flow of nitrogen leads to an increase in the surface area to 555 m^2/g but the adsorption capacity for chromium (III) was drastically reduced to 2.5 mg/g. By oxidation, the nature of the carbon surface changed from being hydrophobic to hydrophilic showing a low nitrogen surface area and a high adsorption capacity for chromium (III). Thermal treatment at higher temperatures removes most of the carbon-oxygen groups which are the active sites of chromium (III) sorption (ion exchange sites) giving a low adsorption capacity but, in contrast, the surface area of nitrogen increased by this treatment which also decreased the hydrophilicity of the oxidized carbon surface (92).

Activated carbon (steam and zinc chloride activated) prepared from rice husks followed by treatment with sulphuric acid (93) showed a higher sorption of mercury (II), lead (II) and cadmium (II). Sorption of these metals increased by increasing the concentration of the sulphuric acid used due to the increased surface acidity and the oxygen content on the carbon surface. Steam activated carbon without acid treatment did not adsorb a measurable amount of metal ions even though the nitrogen surface area was high (420 m^2/g). With acid treatment, the steam activated carbons showed an increase in surface area to 520 m^2/g with mercury (II), cadmium (II) and lead (II) sorption capacity reaching 0.075, 0.074 and 0.1 mmol/g. On the other hand as a result of sulphuric acid treatment, the zinc chloride activated carbon (93) surface area increased from 735 (without acid treatment) to 750 m^2/g and the metal uptake capacity increased from 0.02 to 0.117 (mmol/g) for mercury (II), 0.025 to 0.125 for lead (II), and 0.04 to 0.16 for cadmium (II). From this study, it was concluded that the chemistry of the carbon surface is a prominent factor which determines the sorption capacity for these metal ions while in contrast, the surface area is not a controlling factor. In general, it can be concluded that the active surface area for a particular adsorbate depends on the nature of the adsorbate and the mechanism of sorption (70).

2.3.2.4. Effect of temperature

Temperature is also considered as an important factor affecting metal adsorption, with the efficiency increasing on raising the temperature (65). A similar influence of temperature has been previously reported for heavy metal adsorption onto activated carbon (60). Ragi and Anirudhan found that adsorption of chromium (VI) (94) and mercury (II) (95) on carbon increased by raising the temperature. This was suggested as relating to the increase of the active centres for sorption with temperature and to a change in pore size of the sorbent and / or enhanced pore diffusion (94,95).

2.3.3. Mechanism of metal ion sorption

In general, metal ions are sorbed onto solid surfaces such as biosorbents, active carbon and ion exchangers via different mechanisms, which include: adsorption, ion exchange, complexation, precipitation and reduction. In case of biosorbents, the mechanism cannot be considered as a single process but a collective action by many of these processes as noted in Chapter 1, section 1.4.10. The mechanism of heavy metal sorption on peat, lignite and activated carbons is discussed in Chapter 5, section 5.2.

2.4. Flax Shive

2.4.1. Introduction

Flax *(linum usitatissimum)* has been grown since the beginning of civilization. Remains of flax plants and some of its manufactured products including seeds, fibres and ropes have been found in the refuse of Stone Age dwellings in Switzerland (97). It was a major textile raw material in Egypt during the high periods of Egyptian civilization (97).

Flax continued to be one of the major fibres used in Europe throughout the Middle Ages. Up to the industrial revolution, flax was grown throughout most of Europe, Asia and North Africa (98).

The plant has two main uses, fibre and oil seed, and these end uses determine the way in which the plant is cultivated (96):

> for oil-production (97), the plants are placed further apart so that they grow shorter in length (60 cm) with more branches in stem and more seed heads. The plant is then called linseed (100) or flaxseed (101). In North America (Canada and United States) the plant is grown mainly for its seeds. Linseed oil is mainly used for making paints, putty, varnishes, oil cloth and ink (100).

for fibre production, the plants are cultivated very close together so they branch only in the top and produce a long fibrous stalk (100 cm) and the plant is now called flax (100) or fibre flax (101). The fibre produced has been used in household textiles, furnishing fabrics and linen clothing. Fibre is sometimes a by-product of linseed production and seed is an important by-product of flax (101).

In 1988, Western European production of flax fibre comprises only 13 % of World production (98), the remainder being mostly produced in Eastern Europe, China with smaller quantities in Egypt and South America (table 2.2).

In addition to the former Soviet Union, Eastern European countries in which flax plant is grown include Hungary, Poland and Romania, while Western European countries include France, Belgium, Germany, Netherlands, Austria and Northern Ireland (98).

Country	Flax Produced (tonnes)
Former USSR	450,000
Other Eastern & European Countries	100,000
Western European Countries	100,000
China	100,000
Others	20,000

Table 2.2. World flax production [1988] (98).

At present, in Western Europe *Linum* is grown mainly for fibre to produce linen, the harvested seed can be used for oil production for industrial purposes. Only in Great Britain (24,000 hectares in 1989) and the former Federal Republic of Germany (FRG) and Denmark (less than 2,000 hectares in 1989) *Linum* is grown for seed oil production (99). In 1989, production areas of fibre flax (99) were 59,323 ha in France, 11,568 ha in Belgium, 5,560 ha in Netherlands, 2,175 ha in the FRG and 450 ha in Austria totaling 79,076 ha within Western Europe. Recently, *linum* has featured within the EU as a crop which attracts significant subsidies and hence many English fields are covered with blue flowers in the early Summer.

During the processing of flax, flax shive is produced as a by-product in addition to seeds and tows (short fibres). Flax shive is a woody by-product which is separated from the retted flax straw by a process referred to as scutching which involves two operations (102):

braking (crushing or breaking) involves crushing the woody components into small pieces of less than 1 cm length; and

swingling, which is the removal of the shive using tangential scraping of the broken stems.

Component*	%
Cellulose	46
Hemicellulose	26.2
Lignin	23.1
Nitrogen	0.2
Lipid	1.2
Ash	3.1

*Chemical analysis data were obtained from the provider of flax shive " Natural Fibre Organisation NFO", Church Court, Clewers Hill, Waltham Chase, Hampshire SO32 2LN (Private communication with Mr. Harry Gilbertson).

Table 2.3. Chemical analysis of flax shive.

For every ton of fibre produced, 2.5 tonnes of shive will be left after scutching (103). Due to the nature of shive components, its exploitation has been limited. It consists largely (90-98 %) of three polymeric materials: cellulose, hemicellulose and lignin (table 2.3).

2.4.2. End use and application of flax shive

During the production of fibre from flax straw, many waste products can cause pollution of the environment and rivers (103) and methods of proper disposal is often expensive.

Lignocellulosic materials such as flax shive are of no nutritional value to ruminant animals because the cellulose is not easily digested due to the high lignin content. If the shive is to be used as animal feed, it has to be first upgraded (103) with a biological or a chemical treatment.

The flax shive (103) may be used as a source of energy as the heat content of flax shive is estimated to 18.4 kJ/g which compares well with other lignocellulosic materials such as wood (19.7 kJ/g), peat (20.9 kJ/g) and cellulose (17.6 kJ/g).

Flax shive can also be used as a thermal insulator. In addition, good quality shive can be mixed with bonding agents such as urea formaldehyde based adhesive and wax emulsion, and compressed to form shive board (103).

Flax shive is considered to be a waste product and a problem in itself for disposal. In this project flax shive is treated chemically to produce a carbon material to be used for heavy metal removal from waste-water.

CHAPTER 3. MATERIAL AND METHODS

3.1. Experimental Materials

3.1.1. The sorbents

The carbon sorbents are manufactured by the dehydration of flax shive using different concentrations of sulphuric acid at varying temperatures, reaction times and differing amounts of sulphuric acid.

3.1.1.1. Preparation of the sorbents

3.1.1.1.1. *Materials used*

Sulphuric acid: (98%, sp. g. 1.84 Breckland scientific supplies);

Flax shive: Supplied by NFO "Natural Fibre Organisation, Church Court, Clewers Hill, Waltham Chase, Hampshire SO32 2LN" as pieces which were different in diameter, length and strength. The diameter ranged from ~0.1 to ~0.3 cm and the length from ~0.5 cm to ~2 cm. The chemical structure of the flax shive is shown in table 2.3 in section 2.4.1. Apparent density of flax shive is ~ 0.17 g/ml.

Flax shive was washed with a stream of distilled water through a mesh of 1mm diameter to remove dirt, dust and any superficial impurities. The shive was then dried at 65-70 °C to constant weight.

3.1.1.1.2. *Preparation method of the carbon sorbents*

Clean air-dried flax shive (15.0 g) was weighed in a clean dry beaker of capacity 1dm^3. Sulphuric acid (12 mol/dm^3) was added to flax shive in a ratio of 1:9 (wt of shive: volume of sulphuric acid). The mixture was then heated to 155-160 °C for 15 to 20 minutes with occasional stirring. The temperature was kept in this range (155-160 °C) for a reaction time of 25-30 minutes. The resulting black mixture was allowed to cool; and then filtered using a Buchner funnel under vacuum. The black spent sulphuric acid (black liquor) was filtered off. The carbonised material was washed several times with distilled water and stored under distilled water for 24 hours. The carbon was filtered and washed again several times until the pH of the wash water was between 4-5 and did not give a precipitate with barium chloride solution.

For work under wet conditions the carbonised product was stored under distilled water which was replaced from time to time (twice a week) to avoid any possible bacterial effect. The pH of the supernatant solution decreased to 2-2.5 resulting from the ion exchange character of the material. Before use for the sorption of metal ions, the wet carbon was washed with a stream of distilled water between two sieves of mesh size 1 mm and 0.212 mm to remove fine particulates and to select a suitable size range for the experiments. The sample was transferred to a Gooch crucible and left under suction for 30 minutes. Samples were then weighed to measure the moisture content and to use for the sorption experiments.

For work under dry conditions the carbonised product was dried in an oven at 120 °C overnight to constant weight, transferred to a desiccator to cool and finally stored in a dry, clean and well closed polyethylene jar. The carbon was ground to between 1 mm and 0.212 mm sieves to be used in the sorption experiments.

Optimisation of the preparation was achieved by varying the following parameters: concentration of sulphuric acid; reaction time; temperature and the ratio of shive to the amount of sulphuric acid (wt: vol.). The process described above was repeated for the following four different series to optimise the preparation conditions for the sorption of different metal ion systems.

Effect of reaction time:
~15 g shive + 12 mol/dm^3 sulphuric acid (in a ratio of 1:9, wt: vol.) at 155-160 °C for 10, 20, 30, 45 and 60 minutes.

Effect of temperature:
~15g shive + 12 mol/dm^3 sulphuric acid (in a ratio of 1: 9, wt: vol.) at 100, 120, 140, 160, 180 and 200 °C for 25 minutes.

Effect of ratio of reactants:
~15 g shive + 12 mol/dm^3 sulphuric acid with relative ratios 1:3, 1:5, 1:7, 1:9 and 1:12 at 155-160 °C for 25 minutes.

Effect of sulphuric acid concentration:

~15 g shive + 10, 12, 14, 16 and 18.2 mol/dm^3 H_2SO_4 in a ratio of 1: 9 at 155-160 °C for 25 minutes.

The samples were washed, dried and stored as mentioned above. The samples used in the optimisation of the preparation conditions were all used in the dry state. The carbon sorbents, wet or dry, were used within 20 days from the preparation time to minimise any possible ageing effect on the sorbents.

3.1.2. Sorbates

The metals chosen for investigation include mercury, chromium, palladium, manganese, iron, cadmium, zinc, nickel, cobalt, lead and copper. Corresponding soluble metal salts included chloride, sulphate and nitrate. The salts detailed in table 3.1 were all of analytical grade. Suitable weights of metal salts were dissolved in distilled deionised water to prepare the metal concentrations required.

3.2. Analytical Methods

3.2.1. Moisture content

The moisture content was measured by oven-drying (104).

Procedure:

A dry, clean, empty glass sample tube with a suitable glass cover was weighed to the nearest 0.1 mg and approximately 1.0 g of the prepared carbon product added, the sample was left under suction drying in air for 30 minutes to remove the water from between the particles. Then the exact weight of the sample was determined and the glass sample tube and cover were put in a pre-heated oven at 120 °C for 24 hours, after which time, the sample tube was covered and transferred to a desiccator and weighed again when cold at room temperature. A drying time of 24 hours was found to be sufficient to have constant weight.

3.2.2. Inductively Coupled Plasma - Atomic Emission Spectrometry (ICP-AES)

A Perkin Elmer Plasma 40 Emission spectrometer was used for the analysis of residual concentrations of metal ions in solution after contacting with the carbon sorbents.

Metal	Symbol	Valency	Atomic weight (g/mole)	Salt formula	Salt mol. wt. (g/mole)	Initial concn. (mg/dm^3)
Mercury	Hg	2+	200.59	$HgCl_2$	271.50	6000
		2+	200.59	$Hg(NO_3)_2.xH_2O$	~ 342.6 (x~1)	1000
Chromium	Cr	6+	51.996	$K_2Cr_2O_7$	294.19	1000
		3+	51.996	$CrCl_3.6H_2O$	266.45	1000
Gold	Au	3+	196.970	$AuCl_3$	303.33	1500
Silver	Ag	1+	107.87	$AgNO_3$	169.88	1000
Palladium	Pd	2+	106.40	$PdCl_2$	177.31	1000
Platinum	Pt	2+	195.1	$Na_2PtCl_4.H_2O$	382.88	1000
		4+	195.1	$Na_2PtCl_6.6H_2O$	561.88	1000
Iron	Fe	3+	55.874	$FeCl_3$	162.2	1000
Manganese	Mn	7+	54.94	$KMnO_4$	158.04	1000
Copper	Cu	2+	63.55	$CuSO_4.5H_2O$	249.55	1000
Lead	Pb	2+	207.2	$Pb(NO_3)_2$	331.2	1050
Zinc	Zn	2+	65.38	$Zn(NO_3)_2.6H_2O$	297.47	821
Cobalt	Co	2+	58.933	$CoCl_2.6H_2O$	237.933	1000
Cadmium	Cd	2+	112.403	$3CdSO_4.8H_2O$	769.56	1000
Nickel	Ni	2+	58.69	$NiCl_2.6H_2O$	237.71	1000

Table 3.1 Data for metal salts

Metal	λ max (nm)	Metal	λ max (nm)	Metal	λ max (nm)
Ag	328.068	Cr	205.552	Pd	340.458
Au	242.795	Hg	253.652	Pt	214.423
Cd	214.438	Mn	257.610	Zn	213.856
Co	238.892	Ni	232.003		
Cu	324.754	Pb	220.353		

Table. 3.2 The wavelength (λ max) chosen for metal concentration measurements.

3.2.3. UV/VIS spectrophotometry

A PU 8720 UV/VIS scanning spectrophotometer (Philips) was used for the analysis of chromium (VI) concentrations. The Cr (VI) content was measured by the absorption of the red purple coloured complex developed by the reaction of chromium (VI) with 1,5-diphenylcarbazide (0.25%) in acidified solution as follows (105):

The diphenylcarbazide solution was prepared by dissolving 0.25 g of 1,5-diphenylcarbazide in 100 cm^3 of 50% acetone. To 15 cm^3 of chromium (VI) solution in the concentration range of 0.2-0.5 ppm, sufficient 3 mol/dm^3 sulphuric acid was added to make the concentration about ~0.1 mol/dm^3 when subsequently diluted to 25 cm^3. 1 cm^3 of the reagent, 1,5-diphenylcarbazide was added and the mixture was diluted to 25 cm^3 with distilled deionised water. The solution was swirled to mix and was permitted to stand 15 minutes for full colour development. Absorbance was then measured within the first 30 minutes (106) after the addition of the diphenylcarbazide solution at a wavelength of 540 nm in a 1 cm cuvette.

3.2.4. X-ray powder diffraction

X-ray powder diffraction was carried out for carbon samples using a Philips PW 1730 generator with a Philips 1050/25 powder goniometer, and Philips PW 1390 measuring electronics. Copper Kα, using a nickel filter, was used as the incident radiation. The analysis was carried out by Mr. C. Lilley, X-ray analysis unit, Chemistry Department, Faculty of Natural Sciences, University of Hertfordshire.

3.2.5. Scanning electron microscope analysis

The dried adsorbents C160 and C200 were examined using a Camscan CS44 scanning electron microscope photographs to obtain the textural and surface information before sorption and to check for any precipitation of metals or compounds as a result of reduction by the sorption process.

Small pieces of the sorbent samples were mounted on a circular aluminium stub using a thin layer of adhesive. The specimen was rendered conductive by evaporation of a thin layer of carbon over the surface using Edwards E12E vacuum coating unit. The prepared sample was then placed in the microscope chamber and subjected to a 20 kV accelerating voltage. The analysis has been carried out by Mr. C. Lilley, Electron microscope unit, Chemistry Department, Faculty of Natural Sciences, University of Hertfordshire.

3.2.6. Electron microprobe elemental analysis

The analysis was carried out using a Camscan Editor energy disperse analysis system in the standardless mode (manufacturer's calibrations). The analysis has been also carried out by Mr. C. Lilley, Electron microscope unit, Chemistry Department, Faculty of Natural Sciences, University of Hertfordshire.

3.2.7. Surface area determination

The surface area of some carbon sorbents was measured in the laboratories of MCA Services, Units 1A & 1B, Melbourn Science Park, Melbourn, S. Cambridgeshire SG8 6EJ U.K. The size of the carbon used was between 1 mm and 0.212 mm and the surface area was measured via nitrogen adsorption (volumetric technique / Sorptoamatic). Activation and degassing were carried out at 120 °C for 3 hours under vacuum.

3.2.8. Infra-red spectroscopy

Infra-red spectroscopy was used to determine the surface functional groups on the surface of the adsorbents. The adsorbent samples were dried in the oven overnight to remove any water retained by adsorption from the air, which could interfere with observation of hydroxyl groups on the surface. This was followed by encapsulation into dry potassium bromide (KBr) discs. The discs were scanned in transmission mode using a Perkin Elmer Paragon 1000 FT-IR spectrometer through a wavelength range from 4000 to 800 cm^{-1} with background subtraction, and the number of scans used was 16.

3.2.9. pH monitoring

The pH value of solution was measured using a PHM 64 research pH meter, (Radiometer Ltd). The pH meter was calibrated using standard pH 4 and pH 7 buffers prior to the measurement of the initial or final pH in the batch experiments.

3.2.10. Elemental analysis: (CHN and S)

Elemental analysis of carbon, hydrogen, nitrogen and sulphur content of some carbon sorbents were performed by MEDAC Ltd., Brunel Science Centre, Cooper's Hill Lane, Englefield Green, Egham, Surrey TW20 0JZ, UK, using standard analytical methods. The samples C160 and C200 were analysed.

3.2.11. Ash content (107)

A clean crucible was ignited in the muffle furnace at 650 ± 20 °C for 1 hour, placed in a desiccator until room temperature was reached, the crucible was then weighed to the nearest 0.1 mg. About 6 grams of the sorbent (dried at 120 °C for two hours) was placed in the crucible and reweighed. The crucible with the adsorbent sample was placed in the muffle furnace at 650 ± 20 °C for 9 hours. The crucible was then placed in the desiccator to cool to room temperature. The crucible including ash was weighed to the nearest 0.1 mg.

3.3. Experimental Methods

Experimental work was carried out under good laboratory practice fulfilling the University safety regulations.

3.3.1. Optimisation for metal sorption and characterisation of some sorbents

After preparation washing and drying, the carbon sorbents were ground to a size between, 1 mm - 0.212 mm and stored in a desiccator under vacuum prior to the following experiments being carried out. Results of this experimental part are summarised and discussed in Chapter 4.

3.3.1.1. Sorption of mercury (II) and cadmium (II) from aqueous solution

Experimental procedure:

Samples of the carbons (~0.0660) g were added to a mercuric chloride solution (50 cm^3 of 200 mg/dm^3) at an initial pH of 5.00. For the sorption of cadmium, carbon (0.1000 g) was added to a cadmium sulphate solution (50 cm^3 of 100 mg/dm^3) at pH 6.0. The samples were shaken continuously in an incubator shaker (Controlled Environment Incubator Shaker, New Burnswick Scientific Co., Inc., Edison, N. J. USA) at a shaking rate of 150 rpm at 25 °C.

Preliminary kinetic experiments for cadmium (II) and mercury (II) from solution using dried carbon named as C160 showed that the equilibrium time was attained for cadmium (II) in about 3 hours and for mercury (II) in around 5 days (120 hours). Subsequent experiments on mercury (II) sorption were left to attain equilibrium in the shaker incubator for 120 hours, and cadmium samples were left in the incubator for 10 hours.

Once equilibrium had been attained, the solution was sampled, approximately 10 to 15 cm^3 were separated and 1 cm^3 of 0.5 mol/dm^3 nitric acid was added to the samples to minimise metal sorption losses on the glass and finally diluted to the required volumes to give concentrations in the range of the standards used and analysed in the ICP to determine the residual metal ion concentration. The final pH was also measured.

3.3.1.2 Cation exchange capacity

Cation exchange capacity (CEC) is a measure of the total amount of exchangeable cations that can be held by an adsorbent. The procedure used was a standard ASTM method (108). The theory of the test is as follows: the surface activity of colloidal carbon particles is mainly due to the functional groups carrying a negative charge. The negative charge results in the binding of hydrogen ions to the particle's surface. The unbound hydrogen or free hydrogen ions accounts for the acidity of the carbon while the bound hydrogen ions are considered potential acidity. Both forms are in chemical equilibrium and when the free hydrogen ions are neutralised or removed from the carbon, the potential hydrogen ions are replaced by other ions carrying positive charges, such as Ca^{2+}, Mg^{2+} and Na^+. When positive ions (cations) of one species are replaced by other positive charges on the surface of the particle, the process is called cation exchange. The total amount of all positive charges or cations adsorbed by the carbon is called cation exchange capacity. The quantity is expressed as meq/100g of dry sorbent or as here CEC is expressed as meq/g.

Procedure:

An accurately weighed sample of the dried sorbent (0.6 g) was placed in a 100 cm^3 flask, and after hydrochloric acid (AnalaR grade (50 cm^3 0.5 mol/dm^3)) was added the flask was shaken in a mechanical shaker incubator for one hour. This was followed by filtration using a fluted filter paper and the solid washed with distilled deionised water until a sample (10 cm^3) of the wash water showed no precipitate with 1 % silver nitrate solution (3 cm^3). The moist sorbent was then transferred to a clean 100 ml flask and shaken in a mechanical shaker incubator for one hour at room temperature with barium acetate solution (50 cm^3 0.25 mol/dm^3). The solution was then filtered with a glass Gooch G4 crucible and washed with distilled deionised water (3 x 50 cm^3). The sorbent was discarded and the filtrate and washings were titrated with 0.1 mol/dm^3 sodium hydroxide using phenolphthaline as indicator.

The CEC was calculated as follows,

$$mequiv./g\,dry\,sorbent = (cm^3\,x\,molarityNaOH)/g\,sample \qquad (3.1)$$

3.3.1.3. Acidity of the sorbents (109,110)

A sample of sorbent 0.100g was mixed with distilled decarbonated water (20 cm^3) and 2 drops of acetone, to facilitate wetting of the sample, in a clean dry round Quickfit flask. The flask was fitted with a suitable reflux condenser and the mixture was boiled for 15 minutes. The mixture was left to cool while the cold water was still allowed to run through the condenser. The electrode of a standardised pH meter was washed with distilled deionised water and then placed in the sludge, and rotated gently until constant pH was obtained to the nearest 0.01 unit.

3.3.1.4. Base neutralisation capacity

Neutralisation of 0.1 mol/dm^3 sodium bicarbonate, sodium hydroxide, sodium ethoxide and 0.05 mol/dm^3 sodium carbonate, by C160 and C200 in their dry state was studied by mixing 0.25 g portions with 50 cm^3 of the respective solution in 100 cm^3 Quickfit polyethylene bottles. The suspensions were flushed with nitrogen gas to remove oxygen present (111). This step was essential to circumvent the possibility of base–catalyzed auto-oxidation of carbons in the presence of oxygen (112). The suspensions were shaken mechanically for 72 hours covering the equilibrium time. The fall in concentration of each solution was determined by titration of an aliquot of the supernatant liquid against 0.1 mol/dm^3 HCl.

3.3.1.5. Ageing effect

Effect of the ageing upon the prepared carbon has been studied for dry carbons C160 and C200 under storage conditions in air. Also wet samples of both carbons were stored under aqueous acidic solution consisting of distilled water and few drops of concentrated sulphuric acid (5 drops in 1dm^3) to avoid any possible bacterial growth. The aqueous acid solution was changed every 2-3 weeks. Wet carbon, before use, was filtered, washed until free from acid and the moisture content measured as mentioned previously. A sample of C160, moistened with residual sulphuric acid (without washing) and then sealed was left for 30 months and then tested for the effect of ageing on its reactivity. The criteria of carbon activity tested for ageing effect were:

1. cation exchange capacity.
2. cadmium (II) sorption.
3. mercury (II) sorption.
4. base neutralisation capacity.

For base neutralisation capacity, dry sorbents only were used and for other tests both forms of sorbent, wet and dry, were used.

3.3.2. Sorption of metals from aqueous solutions

A range of metals have been studied and it was found that these could be divided into two groups: those for which sorption was fast and followed an ion exchange mechanism; and those where slow approach to equilibrium was observed which follows a mechanism of ion exchange / sorption coupled with reduction. Because of this difference in behaviour the experimental procedures and ensuing results have been separated.

3.3.2.1. Metal ions following ion exchange mechanism

Those metals which behave similarly to cadmium (II) showing fast kinetics such as chromium (III), cobalt (II), copper (II), nickel (II), lead (II) and zinc (II) are included. The following experiments were carried out, and the results are given in Chapter 5.

3.3.2.1.1. *Effect of time*

200 ml of ~ 50 mg/dm^3 of the metal solution were added to about 0.2 g of dry C160 and C200 (and their equivalent weight in wet form). Initial pH ranges of ~ 4–5 were used for most of metal ion solutions and sorption was followed for up to 8 hours.

3.3.2.1.2. *Effect of initial pH*

This experiment was carried out for cadmium (II) ions. A sample, 0.1 g of dry C200 (and the equivalent weight in wet form), was added to cadmium sulphate solutions (50 cm^3) of different concentrations in a clean dry polyethylene jar. The pH was adjusted before hand using drops of dilute NaOH and H_2SO_4. Samples were shaken until equilibrium was reached (10 hours), the metal ion concentration measured before and after the sorption process and the pH was measured at the end of the experiment.

3.3.2.1.3. *Effect of light metal ions*

At 25 °C, a sample of dry C200 (~ 0.1 g), or the equivalent weight of the wet carbon, was added to cadmium sulphate solution (50 cm^3 160 mg/dm^3) with different concentrations of some light metal ions. i. e. Na^+, K^+, Mg^{2+} and Ca^{2+} in their chloride form. Samples were shaken until equilibrium was achieved (10 hours) and the solution analysed for metal ion content.

3.3.2.1.4. *Sorption capacity and temperature effect*

At 25 °C, a sample of dry C160, C200 or the equivalent weight of the wet sorbent was added to the metal ion solution (50 cm^3) of different concentrations in a clean polyethylene jar and shaken until equilibrium had been reached (10 hours). The process was repeated for cadmium (II) at 35 and 45 °C. Once equilibrium was reached, 10 hours shaking, the solution was sampled and analysed for metal content.

3.3.2.2. Metal ions with sorption-reduction mechanism

This series of metals behave differently from those sorbed via ion exchange and similarly to mercury (II) showing a slow kinetic process. These metals include mercury (II), chromium (VI), gold (III), silver (I), platinum (II), platinum (VI), palladium (II), manganese (VII), and iron (III). Results of these experiments are given in Chapter 6.

3.3.2.2.1. *Effect of time*

C160 was chosen to investigate this group of metal ions. A sample of dry C160 or the equivalent amount of the wet sorbent was added to the metal ion solution (200 cm^3 of ~ 100 mg/dm^3 except gold (III) for which 100 ml were used) and the sorption was followed for up to 240 hours. pH adjustment was carried out by dropwise addition of an acid or sodium hydroxide. Experimental conditions are summarised within table 3.3.

Metal	Metal form	Volume (cm^3)	Wt Carbon C160 Dry (g)	pH	pH adjustment
Hg (II)	$HgCl_2$	200	~ 0.130	5.00	HCl, NaOH
Cr (VI)	$K_2Cr_2O_7$	200	~ 0.130	1.50	H_2SO_4, NaOH
		200	~ 0.255	4.50	H_2SO_4, NaOH
Au (III)	$AuCl_3$	100	~ 0.020	2.00	HCl, NaOH
Pd (II)	$PdCl_2$	200	~ 0.103	2.00	HCl, NaOH
Ag (I)	$AgNO_3$	200	~ 0.130	5.00	HNO_3, NaOH
Pt (II)	Na_2PtCl_4	200	~ 0.130	5.00	HCl, NaOH

Table 3.3. Experimental conditions applied for metal ions experiencing sorption-reduction on the carbon surface.

An aliquot of supernatant was withdrawn at different time intervals and residual metal concentration was analysed by Inductively Coupled Plasma - Atomic Emission Spectroscopy (ICP - AES), using a Perkin Elmer Plasma 40 Emission spectrometer.

In the case of chromium experiments, in addition, chromium (VI) has been measured by absorption of the reddish purple colour developed by reaction with 1,5-diphenylcarbazide in acidified solution (105). Absorbance was then measured at a wavelength of 540 nm. Chromium (III) was calculated as the difference between total chromium measured by ICP and chromium (VI) measured spectrophotometrically.

3.3.2.2.2. *Effect of initial pH*

The effect of pH was studied for mercury (II) and chromium (VI).

i. *Mercury (II)*

A sample range of dry carbon C160 (~ 0.064-0.070 g), or the equivalent weight of the wet sorbent, was added to mercuric chloride solution (50 cm^3) in a clean dry polyethylene jar. The pH was adjusted using drops of NaOH and HCl. The metal concentration was measured before and after the sorption process and the pH was measured in the end of the experiment.

ii. *Chromium (VI)*

A sample range of dry carbon C160 (~ 0.066-0.070 g), or the equivalent weight of the wet sorbent, was added to chromium (VI) solution (50 cm^3) in a clean dry polyethylene jar. The initial pH was adjusted using drops of sodium hydroxide and sulphuric acid. The pH range in this study was from 1.5 – 9.0. The pH was measured at the end of the experiment and chromium concentration was measured before and after the sorption process for both total chromium and chromium (VI) as described above.

3.3.2.2.3. *Light metal ion effect*

This experiment was carried out only for mercury (II). At 25 °C, a sample of dry C160 (~ 0.064-0.070 g), or the equivalent weight of the wet carbon, was added to mercuric chloride solution (50 cm^3 300 mg/dm^3) with different concentrations of some light metal ions. e. g. Na^+, K^+, Mg^{2+} and Ca^{2+} in their chloride form.

3.3.2.2.4. *Sorption capacity and temperature effect*

Sorption capacity was measured for mercury (II), chromium (VI), silver (I) as follows: At 25 °C, a sample of dry C160 (~ 0.064-0.070 g) or the equivalent weight of the wet sorbent, was added to a solution of the metal at different concentrations in a clean polyethylene jar, shaken until equilibrium was reached, and residual concentrations have been analysed.

Initial pH was 6.5 for mercury (II) [mercuric chloride], 3.0, 5.0 and 7.0 for chromium (VI) [potassium dichromate], and 5.0 for silver (I) [silver nitrate].

For gold (III), 40 ml of the desired gold concentrations with ~ 20 mg of the carbon (or its equivalent weight of the wet form) have been used. The initial pH was 2.00. Equilibrium times for mercury (II), chromium (VI), gold (III) and silver (I) were (80, 120), (96, 120), (48, 72) and (160, 185) hours for wet and dry C160 respectively.

The process was repeated at 35 and 45 °C for mercury (II) and chromium (VI) and only at 45 °C for silver (I) and gold (III).

Similar weights of carbons were used for 50 cm^3 of different concentrations of mercuric nitrate solution of initial pH 3.0 at 25 °C only for equilibrium times as that for mercury (II) chloride (80 hours for wet and 120 hours for dry C160).

Experimental data are shown in table 3.4

Metal species	Volume (cm^3)	Carbon wt C160 (g)	Initial pH	Equilibrium time (hours)		Temperature (°C)
				wet	Dry	
$HgCl_2$✫	50	0.064-0.070	6.5	80	120	25, 35, 45
$HgNO_3$*	50	0.064-0.070	5.0	80	120	25
$K_2Cr_2O_7$**	50	0.064-0.070	3, 5, 7	96	120	(at pH 3) 25, 35, 45
$AuCl_3$✫	40	0.014-0.019	2.0	48	72	25, 45
$PdCl_2$✫	40	~ 0.05	2.0	70	120	25
$AgNO_3$*	50	0.064-0.070	5.0	160	185	25, 45
Na_2PtCl_4✫	50	~0.066	6.5	240	240	25
Na_2PtCl_6✫	50	~0.066	5.0	240	240	25
$KMnO_4$**	50	0.02-0.03	1.3	72	72	25
$FeCl_3$❖	50	0.10-0.12	2.4	240	240	25

* pH was adjusted by drops of HNO_3/NaOH

** pH was adjusted by drops of H_2SO_4/NaOH

✫ pH was adjusted by drops of HCl/NaOH

❖ $FeCl_3$ solution was flushed with a stream of nitrogen to make sure that there was no oxygen in solution left.

Table 3.4. Sorption capacity conditions applied for metal ions behaving differently to ion exchange.

For manganese (VI), $KMnO_4$, the following experiment as in table 3.4 was carried out, a solution of 1000 mg/dm^3 (0.018 mol/dm^3) was prepared, and acidified by sulphuric acid, (pH 1.3). A suitable weight of wet C160 equivalent to 0.02 g or ~0.03 g of the dry material was added to 50 cm^3 of the solution. The sorption system was shaken for 72 hours and filtered through a millipore cellulose ester 0.22 μm filter. The idea of filtration was to remove the carbon with permanganate sorbed together with the precipitated manganese dioxide from the solution. The filtrate contained both non-sorbed and the reduced soluble form, i.e. manganese (II). The method of analysis can be summarized as follows:

(I) Initial Mn was measured using ICP.

(II) Residual manganese in the filtrate containing both manganese (II) and permanganate. The total manganese was measured by ICP analysis after acidifying 5 cm^3 of the filtrate with sulphuric acid (5 cm^3 4 mol/dm^3), diluted to 25 cm^3 in a volumetric flask.

(III) Permanganate remaining in solution was measured iodometrically:
10 cm^3 of the filtrate was acidified with 6 mol/dm^3 sulphuric acid and ~1g potassium iodide added. The resulting iodine was analysed by titration with standardised 0.05 mol/dm^3 thiosulphate. Starch solution was added near the equivalence point.

Calculation:

Manganese (II) content of filtrate = total manganese(II) in solution - permanganate content (III).

sorbed/reduced manganese = total initial concentration (I) - total filtrate concentration (II).

The experiment with iron (III) was shaken continuously in the incubator for 11 days and then the solution was filtered and analysed as follows (105):
To measure iron (II), 10 cm^3 of the iron solution was acidified with 20 cm^3 1 mol/dm^3 sulphuric acid and 3 cm^3 phosphoric acid. The solution was titrated with potassium dichromate (9.617x10^{-3} mol/dm^3) using diphenyl amine as indicator. In another titration, the equilibrium iron (III) was reduced to iron (II) (105) and total iron (II), which is the total iron content at equilibrium, was then measured using the dichromate titration as mentioned above (105). Initial iron solution was also measured by the same method.

3.3.3. Carbon dioxide determination

Reduction of mercury is accompanied by oxidation of the carbon sorbent to carbon dioxide. The carbon dioxide was flushed out of solution by a stream of nitrogen gas, in a closed system into Dreschel bottles containing barium hydroxide solution. Barium hydroxide reacts with the evolved carbon dioxide to give a precipitate of barium carbonate. Weighing the barium carbonate at the end of the reaction gives the amount of carbon dioxide evolved from the reaction mixture.

The apparatus shown in figure 3.1 was set up as follows:
A 3-necked round bottom flask was fitted with a nitrogen bubbler in one arm, a stopper in the top and the third arm was connected to four Dreschel bottles in series. The second, third and fourth bottles were intended to retain any carbon dioxide which did not react in the first bottle.

Mercuric chloride solution (200 cm^3 of 6000 mg/dm^3) and 5% barium chloride solution were prepared in decarbonated water which in turn was prepared from distilled water by heating to boiling under a nitrogen gas atmosphere, and then left to cool to room temperature. The flask containing the decarbonated water was then carefully closed. Each Dreschel bottle was filled with decarbonated water (40 cm^3), 5% barium chloride (20 cm^3), few drops of phenolphthalein and one or two drops of carbonate-free sodium hydroxide, (approximately 1mol/dm^3).

Carbonate-free sodium hydroxide was prepared as follows (105): A concentrated solution was prepared in decarbonated water by dissolving AR sodium hydroxide pellets from a newly opened bottle in an equal weight of water. The mixture was immediately sealed, shaken and allowed to stand. The sodium carbonate remains insoluble and the supernatant liquid was withdrawn and diluted to the required concentration in decarbonated water and immediately closed.

Nitrogen was flushed through the mercury (II) chloride solution for around 30 minutes to remove any carbon dioxide from the system. The apparatus was assembled as in figure 3.1 and about 0.85 g on the dry basis of a wet sample of carbon C160 was added to the mercury (II) chloride solution, the system was closed immediately and apparatus flushed with nitrogen.

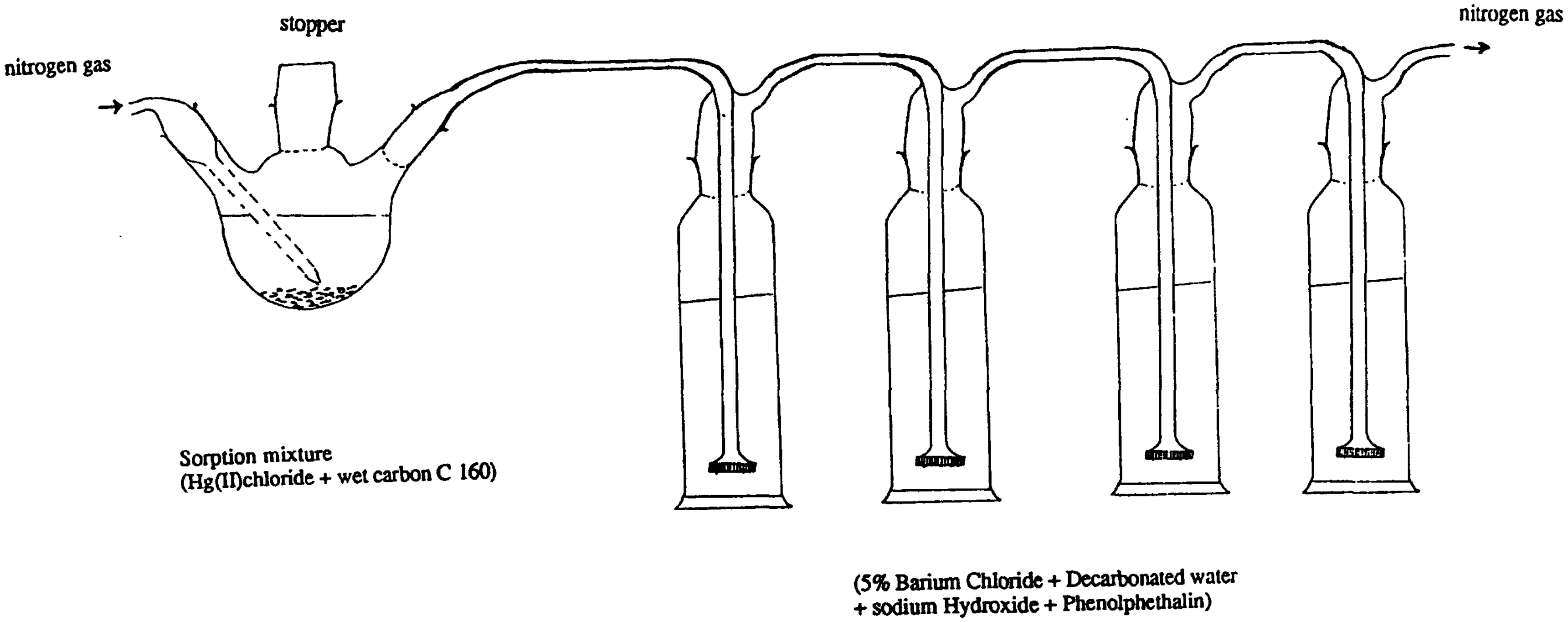

Fig. 3.1. A system for the collection of carbon dioxide evolving from the sorption reaction of Hg (II) and wet carbon C160.

The temperature of the reaction mixture was kept at about 60 °C during the sorption process by immersing the vessel in a water bath. The pH of the reaction mixture was readjusted several times to maintain a pH of 5-6. The only check needed during the experiment was to ensure that the solution in the Dreschel bottles remained pink (alkaline) so that the barium carbonate formed does not redissolve. A few drops of sodium hydroxide were added to the barium solution when required under the condition that the bubbler stayed under the surface of the barium solution so that no carbon dioxide was lost.

The reaction was run continuously for 72 hours. At the end of the experiment, the apparatus was disconnected, the mercury solution was filtered through a clean and dry Gooch G4 crucible, and the residual concentration of mercury (II) was measured by ICP. The barium solution / barium carbonate precipitate from the Dreschel bottles (the majority of which was concentrated in the first bottle) was collected in a well-closed container and left for 24 hours to allow particle growth and then filtered through a dry and pre-weighed glass fibre microfilter (particles above 1.2 μm retained). The glass fibre was dried at 105 °C for two hours, transferred to the desiccator until cool and reweighed to constant weight. The weight of barium carbonate was measured.

3.3.4. The cumulative metal sorption capacity

The cumulative metal sorption capacity of C160 was carried out using the semi-continuous batch sorbent system as follows. A 50 cm^3 solution of 100 mg/dm^3 of cadmium (II), sulphate media of pH 6.00 was mixed with ~0.1 g of dry C200 and left for 10 hours to equilibrate. The sorbent was separated by filtration, and mixed with a new aliquot of the same initial solution. A sample of the filtrate was separated to be analyzed using the ICP. The process was continued for 7 cycles.

For mercury, a 50 cm^3 solution of 500 mg/dm^3 of mercury (II), chloride media, at a pH of 4.5, was mixed with ~0.105 g or its equivalent in the wet form for the equilibrium time (80 hours for wet, 120 hours for dry). After filtration of the solution, the experiment was repeated using fresh aliquots of the mercury solution for 12 cycles.

The experiment was also carried out for mercury (II) from natural water containing various concentrations of sodium, potassium, calcium and magnesium ions at an initial pH 6.6. Wet sorbent was used and the experiment was repeated for 6 cycles.

3.3.5. Column studies

A fixed bed of the sorbent was prepared as represented schematically in figure 3.2. A glass column with a sintered glass disc at the bottom was used. The column was prepared by placing a 0.5 cm of clean sand over the sintered glass disc, followed by suitable weight of carbon sorbent (if dry sorbent was used it was previously immersed in deionised water for 2 hours) added to the column, which was filled with distilled water; and the column was gently tapped to facilitate uniform packing of the bed. The process was continued until all the carbon was loaded. After the column was prepared, the metal solution was pumped through the bed from top to bottom at a suitable rate via a peristaltic pump (ISMATEC, IPN-8). Samples of the effluent were collected automatically in suitable sample tubes held in sample collector (2112 REDIRAC fraction Collector, LKB, BROMMA). Samples were analysed by ICP for metal ion concentration.

3.3.5.1. Cadmium (II) sorption using a fixed bed column sorption system

A sample of C200 dry carbon (1.5 g) was immersed in distilled water for about two hours for wetting. The carbon sample was then loaded in a column of 0.55 cm diameter, length 8.5 cm (bed volume 8.1 cm^3). Cadmium (II) solution (85 mg/dm^3 cadmium at pH 6.00) was pumped through the column at a flow rate of 2.6 cm^3/minute, remaining in contact with the carbon for 3.12 minutes. The pH of the final solution was about 4.0. After column loading reached a plateau, the column was washed with 0.5 mol/dm^3 sulphuric acid at a rate of 2.6 cm^3/minute for 80 minutes (~26 bed volumes) and then washed with distilled deionised water to free the column from sulphuric acid until no precipitation with barium chloride solution and no change in methyl orange occurred. The column was then connected again to the cadmium solution of the same concentration and pH. The loading cycle was repeated 7 times.

3.3.5.2. Mercury (II) sorption using a fixed bed column sorption system

A wet sample of C160 (equivalent to ~ 1 g on a dry basis) was loaded in a column of radius 0.67 cm and length 11.02 cm mercury (II) chloride solution of 200 mg/dm^3 of pH

4.5. Mercury (II) solution was pumped thorough the column in a flow rate of 1.11 cm^3/minute, remaining in contact with the sorbent for 14 minutes. The process was carried out in both a continuous and intermittent regime. In the intermittent regime, mercury solution flowed for 4 hours continuously and then the system was stopped for 8 hours, and the process was repeated for a number of bed volumes equal to the continuous regime.

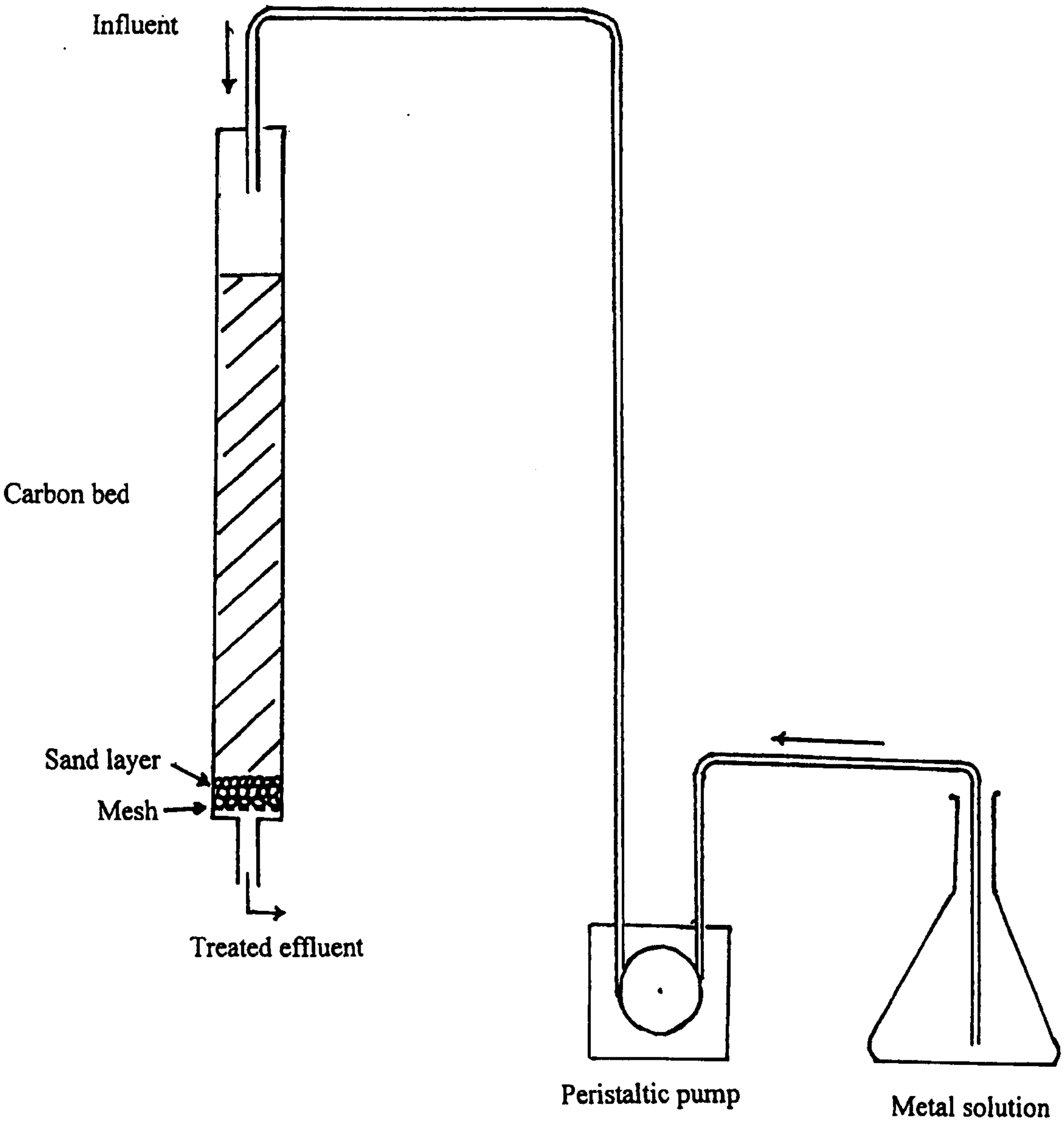

Figure 3.2. Schematic representation of carbon column for metal treatment.

3.4. Data Analysis

Sorption experiments were repeated at least three times. The preparation of carbon sorbents under different conditions was carried out twice and the test experiments for optimisation were repeated three times. Standard deviations and analytical errors were calculated and the maximum analytical error was found to be < 5 %.

CHAPTER 4

RESULTS AND DISCUSSION I. PREPARATION AND CHARACTERISATION OF CARBON BY REACTION WITH SULPHURIC ACID AND ITS OPTIMISATION FOR HEAVY METALS SORPTION FROM AQUEOUS SOLUTIONS

4.1. Introduction

Flax shive is a woody material, which contains, as major components, cellulose, hemicellulose and the non-carbohydrate compound, lignin, table 2.3 (chapter 2, section 2.4). Some information about these three components, which may be useful to understand their role in the preparation of carbon by dehydration, is presented below:

4.1.1. Cellulose and hemicellulose

Cellulose is the main component of the cell wall in plants. It consists of repeat units of anhydro-β-D-glucopyranose linked together by β-1,4-glucosidic bonds, as shown in figure 4.1.

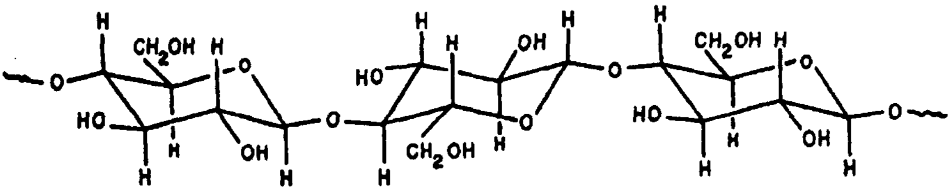

Figure 4.1. Structure of a molecule of cellulose

Two kinds of hydrogen bonds are known within the native cellulose (113):

intra-chain hydrogen bonding between C-2 hydroxyl hydrogen and the pyranose ring oxygen atom on one side of each pyranose residue and also between C-3 hydroxyl hydrogen and the C-6 hydroxyl oxygen atom on the other side;

inter-chain hydrogen bonding where cellulose chains are linked laterally by inter-chain hydrogen bonding occurring between C-6 hydroxyl hydrogen atom on one chain and the C-3 hydroxyl oxygen atom on the other (113). The reaction site for the hydrolysis of cellulose (113) is the glucosidic linkage between the anhydroglucopyranose units while for oxidation, esterification and etherification the reaction sites are the hydroxyl groups on C-2, C-3 and C-6.

Cellulose is very susceptible to oxidising agents due to the presence of three hydroxyl groups in each anhydroglucose unit. Oxidising agents cause cellulose to break down to the lower molecular weight material, oxycellulose (114,115). Oxidation of cellulose adds aldehyde, ketone and carboxylic functional groups in the structure (114). Addition of oxygen to the oxygen bridge forms a peroxide which is followed by scission of the macromolecule at this point. The resulting non-homogeneous product has a high reducing capacity and a lower mechanical fibre strength (114).

Hemicellulose refers to the readily hydrolyzable carbohydrate of the cell wall (114), and consists of shorter chain polysaccharides than cellulose. Hemicelluloses (114) include mainly pentosans and hexosans. Pentosans have five carbon atoms in the repeat unit $(C_5H_8O_4)_n$, where n is the degree of polymerisation. On hydrolysis, it gives pentoses such as xylose and arabinose. Hexosans are carbohydrates with six carbon atoms in the repeat unit $(C_6H_{10}O_5)_n$, which on hydrolysis, gives hexoses (e.g. galactose and mannose). The role of hemicelluloses, in general, is to provide a linkage between lignin and cellulose (116).

4.1.2. Lignin

Lignin, is one of the principal constituents of the woody structure. It acts as a cementing agent to bind the matrix of cellulose fibres together into a rigid structure (117). Lignin is a natural polymer containing carbon, hydrogen and oxygen. It is composed of phenylpropane units bonded to each other via C-C and C-O-C bonds, see figure 4.2, and it is heterogeneous and chemically complex. It is associated with, and to some extent covalently bonded to, plant cell wall hemicelluloses (118). The exact chemical structure of lignin as it occurs in plants is not known. The functional groups available in lignin include hydroxyl, methoxy and carbonyl, ethylenic double bonds and dioxymethylene groups (117,114).

Compared with cellulose and other wood polysaccharides, lignin is more easily oxidised (114) and is susceptible to a wide range of oxidants. Thus molecular oxygen degrades lignin to aromatic aldehydes and carboxylic acids, while nitric acid degrade the aromatic rings of lignin (119). Oxidation of lignin usually yields products of extensive oxidation, such as

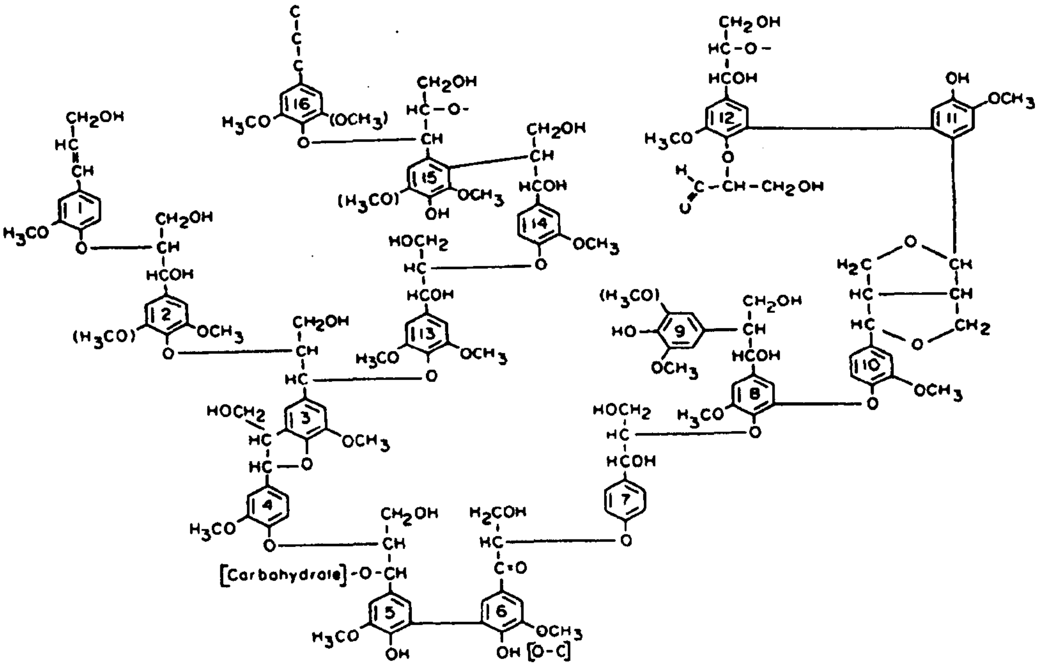

Figure 4.2. Structure of lignin. (118), [It is not a quantitative accurate depiction of the various substructures (118)].

carbon dioxide, acetic acid, malonic acid, succinic acid and oxalic acid. Such products are obtained by treating lignin with hydrogen peroxide in neutral and weakly acidic media (114).

4.1.3. Effect of sulphuric acid on flax shive

As noted above, flax shive contains both carbohydrates and lignin and the effect of sulphuric acid on these materials is different. Thus hemicelluloses are readily hydrolysed by dilute acids and bases, even water at high temperatures causes the conversion of hemicellulose into soluble products (120). Cellulose, as a result of its high crystallinity and cohesive density, is insoluble in water (113) and more resistant to dilute acids (120) however strong acids, strong alkalis, and concentrated salt solutions can swell and even dissolve cellulose (116).

Concentrated sulphuric acid behaves as an extremely strong dehydrating agent, decomposing carbohydrates by the removal of water. Sugar, for example, in contact with concentrated sulphuric acid reacts and leaves a carbonaceous material as shown in equation 4.1 (48).

$$C_{12}H_{22}O_{11} \xrightarrow{H_2SO_4} 11\,H_2O\,(H_2SO_4) + 12\,C + \text{heat.} \qquad (4.1)$$

By mixing concentrated sulphuric acid at room temperature with carbohydrates (cellulose and sugars), a black colloidal suspension of varying particle size is obtained (95). Concentrated sulphuric acid also acts as a strong oxidising agent because of its tendency to lose an atom of oxygen to form sulphurous acid, H_2SO_3, which readily decomposes to sulphur dioxide and water (121).

Nikitin observed that concentrated sulphuric acid (72 % and above) rapidly dissolved cellulose in the cold, forming clear solutions. When the solutions were allowed to stand, they blackened as a result of carbonisation of cellulose. The same effect may be attained by increasing the temperature (114).

Dilute or concentrated sulphuric acid, when used at higher temperature, causes carbonisation of the woody material. Hanzawa *et al* (51) prepared carbon from saw-dust by treatment with sulphuric acid. The concentration of sulphuric acid ranged from dilute acid concentrations (1, 5, 15 and 40 %) to the concentrated form of the acid (70, 98 %) at 120 °C for 8,14 and 24 hours and at 150 °C for 4 and 8 hours. It was found that low concentrations such as 1% were not sufficient to cause carbonisation and with 15 and 40 % sulphuric acid, the yield of the carbon was lower than that obtained when using other higher concentrations.

Preliminary studies in this work showed that using 4, 6, 8 mol/dm^3 sulphuric acid carbonisation did take place but the yield of the carbon and the sorption capacity for both cadmium (II) and mercury (II) were low.

It can be concluded that three processes may occur at relatively high temperatures by mixing sulphuric acid with flax shive carbohydrates (cellulose and hemicellulose) namely swelling and hydrolysis, carbonisation, and partial oxidation.

On the other hand, lignin behaves differently from the carbohydrate components. When treating powdered wood with sulphuric acid, the polysaccharides (as mentioned above) are hydrolysed whereas lignin is obtained as a non-hydrolysed dark coloured residue (114). This material, obtained from using 64-72 % sulphuric acid, is called Klason lignin (118).

Optimising the preparation conditions of carbon by dehydration of any woody structure is a difficult task since it depends on the nature of the raw material used, the method of treatment, and the intended use of the carbon. From this study it is also evident that the method of preparation influences the formation of active groups on the carbon which affects the sorption behaviour with different metals. Pichugin *et al* (57) investigated the preparation of carbon from flax shive by dehydration using sulphuric acid, basing the optimisation on mercury (II) sorption and the yield of the sorbent (58). Carbon prepared using 12 mol/dm^3 sulphuric acid at 150-155 °C with a weight ratio of 1: 5-6 shive: acid and a reaction time for 15-20 minutes was recommended from these studies (58).

In the present work, 12 mol/dm^3 sulphuric acid was chosen to investigate the effect of temperature, weight-volume ratio (flax shive: sulphuric acid) and the reaction time on the resulting carbon sorbents. Three main factors were chosen to assess the preparation of a suitable sorbent for different metal systems:

sorption capacity of metal ion from solution using mercury (II) and cadmium (II);
yield of the carbon;
acid and energy consumption.

4.2. Yield

The effect of reaction time on the carbon reflects a slight decrease in yield as shown in table 4.1. Changing the weight-volume ratio of reactants shows very little variation in the yield, table 4.1, although it was found that lower ratios such as 1:3 were not capable of carbonising some hard pieces of the flax shive. It also appeared that with the ratio of 1:5 there was virtually no residual acid left and some hard pieces of shive were not well carbonised. Data are also shown in appendix I, table 4.1.

Variation of acid concentration and temperature both showed a significant and similar effect on the yield. While with 10 mol/dm^3 sulphuric acid the yield was low, it reached a maximum at 12 mol/dm^3 and then gradually decreased until 18.2 mol/dm^3, i.e. concentrated sulphuric acid. The filtrate in the case of 10 mol/dm^3 sulphuric acid was blacker than the other concentrations used. Using the optimal concentration of the acid (12 mol/dm^3) at different reaction temperatures, it was found that at 100 °C a low yield was obtained and the filtrate was very black. The yield gradually increased as the temperature increased until at 160 °C the yield was a maximum. Further increase in the temperature gave a decreasing yield. It was also observed that the filtrate became less dark as the temperature increased.

Reaction Time (min.) [a,b,c]	Yield %	Reaction Temp. (°C) [a,b,d]	Yield %	Ratio of flax shive : H_2SO_4 (wt : v) [a,c,d]	Yield %	H_2SO_4 concn. (mol dm^{-3}) [b,c,d]	Yield %
10	60.2	100	50.4	1 : 5	57.3	10	46.7
20	59.0	120	54.8	1 : 7	58.2	12	58.3
30	58.5	140	57.0	1 : 9	58.3	14	56.9
45	58.2	160	58.3	1:12	57.6	16	53.4
60	58.0	180	54.2			18.2	51.3
		200	50.2				

a. sulphuric acid concentration 12 mol dm^{-3}; b. flax shive: H_2SO_4 ratio 1:9; c. reaction temperature 160 °C; d. reaction time 25 minutes.

Table 4.1. Yield of carbon sorbents as a function of preparation conditions.

4.3. Cation Exchange Capacity

Cation exchange capacity (CEC) studies were undertaken to obtain information about the total amount of exchangeable cations that can be bound by a particular sorbent sample. The experimental ASTM procedure and theory are described in section 3.3.1.2. The sorbent was protonated by the hydrochloric acid and the excess acid removed by washing with distilled water leaving the sorbent with protonated functional groups. Barium ions were used to replace the protons on the sorbent and the resultant acidic solution titrated with sodium hydroxide in the presence of an indicator. The results were expressed as meq/g.

The results, in table 4.2 and figures 4.3 - 4.6, show that CEC increases as the reaction time increases while there is no significant change in CEC with the change in ratio of flax shive to sulphuric acid in the range 1:5 - 1:12. However the cation exchange capacity shows a large increase as the temperature was raised while maintaining the other variables constant, so that using 12 mol/dm^3 sulphuric acid an approximate three fold increase in CEC for the carbon prepared at 200 °C was observed when compared with that prepared at 100 °C.

Reaction Time (min.) [a,b,c]	CEC (meq g^{-1})	Reaction Temp. (°C) [a,b,d]	CEC (meq g^{-1})	Ratio of flax shive: H_2SO_4 (wt : v) [a,c,d]	CEC (meq g^{-1})	H_2SO_4 concn. (mol dm^{-3}) [b,c,d]	CEC (meq g^{-1})
10	1.47	100	1.00	1:5	1.43	10	1.18
20	1.50	120	1.19	1:7	1.65	12	1.72
30	1.71	140	1.35	1:9	1.71	14	2.42
45	2.03	160	1.71	1:12	1.69	16	2.77
60	2.12	180	2.31			18.2	2.94
		200	2.78				

a. sulphuric acid concentration 12 mol dm^{-3}; b. flax shive: H_2SO_4 ratio 1:9; c. reaction temperature 160°C; d. reaction time 25 minutes.

Table 4.2. Cation exchange capacity of the carbon sorbents as a function of preparation conditions.

Similar CEC results were found when the effect of acid concentration was investigated. As the concentration of the sulphuric acid increased the CEC increased, increasing approximately three fold from 10 to 18.2 mol/dm^3 acid. Data are also shown in appendix I, table 4.2.

4.4. Acidity of the Sorbents

The pH of the aqueous slurry of the carbon material provides a convenient indicator of the surface groups on carbon. The pH of the carbon is mainly related to the concentration of carboxylic groups with only a very slight addition from sulphonic groups due to the low concentration of sulphur in the carbon structure. As the concentration of such functional groups increases on the carbon surface, the pH of the carbon decreases. A carboxylic group on carbon acts as a Bronsted acid in water according to the following equilibrium reaction (122):

$$—COOH + H_2O = —COO^- + H_3O^+$$

The experimental ASTM procedure for the pH determination of granular activated carbon and carbon black was used as discussed in section 3.3.1.3. In this study ~0.1 g of the carbon sorbents were used which is less than that specified in the ASTM method.

Reaction Time (min.) [a,b,c]	pH	Reaction Temp. (°C) [a,b,d]	pH	Ratio of flax shive : H_2SO_4 (wt : v) [a,c,d]	pH	H_2SO_4 concn (mol dm^{-3}) [b,c,d]	pH
10	3.18	100	3.35	1 : 5	3.10	10	3.24
20	3.11	120	3.26	1 : 7	3.05	12	3.06
30	3.03	140	3.11	1 : 9	3.05	14	3.02
45	3.01	160	3.05	1 : 12	3.05	16	3.00
60	2.95	180	3.01			18.2	2.79
		200	2.85				

a. sulphuric acid concentration 12 mol dm^{-3}; b. flax shive: H_2SO_4 ratio 1:9; c. reaction temperature 160°C; d. reaction time 25 minutes

Table 4.3. pH values of the carbon sorbents as a function of preparation conditions.

This was because of the higher content of the functional groups in the carbons prepared in this work. Table 4.3 shows the pH values of the carbon sorbents prepared. A slight decrease in the pH value was found as the reaction time increases, but there is no real significant change when different ratios of sulphuric acid are used. An obvious change in the pH was obtained by increasing the temperature and increasing the concentration of the sulphuric acid. These results are similar to those found for the cation exchange capacity, figures 4.3 - 4.6, (appendix I, table 4.3).

4.5. Moisture Content

The moisture content for the whole range of carbon sorbents is very similar with values ranging from ~83% to 88%, table 4.4. This moisture is present due to the swelling of the carbons during preparation and washing (appendix I, table 4.4).

Reaction Time (min.) a,b,c	Moisture (%)	Reaction Temp (°C) a,b,d	Moisture %	Ratio of flax shive :H_2SO_4 (wt : v) a,c,d	Moisture (%)	H_2SO_4 concn. (mol dm^{-3})^{b,c,d}	Moisture (%)
10	84.2	100	85.0	1 : 5	83.2	10	84.2
20	86.1	120	84.8	1 : 7	87.0	12	86.6
30	86.7	140	86.4	1 : 9	86.7	14	86.7
45	86.4	160	86.9	1 : 12	87.6	16	86.4
60	84.9	180	85.2			18.2	84.9
		200	85.3				

a. sulphuric acid concentration 12 mol dm^{-3}; b. flax shive: H_2SO_4 ratio 1:9; c. reaction temperature 160°C; d. reaction time 25 minutes.

Table 4.4. Moisture content of carbon sorbents as a function of preparation conditions.

4.6. Sorption of Cadmium (II)

Sorption of cadmium (II) by the carbons prepared under different conditions, as described above, shows similar results to that of cation exchange capacity and pH values. Results are shown in table 4.5, appendix I and also in figures 4.3 - 4.6.

As the reaction time increases cadmium (II) uptake increases. Sorption shows that there is a slight decrease for the carbon prepared using the 1:5 weight-volume ratio while it is approximately the same for the other weight-volume ratios. There is a large increase in uptake as the reaction temperature increases. Thus, there is a three-fold increase in cadmium (II) uptake onto the carbon prepared at 200 °C compared to the value obtained with that prepared at 100 °C, similar to the CEC results. A similar three-fold increase was also found as the concentration of the sulphuric acid increases, from 10 to 18.2 mol/dm^3. The pH of the cadmium solution after sorption was measured (appendix I, table 4.5) and as the amount of cadmium (II) sorption increased the final pH decreased. The relatively fast kinetics, the similarities to the cation exchange capacity results, and the pH of the final solutions indicate that the mechanism of sorption of cadmium (II) onto the carbons is most probably due to an ion exchange process.

4.7. Sorption of Mercury (II)

The sorption of mercury (II) onto the carbon sorbents behaves in a different way from that found for cadmium (II) and the cation exchange capacity data. This perhaps indicates a different sorption mechanism between cadmium (II) and CEC results on one hand and mercury (II) on the other. The kinetic studies show that equilibrium is attained after about 120 hours for mercury (II), whereas for cadmium (II) is around 3 hours.

The results of the mercury (II) sorbed by different carbons are shown in table 4.6, appendix I, and in figures 4.3-4.6. The first feature to note from these figures is that the uptake of mercury (II) is very much higher than cadmium (II) under the same conditions.

Carbons prepared at the lowest reaction time, 10 minutes, show lower mercury (II) uptake than those prepared at 20 minutes but no significant increase in the mercury (II) uptake was observed for longer reaction periods. Changing the relative amount of 12 mol/dm^3 sulphuric acid shows no real significant change in the mercury (II) sorption.

With respect to the carbons prepared at different reaction temperatures, the mercury (II) uptake increases with temperature up to 160 °C after which it is approximately constant for sorbents prepared at higher temperatures. The difference in mercury (II) uptake at 160 °C compared to that at 100 °C is less than two fold.

Carbons prepared with 10 mol/dm^3 sulphuric acid show a slightly lower sorption value than that prepared by 12 mol/dm^3 acid but no significant change occurs when high sulphuric acid concentrations are used.

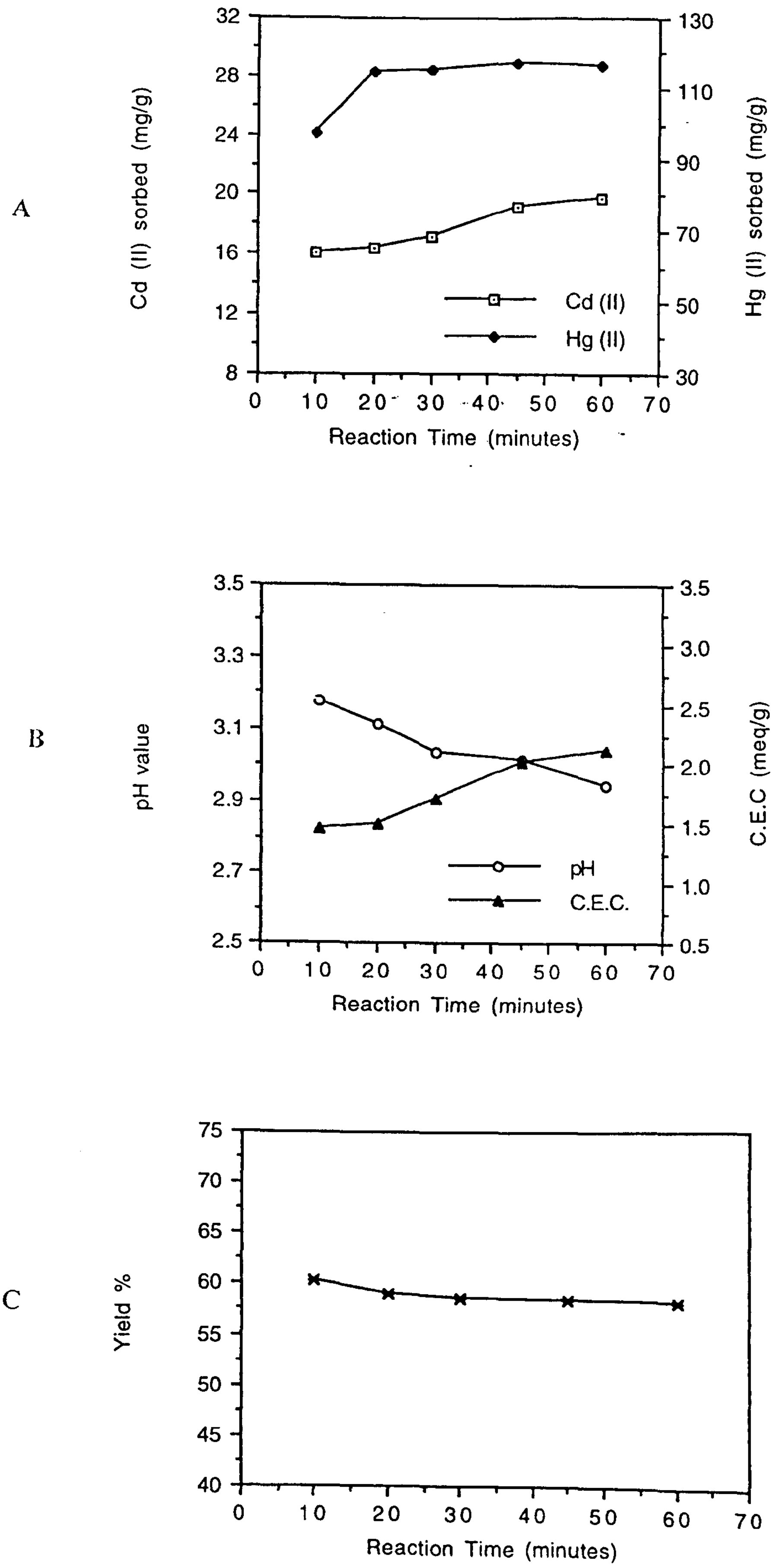

Figure 4.3. Effect of reaction time on the properties of carbon sorbents. 15 g shive + 12 mol dm^{-3} sulphuric acid (in a ratio of 1:9, wt: vol.) at 155-160°C for 10, 20, 30, 45 and 60 minutes.

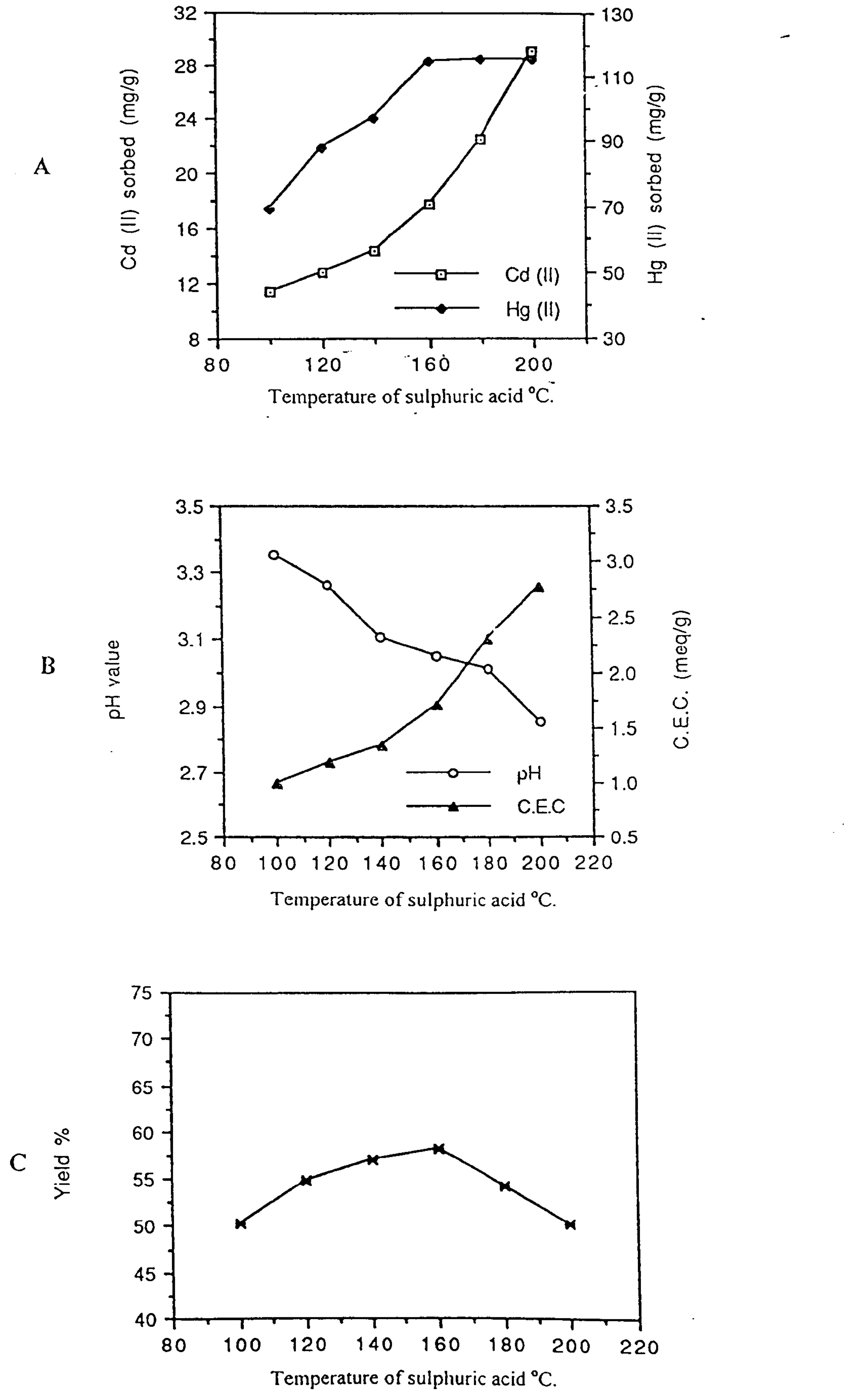

Figure 4.4. Effect of sulphuric acid temperature on the properties of carbon sorbents. 15g shive + 12 mol dm^{-3} sulphuric acid (in a ratio of 1: 9, wt: vol.) at 100, 120, 140, 160, 180 and 200°C for 25 minutes.

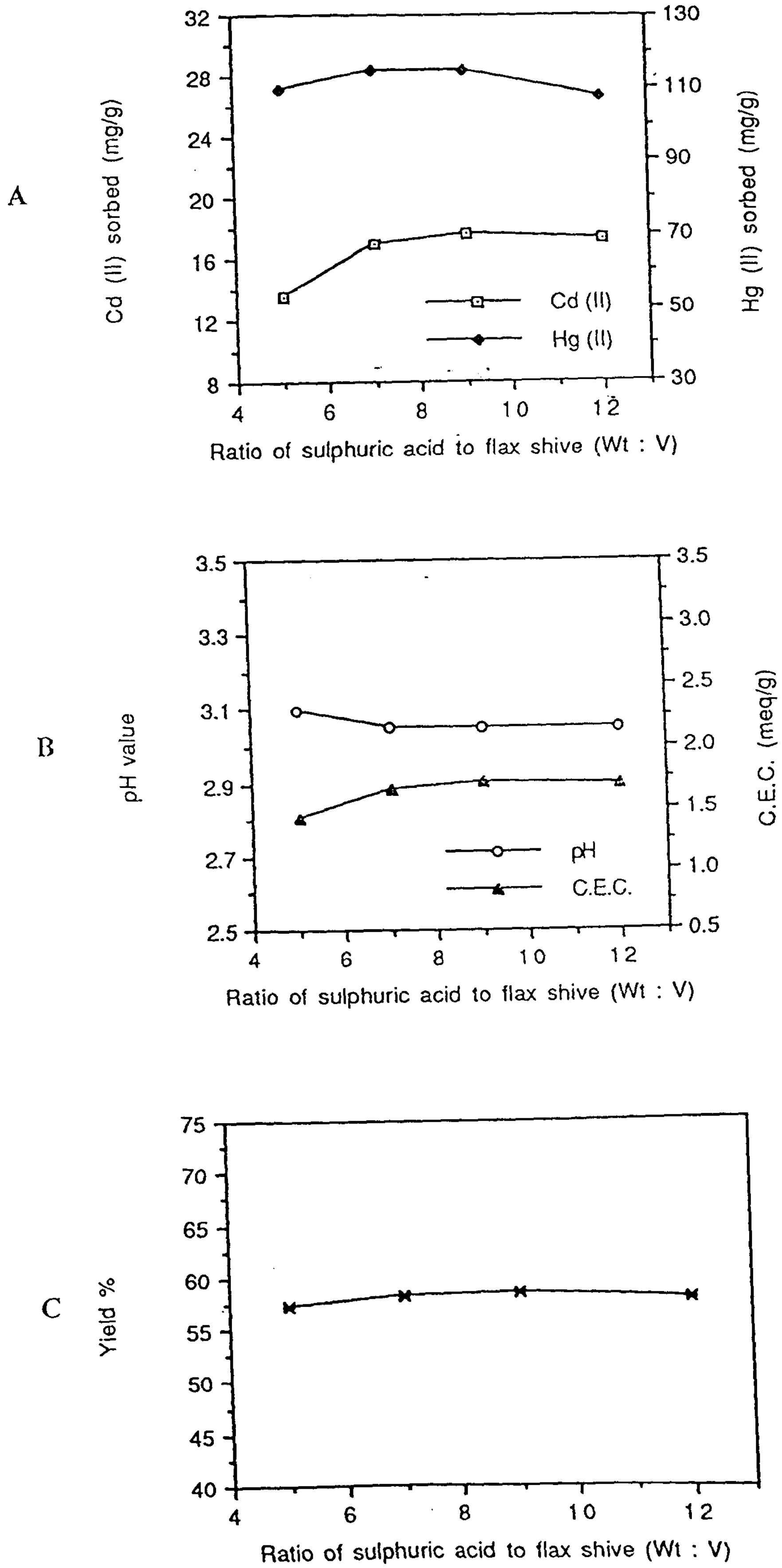

Figure 4.5. Effect of ratio of flax shive to sulphuric acid (12 mol dm^{-3}) on the properties of carbon sorbents. 15 g shive + 12 mol dm^{-3} sulphuric acid with relative ratios 1:3, 1:5, 1:7, 1:9 and 1:12 at 155-160°C for 25 minutes.

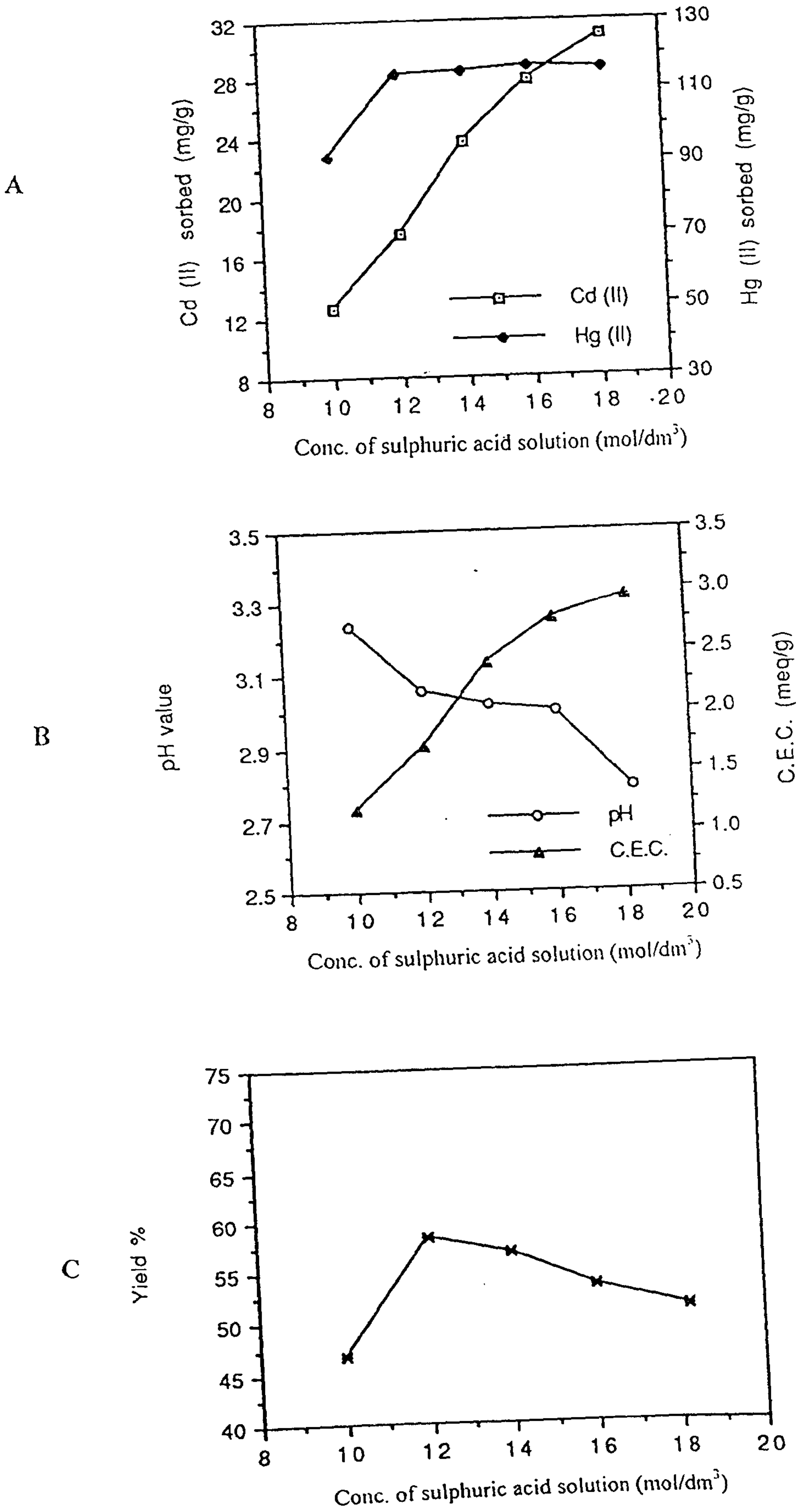

Figure 4.6. Effect of sulphuric acid concentration on the properties of carbon sorbents.
15 g shive + 10, 12, 14, 16 and 18.2 mol dm^{-3} H_2SO_4 in a ratio of 1: 9 at 155-160°C for 25 minutes.

4.8. Discussion: the effect of sulphuric acid on flax shive

Comparing the difference in yield of carbons obtained by varying the reaction time and the weight-volume ratio of flax shive to the acid on one side, and varying the temperature and concentration of the acid on the other, the latter are more effective in producing a high yield.

Reaction time has, in general, little effect on the yield and other related studies, while the weight-volume ratio has virtually no effect on yield and other properties. Thus it can be concluded that there are two main factors affecting the yield and properties such as cation exchange capacity, pH and cadmium (II) sorption. These two factors are reaction temperature and the concentration of the sulphuric acid. The difference between these results and those obtained by Komoto (56) may be related to the different conditions of preparation and the different starting materials.

Three processes can take place by the reaction of sulphuric acid with flax shive, which may be considered as a woody material: swelling and hydrolysis, carbonisation and partial oxidation. The extent of each process depends mainly on temperature and concentration of the acid and to some extent on the reaction time. Room temperature and low sulphuric acid concentration enhances hemicellulose hydrolysis and causes cellulose to swell.

With low concentrations of sulphuric acid at high temperature, carbonisation occurs and this process increases as sulphuric acid concentration increases. Partial oxidation of the carbonised product also takes place at high temperature and high acid concentration. These processes can be used to explain the above results.

With respect to reaction time, it is found that increasing reaction time decreases the yield and pH slightly, while sorption of cadmium (II) and the cation exchange capacity increase slightly. This can be explained by the evaporation of water during preparation and the resulting concentration of acid leading to an increase in oxidation. This in turn leads to partial fragmentation of the carbon skeleton, hence a slight decrease in the yield, and an increase in the carbon-oxygen groups on the surface of the product which act as additional cation exchange groups. This was clearly shown from the change in the cation exchange capacity, pH and cadmium sorption results.

Varying reaction temperature using 12 mol/dm^3 sulphuric acid, the yield follows a parabola. At lower temperatures, e.g. 100 °C, hydrolysis takes place to a large extent for hemicellulose which acts as a binding agent between cellulose and lignin (116). This leads to a loss of lignin from the reacting shive pieces and the filtrate becomes much darker than at higher temperatures and a low yield is found. Oxidation at such low temperatures is not significant. This is shown clearly from the results of cation exchange capacity, pH and cadmium (II) sorption. As the temperature increases, evaporation of water takes place and the acid becomes more concentrated, and so carbonisation of the polysaccharides occurs to a larger extent, until it reaches a maximum at 160 °C. In this case, lignin seems to be encased inside the carbon particles where it is retained and so the filtrate shows less blackening. This oxidation again leads to an increase in the carbon-oxygen groups as shown by CEC, pH and cadmium (II) sorption. As the temperature increases further to 200 °C, the oxidation process continues to create more carbon-oxygen groups and also maybe fragments of lower molecular weights from the carbon particles to give a lower yield of carbon with higher CEC, cadmium sorption, and lower pH value.

Similar results have been found with the change of the concentration of the sulphuric acid. Using 10 mol/dm^3 sulphuric acid, hydrolysis seems to occur to a large extent, lignin fragmentation takes place leading to release from the carbons and as a result, more blackening of the filtrate is found and lower yields. Using 12 mol/dm^3 acid a maximum in yield is found similar to that with reaction temperature. With higher concentration of the acid, oxidation of the carbonised product takes place which produces a higher concentration of the carbon-oxygen groups on the surface of the carbon. Probably fragmentation to lower molecular weight compounds also takes place to give lower yields. CEC, pH and cadmium sorption shows greater increase in the functional groups than treatment with lower acid concentration.

As mentioned earlier, the following three main factors were considered in the selection of a suitable sorbent for different metal systems: sorption of metal ion from solution (mercury (II) and cadmium (II)), percentage yield of the carbon, and acid and energy consumption. The two carbons selected for further study were carbon C160 and C200. Both of these samples used the same sulphuric acid concentration (12 mol/dm^3) and weight: volume ratio of flax: acid of 1:9 but varied in their reaction temperature. Thus C160 was treated at 160 °C for 25-30 minutes and C200 was treated at 200 °C, also for 25-30 minutes.

C200 showed a good performance for cadmium (II). Metal ions behaving similarly to cadmium (II) and which follow the CEC results, and did not show reduction, are summarised in Chapter 5. The sample C160 was shown to be best suited for the sorption of metals such as mercury (II) which reduced on the carbon surface. Mercury (II) and metal ions that behave similarly are discussed in Chapter 6.

4.9. Base Neutralisation Capacity

Surface functional groups on carbon mainly depend on the precursor materials and the treatment method followed to produce the carbon material. Since the precursor material here is flax shive, which is composed mainly of cellulose, hemi-cellulose and lignin which have high oxygen content, in addition to sulphuric acid treatment (dehydration/ oxidation), different function groups are created on its surface during the process.

The various surface functional groups available on the carbon surface can be determined using selective neutralisation by equilibration with a series of bases of increasing strength. Boehm (123) differentiated the acidic groups on oxidized charcoal and carbon black by selective neutralisation techniques using $NaHCO_3$, Na_2CO_3, NaOH and NaOEt.

$NaHCO_3$ neutralises strongly acidic groups which were postulated as carboxylic groups; whereas those neutralised by Na_2CO_3 but not by $NaHCO_3$ were believed to be lactones, sodium carbonate allows lactone groups to open and form carboxyl groups which are neutralised (122). The weakly acidic groups neutralised by NaOH but not by Na_2CO_3 were postulated as phenols. The reaction with NaOEt was not considered as a true neutralisation reaction since it did not involve exchange by H^+ or Na^+ ions (124). The groups reacting with NaOEt but not with NaOH were suggested to be carbonyl (124), (quinoid–type) (122), groups. For a given carbon, the amounts of different bases neutralised vary in the order: NaOEt >NaOH > Na_2CO_3 > $NaHCO_3$.

However, Rivin (125) has cautioned that the selective neutralisation technique sets arbitrary limits on acidity ranges for each group which may not be realistic for all carbons. He has argued that the acidity of surface groups may depend upon the carbon crystallites to which they are attached and to their point of attachment. Thus it is probable that the same acidic functional group, depending on its location, may have different acidic strengths.

Tessmer *et al*, (126), noted that the determination of the acidic functional groups by the base neutralisation method accounts for only about 50% of the total oxygen content of the carbon and that the remainder of the total oxygen content may be in the form of ether-type oxygen or less reactive carbonyl groups.

In this work these bases were put in contact with the carbon samples for 72 hours under continuous shaking. It was observed that a yellowish brown colour was released in a solution of NaOH and a lower intensity of such colour was observed in carbonate and bicarbonate solutions. In the case of NaOEt, virtually no release of this colour into the solution was seen. The colour was more intense in the case of C200 than C160. The colour being released could be due to the solubility of some lignin in the base (115).
Neutralisation data are shown in table 4.5a confirming the sequence mentioned above.

Carbon	$NaHCO_3$, meq/g	Na_2CO_3, meq/g	NaOH, meq/g	NaOEt, meq/g
C160	2.44	3.52	5.46	5.9
C200	3.52	5.09	7.14	7.62

Table 4.5a. Base neutralisation capacity data.

From table 4.5a, different surface function groups can be estimated (111) as in table 4.5b. As shown in tables 4.5a,b, base neutralisation capacities, and consequently the functional groups on carbon surface for C160 for all bases used are less than that of C200. This is explained by the presence of more functional groups on the C200 surface as a result of greater oxidation during preparation.

Carbon	Carboxylic (meq/g)	Lactonic (meq/g)	Phenolic (meq/g)	Carbonyl (meq/g)
C160	2.44	1.08	1.95	0.46
C200	3.52	1.56	2.06	0.47

Table 4.5b. Estimated surface groups on carbon surface.

4.10. Elemental Analysis

Elemental analysis included CHN (and sulphur analysis) and electron microprobe elemental analysis. The results of the analysis of carbon, hydrogen, nitrogen and sulphur are shown in table 4.6. Carbon comprises about 60% of the total composition in both samples with a small increase in C160. Hydrogen in C200 is less than in C160 while sulphur is a little higher in C160 than in C200. Nitrogen which was found in the composition of flax shive as a minor component (table 2.3 Chapter 2) does not appear in the composition after the treatment process. The little nitrogenous material which is present may be oxidised and escape as oxides of nitrogen during treatment. The total percent of C, H and S in C160, 64.20%, is a little higher than in C200, 63.02%. This suggests that there may be more oxygen in C200 than C160 which is indicated by higher CEC in the former sample arising from an increase in C—O functional groups.

Sorbent	Element wt %				
	C	H	N	O	S
C160	59.87	3.20	-		1.13
	66.38 $_m$		-	32.20 $_m$	1.42 $_m$
C200	59.58	2.60	-		0.84
	64.82 $_m$		-	34.03 $_m$	1.15 $_m$

($_m$) refers to the microprobe elemental analysis which was performed in a standardless mode and wt percentage was measured excluding the other components including hydrogen and other trace metals.

Table 4.6. Elemental analysis and microprobe elemental analysis for C160 and C200.

Electron microprobe elemental analysis, even though it was performed in a standardless mode, excluding hydrogen and other trace metals in the structure, showed a similar pattern for carbon and sulphur as the elemental analysis results (table 4.6). The derived oxygen results from the above elemental analysis are also supported by this study.

4.11. Surface Area

The surface area of both of carbon C160 and C200 of respective apparent density of 0.243 and 0.278 mg/cm^3, was measured by nitrogen adsorption by MCA services. Sample particles ranging from 1 mm - 212 μm, were activated at 120 °C for 3 hours under high vacuum to ensure the desorption of any sorbed gases or vapours. The higher temperatures that are used for activated carbons (200-350 °C) were avoided to minimise any possible chemical changes which could take place at the carbon surface.

The surface area was calculated from the equation outlined by Brunauer, Emmet and Teller (45,127). The BET equation is:

$$\frac{P}{(P_o - P)V} = \frac{1}{V_m C} + \frac{C-1}{V_m C} \cdot \frac{P}{P_o} \qquad (4.2)$$

Where , V = volume of nitrogen adsorbed expressed in cubic centimetre per unit weight of the solid surface (g).

V_m = monolayer capacity of the solid.

P = equilibrium pressure of nitrogen.

P_o = Saturated vapour pressure of nitrogen.

P/P_o = relative pressure.

$$C \approx e^{-(E_1 - E_L)/RT}$$

C is a measure of the heat of adsorption of the first adsorbed layer of nitrogen (E_l) and the heat of liquefaction of nitrogen (E_L).

Compared to activated carbon, the products obtained by dehydration of flax shive, table 4.7, show a much lower surface area. Prior to activation, thermally prepared carbon is practically inactive and it has a surface area of the order of several m^2/g (44).

Carbon	V_m (cm^3/g)	surface area (S_{BET}) (m^2/g)	BET$_C$
C160	4.364	19	610
C200	5.051	22	537

Table 4.7. Nitrogen surface area, monolayer capacity and BET constant of carbon C160 and C200.

The surface area of the carbons C160 and C200 shows not much difference from that of peat, which is around 27 m^2/g, and lower than that of lignite which is around 100 m^2/g (74). The untreated peat and lignite contain many complex organic waxes and esters and these result in the peat and lignite having a closer non-porous structure with little or no micropores (128).

Activated carbon upon treatment with oxidising agents shows a decrease in surface area (47). This is related to the presence of carbon-oxygen groups on the surface of the carbon, which occupy a proportion of the carbon surface.

The carbons produced by dehydration, C160 and C200, keep the fibrous woody structure and the available pores seem to be the tubular pores arising from the dehydrated tissue of the woody material. By compaction of the carbon as a result of drying the opportunity for micropores is either very low or non-existent. So that few or no micropores are available within the carbon particles. This kind of carbon has a very high organic content with such compounds as lignin, esters, humic substances and waxes probably present. These materials in addition to the presence of the high content of carbon-oxygen functional groups, leads to the observed low surface areas.

4.12. Ash Content

The ash content of C160 (0.51%) seems to be less than C200 (0.87%). This may be related to the lower yield of the carbon prepared at 200 °C, C200, and so the percentage of ash seems to be relatively higher than in C160.

4.13. Scanning Electron Microscopy

The SEM Camscan CS44 was used to obtain surface and textural information of the carbons C160 and C200 as described in section 3.2.5. Photographs of the sorbents taken at different amplifications are presented in figures 4.7 and 4.8. Both carbons seem to keep the plant structure as shown from the cross-section photographs and the morphology of the surface.

4.14. X-ray Powder Diffraction

The X-ray diffraction spectra were determined using copper Kα radiation and Ni filter as described earlier. The X-ray results shown in figures, 4.9, 4.10, show no identified peaks and thus both carbons seem to be amorphous in structure.

4.15. FTIR Studies

Even though the carbonised materials, C160 and C200, are rather complex, FTIR still can give some information about the probable functional groups on the surface. FTIR spectra for C160 and C200 are shown in figure 4.11. The intense and broad bands at 3388 cm^{-1} and 3387 cm^{-1} in C160 and C200 respectively are connected with the (O—H) stretching vibrations. The OH groups are associated by means of hydrogen bonds since the frequency of free OH groups is sharp and located above 3500 cm^{-1} (129). The OH groups on the carbon probably interact with water adsorbed by the carbon samples as suggested by Zawadzki (130). The shoulders at 2924 cm^{-1} and 2849 cm^{-1} in both spectra denote the presence of stretching C—H vibrations in CH_2 group (131). The intense broad band at 1702 cm^{-1} for C160 and at 1707 cm^{-1} for C200 suggests the presence of stretching C═O vibrations in configurations such as lactone, quinone (129), and carboxylic acids (131).

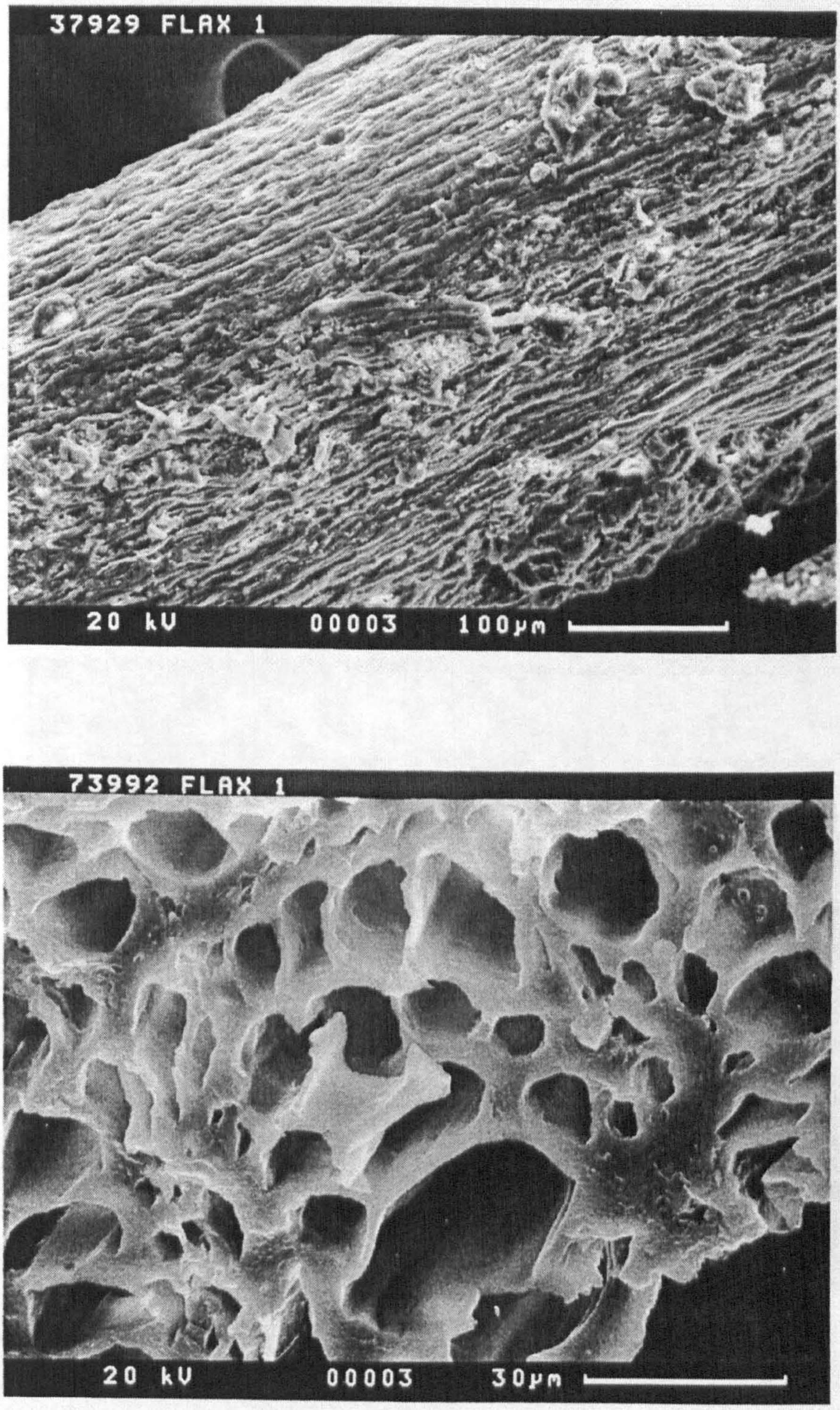

Figure 4.7. Scanning electron microscope photographs of the carbon C160.

A) Exterior surface B) Cross section

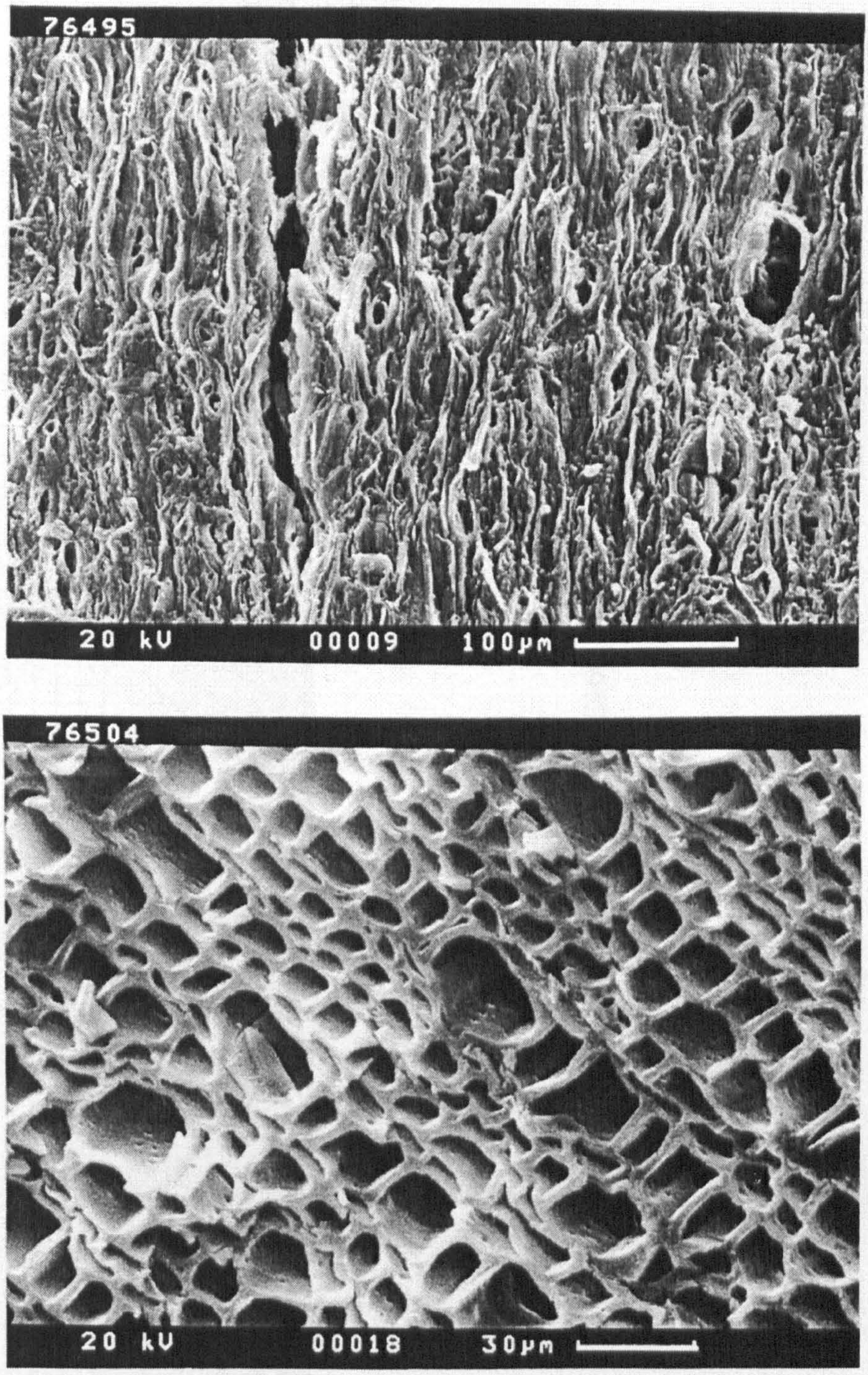

Figure 4.8. Scanning electron microscope photographs of the carbon C200

A) exterior surface B) cross section

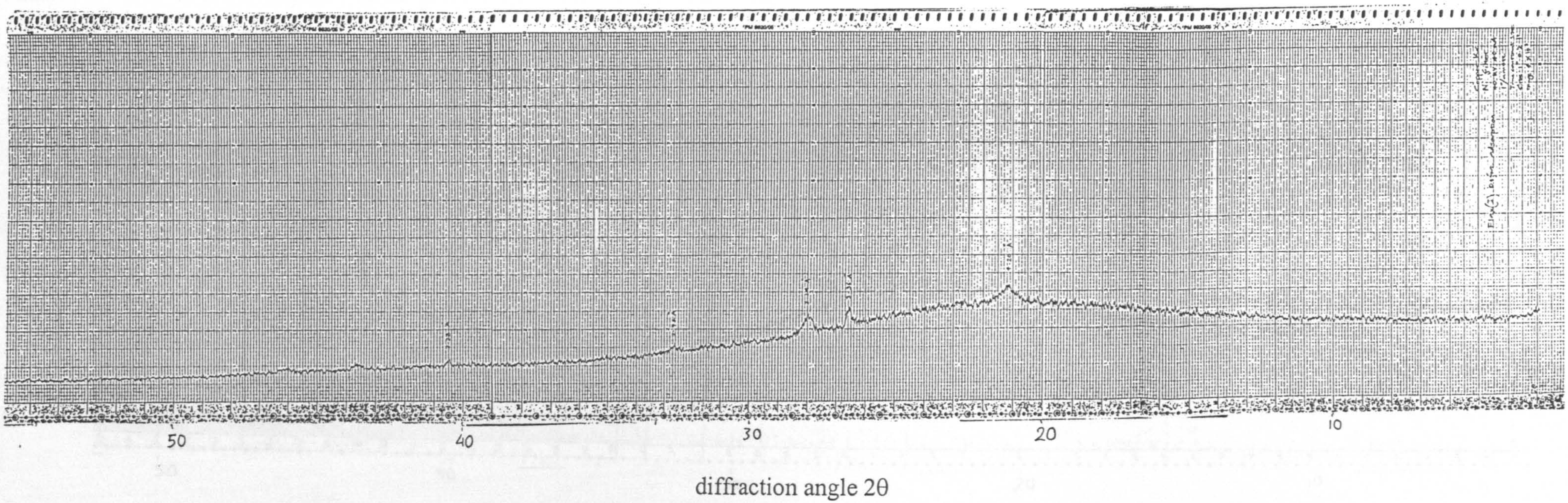

Figure 4.9. X-ray diffraction pattern of carbon C160.

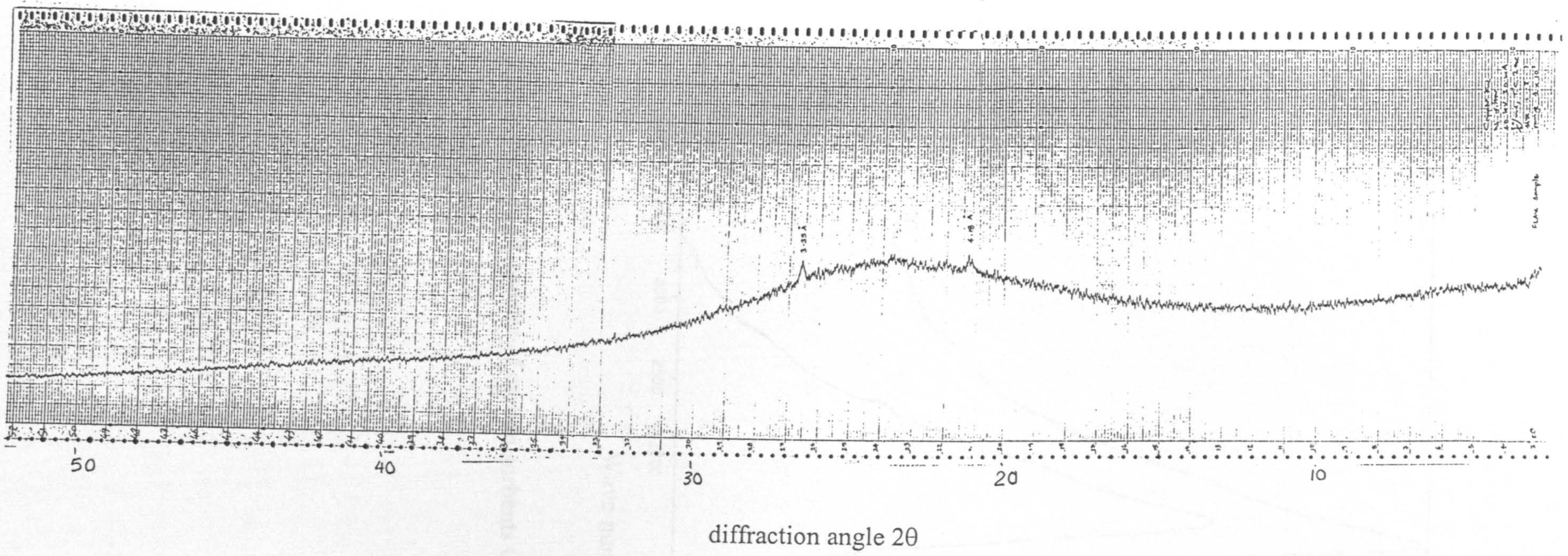

Figure 4.10.. X-ray diffraction pattern of carbon C200.

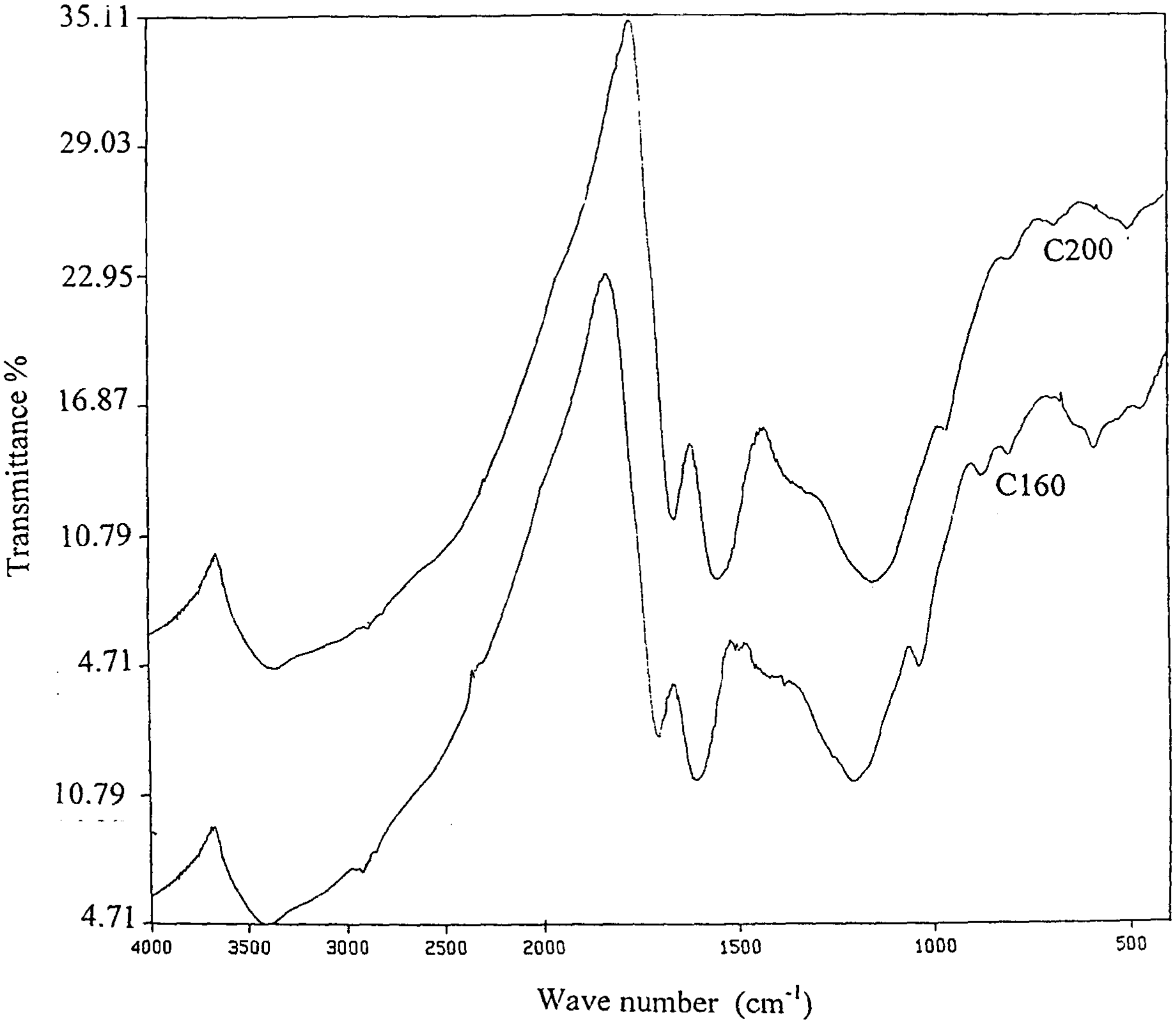

Figure 4.11. FTIR spectra of carbon sorbents C160 and C200.

The intense band around 1600 cm^{-1} for both carbons, C160 at 1610 cm^{-1} and C200 at 1604 cm^{-1}, may be due to the asymmetric and symmetric stretching COO^- vibrations or to skeletal C═C aromatic vibrations (129,132). Bands also appearing in the range 1600 cm^{-1} range in spectra of carbonaceous films were attributed to vibrations in iono-radical structure (130,133) and in coal spectra to hydroxyl groups along with conjugated C═C (134).

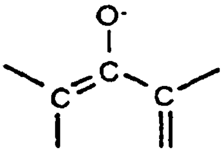

Figure 4.12 iono-radical structure

The various bands and shoulders from 1300-900 cm^{-1} are variously ascribable to stretching C—O vibrations in hydroxyl groups and ether type structures (129); aromatic ether or epoxy groups (C160 1209 cm^{-1}, C200 1222 cm^{-1}) (129). ═C—O symmetric stretching 1038 cm^{-1} (129) and phenolic OH or aliphatic OH could also occur in this range (129,132).

As shown in figure 4.11, the band ~ 3390 cm^{-1}, ~ 1700 cm^{-1}, 1600 cm^{-1}, and ~ 1210 cm^{-1} are more intense and a slightly wider in the carbon C200 than in C160 which could reflect the greater concentration of C═O and COO^- as a result of more oxidation to the carbon surface at 200 °C.

4.16. Ageing Effect

It was important in this study to check the ageing effect on the carbon sorbents (C160 and C200) being contacted with air occasionally for the dry materials, and for the wet samples stored under deionized distilled water for the period of study which lasted for one year. It was important for the material stored under wet conditions to change the water from time to time to avoid any bacterial growth on the carbon sorbents. A sample of C160 was also stored under acidic condition (moistened with residual sulphuric acid after preparation) by being sealed and left for 30 months and then being tested for any ageing effect.

In other studies, activated carbon, oxidised by hydrogen peroxide treatment, was exposed to ambient air for two years and was tested for any ageing effects by titration with different bases and with hydrochloric acid (135). The carbon showed no change in the functional groups on the surface after storing for two years. Thus activated carbon, from this study, seems to be resistant towards ageing.

The ageing effect for the carbons under investigation was tested by following the changes in the cation exchange capacity, mercury (II) and cadmium (II) removal for a period of one year, and in base neutralisation capacity which was carried out for the carbons after preparation and at the end of the storing test period. The dry carbon C160 and C200 had a moisture content of ~7% under such conditions. Acidic stored samples under wet conditions were washed with distilled deionised water (as in Chapter 3, section 3.1.1.1.2.), filtered and kept as wet in distilled deionised water, and a sample was separated, dried in oven and used as a dry carbon.

Cadmium sorption increases slightly with time for both forms of the carbons, wet and dry, showing a slightly greater increase for the dry carbons than the wet ones which were stored under dilute acid conditions, (figure 4.13). CEC (cation exchange capacity) results show a similar trend to that for cadmium (II) sorption on carbon sorbents, increasing with time, with a slightly higher capacity for dry sorbents than for wet ones, figure 4.14.

The neutralisation capacity for all bases used increases with ageing for both carbon sorbents, table 4.8a. This shows that the carbon surface tends to be oxidized by ageing, in open air, increasing the surface acidity. While a sample of C160, stored for 30 months moistened with sulphuric acid, shows virtually no variation to the freshly tested samples. Also, C200 still shows more removal capacity for cadmium (II) and for CEC.

Carbon	$NaHCO_3$, meq/g	Na_2CO_3, meq/g	NaOH, meq/g	NaOEt, meq/g
C160*f*	2.436	3.517	5.462	5.921
C200*f*	3.518	5.086	7.144	7.618
C160a	2.866	3.831	6.312	6.669
C200a	4.444	4.871	8.040	8.372
C160*s*	2.424	3.415	5.552	6.103

Table 4.8a. Base neutralisation capacity data. (*f* freshly prepared, *a* after one year of preparation, *s* stored in residual sulphuric acid for 30 months).

The concentration of each individual functional group could therefore be estimated from the differences in these values (111,135) as shown in table 4.8b. The increase of concentration of the functional groups on the surface, mostly those capable of sorbing metals such as -COOH and -OH, could be related to the oxidation of carbon by air.

Carbon	Carboxylic (meq/g)	Lactonic (meq/g)	Phenolic (meq/g)	Carbonyl (meq/g)
C160*f*	2.436	1.081	1.945	0.459
C200*f*	3.518	1.564	2.058	0.474
C160*a*	2.866	0.965	2.482	0.357
C200*a*	4.444	0.427	3.1687	0.332
C160*s*	2.424	0.991	2.137	0.551

Table 4.8b. Functional groups on the carbon surface. (*f* freshly prepared, *a* after one year of preparation, *s* stored in residual sulphuric acid for 30 months).

Mercury (II) capacity, on the other hand, shows a highly significant decrease with ageing and a greater decrease for dry than wet sorbents. Wet sorbents show little decrease compared to the dry ones, figure 4.15. Also, C160 moistened with acid for 30 months shows approximately no change compared to that freshly prepared (appendix I, tables 4.7- 4.9). In addition, the monolayer capacity from the Langmuir isotherm was calculated and was found to be 323 and 286 mg/g for wet and dry samples respectively which is quite similar to that the freshly prepared ones (wet: 345, dry: 303 mg/g) of C160, as shown later in table 6.2,

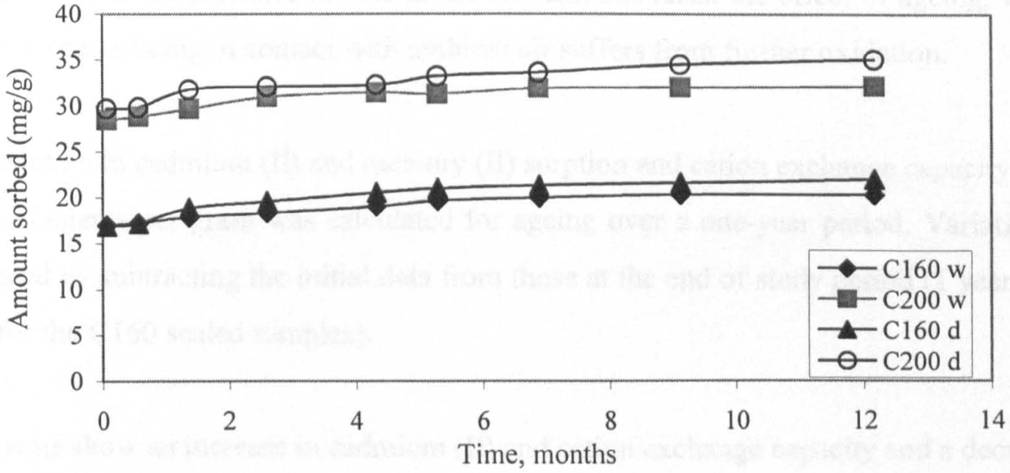

Figure 4.13. Effect of ageing on cadmium (II) sorption on C160 and C200.

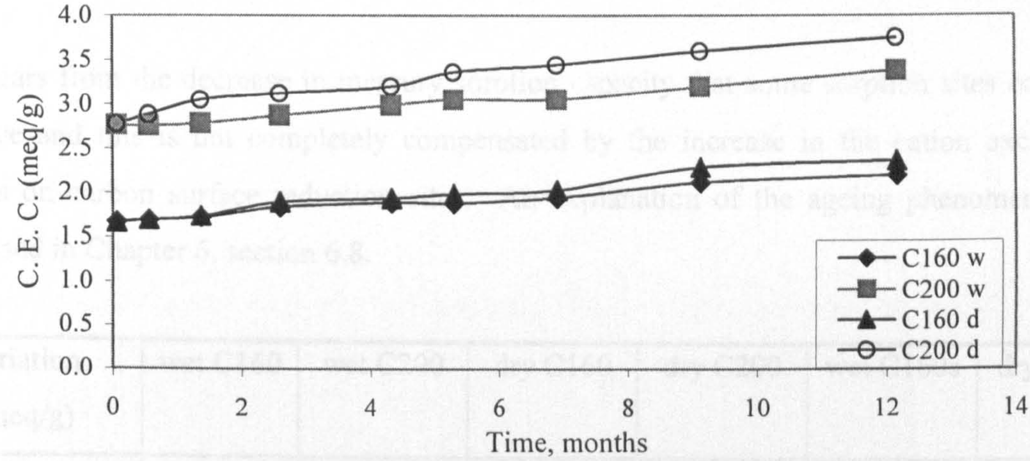

Figure 4.14. Effect of ageing on cation exchange capacity of C160 and C200.

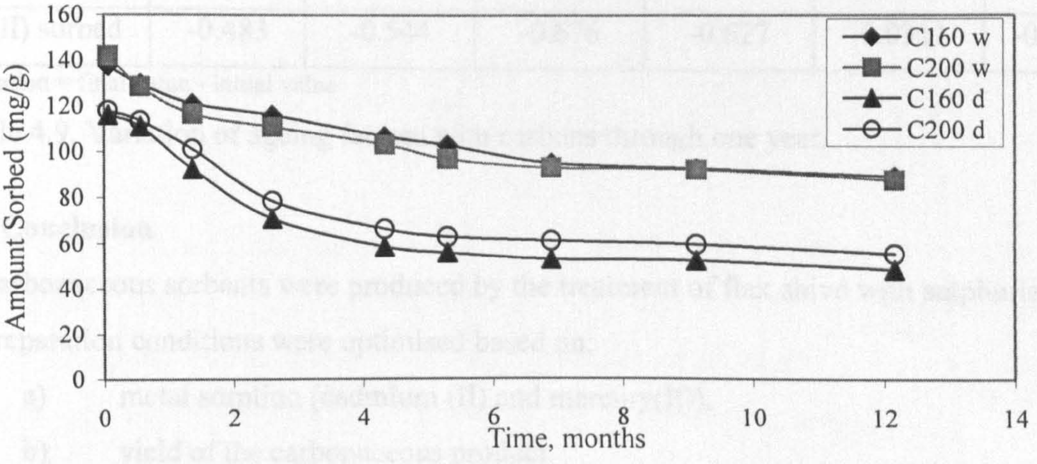

Figure 4.15. Effect of ageing on mercury (II) sorption on C160 and C200.

Chapter 6. Thus the presence of acid in the wet carbons resist the effect of ageing, whereas the dry sorbents being in contact with ambient air suffers from further oxidation.

The variation in cadmium (II) and mercury (II) sorption and cation exchange capacity data in milliequivalents per gram was calculated for ageing over a one-year period. Variation was calculated by subtracting the initial data from those at the end of study period (1 year, or 2.5 years for the C160 sealed samples).

The results show an increase in cadmium (II) and cation exchange capacity and a decrease in mercury (II) sorption (table 4.9). On the other hand, when stored under more concentrated sulphuric acid conditions (C160s) no significant variation is shown.

It appears from the decrease in mercury sorption capacity that some sorption sites became inactive and this is not completely compensated by the increase in the cation exchange groups on carbon surface reduction sites. An explanation of the ageing phenomenon is discussed in Chapter 6, section 6.8.

variation (meq/g)	wet C160	wet C200	dry C160	dry C200	wet C160s	dry C160s
Cd (II) sorbed	+0.5300	+0.6200	+0.713	+0.974	+0.0059	+0.0023
C. E. C.	+0.0598	+0.0658	+0.0909	+0.0955	+0.04	+0.024
Hg (II) sorbed	-0.483	-0.544	-0.676	-0.627	-0.0311	-0.07708

Variation = final value - initial value

Table 4.9. Variation of ageing factors with carbons through one year.

4.17. Conclusion

(1) Carbonaceous sorbents were produced by the treatment of flax shive with sulphuric acid. Preparation conditions were optimised based on:

- a) metal sorption (cadmium (II) and mercury(II)).
- b) yield of the carbonaceous product.
- c) energy and acid consumption.

The optimised conditions for preparation were: 12 mol/dm^3 sulphuric acid; ratio shive: acid 1:9 (wt (g) : vol. (cm^3)), reaction time 25-30 minutes with reaction temperatures 160 °C for C160 and 200 °C for C200.

(2) Processes that take place on flax shive upon sulphuric acid treatment include: carbonisation by dehydration, swelling and fragmentation, and partial oxidation of the surface.

(3) The carbon sorbent retains its fibrous structure and as the sorbent appears to be amorphous, no significant presence of carbon crystallites is likely.

(4) The carbon material produced possesses a high concentration of carbon-oxygen functional groups on the surface; such as -OH, -COOH; capable of acting as ion exchange sites. Cation exchange capacity is favoured by high reaction temperatures, e.g. 200 °C and such materials are most suitable for the sorption of metal ions such as cadmium which follow an ion exchange mechanism.

(5) Carbon C200 possesses more carbon-oxygen functional groups on the surface than C160 and shows higher cation exchange and base neutralisation capacities.

(6) Carbon C160 is suitable for the removal of mercury (II) from aqueous solution which has a different mechanism from that for cadmium (II) (i.e. not purely ion exchange).

(7) The carbon sorbents possess low nitrogen surface areas, probably due to the presence of a large residual organic content in the carbon structure.

(8) Storing the carbon materials in ambient air leads to a slight increase in the cadmium (II) sorption as well as cation exchange capacity. Also base neutralisation capacity data show that air ageing increases the surface concentration of functional groups. On the other hand, mercury (II) sorption shows a decrease with ambient air-ageing.

(9) Storing the carbon in contact with residual acid from preparation under sealed conditions seems to retain the properties of the carbon material especially the cadmium and mercury sorption and cation exchange capacities.

(10) C200 is recommended for applications for the removal of cadmium (II) and metal ions behaving similarly, from aqueous solution. C160 is recommended for mercury (II) and other metals behaving in a similar manner to mercury (II).

(11) The carbon material is an efficient cheap alternative sorbent to activated carbon for removing heavy metals from aqueous solution.

CHAPTER 5

RESULTS AND DISCUSSION II. APPLICATION OF CARBON BY DEHYDRATION FOR METAL REMOVAL FROM AQUEOUS SOLUTION VIA ION EXCHANGE

5.1. Introduction

To understand the adsorption of trace metals from aqueous solution onto the carbon sorbents, information is required on:

the equilibrium adsorption and related equilibrium adsorption isotherms;

comparison of the adsorption behaviour of the material prepared in this work with other carbonaceous material such as peat, lignite and activated carbon.

5.1.1. Equilibrium adsorption theory

Positive adsorption on a solid - liquid system reflects the ability of certain solids to preferentially concentrate specific substances from solution onto their surfaces and so facilitate their removal from solution. The maximum extent of adsorption which may be achieved under a given set of conditions, is determined by the equilibrium established between the solution and sorbed phases. At equilibrium, there is a defined distribution of solute between the liquid and the solid phase and when all the variables are essentially constant except the concentration of the metal ion, correlation between the metal ion concentration adsorbed and the residual concentration left in solution can be represented by one or more of a series of adsorption isotherms. The Langmuir isotherm is one of the most relevant isotherms representing such relations.

5.1.1.1. Langmuir adsorption isotherm

The Langmuir equation is the most widely used isotherm equation for modelling equilibrium data for dilute solutions (136) and can be used to explain the sorption of metal ions onto the carbon prepared in this work.

A basic assumption of the Langmuir theory (45,137) is that sorption takes place at specific sites within the adsorbent. It can be assumed here that, once a metal ion occupies a site, no further adsorption can take place at this particular site. At equilibrium, when all sites within the adsorbent become saturated no further sorption can take place and the approach to the saturated monolayer can be represented by Langmuir equation, equation 5.1.

$$X = \frac{X_m bCe}{(1 + bCe)} \qquad (5.1)$$

$X = x/m$, the amount of solute adsorbed, x, per unit weight of adsorbent m;

Ce = equilibrium concentration of the solute;

X_m = the amount of solute adsorbed of unit weight of adsorbent required for monolayer coverage of the surface, or monolayer capacity;

b = the adsorption equilibrium constant which is temperature dependent and related to the heat of adsorption following the equation given below (29,45,138):

$$(b \; \alpha \; e^{-\Delta H/RT})$$

Or $$b = b_o e^{\frac{-\Delta H}{RT}} \qquad (5.2)$$

where b_o is a constant, ΔH is the heat of adsorption and R is the gas constant.
As shown by equation 5.1, X approaches X_m asymptotically as Ce approaches infinity.

A linear form of the equation can be derived:

$$\frac{Ce}{X} = \frac{1}{(b.X_m)} + \frac{Ce}{X_m} \qquad (5.3)$$

Plotting Ce/X against Ce gives a straight line of a slope $1/X_m$ and an intercept of $1/bX_m$. X_m, the monolayer capacity, defines the total capacity of the adsorbent for a specific adsorbate (46).

5.1.1.2. Isotherm shape analysis

The isotherm shape may be considered with a view to predicting if an adsorption system is "favourable" or "unfavourable". Hall *et al* (139) noted that the essential characteristics of a Langmuir isotherm can be expressed in terms of a dimensionless constant separation factor or equilibrium parameter (R_s) which is defined by equation (5.4).

$$R_s = \frac{1}{(1 + bC_o)} \qquad (5.4)$$

where, R_s is the separation factor or the equilibrium parameter and C_o is the initial concentration of metal ions. This factor, R_s, is a direct function of the Langmuir constant b. According to its value, the parameter indicates the shape of the isotherm as follows:

R_s value	Types of the isotherm
$R_s>1$	Unfavourable
$R_s = 1$	Linear
$0<R_s<1$	Favourable
$R_s = 0$	Irreversible

Table 5.1. Effect of separation factor on isotherm shape

5.1.2. The mechanism of metal ion uptake on peat, lignite and activated carbon

On materials such as activated carbons, peat and lignite, the mechanism of metal uptake cannot be easily related only to a single process due to the complexity and surface heterogeneity of the solid. Metal sorption onto such materials can be related to the collective action of a number of processes, such as adsorption, ion exchange, complexation or surface chemical reaction followed by metal fixation by precipitation. In fact some of these could predominate as the main process depending on the chemical nature of the surface of the sorbent material.

The carbon prepared by reaction with sulphuric acid with agricultural waste material (flax shive) which is the subject of this study, has similar properties to those mentioned above:

it has an agricultural origin (flax shive, a by-product of flax processing);

it is a carbonaceous material with a carbon content ~60%;

it has functional groups on the carbon surface, mostly carboxylic, phenolic, lactonic and carbonyl species with a cation exchange capacity of 1.65 meq/g for C160 and 2.85 meq/g for C200;

the carbonaceous product contains lignin and humic substances as a result of sulphuric acid treatment of the shive.

For the reasons mentioned above, it is assumed that a relation between such carbons and those known in the literature namely peat, lignite and activated carbon will be useful and helpful to locate the carbon formed by dehydration among other carbon sorbents.

When a metal ion in solution collides with a solid surface only a limited number of outcomes are possible. These are as follows:

1. The molecule may be rebound from the solid surface;
2. The molecule may be adsorbed;
3. Reaction may take place between the incoming cation and chemical species present on the solid such as ion exchange, complexation, and oxidation-reduction reactions.

In general, it can be concluded that metal ions can be retained on the surface of such sorbents via processes such as adsorption, ion exchange, complexation and oxidation-reduction reactions.

5.1.2.1. Basic principles

5.1.2.1.1. *Adsorption*

Adsorption from solution is a general term describing the uptake of certain species onto solid adsorbents. Types of adsorption include physical and chemical adsorption as discussed in Chapter 2, section 2.2.

5.1.2.1.2. *Ion exchange*

Ion exchange is a reversible process which is considered as a special case of adsorption based on electrostatic interactions between the incoming metal cations and charged sites on the surface of the adsorbents (29, 140), Chapter 1, section 1.4.2.

5.1.2.1.3. *Complexation*

Complexation or complex formation describes the interaction between a metal cation (M) which is an electron acceptor and a ligand (L) which is an electron donor, having at least one pair of unshared electrons available for bond formation. Complexation is an equilibrium process as shown by equation 5.5.

$$iM + jL \Leftrightarrow M_iL_j \qquad (5.5)$$

where i and j are determined by the respective valences of the reactants.

The metal can form a number of such complexes up to the maximum coordination number of the metal. A chelate is a particular type of complex formed when a cation is bonded by two or more donor groups contained in a single ligand. The species formed as a result of coordination can be electrically positive, neutral or negative. e.g. copper (141): $Cu\,(NH_3)_4^{2+}$, $Cu(NH_2CH_2COO)_2$, $CuCl_4^{2-}$.

The formation constant k_f can be derived from equation 5.5 by application of the law of mass action:

$$k_f = \frac{\lfloor M_i L_j \rfloor}{[M]^i [L]^j} \qquad (5.6)$$

where $\lfloor M_i L_j \rfloor$, $[M]^i$, $[L]^j$ are the molar concentrations of the complex, metal ion and ligand respectively.

5.1.2.1.4. *Oxidation reduction reaction*

In addition to adsorption, ion exchange and complexation, metal ions can be sorbed and fixed on the carbon surface and within pores via reduction reactions either to elemental forms or to lower oxidation states. Lower oxidation states of metal ions can be sorbed via adsorption, ion exchange and/or complexation. They also can interact with anions available in aqueous solutions leading to a possible chemical reaction such as chemical precipitation on carbon surface. A comprehensive study for some metal ions that experience redox reactions on a carbon surface is summarized in Chapter 6.

5.1.2.2. Mechanism of metal sorption, onto activated carbon, peat and lignite (literature survey)

Metal ions, in general, can be bound to the solid surface of peat, lignite and activated carbons via adsorption, ion exchange, complexation and reduction to lower oxidation states followed by precipitation or some other sorption processes. Comparing the results of metal sorption onto such sorbents is rather difficult. This is because of the variation among authors in the methods of pretreatment used, the type of the adsorbent and the experimental conditions used.

Activated carbons have been used widely for the removal of heavy metals from aqueous solutions (142). Granular activated carbon (143), upon acid rinsing (0.1 mol/dm^3 HNO_3) followed by base rinsing (0.1 mol/dm^3 NaOH), retained a high pH value of the carbon surface (pH ~11). Sorption of lead onto such carbon was high and was explained by adsorption, surface precipitation as $Pb(OH)_2$ due to an interaction of Pb^{2+} with OH^- ions retained inside the carbon following such treatment. Solution pH considered to be highly prominent factor (143).

Adsorption of metals such as cadmium (II) (144), and copper and nickel (69) on activated carbons is predominantly due to electrostatic interactions between the metal ions and the adsorption sites on surface. High adsorption of copper (II) and nickel (II) onto activated carbon as the pH increases is explained on the basis of a decrease in competition between the proton and metal species for the surface sites, and by the decrease in positive surface charge, which results in a lower Coulombic repulsion of the sorbing metal (69). Similar results were found for lead (II) on activated carbons that were prepared from olive stones (64).

Sorption of copper (II) onto activated carbon after treatment with nitric acid showed an increase in the amount of copper (II) sorbed. This was accounted for by the formation of more ion exchange groups on the surface as a result of oxidation by the nitric acid (70). Similar behaviour of activated carbon treated with nitric acid has been found for the adsorption of cobalt (II), copper (II) and sodium (I) (145).

Mostafa (93) found that the removal of mercury (II), lead (II) and cadmium (II) on an activated carbon surface was significantly increased as a result of sulphuric acid treatment. This was due to the increase of surface acidity as carbon-oxygen groups capable of behaving as ion exchange centres were formed.

Saw-dust based activated carbon was prepared by treatment of the saw-dust from wood from rubber tree *(Hevea brazeliansis)* with concentrated sulphuric acid (1:1.8, by weight) with the mixture kept in an air oven at 150 °C for 24 hours (146). After being washed with distilled water it was soaked in 1% sodium bicarbonate solution overnight. The material after such treatment shows a good adsorption efficiency for cadmium (II) and lead (II) from aqueous solution. Such a carbonaceous material treated with sodium bicarbonate has the characteristics of a weak ion exchange resin in the sodium form. The resulted carbon surface has –COH and -CO as major groups. Sorption of metal ions is extremely low at low pH, ~2, and this is related to the higher concentration of hydrogen ions present in the reaction mixture competing with the metal cations for adsorption sites but higher adsorption is shown by raising the pH to pH 8 (146). Raising the pH even more decreases metal sorption and this is related to the formation of soluble metal hydroxy complexes (146). The chemical bonding results from the sharing of free electron pairs between the surface oxygen atom and the metal atom or the formation of an O-M (II) bonding (60,146).

Sorption of cadmium (II), copper (II), nickel (II) and zinc (II) onto hydrous activated carbon (60) has also been investigated. The sorption reaction was explained by reaction between the metal ions and their hydroxospecies with the formation of surface complexes with the carbon via hydrogen bonding between the C—O groups on the carbon surface and the hydroxospecies of the metals.

Cadmium (II) and zinc (II) adsorption on activated carbon was studied by Marzal *et al* and the mechanism was related to metal complexation on the carbon surface. It was assumed from this study that bidentate bonding shows a better fit to the experimental data than monodentate (65).

Peat is a complex material containing lignin, cellulose and polyuronic, humic and fulvic acids constituents which bear a rich array of polar functional groups such as alcohols, aldehydes, carboxylic acids, ketones and phenolic hydroxides. These functional groups are mainly responsible for metal sorption (136). The nature of metal binding onto peat has received extensive investigation but a common consensus on the exact mechanism has yet to be reached (136).

Peat is reported to have excellent ion exchange properties being similar to natural zeolites (147). Metal uptake onto such natural sorbent was believed to be an ion exchange process taking place at acidic sites that have resulted from humification process (148), and so, for peat, metals can react with carboxylic and phenolic acid groups of fulvic and humic acids to release protons or, at sufficiently high pH, with the resulting anion sites to displace an existing metal (148). In addition, Aho and Tummavuori (149), and Bunzl *et al* (150) have found that metal ions were sorbed onto peat via ion exchange with one divalent metal ion being exchanged for two hydrogen ions.

Other authors have reported that the mechanism is both ion exchange and complexation (151). Cupric ion was found to be sorbed onto peat with a mechanism related to ion exchange and adsorption-complexation (152).

Sorption of cadmium (II) and copper (II) on bone char, peat, lignite, activated carbon, peat char and lignite char has been investigated (153). Sorption capacities followed a similar trend for both metals for specific adsorbent samples. For cadmium (II), bone char was the most effective sorbent (100 mg/g) followed by peat (60 mg/g). Lignite and activated carbon showed a good performance having cadmium sorption capacities of 40 mg/g. The poorest metal adsorbents in the study for cadmium were peat char and lignite char with 1 mg/g and 5 mg/g respectively. These low results were related to the charring process burning off the vast majority of the functional group associated with the binding of metal ions onto peat and lignite. The low metal sorption capacity reflected by peat char and lignite char compared to activated carbon was also related to their lower surface areas compared to that of activated carbon. An exchange sorption mechanism was suggested to be predominant in these materials (153). In another study, Allen *et al* (154) investigated the sorption of cadmium (II), zinc (II), copper (II), lead (II), and aluminum (III) onto seventeen sorbents composing of a variety of peat, lignite, bone char, activated carbons, peat char and lignite char. Similar trends of metal sorption were obtained and the suggested mechanism was related predominantly to an exchange sorption.

Copper sorption onto acid washed peat was studied by Bowen and McBride (155) who found that humic acids bind most divalent metals largely as hydrated metal ions. An exception was copper where the authors considered the binding of copper ions involved the exchange of one or two aquoligands by carboxylate oxygens (155).

Lignite as a soft low-ranking brown coal, has natural ion exchange properties because of the presence of carboxylic, phenolic and sulphonic functional groups attached to a highly cross-linked structure of aromatic compounds. Some lignites also contain carbonyl groups (156, 157). In another study, sorption of copper onto sulphonated lignite was attributed to the exchange with the protons available on carbon surface from the functional groups, -COOH and -SO_3H (158).

Brown (74) found that metal ion binding to peat and lignite seems mostly to follow an ion exchange type of adsorption reaction with the binding of ions by polyacidic functional groups such as carboxyl and hydroxyl (probably phenolic) groups.

Eligwe *et al* (157) studied the adsorption of mercury (II), cadmium (II) and lead (II) on lignite. Sorption was highly dependent on pH and the mechanism of metal (II) sorption was related to ion exchange on the lignite surface mainly at carboxylic and phenolic sites.

Sorption of copper (II) on peat and lignite has also been carried out by Ong and Swanson (159). They found that the humic acids extracted from peat and lignite are able to complex copper ions in solution. The sorption of copper onto peat and lignite from which humic acids are removed, did not as expected decrease but on the contrary it increased. Accordingly, the sorption of copper could not be explained solely by the formation of humic acid complexes. The increase of copper adsorption onto peat and lignite from which humic acids had been removed, was explained as a consequence of the increased surface area of the peat by their extraction. The authors concluded that adsorption of copper by peat and lignite can be considered as an attraction between the negatively charged sites on the surface and the positively charged metal ions. Also they found that adsorption of copper decreased as the degree of metamorphism increased following compaction of the surface area. The order of capacity was peat> lignite > coal.

In the following, the results and discussions of the current experiments on a series of metals including cadmium (II), copper (II), chromium (III), cobalt (II), nickel (II), lead (II), and zinc (II) are to be discussed. These metal ions show similar adsorption behaviour on the carbons under investigation (C160 and C200), it is convenient to put them together within this Chapter.

5.2. Kinetics of Sorption

5.2.1. Kinetics of cadmium (II) sorption

In the adsorption of materials from solution by porous sorbents, there are three consecutive stages to be considered. The first of these is the transport of the adsorbate to the exterior surface of the adsorbent, the second, with the exception of a small amount of adsorption on the exterior surface, is the diffusion of the adsorbate into the pores of the adsorbent, and the third step is the adsorption in the interior surfaces of the adsorbent (161). Adsorption steps are usually rapid and the rate of adsorption (161) is mainly related to the first and second steps but with sufficient mixing, it would appear that diffusion of the adsorbate into the porous structure should control the rate of adsorption.

Sorption kinetics were investigated for cadmium (II) solution, with an initial pH value 6.0, onto carbon sorbents C160 and C200 at 25 °C until equilibrium is attained. Primary investigation of time to equilibrium showed fast removal kinetics, thus equilibrium was almost attained within the first two hours and samples were left under shaking for about 10 hours to ensure equilibrium had been reached.

The kinetics of cadmium (II) sorption onto carbons C160 and C200 are shown in figure 5.1a,b, with the wet samples reaching equilibrium a little faster than the dry sorbents. Since the moisture content of the wet form is relatively high (> 80%), this reduction in rate for the dried sample is probably related to shrinking and compaction of the carbon upon drying resulting in narrower pores for the diffusion of the metal ions. It was also observed that little swelling of the dry material occurred when placed in aqueous solutions. Wet sorbents also show a slightly higher uptake of cadmium (II) compared to the dry ones. It is obvious from figure 5.1a,b that the C200 shows higher uptake of cadmium (II) compared to C160. This could be related to the presence of more ion exchange sites on the C200 surface being developed as a result of the preparation conditions applied. The uptake of cadmium (II) was found to vary almost linearly with the half power of time, $t^{0.5}$, in the initial stages of sorption as shown in figure 5.2. Similar results were found by Ozer *et al* (160) applying the equation 5.7.

$$X = k_d t^{0.5} \qquad (5.7)$$

where X indicates the metal sorbed (mmol g^{-1}) and k_d is the rate constant of pore diffusion.

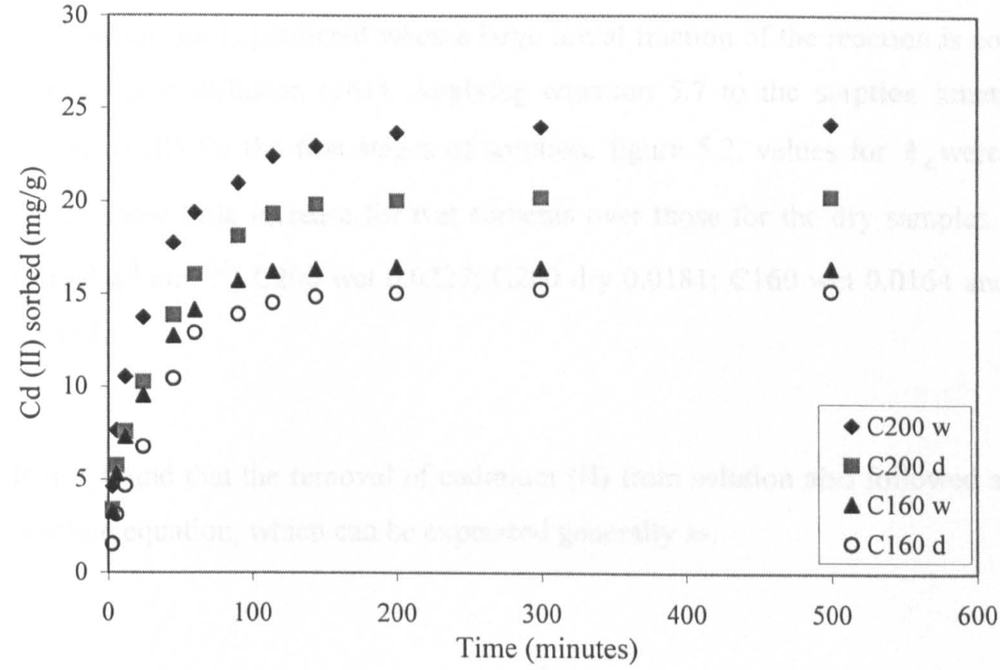

Figure 5.1a. Kinetics of cadmium (II) sorption on carbon sorbents at 25 °C.

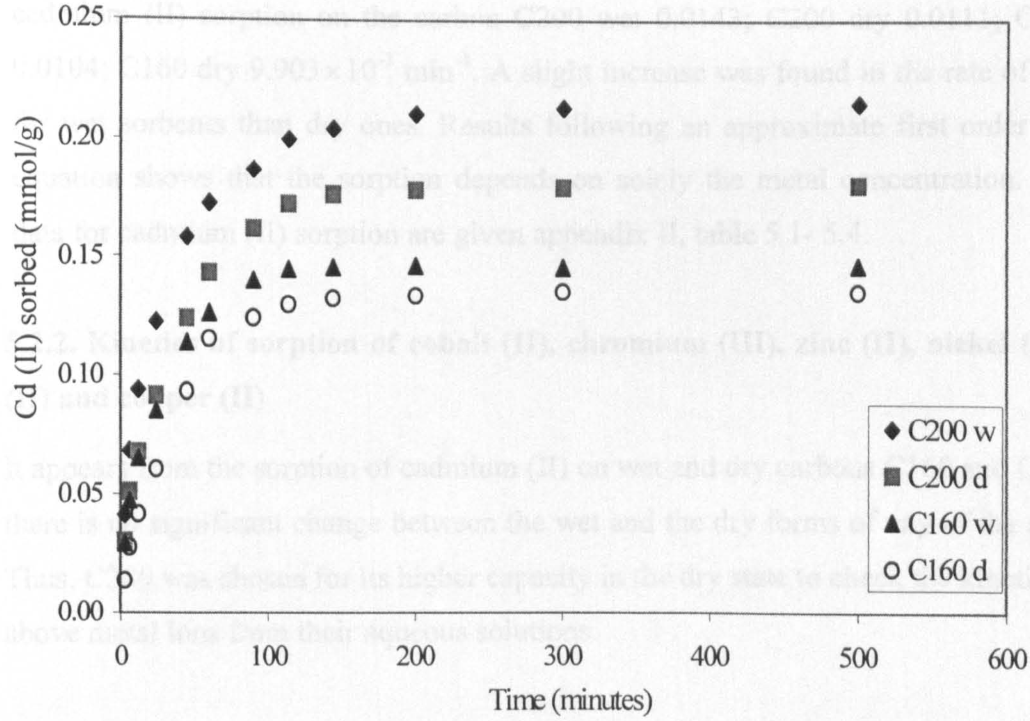

Figure 5.1b. Kinetics of cadmium (II) sorption on carbon sorbents at 25 °C.

Such behaviour is predicted when a large initial fraction of the reaction is controlled by intra-particle diffusion (161). Applying equation 5.7 to the sorption kinetics data of cadmium (II) for the first stages of sorption, figure 5.2, values for k_d were calculated which show little increase for wet sorbents over those for the dry samples. k_d values (mmol g^{-1} $min^{-0.5}$) C200 wet 0.0227; C200 dry 0.0181; C160 wet 0.0164 and C160 dry 0.0155.

It was found that the removal of cadmium (II) from solution also followed a first-order reaction equation, which can be expressed generally as:

$$\log C_t = \log C_o - \frac{k_1}{2.303} \cdot t \qquad (5.8)$$

where C_t is the concentration of cadmium (II) at time t, C_o is the initial concentration of cadmium (II) and k_1 is the rate constant of sorption at 25 °C. The results of the kinetic experiment, figure 5.3, show an approximately linear decrease of the $\log C_t$ as a function of time for both sorbents in their different forms. The rate constants for cadmium (II) sorption on the carbon C200 wet 0.0143; C200 dry 0.0111; C160 wet 0.0104; C160 dry 9.903×10^{-3} min^{-1}. A slight increase was found in the rate of sorption for wet sorbents than dry ones. Results following an approximate first order reaction equation shows that the sorption depends on solely the metal concentration. Kinetic data for cadmium (II) sorption are given appendix II, table 5.1- 5.4.

5.2.2. Kinetics of sorption of cobalt (II), chromium (III), zinc (II), nickel (II), lead (II) and copper (II)

It appears from the sorption of cadmium (II) on wet and dry carbons C160 and C200 that there is no significant change between the wet and the dry forms of any of the sorbents. Thus, C200 was chosen for its higher capacity in the dry state to check the kinetics of the above metal ions from their aqueous solutions.

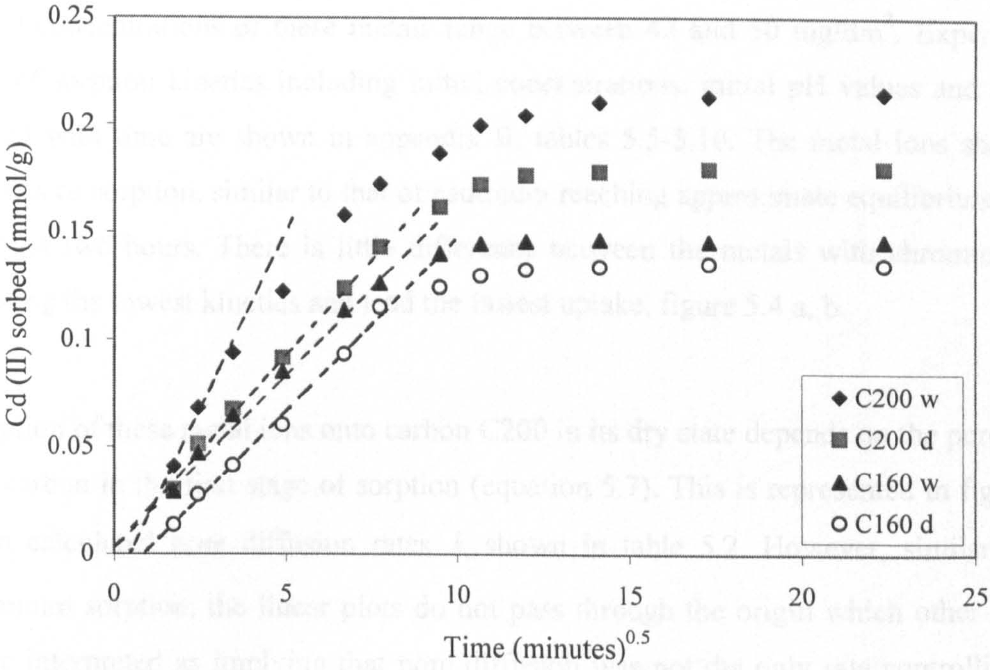

Figure 5.2. A Plot for the rate of pore diffusion of cadmium (II) on carbon sorbents at 25 °C.

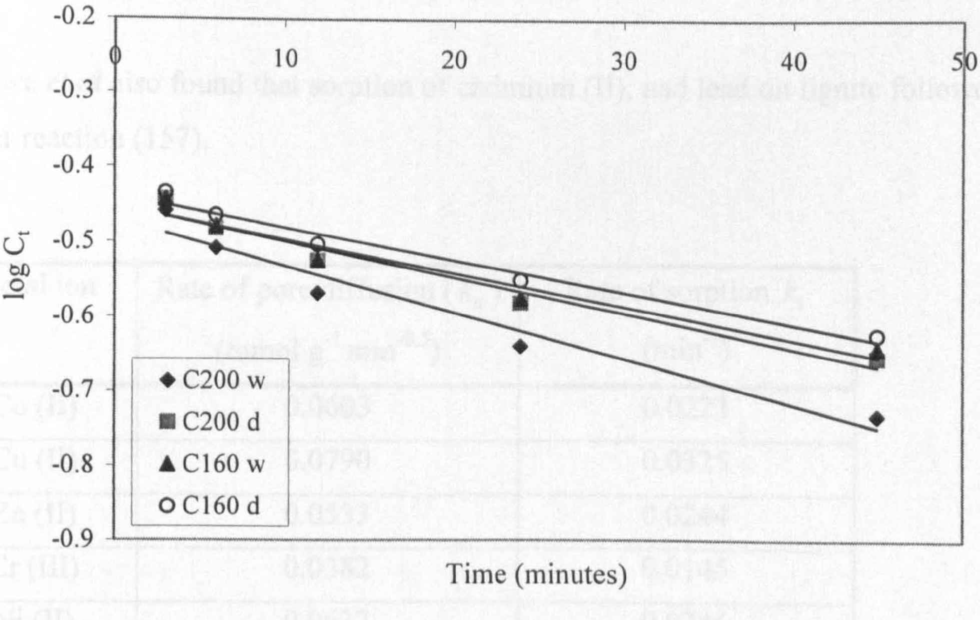

Figure 5.3. A Plot for the first order reaction for cadmium (II) sorption on carbon sorbents at 25 °C. (C_t is expressed as mmol/dm^3).

Initial concentrations of these metals range between 42 and 50 mg/dm^3. Experimental data of sorption kinetics including initial concentrations, initial pH values and amount sorbed with time are shown in appendix II, tables 5.5-5.10. The metal ions show fast kinetics of sorption, similar to that of cadmium reaching approximate equilibrium within the first two hours. There is little difference between the metals with chromium (III) showing the lowest kinetics and lead the fastest uptake, figure 5.4 a, b.

Sorption of these metal ions onto carbon C200 in its dry state depends on the porosity of the carbon in the first stage of sorption (equation 5.7). This is represented in figure 5.5 with calculated pore diffusion rates k_d shown in table 5.2. However, similar to the cadmium sorption, the linear plots do not pass through the origin which other authors have interpreted as implying that pore diffusion was not the only rate controlling step (160, 188).

Sorption of the metal ions in solution onto carbon C200 also followed the first order reaction equation represented (equation 5.8), as shown in figure 5.6 indicating that the sorption depends on the metal ion concentration. The rate of sorption k_1 was calculated and tabulated in table 5.2.

Eligwe *et al* also found that sorption of cadmium (II), and lead on lignite followed a first order reaction (157).

Metal ion	Rate of pore diffusion (k_d) (mmol g^{-1} min$^{-0.5}$)	Rate of sorption k_1 (min^{-1})
Co (II)	0.0603	0.0223
Cu (II)	0.0790	0.0325
Zn (II)	0.0533	0.0244
Cr (III)	0.0382	0.0145
Ni (II)	0.0637	0.0246
Pb (II)	0.0404	0.0495

Table 5.2. Rate of pore diffusion, and rate of sorption of metal ions on dry C200 at 25 ^{0}C.

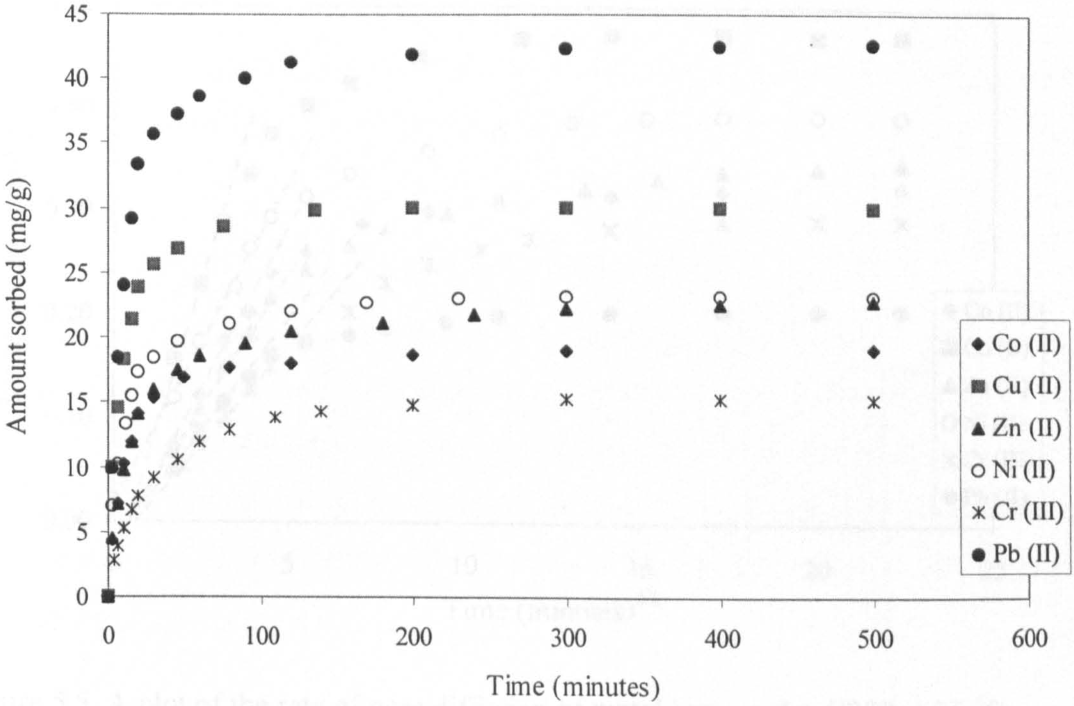

Figure 5.4a. Kinetics of sorption of some heavy metal ions on dry C200 at 25 °C.

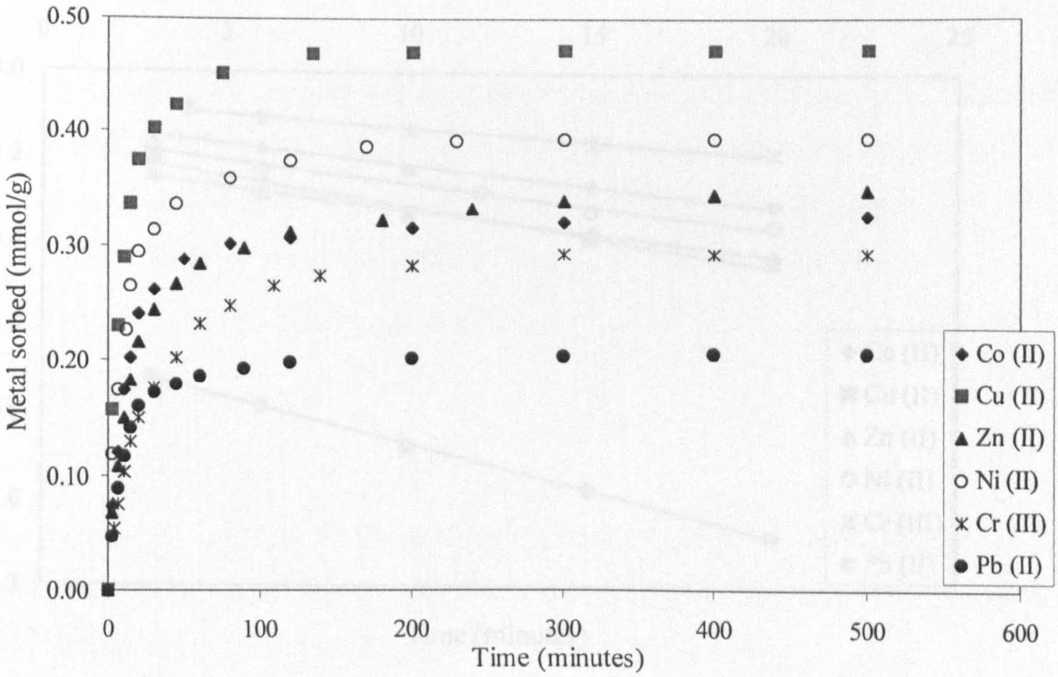

Figure 5.4b. Kinetics of sorption of some heavy metal ions on dry C200 at 25 °C.

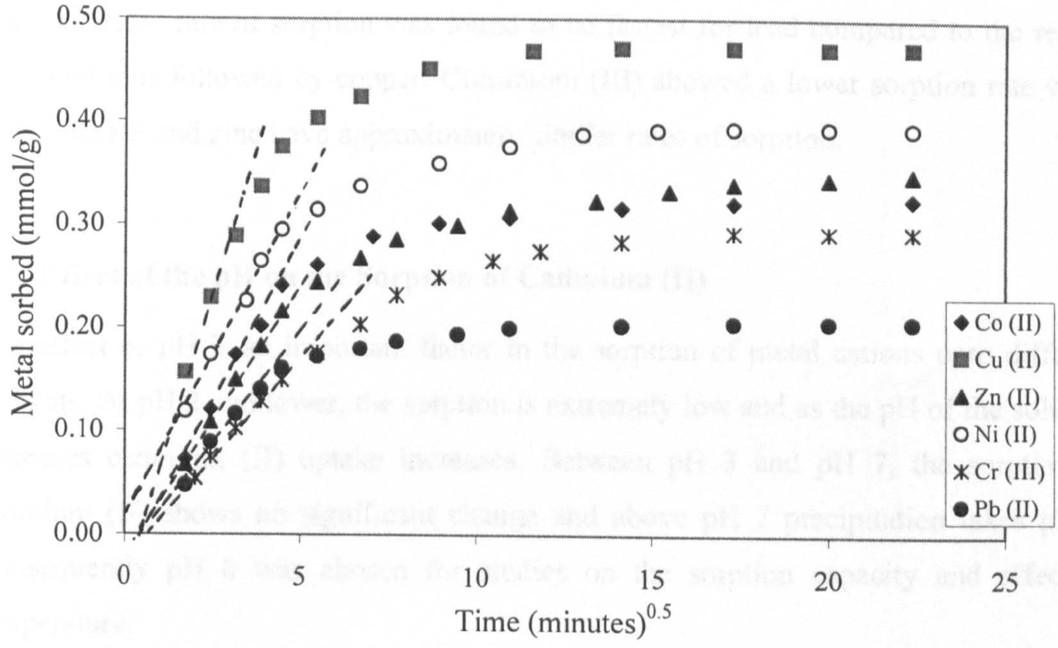

Figure 5.5. A plot of the rate of pore diffusion of metal ions on dry C200 at 25 °C.

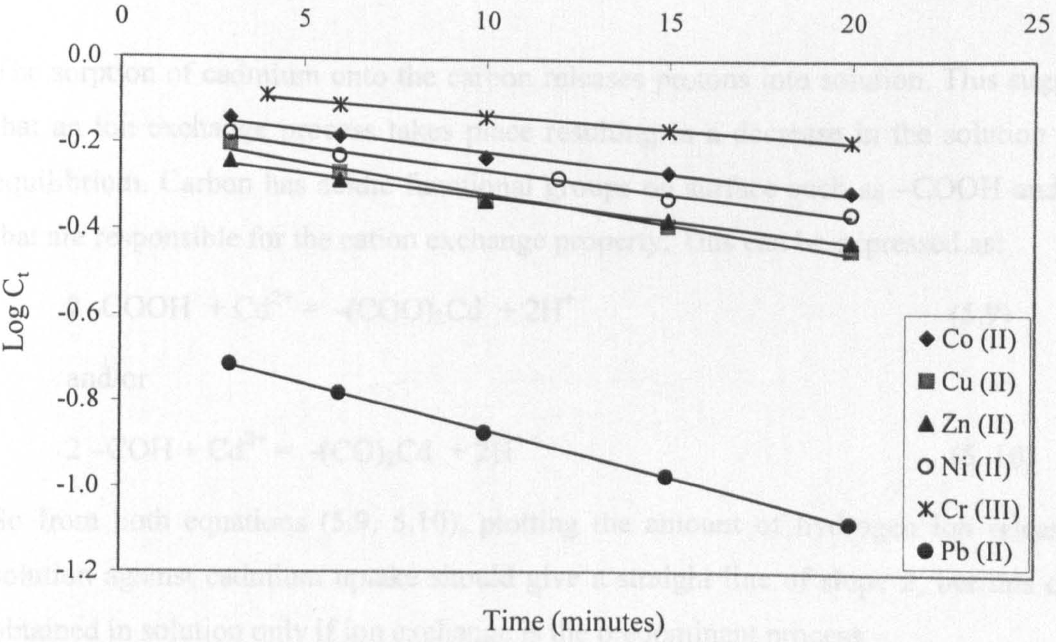

Figure 5.6. A Plot of the first order reaction for metal ions on dry C200 at 25 °C. (C_t is expressed as mmol/dm^3).

The calculated rate of sorption was found to be fastest for lead compared to the rest of the metal ions followed by copper. Chromium (III) showed a lower sorption rate while cobalt, nickel and zinc have approximately similar rates of sorption.

5.3. Effect of the pH on the Sorption of Cadmium (II)

The effect of pH is an important factor in the sorption of metal cations onto different sorbents. At pH 2 and lower, the sorption is extremely low and as the pH of the solution increases cadmium (II) uptake increases. Between pH 3 and pH 7, the sorption of cadmium (II) shows no significant change and above pH 7 precipitation takes place. Consequently pH 6 was chosen for studies on the sorption capacity and effect of temperature.

Starting with different initial concentrations, the sorption of cadmium shows similar trends with pH variation with increased sorption capacity from solutions with higher initial concentrations, figures 5.7 and 5.8. Wet sorbents behave similarly to the dry ones with a little increase in cadmium (II) uptake for the former. Cadmium sorption was accompanied by a consequent decrease in the final pH value of the solutions, figure 5.9. Data for the pH effect are shown in appendix II, table 5.11 and 5.12.

The sorption of cadmium onto the carbon releases protons into solution. This suggested that an ion exchange process takes place resulting in a decrease in the solution pH at equilibrium. Carbon has acidic functional groups on surface such as –COOH and –OH that are responsible for the cation exchange property. This can be expressed as:

$$2\,\text{-COOH} + Cd^{2+} = \text{-(COO)}_2Cd + 2H^+ \qquad (5.9)$$

and/or

$$2\,\text{–COH} + Cd^{2+} = \text{-(CO)}_2Cd + 2H^+ \qquad (5.\ 10)$$

So from both equations (5.9, 5.10), plotting the amount of hydrogen ion released in solution against cadmium uptake should give a straight line of slope 2, but this can be obtained in solution only if ion exchange is the predominant process.

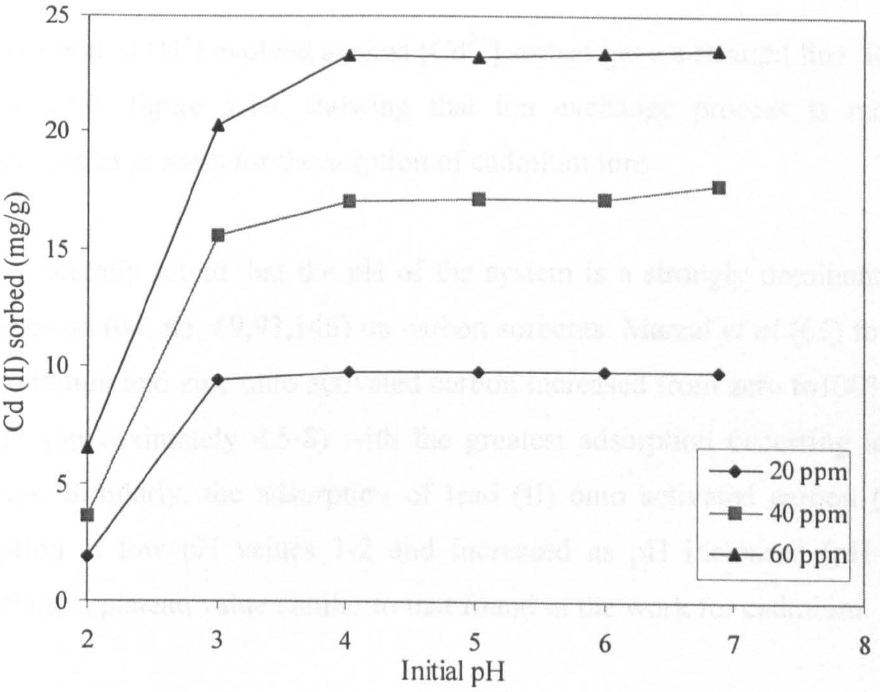

Figure 5.7. Effect of initial pH on the sorption of cadmium (II) on wet C200.

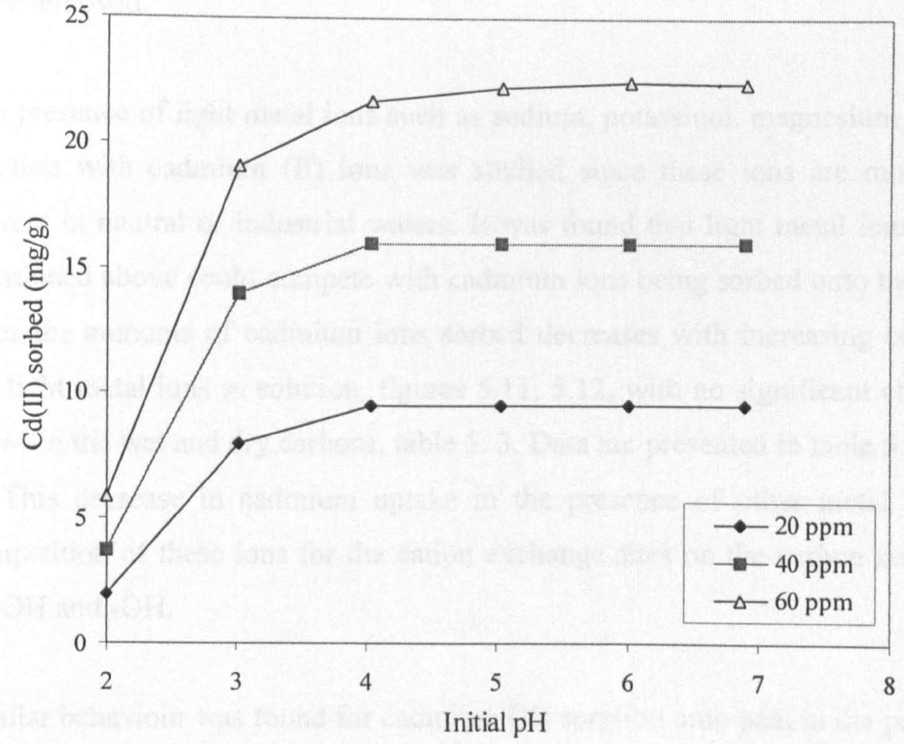

Figure 5.8. Effect of initial pH on the sorption of cadmium (II) on dry C200.

Such a plot of [H^+] evolved against [Cd^{2+}] sorbed gave a straight line, $R^2 = 0.988$, with a slope 2.03, figure 5.10, showing that ion exchange process is most probably the predominant process for the sorption of cadmium ions.

It is generally found that the pH of the system is a strongly dominant factor for metal adsorption (64, 65, 69,93,146) on carbon sorbents. Marzal *et al* (65) found that sorption of cadmium and zinc onto activated carbon increased from zero to100% in a narrow pH range (approximately 4.5-8) with the greatest adsorption occurring at the highest pH values. Similarly, the adsorption of lead (II) onto activated carbon (64) showed low sorption at low pH values 1-2 and increased as pH increased (pH 3 and upwards) reaching a plateau value similar to that found in the work for cadmium.

5.4. Effect of Light Metal Ions on Cadmium (II) Sorption

Generally, in natural water or industrial effluents, the metal ion to be recovered will be found with many other metal ions in many different concentrations. The higher the concentration of foreign ions in solution, the more difficult will be the recovery of a specific metal ion by a non-selective sorbent such as carbon. In general, other metal ions in water do compete for sorption sites on carbon surface with the metal that is required to be removed.

The presence of light metal ions such as sodium, potassium, magnesium and calcium in solution with cadmium (II) ions was studied since these ions are most likely to be present in natural or industrial waters. It was found that light metal ions such as those mentioned above could compete with cadmium ions being sorbed onto the carbon C200. Thus the amounts of cadmium ions sorbed decreases with increasing concentration of the light metal ions in solution, figures 5.11, 5.12, with no significant change observed between the wet and dry carbons, table 5. 3. Data are presented in table 5.13 in appendix II. This decrease in cadmium uptake in the presence of other metal ions is due to competition of these ions for the cation exchange sites on the carbon surface such as -COOH and -OH.

Similar behaviour was found for cadmium (II) sorption onto peat in the presence of such metal ions (136). As a single component, the cadmium sorption monolayer capacity was 188 μmol/g and this decreased in the presence of different concentrations of zinc (II) to

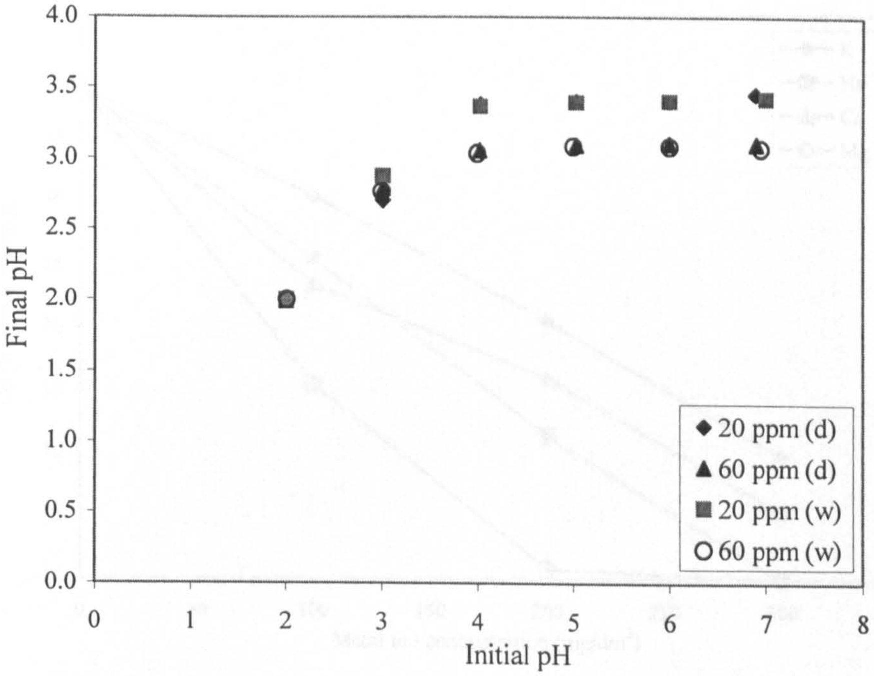

Figure 5.9. Relation between initial pH and final pH for cadmium (II) on C200.

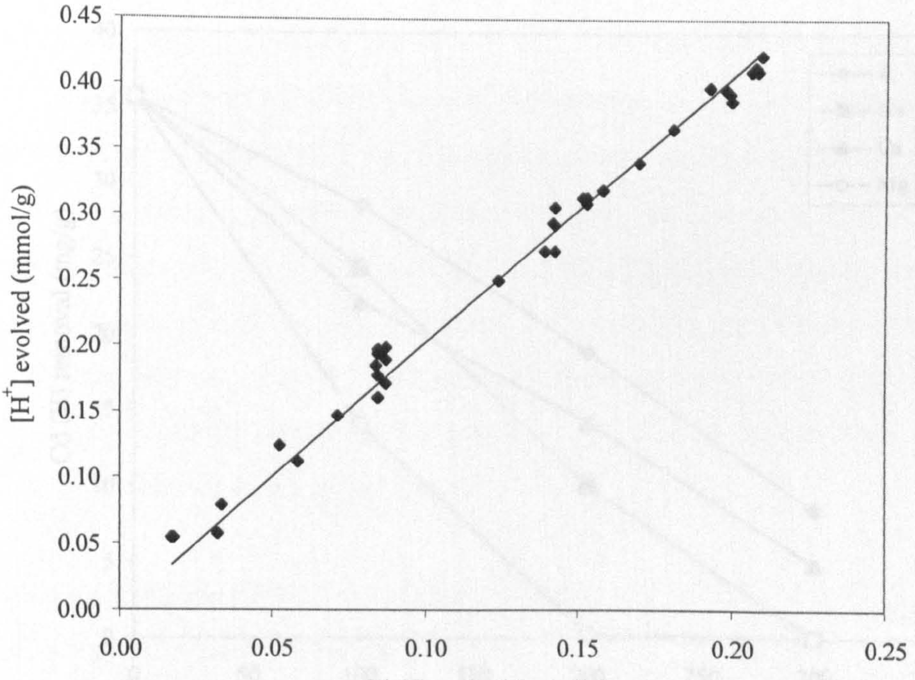

Figure 5.10. Relation between protons evolved in solution and cadmium (II) sorbed on C200.

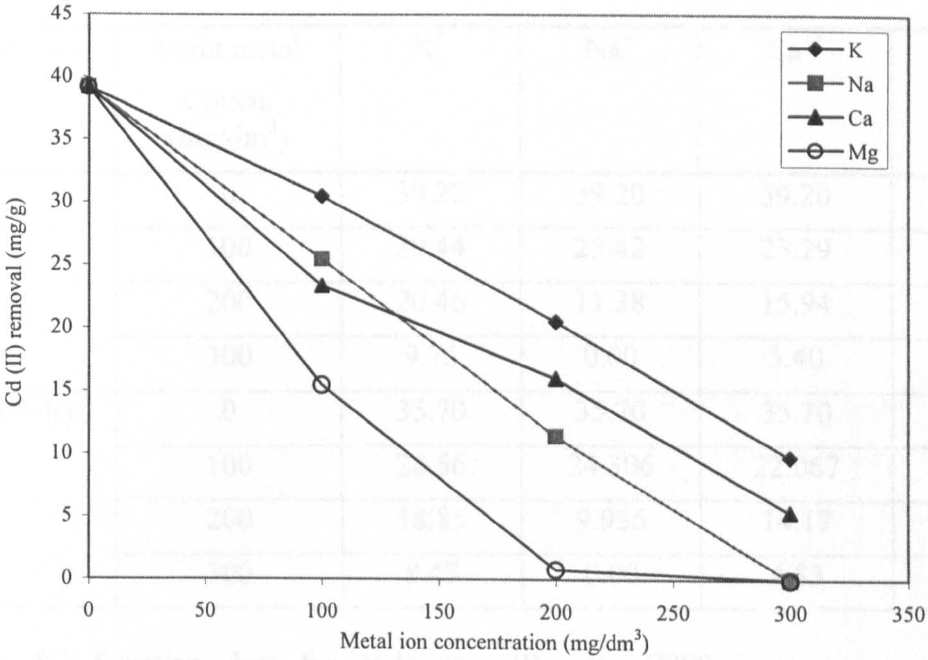

Figure 5.11. Effect of light metal ions on cadmium (II) sorption on wet C200.
(Initial cadmium concentration, 160 mg/dm^3).

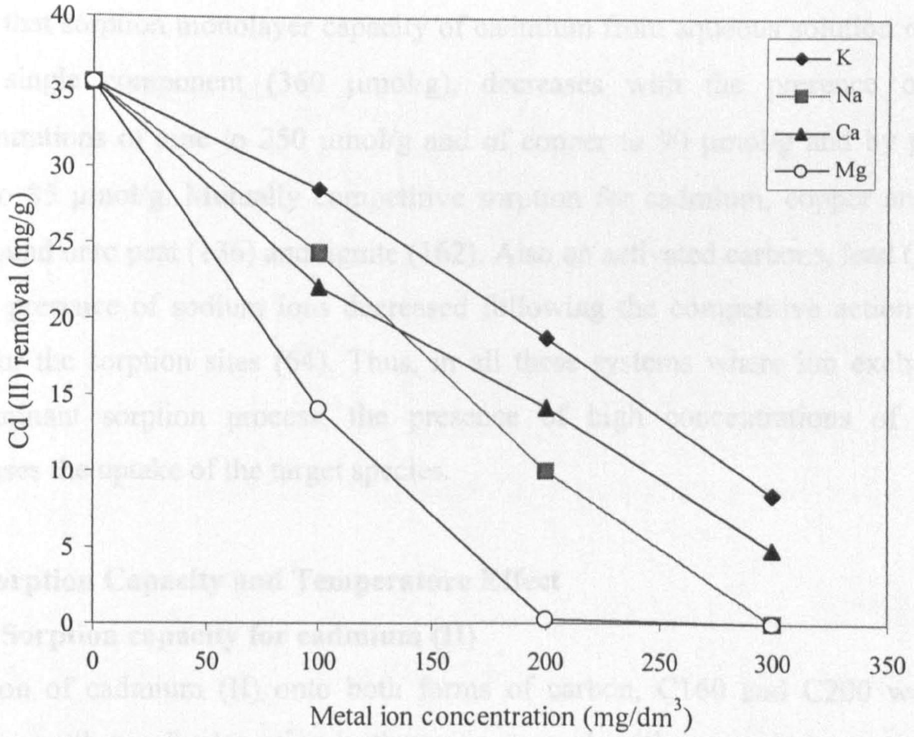

Figure 5.12. Effect of light metal ions on cadmium (II) sorption on dry C200.
(Initial cadmium concentration, 160 mg/dm^3).

C200 wet	Light metal Concn, (mg/dm^3)	K^+	Na^+	Ca^{2+}	Mg^{2+}
	0	39.20	39.20	39.20	39.20
	100	30.44	25.42	23.29	15.44
	200	20.46	11.38	15.94	0.79
	300	9.75	0.00	5.40	0.00
C200 dry	0	35.70	35.70	35.70	35.70
	100	28.56	24.306	22.067	14.11
	200	18.85	9.936	14.17	0.24
	300	8.47	0.00	4.83	0.00

Table 5.3 Sorption data for cadmium (II) onto C200 in presence of different concentrations of light metal ions at 25 °C. (Initial concentration of Cd^{2+} 160 mg/dm^3.)

114 μmol/g and of copper (II) to 91 μmol/g. When both metals ions were added at different concentrations to cadmium (II) to form a ternary solution, sorption of cadmium was found to decrease sharply to a monolayer capacity of 50.2 μ mol/g (136). For equimolar stock solutions of cadmium, copper and zinc sulphate, Allen and Brown (162) found that sorption monolayer capacity of cadmium from aqueous solution onto lignite, as a single component (360 μmol/g), decreases with the presence of different concentrations of zinc to 250 μmol/g and of copper to 90 μmol/g and by presence of both to 85 μmol/g. Mutually competitive sorption for cadmium, copper and zinc was also found onto peat (136) and lignite (162). Also on activated carbons, lead (II) sorption in the presence of sodium ions decreased following the competitive action of sodium ions for the sorption sites (64). Thus, in all these systems where ion exchange is the predominant sorption process, the presence of high concentrations of other ions decreases the uptake of the target species.

5.5. Sorption Capacity and Temperature Effect

5.5.1. Sorption capacity for cadmium (II)

Sorption of cadmium (II) onto both forms of carbon, C160 and C200 wet and dry, follows an "L-type" adsorption isotherm, in general, with increasing capacity for C200 carbon (figures 5.13-5.15). Again the wet sample gave a better performance than that which had been previously dried. Ratios of the amount of cadmium (II) sorbed onto the carbons, dry to wet, are shown in table 5.4. The increase of metal sorption for the wet over the dry samples could be related to the effect of swelling of the carbon. As noted earlier, the wet carbon had a moisture content of (~82 - 87%) which is lost on drying to give a much more compacted form. This process seems irreversible as little swelling of the dry samples is found in water. On shrinking of the carbon, the pores became narrower and some sorption sites could be hidden or became inaccessible to metal ions. By increasing temperature a small increase in cadmium uptake was observed. This could be due to an increase in swelling as a result of higher temperature leading to more ion exchange sites being available for sorption. However, the effect of temperature is marginal for wet and dry carbons.

Carbon type	Temp. of sorption	Langmuir constants			Correlation coefficient	$\frac{DryXm}{WetXm}$
		X_m (monolayer capacity)		b constant dm^3/g		
		mg/g	m mol/g			
Wet C160	25 °C	22.73	0.202	0.0677	0.998	0.93
	35 °C	24.04	0.214	0.07626	0.999	N/A
	45 °C	25.25	0.225	0.0763	0.998	N/A
Dry C160	25 °C	21.05	0.187	0.0673	0.999	
Wet C200	25 °C	44.84	0.399	0.1075	0.998	0.87
	35 °C	45.66	0.406	0.1299	0.998	0.89
	45 °C	46.95	0.418	0.1659	0.997	0.90
Dry C200	25 °C	39.06	0.348	0.0745	0.999	
	35 °C	40.65	0.362	0.0755	0.999	
	45 °C	42.19	0.375	0.0814	0.999	

Table 5.4. Langmuir constants for cadmium (II) sorption on wet and dry carbons at 25, 35 and 45° C.

Figures 5.16 - 5.18 show that the Langmuir equation gives a good representation of the experimental isotherm data. The derived Langmuir constants, table 5.4, show that the monolayer capacity X_m (mmol/g) is a little higher in the case of wet carbon than for the dry samples. See also appendix II, table 5.14-5.16.

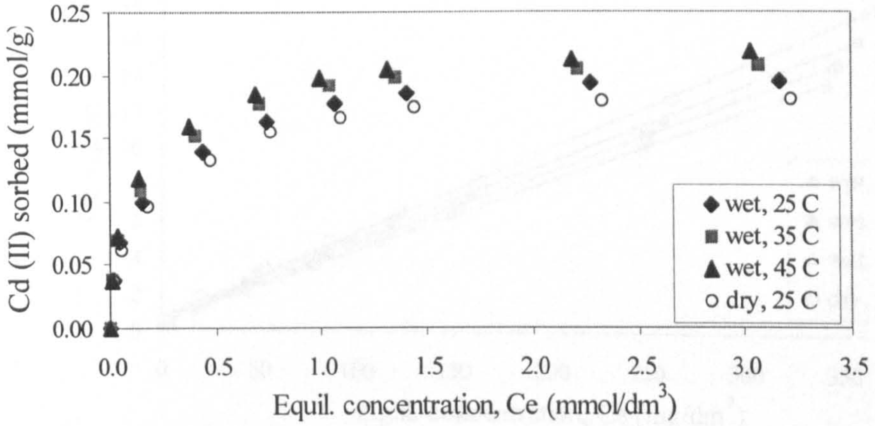

Figure 5.13. Cadmium sorption on C160 at different temperatures.

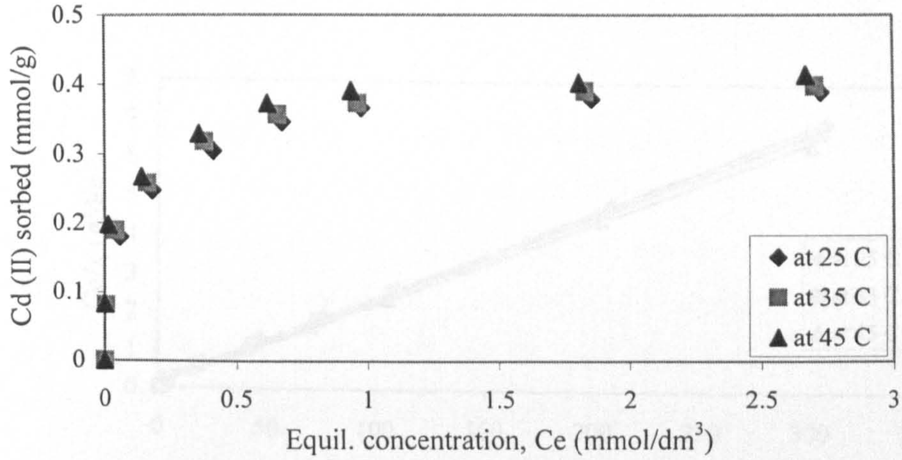

Figure 5.14. Cadmium sorption on wet C200 at different temperatures.

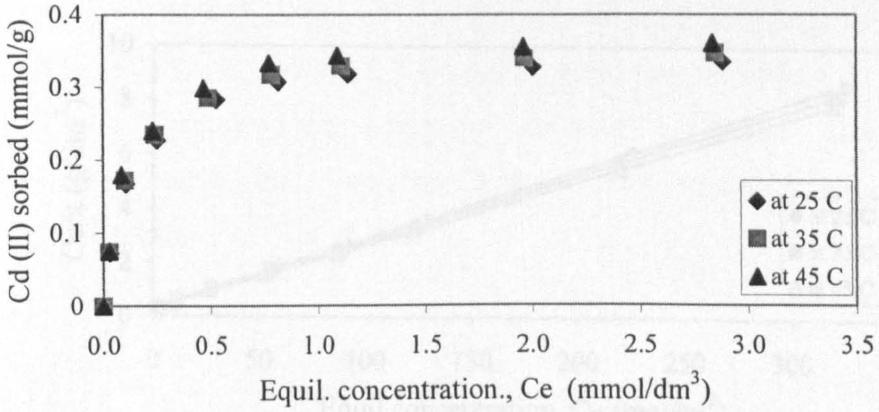

Figure 5.15. Cadmium sorption on dry C200 at different temperatures.

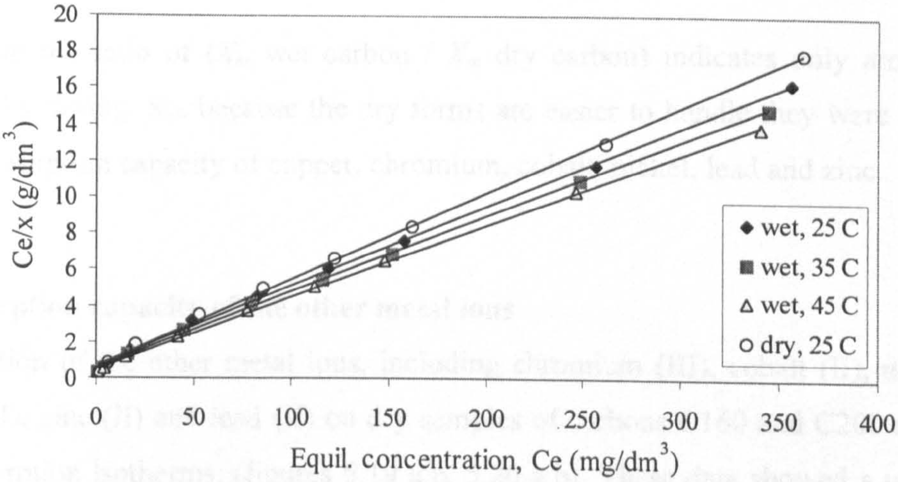

Figure 5.16. Langmuir isotherms for cadmium (II) sorption on C160 at 25, 35 and 45 °C.

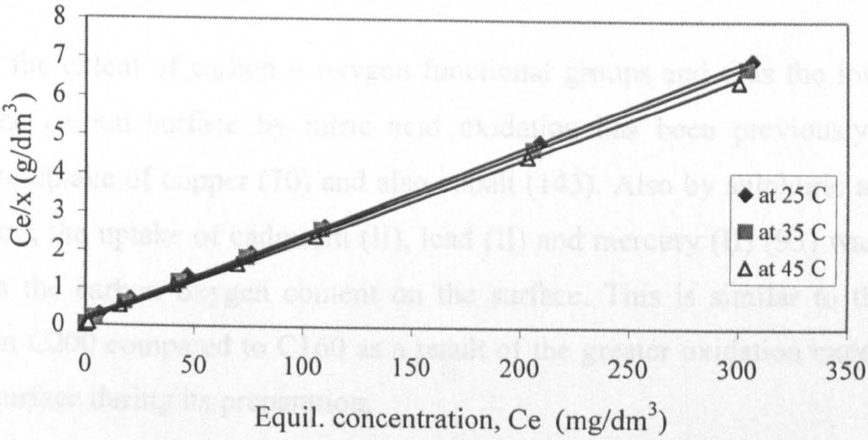

Figure 5.17. Langmuir isotherms for cadmium (II) sorption on wet C200 at 25, 35 and 45 °C.

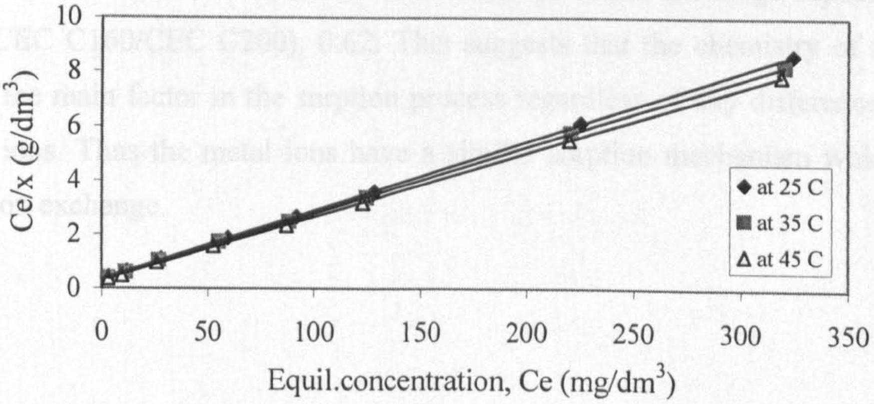

Figure 5.18. Langmuir isotherms for cadmium (II) sorption on dry C200 at 25, 35 and 45 °C.

Comparing the ratio of (X_m wet carbon / X_m dry carbon) indicates only around 10% decrease by drying. So, because the dry forms are easier to handle they were chosen to study the sorption capacity of copper, chromium, cobalt, nickel, lead and zinc.

5.5.2. Sorption capacity of the other metal ions

The sorption of the other metal ions, including chromium (III), cobalt (II), nickel (II), copper (II), zinc (II) and lead (II) on dry samples of carbons C160 and C200 also show L-type sorption isotherms, (figures 5.19 a,b, 5.20 a,b). These data showed a good fit to the Langmuir equation, figures 5.21, 5.22. Similar to cadmium uptake C200 shows higher uptake of metal ions compared to C160 (chapter 4, section 4.3) which could be related to more cation exchange groups being available on C200 due to the more oxidative preparation conditions used. Data are presented in appendix II, table 5.17.

Increasing the extent of carbon – oxygen functional groups and thus the ion exchange sites on the carbon surface by nitric acid oxidation has been previously shown to increase the uptake of copper (70) and also cobalt (145). Also by sulphuric acid surface modification, the uptake of cadmium (II), lead (II) and mercury (II) (93) was due to an increase in the carbon oxygen content on the surface. This is similar to the increase obtained on C200 compared to C160 as a result of the greater oxidation experienced by the C200 surface during its preparation.

Comparing the monolayer capacity data obtained from Langmuir equation (equation 5.1) for C160 to C200 in their dry states, (X_m C160/X_m C200), for the seven metals studied at 25 °C shows that the monolayer capacity of C160 ranges from 54 – 61 % of its value for C200, table 5.5, which is close to that of the ratio of cation exchange capacities of dry carbons (CEC C160/CEC C200), 0.62. This suggests that the chemistry of the carbon surface is the main factor in the sorption process regardless of any differences between the metal ions. Thus the metal ions have a similar sorption mechanism which is most probably ion exchange.

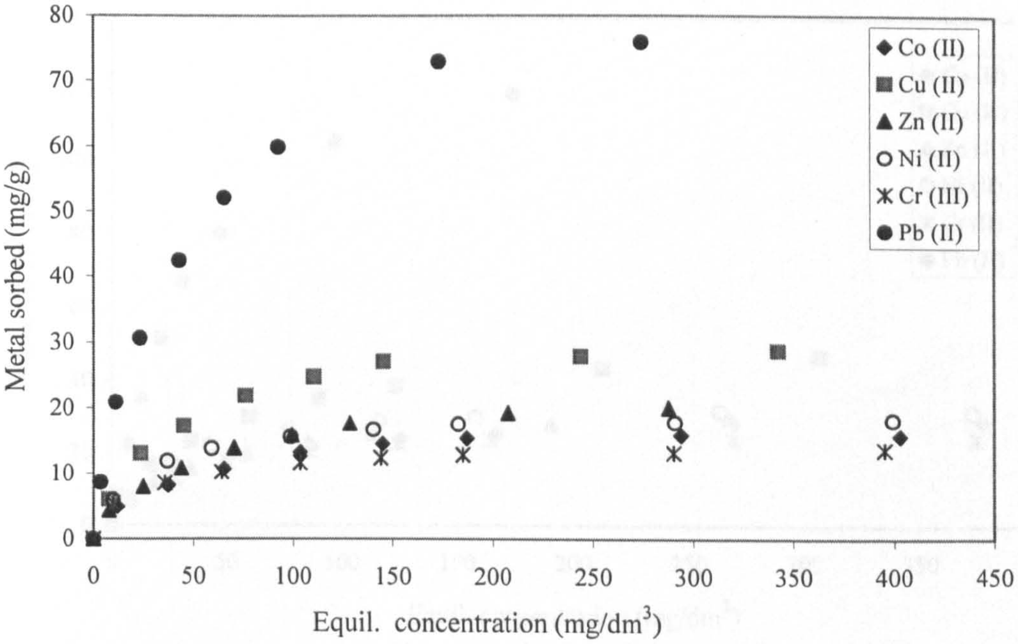

Figure 5.19a. Sorption of metal ions on dry C160 at 25 °C.

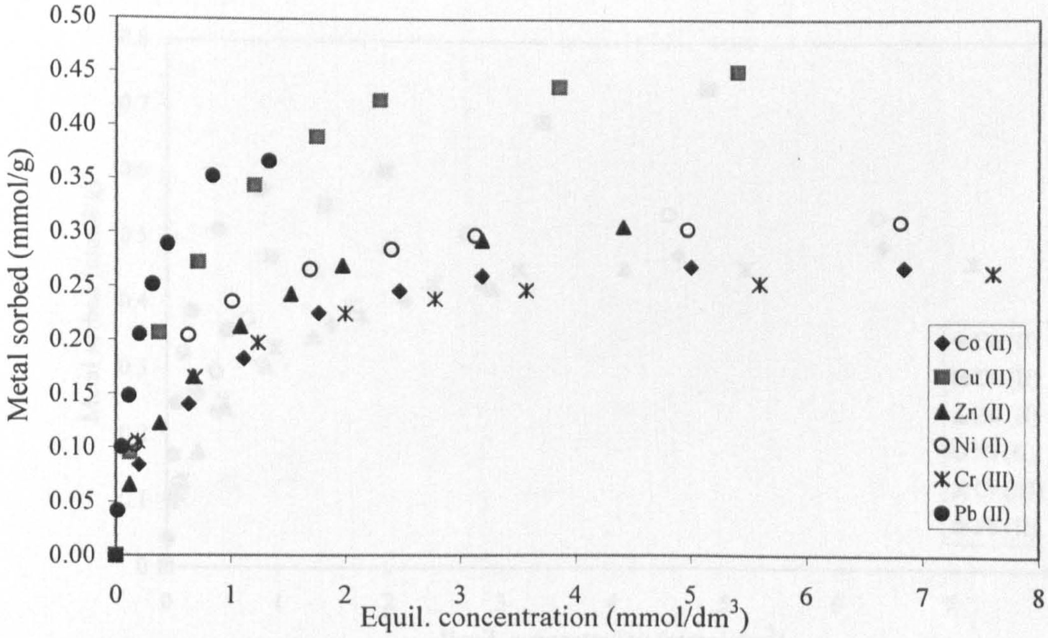

Figure 5.19b. Sorption of metal ions on dry C160 at 25 °C.

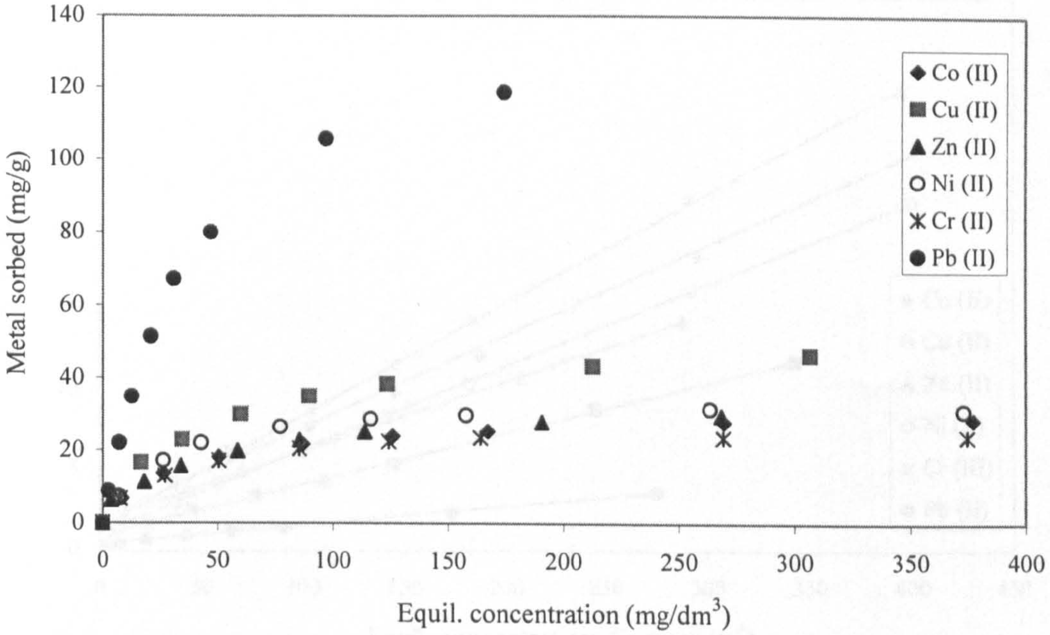

Figure 5.20a. Sorption of metal ions on dry C200 at 25 °C.

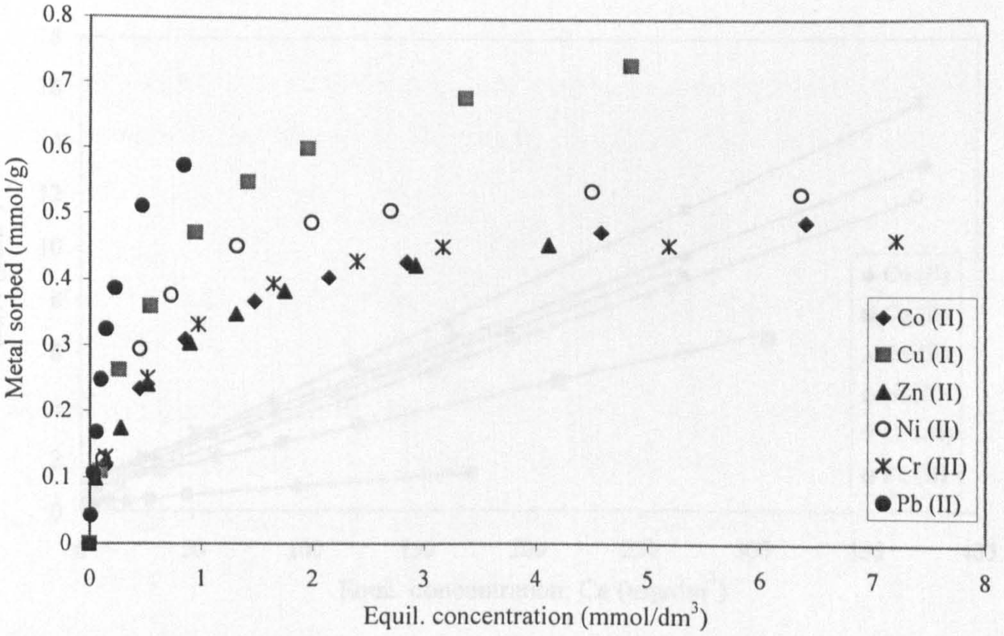

Figure 5.20b. Sorption of metal ions on dry C200 at 25 °C.

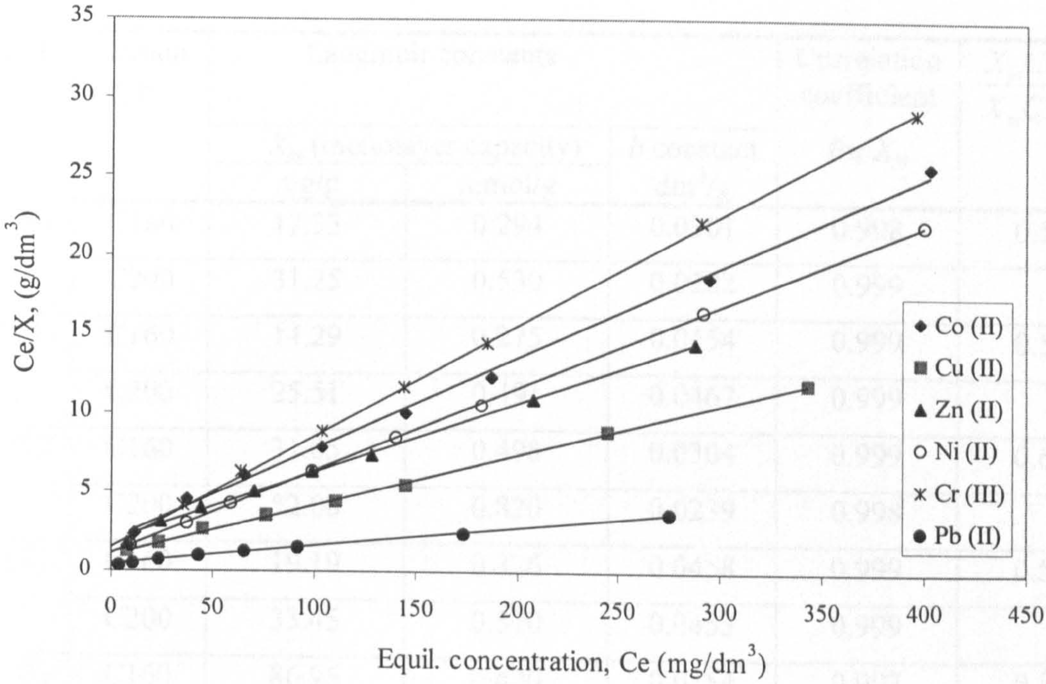

Figure 5.21. Langmuir isotherms for metal sorption on C160 at 25 °C.

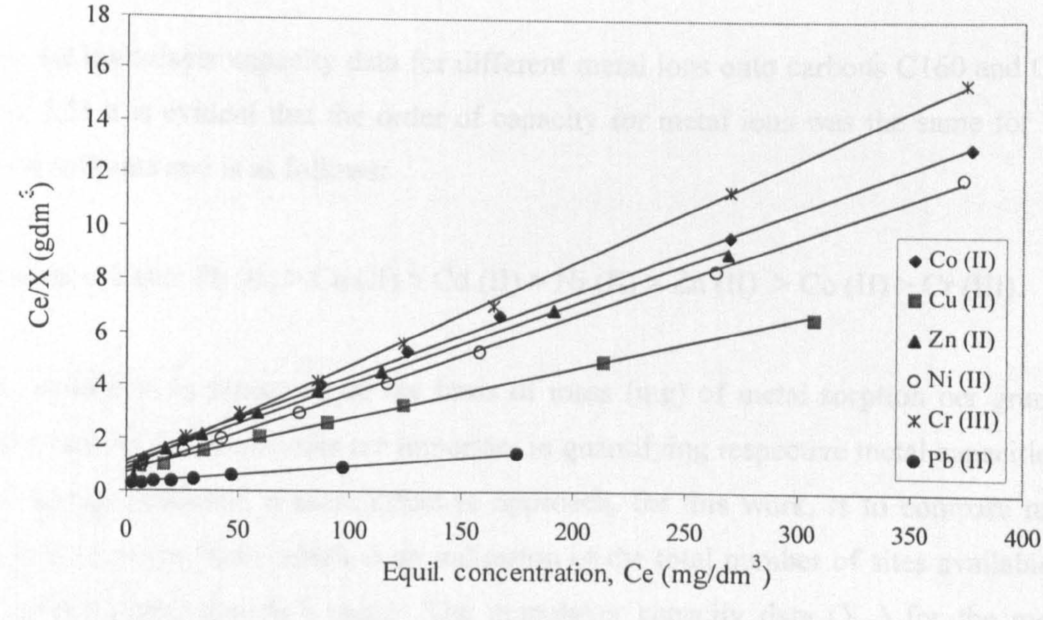

Figure 5.22. Langmuir isotherms for metal sorption on C200 at 25 °C.

Metal	Carbon type	Langmuir constants			Correlation coefficient for X_m	$\frac{X_mC160}{X_mC200}$
		X_m (monolayer capacity)		*b* constant		
		mg/g	mmol/g	dm^3/g		
Co (II)	C160	17.33	0.294	0.0301	0.998	0.55
	C200	31.25	0.530	0.0282	0.999	
Cr (III)	C160	14.29	0.275	0.0454	0.999	0.56
	C200	25.51	0.491	0.0467	0.999	
Cu (II)	C160	31.65	0.498	0.0304	0.999	0.61
	C200	52.08	0.820	0.0239	0.998	
Ni (II)	C160	19.19	0.326	0.0458	0.999	0.57
	C200	33.45	0.570	0.0453	0.999	
Pb (II)	C160	86.96	0.420	0.0254	0.997	0.59
	C200	147.1	0.710	0.0256	0.999	
Zn (II)	C160	18.25	0.279	0.0229	0.997	0.56
	C200	32.47	0.497	0.0320	0.993	
Cd (II)	C160	21.05	0.187	0.0673	0.999	0.54
	C200	39.06	0.348	0.0745	0.999	

Table 5.5. Langmuir sorption parameters for metal sorption on dry C160 and C200 at 25 °C.

From the monolayer capacity data for different metal ions onto carbons C160 and C200 (table 5.5) it is evident that the order of capacity for metal ions was the same for both carbon sorbents and is as follows:

On mass basis: Pb (II) > Cu (II) > Cd (II) > Ni (II) > Zn (II) > Co (II) > Cr (III).

This correlation is presented on the basis of mass (mg) of metal sorption per gram of carbon sorbent and these units are important in quantifying respective metal capacities in 'real' terms. However, a more effective approach, for this work, is to compare metal uptake on a molar basis which is an indication of the total number of sites available on the carbon matrix for each metal. The monolayer capacity data (X_m) for the metals sorption onto carbons on a molar basis is presented in table 5.5. For dry C160, the capacity range is 0.187-0.498 mmol/g, while for dry C200 it is 0.348 – 0.820 mmol/g, showing the higher uptake for C200. Representing the data on a molar basis the metal monolayer capacities data (X_m) fall within a narrower range than on a mass analysis (74). From the data of X_m values in table 5.5, the order of metal capacity follows:

On molar basis: Cu (II) > Pb (II) > Ni (II) > Co (II) > Zn (II) ≈ Cr (III) > Cd (II).

There are many factors that affect the preference for metal ion sorption onto the carbon surface. Factors that can have a strong effect are the system pH and properties of the metal ions such as: ionic potential, ionic radii, electronegativity, hydration capacity, soft and hard acid-base interactions and the chemistry of the metal ions in solution. In addition, the nature and the availability of the active sites on the carbon surface is also an important factor. These factors including different pH values of the system, as shown in table 5.6, make it difficult to explain and to relate to any dominant factor or group of factors. But this will be considered in future work.

Values of the separation factor or equilibrium parameter (R_s) as defined by equation 5.4 are shown in table 5.6. These values are in the range 0.0 and 1.0 thereby indicating "favourable adsorption". Values, which were calculated at the maximum concentration values, gave R_s close to zero; implying that at higher initial concentrations the sorption process will tend to irreversibility (74).

In addition, over the whole range of initial concentrations studied, the R_s values indicate that all the metal sorption systems were "favourable". In general, the degree of favourability is inversely related to the reversibility of the system, giving a quantitative assessment of the affinity of the carbon sorbents for metal ions.

Regarding the minimum values of R_s, it would appear that the process of binding the metal ions onto carbon is strong type or perhaps approaching irreversible. Such observation further supports the suggested ion exchange mechanism which is a strong sorption type.

5.6. Cumulative cadmium sorption capacity

Batch experiments for cadmium (II) onto dry C200 were accompanied by a release of protons and so a decrease of the final pH of solution. Accordingly, it was expected that the equilibrium attained in the Langmuir isotherm experiment will not be the maximum uptake of the metal ion when all the active centres (ion exchange sites) available on surface are occupied by cadmium metal ions.

metal	Sorbent	Temp. °C	Initial pH	C_o mg dm^{-3}	b dm^3/mg	R_s, Separation Factor
Cd (II)	wet C160	25	6.00	10-400	0.0677	0.60 - 0.036
	dry C160	25	6.00	10-400	0.0673	0.60 - 0.036
	wet C160	35	6.00	10-400	0.07626	0.57 - 0.032
	wet C160	45	6.00	10-400	0.0763	0.57-0.032
	wetC200	25	6.00	20-400	0.1075	0.32 - 0.023
	wet C200	35	6.00	20-400	0.1299	0.28 - 0.019
	wet C200	45	6.00	20-400	0.1659	0.23 - 0.015
	dry C200	25	6.00	20-400	0.0745	0.40 - 0.033
	dry C200	35	6.00	20-400	0.0755	0.40 - 0.032
	dry C200	45	6.00	20-400	0.0814	0.38 - 0.030
Co (II)	dry C160	25	5.56	22-435	0.0301	0.60 - 0.07
	dry C200	25		22-435	0.0282	0.62 - 0.075
Cr(III)	dry C160	25	3.15	21-423	0.0454	0.51 - 0.049
	dry C200	25		21-423	0.0467	0.50 - 0.048
Cu (II)	dry C160	25	3.54	20-400	0.0304	0.62 - 0.076
	dry C200	25		20-400	0.0239	0.68 - 0.095
Ni (II)	dry C160	25	4.00	22-436	0.0458	0.50 - 0.048
	dry C200	25		22- 436	0.0453	0.50 - 0.048
Pb (II)	dry C160	25	4.75	21- 426	0.0254	0.65 - 0.085
	dry C200	25		20.5-412	0.0256	0.66 - 0.087
Zn (II)	dry C160	25	4.20	16.4- 328	0.0229	0.73 - 0.117
	dry C200	25		16.4- 328	0.032	0.66 - 0.087

Table 5. 6. Calculated R_s values for adsorption of metals on carbons C160 and C200 at different temperatures.

Thus an experiment to determine the maximum capacity of the sorbent was carried out as mentioned in Chapter 3, section 3.3.4. So, a 50 cm^3 solution containing 100 mg/dm^3 of cadmium (II) in a sulphate media at pH 6.00 was mixed with ~0.1 g of C200 dry and left for the equilibrium time (10 hours). Samples were separated by filtration and the sorbent reused without washing with a new aliquot of the same initial cadmium solution and the sorption of cadmium was followed for seven successive cycles.

The uptake of cadmium (II) onto C200 at 25 °C was shown for each cycle in figure 5.23 and collectively in figure 5.24. From figure 5.23, sorption in cycle 2 and cycle 3 decreases but is still high showing sorption uptake of 20.97 and 16.00 mg/g respectively after the first loading cycle for which the uptake was 31.27 mg/g. Sorption of each cycle continued to decrease until it reached cycle 6 (7.3 mg/g) and cycle 7 (3.05 mg/g). Collectively, cadmium (II) uptake shows about a three fold increase over the first sorption cycle (figure 5.24). Data are shown in appendix II, table 5.18.

When cadmium ions are sorbed on the carbon surface, protons are released into the aqueous solution until equilibrium was attained. This equilibrium does not represent full coverage of ion exchange sites but a lower value due to the hydrogen ions released competing with the incoming cadmium ions. Changing the solution to a new one at pH 6.00 with a higher concentration of cadmium allowed more cadmium ions to be sorbed on the unoccupied active sites and perhaps weaker sites, finally reaching at the end of the seven cycles a capacity of 103.0 mg/g and of course exceeding the X_m values obtained from the Langmuir equation.

5.7. Scanning Electron Microscope Studies (SEM)

Scanning electron microscope photographs for cadmium (II) and other metal loaded samples did not show any kind of surface change compared to carbon samples before use.

5.8. Cadmium (II) Sorption Using a Fixed Bed Column Sorption System

The experimental data in this section are the result of the experiments using the fixed bed column packed with carbon C200 as described in Chapter 3, page 57.

Sorption of cadmium (II) onto carbon C200 in the fixed bed column showed breakthrough after ~ 3 hours (~ 60 bed volume) with an initial solution concentration of 85 mg/dm^3 and initial pH 6.00 as shown in figure 5.25. The final pH of the effluent was

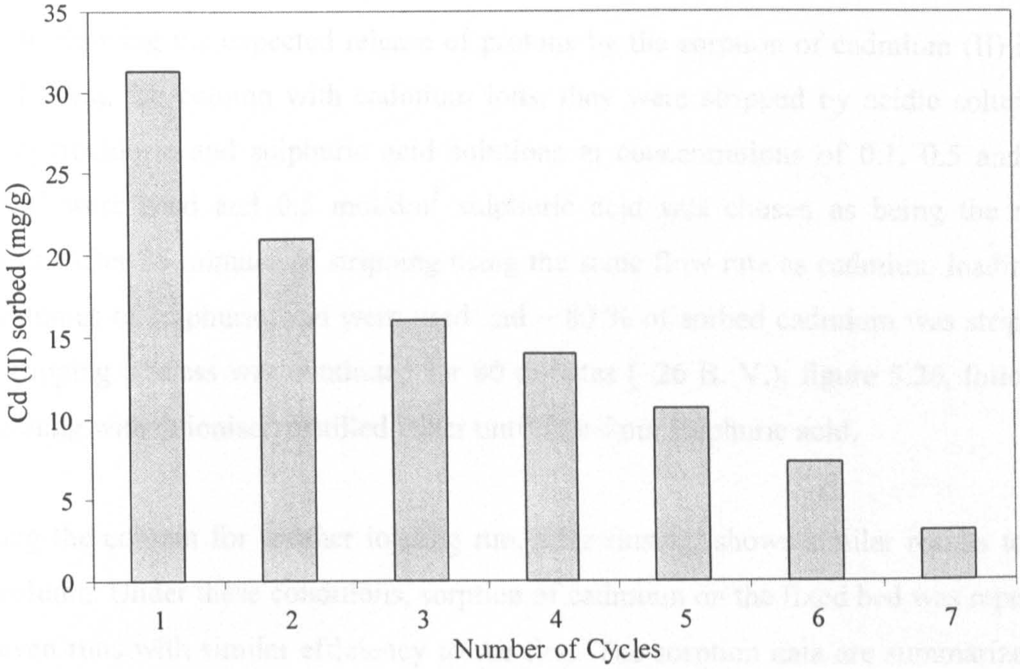

Figure 5.23. Sorption of cadmium on C200 (separately).

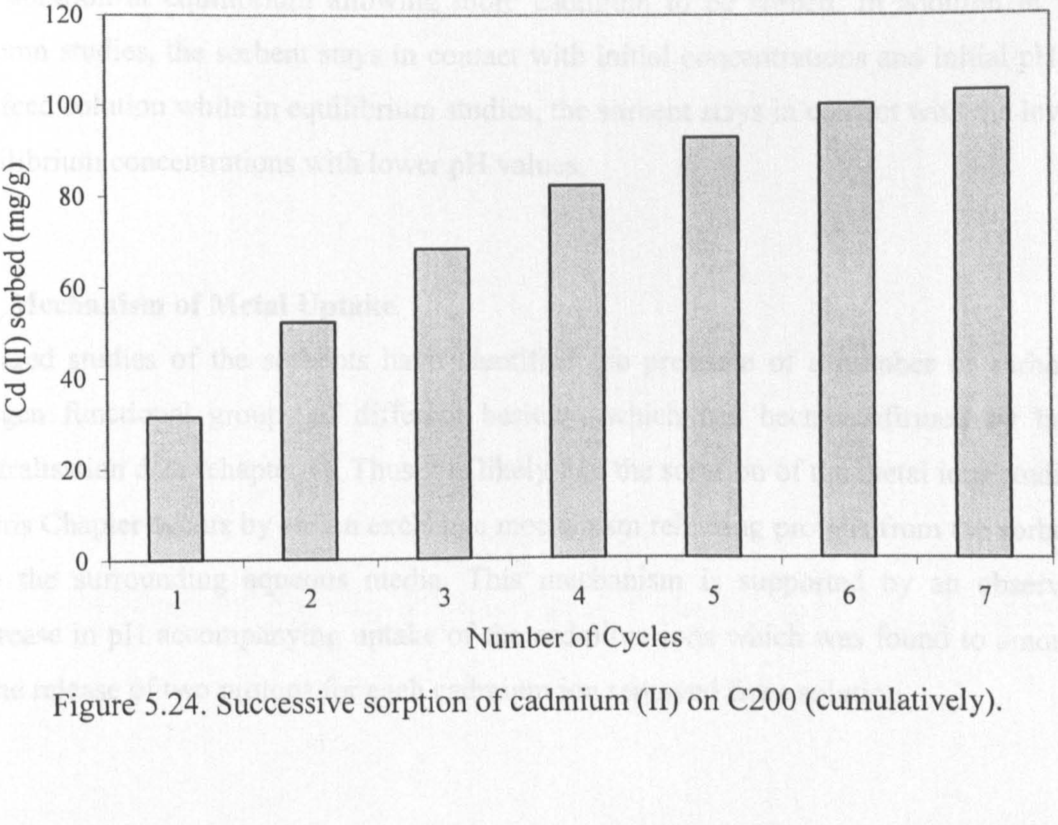

Figure 5.24. Successive sorption of cadmium (II) on C200 (cumulatively).

3.8-4.00 showing the expected release of protons by the sorption of cadmium (II) ions. After loading the column with cadmium ions, they were stripped by acidic solutions. Both hydrochloric and sulphuric acid solutions at concentrations of 0.1, 0.5 and 1.0 mol/dm^3 were used and 0.5 mol/dm^3 sulphuric acid was chosen as being the most efficient. After 25 minutes of stripping using the same flow rate as cadmium loading, 8 bed volumes of sulphuric acid were used and ~ 80 % of sorbed cadmium was stripped. The stripping process was continued for 80 minutes (~26 B. V.), figure 5.26, followed by washing with deionised distilled water until free from sulphuric acid.

Reusing the column for another loading run, after rinsing, shows similar results to the first column. Under these conditions, sorption of cadmium on the fixed bed was repeated for seven runs with similar efficiency to the first. The sorption data are summarized in appendix II, tables 5.19 and 5.20.

The efficiency of reusing the column suggests that ion exchange is the main process available or perhaps the only one. Sorption capacity for columns ranged between 57.2 and 62 mg/g which is higher than the monolayer capacity measured from the Langmuir equation. This is a result of the pH of the effluent being higher than that of the cadmium (II) solution at equilibrium allowing more cadmium to be sorbed. In addition in the column studies, the sorbent stays in contact with initial concentrations and initial pH of the feed solution while in equilibrium studies, the sorbent stays in contact with the lower equilibrium concentrations with lower pH values.

5.9. Mechanism of Metal Uptake

Infrared studies of the sorbents have identified the presence of a number of carbon–oxygen functional groups of different basicity, which has been confirmed by base neutralisation data (chapter 4). Thus it is likely that the sorption of the metal ions studied in this Chapter occurs by an ion exchange mechanism releasing protons from the sorbent into the surrounding aqueous media. This mechanism is supported by an observed decrease in pH accompanying uptake of the cadmium ions which was found to amount to the release of two protons for each cadmium ion removed from solution.

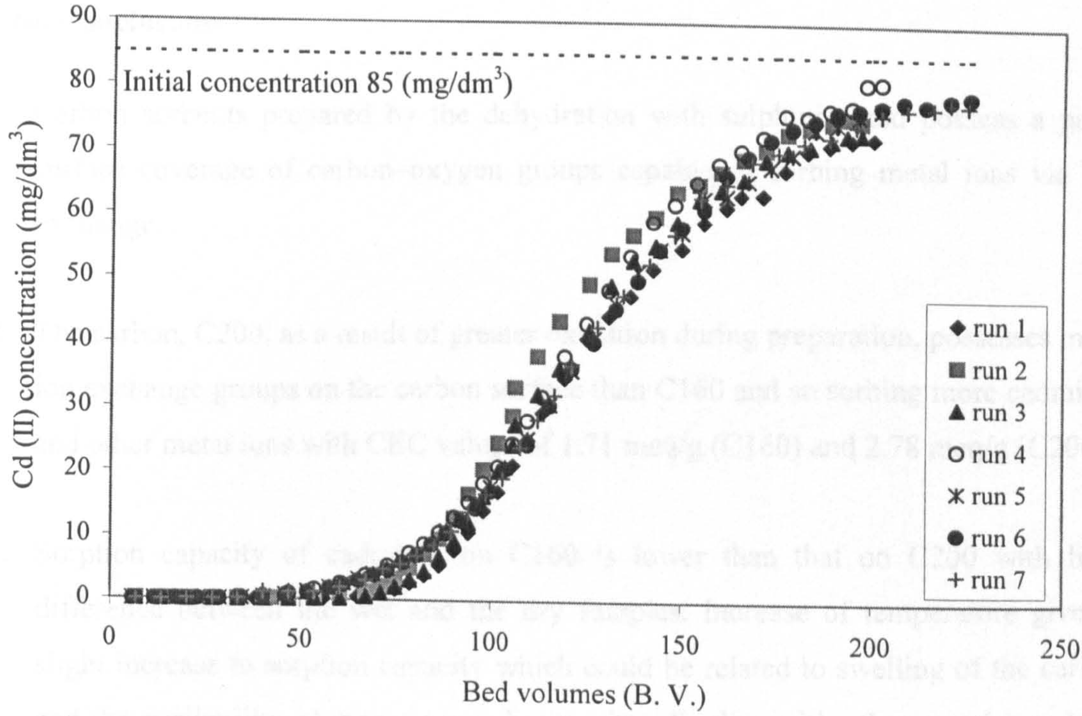

Figure 5.25. Column studies for cadmium (II) uptake on C200, seven runs.

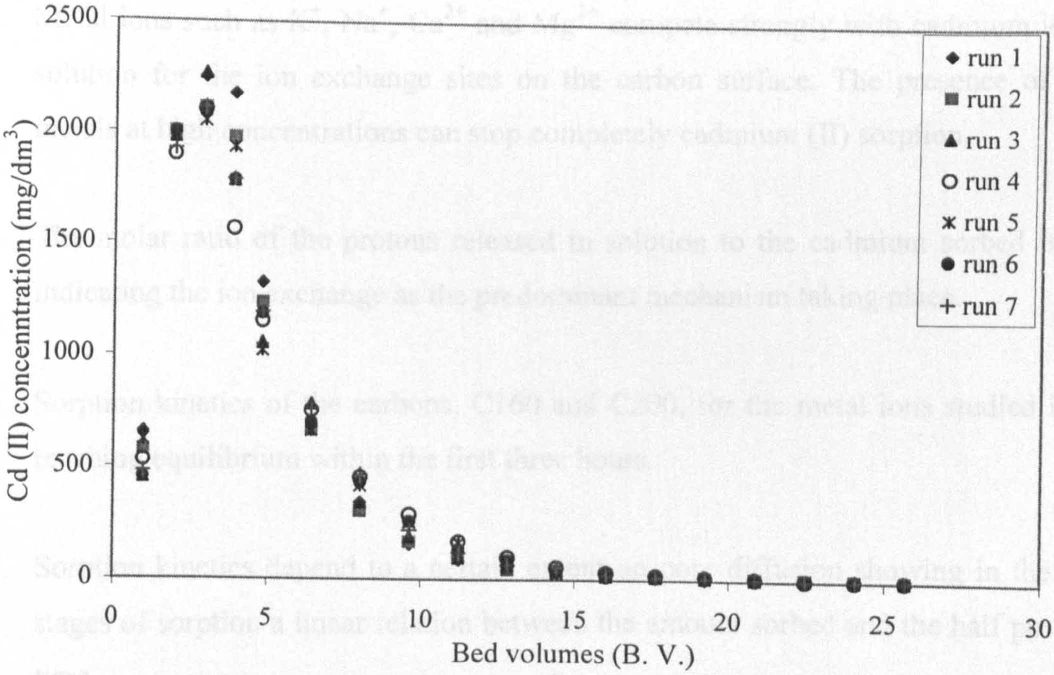

Figure 5.26. Stripping of cadmium (II) from C200 with sulphuric acid (0.5 mol/dm^3).

5.10. Conclusions

1. Carbon sorbents prepared by the dehydration with sulphuric acid possess a polar surface coverage of carbon–oxygen groups capable of sorbing metal ions via ion exchange.

2. The carbon, C200, as a result of greater oxidation during preparation, possesses more ion exchange groups on the carbon surface than C160 and so sorbing more cadmium and other metal ions with CEC values of 1.71 meq/g (C160) and 2.78 meq/g (C200).

3. Sorption capacity of cadmium on C160 is lower than that on C200 with little difference between the wet and the dry samples. Increase of temperature gives a slight increase in sorption capacity which could be related to swelling of the carbon and the availability of more ion exchange sites. Studies with other metal ions have shown a higher sorption capacity for copper (II) and lead (II) and a smaller capacity for cadmium (II) and chromium (III).

4. Metal ions such as K^+, Na^+, Ca^{2+} and Mg^{2+} compete strongly with cadmium ions in solution for the ion exchange sites on the carbon surface. The presence of these metals at high concentrations can stop completely cadmium (II) sorption.

5. The molar ratio of the protons released in solution to the cadmium sorbed is 2.03 indicating the ion exchange as the predominant mechanism taking place.

6. Sorption kinetics of the carbons, C160 and C200, for the metal ions studied is fast reaching equilibrium within the first three hours.

7. Sorption kinetics depend to a certain extent on pore diffusion showing in the early stages of sorption a linear relation between the amount sorbed and the half power of time.

8. Sorption kinetics also fit a first order rate equation indicating that sorption depends on the concentration of metal ions.

9. Sorption of cadmium is highly dependent on the pH of the solution with low sorption at low pH values and reaching a plateau between pH 3-7.

10. The carbon prepared by dehydration could be a cheap efficient sorbent for ion exchanged metal cations.

CHAPTER 6

RESULTS AND DISCUSSION III. SORPTION-REDUCTION OF METAL IONS ON CARBON BY DEHYDRATION WITH SULPHURIC ACID.

6.1. Introduction

Metal ions can be removed on solid sorbents via adsorption, ion exchange, and complexation as summarized in Chapter 5. In addition, oxidation-reduction reactions are important processes for metal uptake onto carbon sorbents. The following sections provide the basic principles of redox reactions together with a literature survey about the involvement of redox processes.

6.1.1. Oxidation reduction reactions

6.1.1.1. Basic principles

Oxidation-reduction (redox reaction) is a process where electrons are transferred from one reactant to another.

$$\text{Thus: } Ce^{4+} + Fe^{2+} = Ce^{3+} + Fe^{3+} \qquad (6.1)$$

This equation can be summarized in the following general equation (141):

$$Ox1 + Red2 = Red1 + Ox2$$

Ox1(oxidizing agent) which is Ce^{4+} is reduced to Red1 (reducing agent), Ce^{3+}; while Red2 (reducing agent) which is Fe^{2+} is oxidized to the Ox2 (oxidizing agent), Fe^{3+}.

Equation 6.1 can be split into two half reactions:

$$Ce^{4+} + e = Ce^{3+} \quad , \quad E^{o} \ +1.72\ V.$$

$$Fe^{2+} = Fe^{3+} + e \quad , \quad E^{o} \ +0.771\ V.$$

Standard electrode potentials of some element systems are shown in table 6.1.

6.1.2. Mechanism of metal sorption onto activated carbon, peat and lignite (literature survey):

In addition to adsorption, ion exchange and complexation for metal uptake on peat, lignite and activated carbons, reduction of metal ions to lower oxidation states is another important process which can occur.

Reduced forms of metal ions can be soluble or insoluble in the aqueous solution. Soluble reduced forms (metal ions with lower oxidation states) could be sorbed via ion exchange, complexation and adsorption on the sorbent surface. Lower oxidation states of the metals may also interact with other species in solution leading to other chemical processes such as precipitation and crystallisation.

Element	Reduction half-reaction	Standard reduction potential E°, volts
Au	$Au^{3+} + 3e = Au\ (s)$	+1.498
	$AuCl_4^- + 3e = Au\ (s) + 4Cl^-$	+1.002
	$Au(CN)_4^- + 3e = Au\ (s) + 4CN^-$	-0.18 (163)
	$Au\ (CN)_2^- + e = Au\ (s) + 2CN^-$	-0.57 (164)
Br_2	$Br_2\ (aq) + 2e = 2Br^-$	+1.0873
Hg	$2Hg^{2+} + 2e = Hg_2^{2+}$	+ 0.92
	$Hg^{2+} + 2e = Hg\ (l)$	+ 0.851
	$Hg_2Cl_2 + 2e = 2Hg^o + 2Cl^-$	+0.2681
	$HgCl_4^{2-} + 2e = Hg^o + 4Cl^-$	+0.48 (165)
	$Hg\ {}^{2}{}_{2}{}^{+} + 2\ e = 2\ Hg\ (l)$	+ 0.7973
	$Hg(CN)_4^- + 2e = Hg(l) + 4CN^-$	-1.60 (166)
	$Hg(CN)_2 + 2e = Hg(l) + 2CN^-$	-1.23 (166)
Ag	$Ag^+ + e = Ag\ (s)$	+ 0.7996
	$Ag(CN)_2 + e = Ag\ (s) + 2CN^-$	-0.382 (167)
Pt	$[PtCl_4]^{2-} + 2e = Pt\ (s) + 4Cl^-$	+0.755
Pd	$[PdCl_4]^{2-} + 2e = Pd\ (s) + 4Cl^-$	+0.591
Cu	$Cu^{2+} + 2\ e = Cu\ (s)$	+ 0.3419
H	$2H^+ + 2\ e = H_2\ (g)$	0.000
Pb	$Pb^{2+} + 2e = Pb\ (s)$	- 0.1262
Co	$Co^{2+} + 2\ e = Co\ (s)$	- 0.28
Ni	$Ni^{2+} + 2e = Ni\ (s)$	- 0.257
Cd	$Cd^{2+} + 2e = Cd\ (s)$	- 0.403
Zn	$Zn^{2+} + 2\ e = Zn\ (s)$	- 0.7618
Mg	$Mg^{2+} + 2\ e = Mg\ (s)$	- 2.372
Na	$Na^+ + e = Na\ (s)$	-2.71
K	$K^+ + e = K\ (s)$	-2.931

note: Unnotified reduction potential values are from (CRC (168) 77th ed.).

Table 6.1. Standard electrode potential of some element systems.

In a study of the literature, examples have been found of reduction occurring on peat, lignite and activated carbon surfaces. Huang (66) studied the adsorption of chromium (VI) onto activated carbon. The adsorption was found to vary with the pH of the solution reaching a maximum at around pH 5-6. The sorption mechanism was explained by two types of surface reaction: reduction from chromium (VI) to chromium (III) which occurs only at pH<6, since no chromium (III) was found in the supernatant when pH was greater than 6, and adsorption of most of the original chromium (VI) and part of the reduced chromium (III), onto the activated carbon surface. Similar behaviour of chromium (VI) sorption has been found on different activated carbons (67) where the study shows that chromium (VI) sorption is pH dependent and the mechanism is adsorption, coupled with reduction at lower pH values.

Another example of the reducing properties of active carbon has been found with other systems. Thus gold (III) as ($AuCl_4^-$) was reduced to metallic gold and the adsorption was shown to follow a first order reduction process (169), and silver (I) in nitrate solution was also reduced to the metallic state Ag^0 (167).

On the other hand, the mechanism of sorption of the complex of these two metals with cyanide species: $Au(CN)_2^-$, $Au(CN)_4^-$, $Ag(CN)_2^-$ was adsorption as ion pairs such as: $M^{n+}[Au(CN)_2^-]_n$, $M^{n+}[Au(CN)_4^-]_n$, $M^{n+}[Ag(CN)_2^-]_n$ (164,167,170). The difference in behaviour of the chloroauric ion and silver cation, and these cyanocomplexes is related to the difference between the reduction potential of those species and that of activated carbon (167,169). Electrochemical reduction is thermodynamically feasible if the equilibrium potential of the metal ion is more positive than the activated carbon surface potential (171). Thus reduction is feasible for gold (III) ($AuCl_4^-$) and silver (I) ($AgNO_3$) but not for the cyanide species, table 6.1. The reduction potentials of activated carbons have been found to lie between 0.40 and 0.08 V (172) as reported by Adams (167).

Another study on the sorption of $AuCl_4^-$, $PtCl_4^{2-}$, $PdCl_4^{2-}$, Ni^{2+} onto activated carbon (171) showed that $AuCl_4^-$, $PtCl_4^{2-}$ and $PdCl_4^{2-}$ could be reduced to their metallic states whereas Ni^{2+} (E^o = -0.257V), not surprisingly, could not be reduced onto the activated carbon surface.

Adams (166) found that the cyanide species of mercury (II), $Hg(CN)_2$ ($E^o = -1.23V$) and $Hg(CN)_4^{2-}$ ($E^o = -1.60V$), are not reduced by activated carbon and so they are adsorbed in their original form. On the other hand, $HgCl_2$ (E^o+0.92V) was reduced to Hg_2Cl_2 onto the carbon surface. This is related to the potential difference between the mercury (II) species and that of the carbon which was estimated to be +0.24 V (166).

Fu *et al* studied the reduction properties of activated carbon fibres (173-176). They found that gold (III) ($AuCl_3$) (173) and platinum (IV) (H_2PtCl_6) (174) were reduced to gold and platinum metals respectively. An extensive study by these authors (175) included, in addition to these metals, silver (I) ($AgNO_3$), mercury (II) ($HgCl_2$), iron (III) ($FeCl_3$) and MnO_4^- ($KMnO_4$). Reduction of gold (III), platinum (IV) and silver (I) to their metallic states and mercury (II) to mercury (I) chloride was confirmed by X-ray diffraction. $KMnO_4$ was found to be reduced to MnO_2 and further to Mn^{2+}. Iron (III) ions showed some reduction by the carbon fibers (175). Because reduction must always be accompanied by an equivalent oxidation process the authors showed (176) that oxidation of the surface of the activated carbon fibres occurs to produce hydroxyl (or phenolic) groups and carbonyl or carboxyl groups. The process also produced carbon dioxide and protons.

The mechanism of sorption of the uranyl ion, UO_2^{2+}, onto lignite has been studied (177). Uranyl complexation with the carboxylic groups was considered to occur as a result of cation exchange with surface carboxyl groups. A reduction mechanism was also observed which was explained by dehydrogenation of hydroxyl and aliphatic hydrocarbon moieties.

Reduction of some metallic cations onto lignite has been investigated (178). It was found that Pd^{2+}, Pt^{4+}, Ag^+ and Fe^{3+} were reduced onto the lignite surface while not surprisingly Cs^+ and Nd^{3+} were not reduced.

Sorption of gold (III) ($AuCl_3$) onto lignite (179) and by humic compounds derived from peat (180) also showed reduction to the metallic state. The process of reduction was accompanied by oxidation of lignite and humic substances respectively. "Previous studies have estimated reduction potentials for humic substances to be +0.5 - 0.7V at pH 0 with values decreasing at ~25 mV/pH unit as pH increases (181, 182)" (180). Fulvic acid was also found to reduce mercury (II) to elemental mercury and iron (III) to iron (II) (183).

In this study, even though redox reactions play a very important role for metal sorption, it is difficult to consider it as the only process contributing to metal sorption on carbon surface. Other processes such as ion exchange and adsorption are also almost certainly participating.

In this study, carbon C160 was chosen to test the metal ions that experience reduction. This is because C160 has similar capacity to C200 for the removal of mercury (II) from chloride media, it has a higher preparation yield and also requires less energy for production. Thus for these reasons, C160 was chosen to study the sorption of mercury (II), chromium (VI), gold (III), palladium (II), silver (I) and platinum (II).

6.2. Mercury (II) Sorption onto Carbon C160

6.2.1. Introduction

Mercury metal and its ionic forms are very toxic. It is included within the Black List in the Directive (76/464/EEC) of the dangerous substances in aquatic environment (9). The maximum acceptable concentration of mercury in all forms in waters is < 1μg/dm^3. Monomethylmercury (CH_3Hg^+) is the most toxic form of mercury (4). Minamata disease, one of the most famous accidental pollution events, was caused by the consumption of sea foods contaminated with methylmercury compounds which followed mercury discharges from the Chisso Company factory at Minamata (184).

Activated carbon has been widely used (62, 63, 68, 71, 73, 185) for the removal of mercury (II) from aqueous solution. Huang *et al* (62) showed that the highest removal of mercury (II) was attained at pH 4-5 and the mechanism of sorption was described by two reactions; adsorption and reduction. The reduced form of mercury (II) was shown to be Hg^o (elemental mercury) since the initial mercury (II) form was nitrate. The reduced mercury was removed from the carbon by volatilization with a stream of nitrogen gas at a high flow rate. It was found that both adsorption and reduction are pH dependent. The initial adsorption rate was very fast, and as the reaction time progresses the contribution of the adsorption reaction decreases and finally becomes overtaken by the reduction reaction.

Removal of mercury (II) from drinking water to comply with the guideline concentration of mercury in the drinking water has been successfully achieved by activated carbon (68). Initial concentrations of mercury (II) were 10 μg/dm^3, 10 times more than its maximum acceptable value (MAC). After treatment with activated carbon the value was below the MAC value.

Other workers (166, 186) have found that mercury (II) chloride was reduced to mercury (I) on the activated carbon surface. Adams (166) also found that the cyanide species of mercury (II), $Hg(CN)_2$ and $Hg(CN)_4^{2-}$, are not reduced by the activated carbon and they are adsorbed in their original form. Reduction of mercury (II) on activated carbon fibres has also been found (175, 176), and Zeng and Fu (187) showed that the adsorption process includes redox reaction, ion exchange, complex formation and precipitation.

Sorption of mercury (II) onto carbon prepared by dehydration from flax fibre waste (flax shive) has been studied by Pichugin (57) and this study formed the basis of the present work.

6.2.2. Kinetics of mercury sorption

The kinetics of mercury (II) sorption is shown in figure 6.1, with the wet carbon sample reaching equilibrium in ~ 80 hours compared to about 120 hours for the dried material. As noted earlier, this reduction in rate for the dried sample is probably related to shrinking and compaction of the carbon on drying giving narrower pores for the diffusion of the mercury (II) ions. Table 6.1 (appendix III) shows these kinetic sorption data.

In the initial stages of sorption, the uptake of mercury (II) was found to vary almost linearly with the half power of time, $t^{0.5}$, according to equation 5.7 (160).

$$X = k_d t^{0.5} \qquad (5.7)$$

where X is the amount sorbed (mmol/g) and k_d is the rate constant for pore diffusion. This relationship is presented in figure 6.2, and such behaviour is predicted when a large initial fraction of the reaction is controlled by intra-particle diffusion (161). The rate constant of mercury (II) sorption on wet carbon shows a higher rate (0.1009 mmol g^{-1} $hr^{-0.5}$) than that of dry material (0.0565 mmol g^{-1} $hr^{-0.5}$). This could be related to the narrower pores developed by drying. However, as with the cadmium results in Chapter 5, the linear plots do not pass through the origin. Similar results have been interpreted as pore diffusion might not be the only rate controlling step (160, 188).

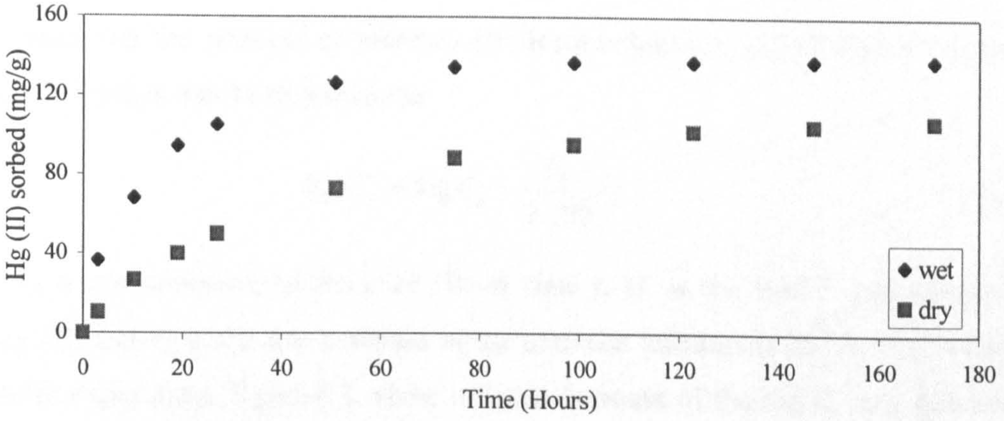

Figure 6.1. Kinetics of mercury (II) sorption (chloride media) on wet and dry carbon C160 at 25 °C.

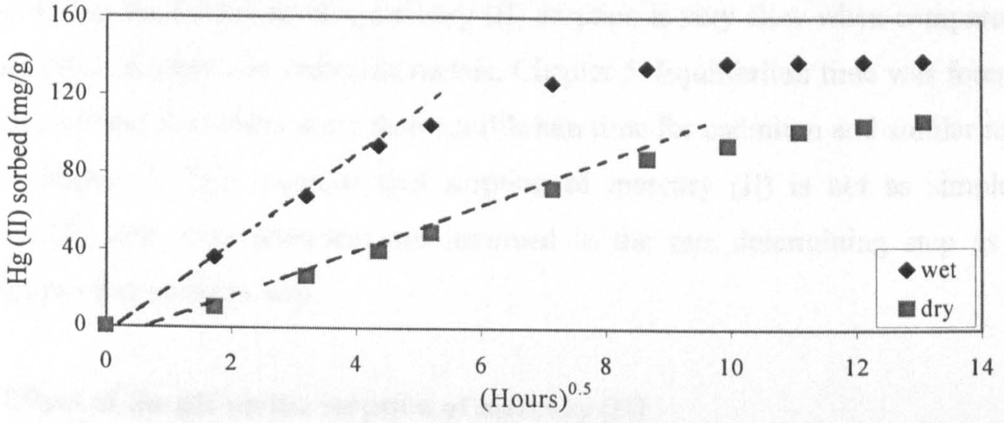

Figure 6.2. A plot of the rate of pore diffusion for mercury (II) sorption on wet and dry C160.

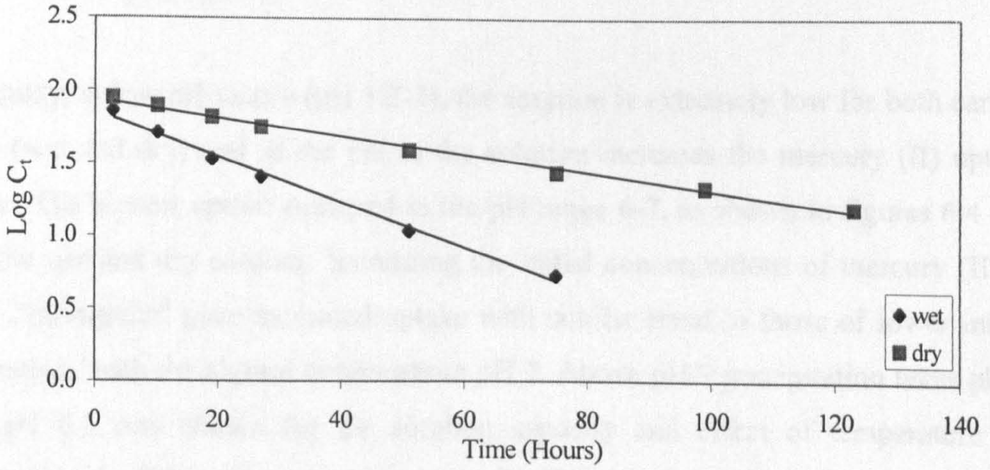

Figure 6.3. A plot of the first order reaction equation for mercury sorption on C160 at 25 °C. (C_t is expressed in mg/dm^3).

It was found that the removal of mercury (II) from solution also followed a first-order rate equation which can be expressed as:

$$\log C_t = \log C_o - \frac{k_1}{2.303} \cdot t \qquad (5.8)$$

where C_t is concentration of mercury (II) at time t, C_o is the initial concentration of mercury (II) and k_1 is the rate constant of the sorption reaction at 25 °C. The results of the kinetic experiment, figure 6.3, show a linear decrease of the log C_t as a function of time for both sets of experiments. The rate constants for mercury (II) sorption on the wet and dry carbon were 0.0359 and 0.0144 h^{-1} respectively.

As shown from the kinetic results, mercury (II) sorption is very slow when compared to cadmium (II) and other non-reducible metals, Chapter 5. Equilibrium time was found to be 40-60 (wet and dry) times more than equilibrium time for cadmium and similar metal ions in Chapter 5. This suggests that sorption of mercury (II) is not as simple as cadmium (II) and other processes are involved in the rate determining step as ion exchange is a fast sorption step.

6.2.3. Effect of the pH on the sorption of mercury (II)

In general, pH is an important factor in the sorption of metal cations onto different sorbents. Mercury (II) removal on carbon sorbents is highly dependent on the pH of the sorption solution (62, 68).

In this study, at low pH values (pH 1.2-2), the sorption is extremely low for both carbon samples (wet and dry) and as the pH of the solution increases the mercury (II) uptake increases. The highest uptake occurred in the pH range 6-7, as shown in figures 6.4 and 6.5 for the wet and dry carbons. Increasing the initial concentrations of mercury (II) to 200 and 300 mg/dm^3 gave increased uptake with similar trend to those of lower initial concentrations with the highest uptake about pH 7. Above pH 7 precipitation takes place and so pH 6.5 was chosen for the sorption capacity and effect of temperature for mercuric chloride. Data are presented in appendix III, table 6.2 and 6.3.

Wet carbon shows higher uptake of mercury (II) than those which had been previously dried. The initial pH of solution for these experiments from nitrate media was 3.0.

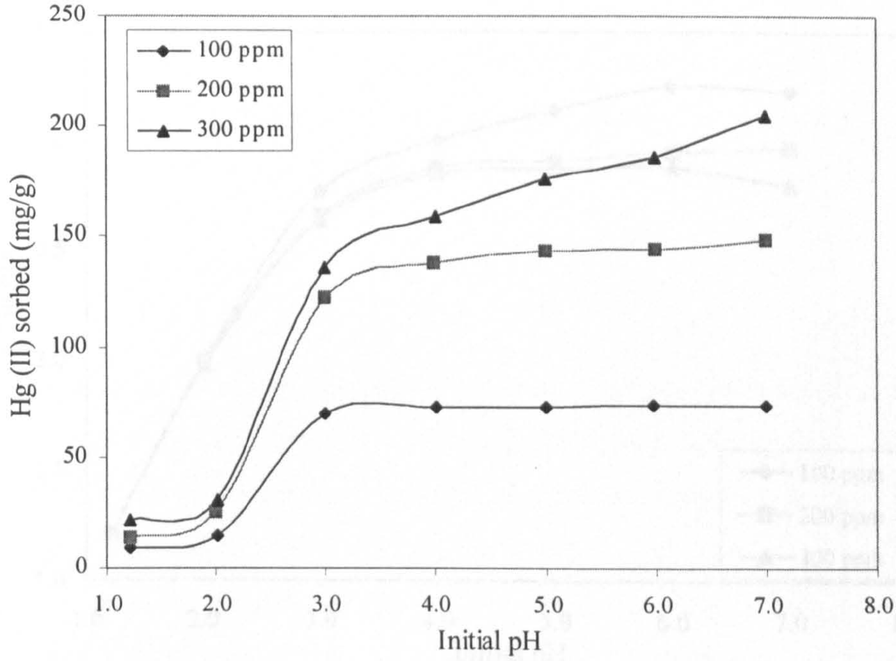

Figure 6.4. Effect of initial pH on the removal of mercury (II) chloride media, on wet C160.

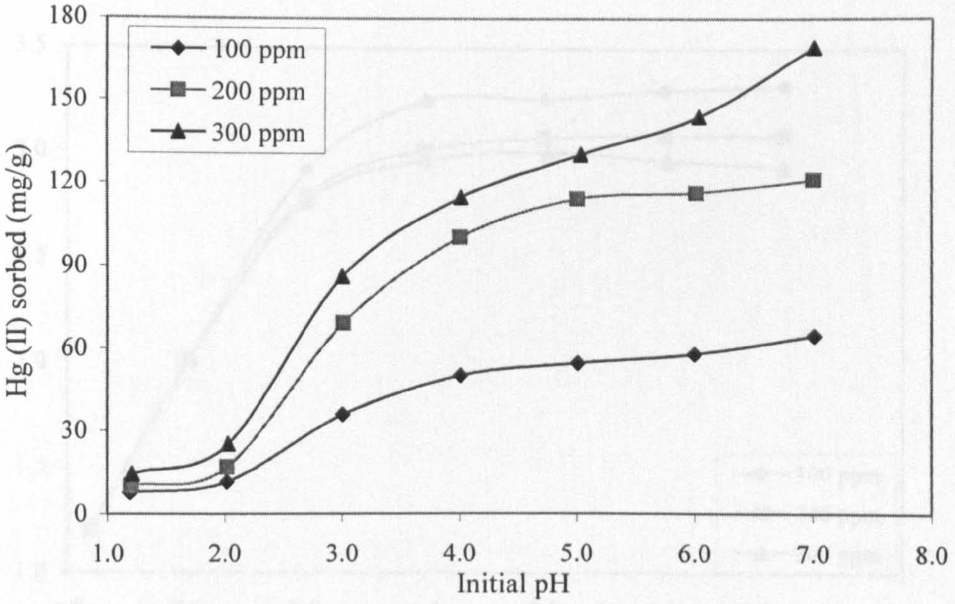

Figure 6.5. Effect of initial pH on the removal of mercury (II) chloride media, on dry C160.

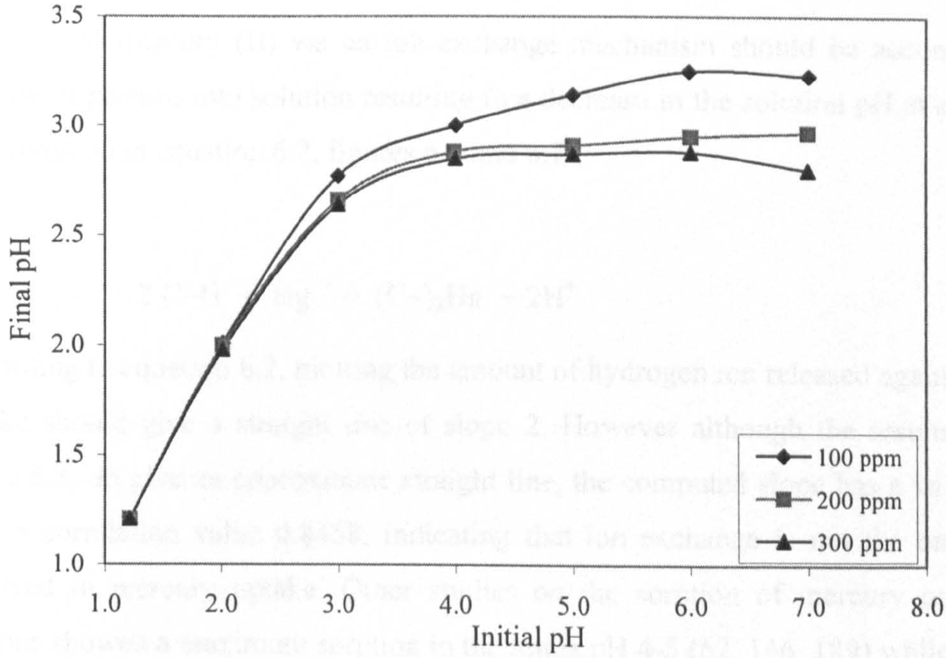

Figure 6.6. Relation between initial pH and final pH for wet C160 with different initial concentrations of mercury (II).

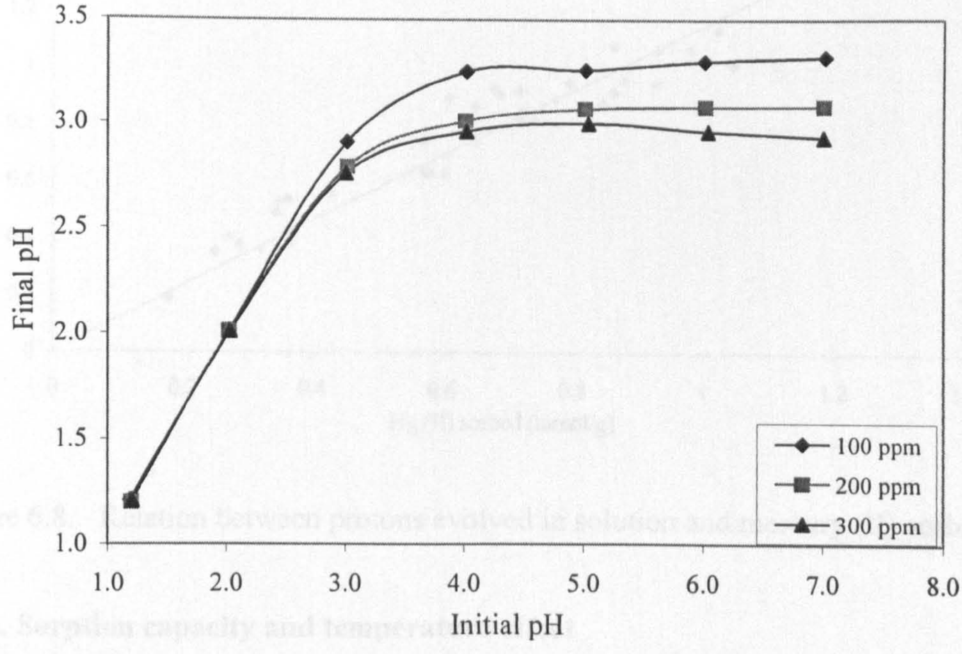

Figure 6.7. Relation between initial pH and final pH for dry C160 with different initial concentrations of mercury (II).

Sorption of mercury (II) via an ion exchange mechanism should be accompanied by release of protons into solution resulting in a decrease in the solution pH at equilibrium as expressed in equation 6.2, figures 6.6 and 6.7.

$$2\ C\text{\textasciitilde}H + Hg^{2+} = (C\text{\textasciitilde})_2Hg + 2H^+ \qquad (6.2)$$

According to equation 6.2, plotting the amount of hydrogen ion released against mercury uptake should give a straight line of slope 2. However although the results obtained, figure 6.8, do give an approximate straight line, the computed slope has a value of 1.17 with a correlation value 0.8458, indicating that ion exchange is not the only process involved in mercury uptake. Other studies on the sorption of mercury on activated carbons showed a maximum sorption in the range pH 4-5 (62, 146, 189) while for others (68), the sorption maximum was found around pH 7. The maximum adsorption of mercury (II) on carbon prepared by acid dehydration of saw-dust (146) was in the range pH 4-8. These values support the results in this study.

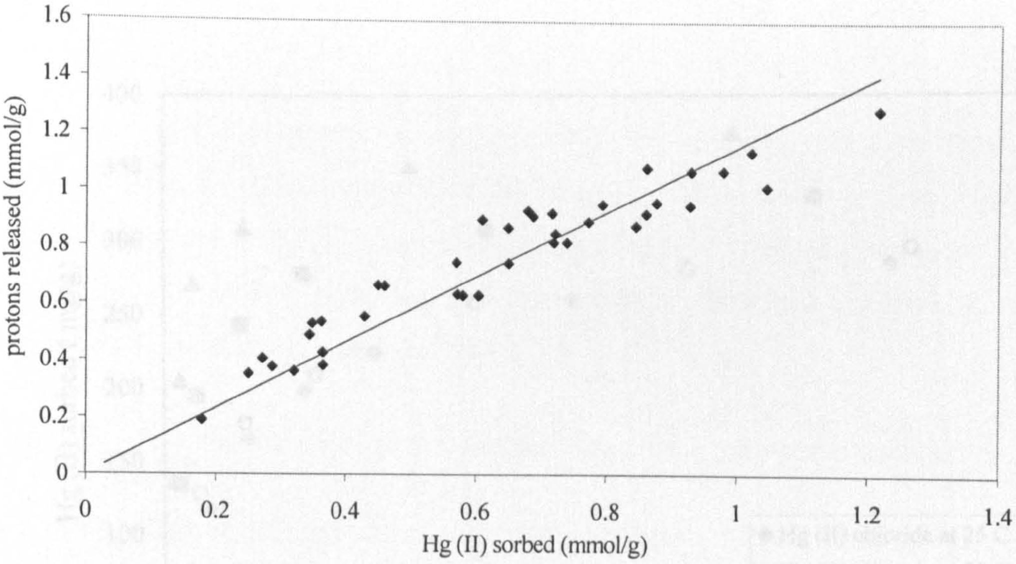

Figure 6.8. Relation between protons evolved in solution and mercury (II) sorbed.

6.2.4. Sorption capacity and temperature effect

Sorption of mercury (II) onto both forms (wet, dry) of the carbon C160 follows an "L-type" adsorption isotherm, with increasing capacity with temperature, figures 6.9 and 6.10. Again the wet sample gave a better performance than that which had been dried.

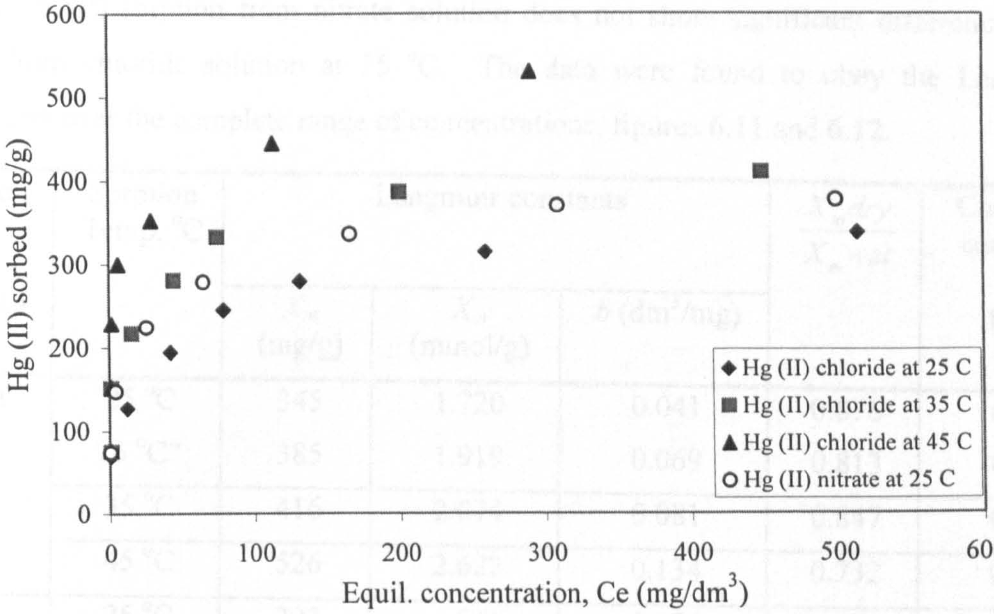

Figure 6.9. Sorption isotherms of mercury (II) on wet C160 at 25, 35 and 45 °C.

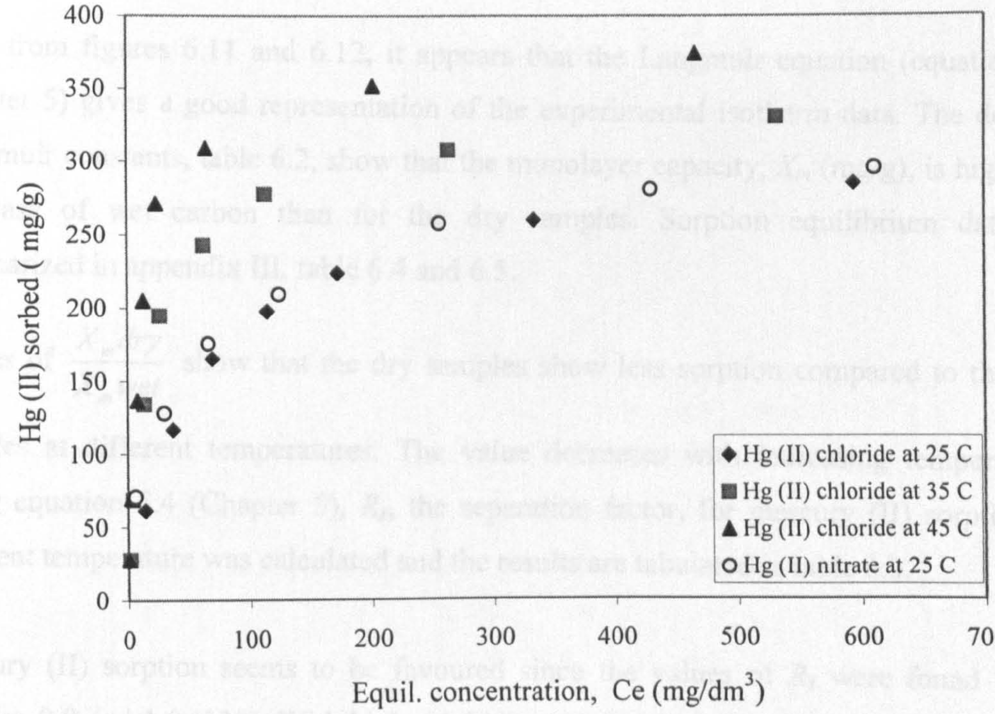

Figure 6.10. Sorption isotherms of mercury (II) on dry C160 at 25, 35 and 45 °C.

Mercury (II) sorption from nitrate solution does not show significant difference from that from chloride solution at 25 °C. The data were found to obey the Langmuir isotherm over the complete range of concentrations, figures 6.11 and 6.12.

Carbon (C160)	Sorption Temp. °C	Langmuir constants			$\frac{X_m dry}{X_m wet}$	Correlation coefficient for X_m
		X_m (mg/g)	X_m (mmol/g)	b (dm^3/mg)		
Wet	25 °C	345	1.720	0.041	0.878	0.996
	25 °C*	385	1.919	0.069	0.813	0.998
	35 °C	416	2.074	0.081	0.847	0.998
	45 °C	526	2.622	0.134	0.732	0.995
Dry	25 °C	303	1.511	0.020		0.995
	25 °C*	313	1.560	0.022		0.997
	35 °C	344	1.715	0.047		0.999
	45 °C	385	1.919	0.079		0.999

* Data for mercury (II) nitrate and the rest for mercury (II) chloride.

Table 6.2. Langmuir constants for mercury (II) sorption onto wet and dry carbon at 25, 35 and 45 °C.

Thus from figures 6.11 and 6.12, it appears that the Langmuir equation (equation 5.1 Chapter 5) gives a good representation of the experimental isotherm data. The derived Langmuir constants, table 6.2, show that the monolayer capacity, X_m (mg/g), is higher in the case of wet carbon than for the dry samples. Sorption equilibrium data are summarized in appendix III, table 6.4 and 6.5.

Values of $\frac{X_m dry}{X_m wet}$ show that the dry samples show less sorption compared to the wet samples at different temperatures. The value decreases with increasing temperature. Using equation 5.4 (Chapter 5), R_s, the separation factor, for mercury (II) sorption at different temperature was calculated and the results are tabulated in table 6.3.

Mercury (II) sorption seems to be favoured since the values of R_s were found to be between 0.0 and 1.0 (139). With higher initial concentrations R_s values are close to zero indicating that at higher initial concentrations the sorption process tends to irreversibility (74).

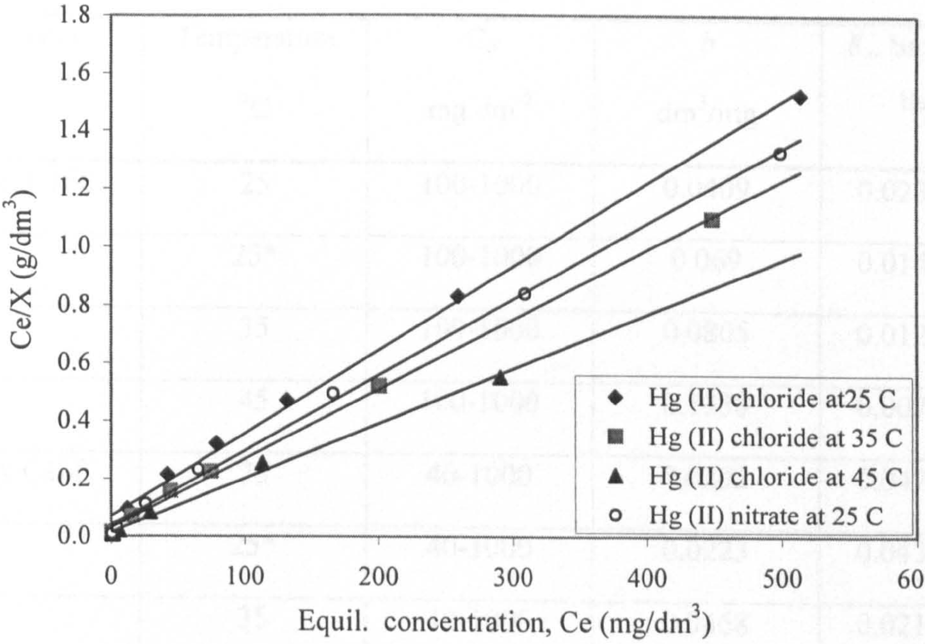

Figure 6.11. Langmuir isotherms for mercury (II) sorption on wet C160 at 25, 35 and 45 °C.

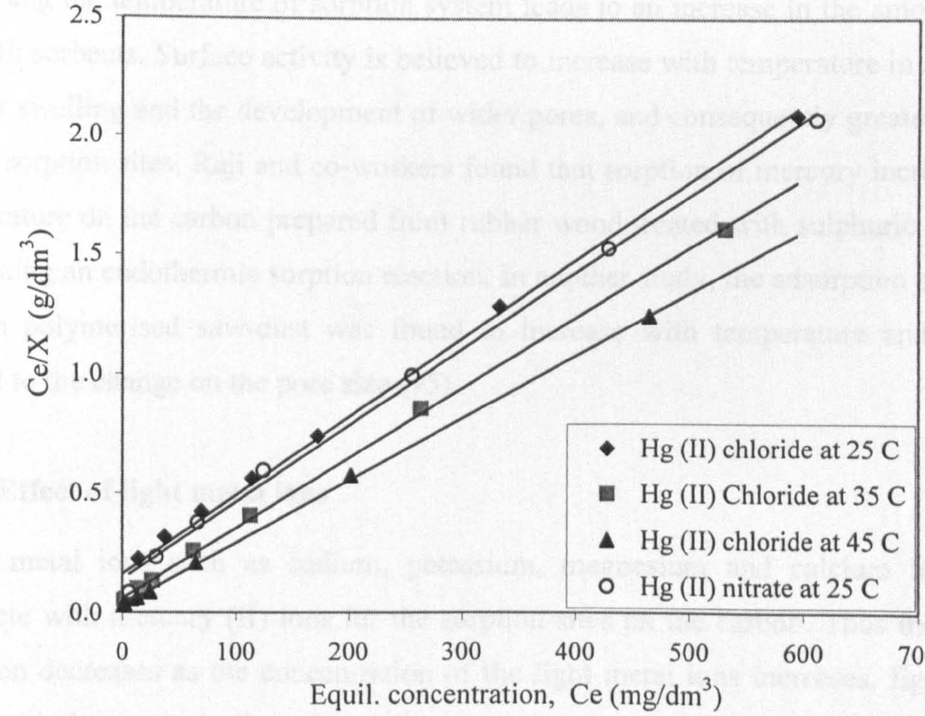

Figure 6.12. Langmuir isotherms for mercury (II) sorption on dry C160 at 25, 35 and 45 °C.

Sorbent	Temperature °C	C_o mg dm^{-3}	*b* dm^3/mg	R_s, Separation factor
Wet C160	25	100-1000	0.0409	0.023-0.196
	25*	100-1000	0.069	0.014-0.127
	35	100-1000	0.0805	0.012-0.110
	45	100-1000	0.1338	0.007-0.070
Dry C160	25	40-1000	0.0202	0.047-0.553
	25*	40-1000	0.0223	0.043-0.529
	35	40-1000	0.0468	0.021-0.348
	45	40-1000	0.0790	0.012-0.240

* refers to mercury (II) nitrate solution, the rest are for mercury (II) chloride solution.

Table 6.3. Separation values for mercury (II) sorption on wet and dry C160 at different temperatures.

Increasing the temperature of sorption system leads to an increase in the amount sorbed for both sorbents. Surface activity is believed to increase with temperature in addition to greater swelling and the development of wider pores, and consequently greater access to active sorption sites. Raji and co-workers found that sorption of mercury increased with temperature on the carbon prepared from rubber wood treated with sulphuric acid (146) suggesting an endothermic sorption reaction. In another study, the adsorption of mercury (II) on polymerised saw-dust was found to increase with temperature and this was related to the change on the pore size (95).

6.2.5. Effect of light metal ions

Light metal ions such as sodium, potassium, magnesium and calcium in solution compete with mercury (II) ions for the sorption sites on the carbon. Thus the mercury sorption decreases as the concentration of the light metal ions increases, figures 6.13, 6.14, with the greatest effect observed with the wet form of the carbon. This decrease in mercury uptake in the presence of other metal ions is due to competition of these ions for the cation exchange sites on the carbon.

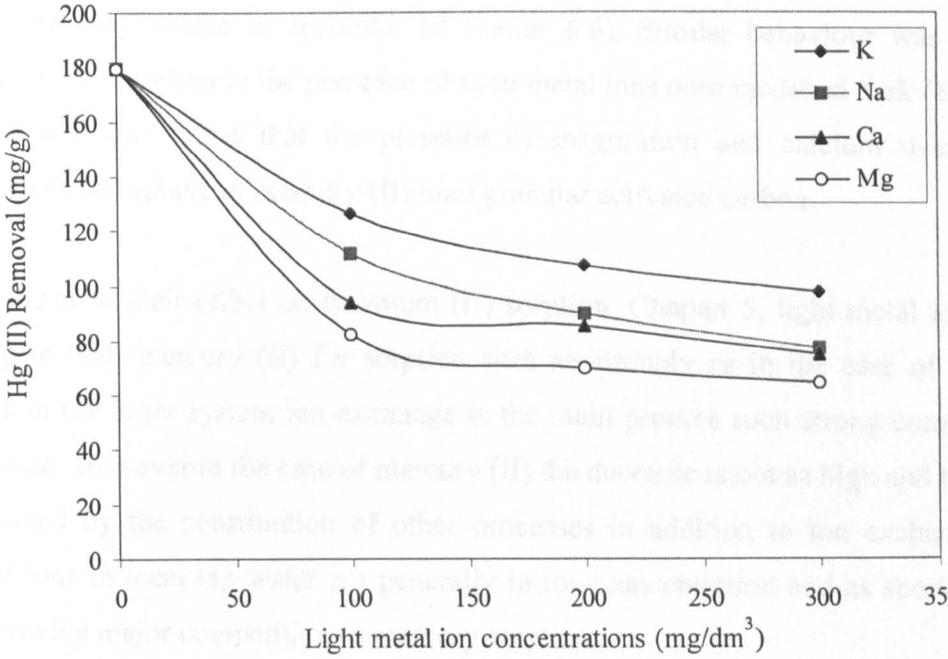

Figure 6.13. Effect of light metal ions on mercury (II) sorption on wet C160.

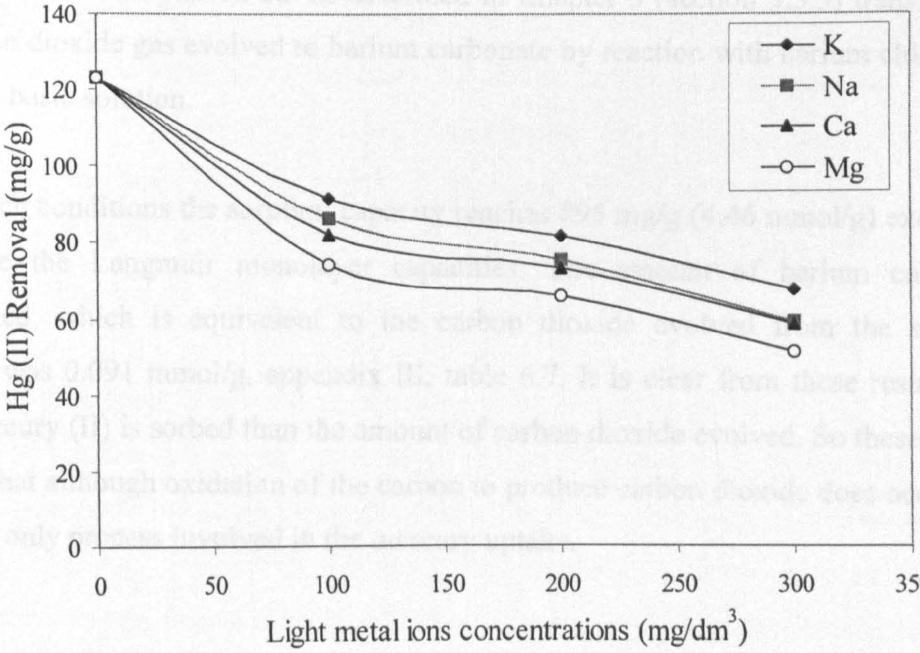

Figure 6.14. Effect of light metal ions on mercury (II) sorption on dry C160.

Data are summarized in appendix III (tables 6.6). Similar behaviour was found for mercury (II) sorption in the presence of such metal ions onto modified bark (87) and Ma *et al* (68) also found that the presence of magnesium and calcium over 50 ppm decreased the uptake of mercury (II) onto granular activated carbon.

Compared to their effect on cadmium (II) sorption, Chapter 5, light metal ions do not compete with mercury (II) for sorption sites as strongly as in the case of cadmium. Since in the latter system ion exchange is the main process such strong competition is expected. However in the case of mercury (II) the decrease is not as high and this can be explained by the contribution of other processes in addition to ion exchange. Light metal ions in local tap water are generally in low concentration and as shown later do not provide major competition to mercury sorption.

6.2.6. Carbon dioxide measurement

Previous studies by Fu *et al* (176) showed that reduction of mercury (II) was accompanied by evolution of carbon dioxide from the carbon sorbent. In the present study, this experiment was repeated with a wet sample of the carbon and an aqueous solution with a high initial concentration of mercury (II) ions (6000 mg/dm^3). The pH was maintained in the range 5-6 and the temperature was kept at 60 °C in a thermostat. The experiment was carried out as described in Chapter 3 (section 3.3.3) transforming the carbon dioxide gas evolved to barium carbonate by reaction with barium chloride in a slightly basic solution.

Under such conditions the sorption capacity reaches 895 mg/g (4.46 mmol/g) exceeding of course the Langmuir monolayer capacities. The amount of barium carbonate precipitated, which is equivalent to the carbon dioxide evolved from the sorption reaction, was 0.091 mmol/g, appendix III, table 6.7. It is clear from these results that more mercury (II) is sorbed than the amount of carbon dioxide evolved. So these results indicate that although oxidation of the carbon to produce carbon dioxide does occur this is not the only process involved in the mercury uptake.

6.2.7. Cumulative mercury (II) sorption capacity

Batch experiments for mercury (II) onto wet and dry C160 were accompanied by a release of protons and so a decrease of the final pH is observed. In addition, from the pH effect it was found that starting with a low pH value such as pH, 1.5 - 2.00, sorption of mercury (II) was extremely low and this was explained by the competition of the protons in solution for the ion exchange sites such as -COOH and –OH (in their ionised forms – COO^- and $-O^-$ respectively) that are available on the carbon surface.

To reach to the 'maximum' capacity of the carbon C160 for mercury (II) a 50 cm^3 solution of 500 ppm of mercury (II), in chloride media, at pH 4.5 was mixed with ~0.105 g of the dry material, or its equivalent in the wet form, for the appropriate equilibrium time (80 hours for wet, 120 hours for dry). The sorbent was separated by filtration, and mixed with a fresh sample (50 ml) of the same initial mercury solution. The process was continued for 12 cycles with both sorbents as mentioned in Chapter 3, section 3.3.4, similar to that performed by Williams *et al* (83).

Mercury (II) uptake showed 182 mg/g for wet C160 and 145 mg/g using the dry sorbent in the first batch experiment. Sorption in cycle 2 shows a decrese in mercury uptake with 137 and 111 mg/g for wet and dry respectively. Sorption of mercury afterwards shows successive lower sorption reaching 44 mg/g and 24 mg/g for wet and dry C160 by the twelfth cycle. Data for mercury sorption separately are presented in figure 6.15. Collectively by the twelfth cycle, mercury (II) shows higher sorption increase reaching 1017 mg/g which is 5.6 times more than that obtained for mercury (II) sorption in the first cycle for wet and 784 mg/g which is about 5.4 fold increase in its capacity more than that found in the first cycle for dry C160, figure 6.16. Data are also shown in appendix III, table 6.8 and 6.9.

Note in this case much more mercury has been sorbed than cadmium and even after twelve cycles the mercury being removed is 10 times higher than cadmium after seven cycles. This supports the suggestion of the involvement of other processes besides ion exchange in sorption. The capacity of the wet sorbent after twelve cycles exceeds 1 g Hg/g sorbent showing that this material would be very effective for mercury removal from aqueous solution.

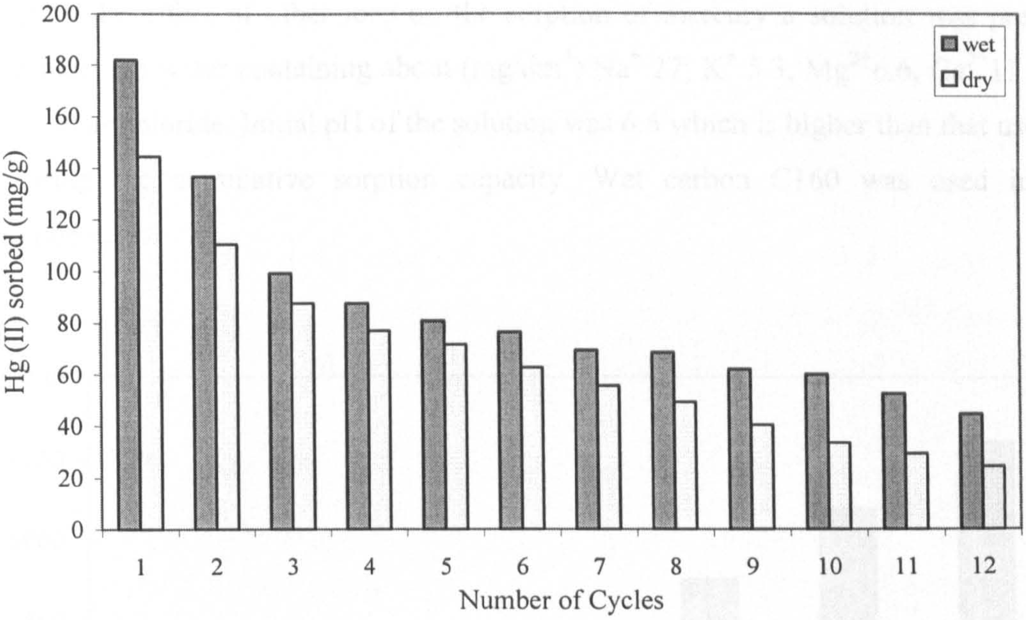

Figure 6.15. Mercury (II) sorption on wet and dry C160 in successive cycles (separately).

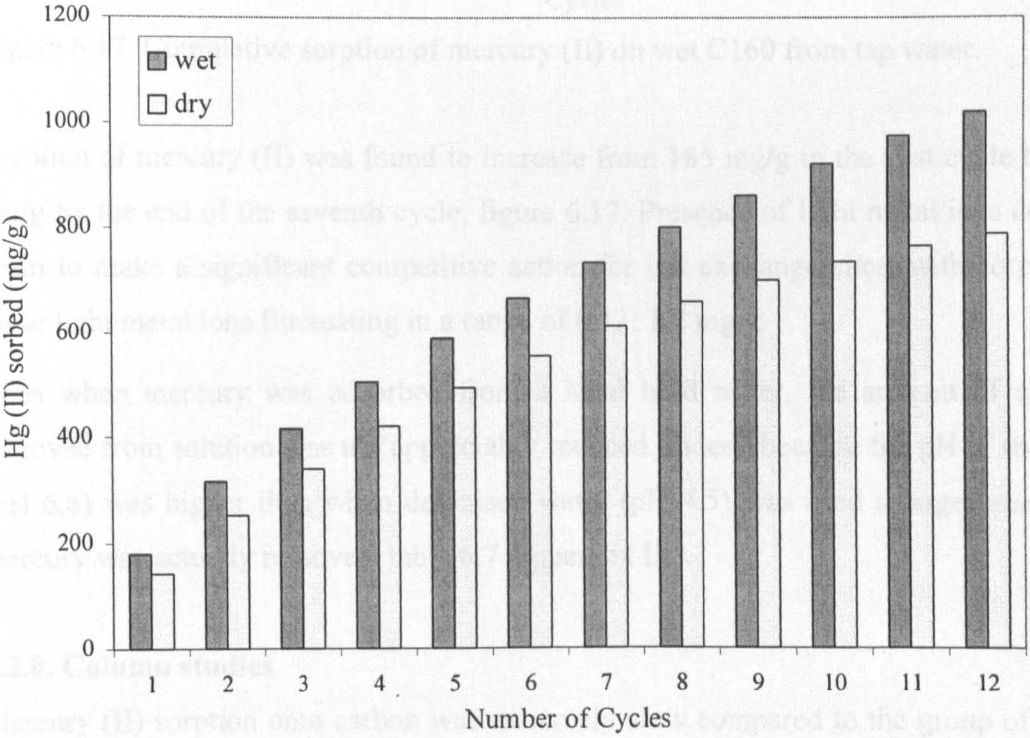

Figure 6.16. Cumulative sorption of mercury (II) sorption on wet and dry C160.

To study the effect of other ions on the sorption of mercury a solution was prepared using local tap water containing about (mg/dm^3) Na^+ 27; K^+ 5.3, Mg^{2+}6.6, Ca^{2+}11.3 and Hg^{2+} 430 as chloride. Initial pH of the solution was 6.6 which is higher than that used for measuring the cumulative sorption capacity. Wet carbon C160 was used in this experiment.

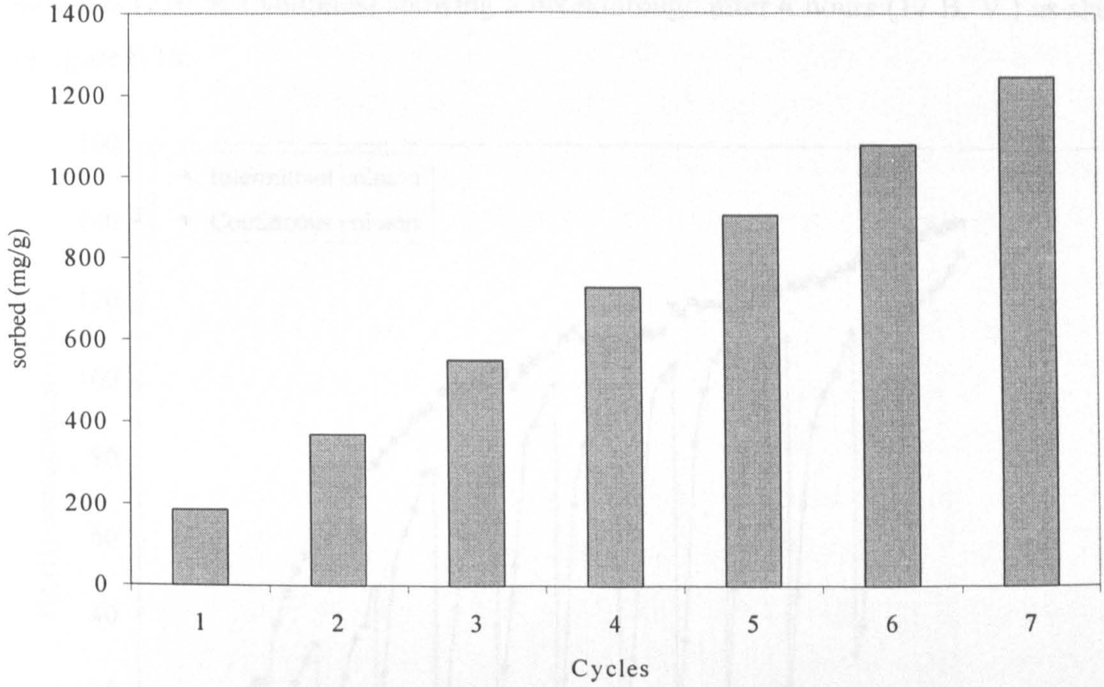

Figure 6.17. Cumulative sorption of mercury (II) on wet C160 from tap water.

Sorption of mercury (II) was found to increase from 185 mg/g in the first cycle to 1243 mg/g by the end of the seventh cycle, figure 6.17. Presence of light metal ions does not seem to make a significant competitive action for ion exchange sites, with sorption of these light metal ions fluctuating in a range of 0.13: 1.2 mg/g.

Thus when mercury was adsorbed from a local hard water, the amount of mercury removed from solution was not appreciably reduced. Indeed because the pH of the water (pH 6.6) was higher than when deionised water (pH 4.5) was used a larger amount of mercury was actually removed, table 6.7 (appendix III).

6.2.8. Column studies

Mercury (II) sorption onto carbon was extremely slow compared to the group of metals studied in Chapter 5. Usually slow kinetics shows a poor performance in column studies because the residence time with the sorbate is not long enough for all metal ions to be sorbed. Thus, sorption of mercury (II) on a fixed bed was not expected to behave as well as cadmium (II). The column was prepared as in Chapter 3, section 3.3.5.2 using a wet weight of C160 equivalent to ~ 1 g on the dry basis in a column of radius 0.67 cm and length 11.02 cm. 200 mg/dm^3 of mercury (II) solution at an initial pH of 4.5 was pumped at a rate of 1.11 cm^3/min resulting in a residence time of 14 minutes for the solution in contact with the carbon sorbent. The column was operated continuously for 48 hours (250 bed volumes) showing a breakthrough after 4 hours (17 B. V.) as shown in figure 6.18.

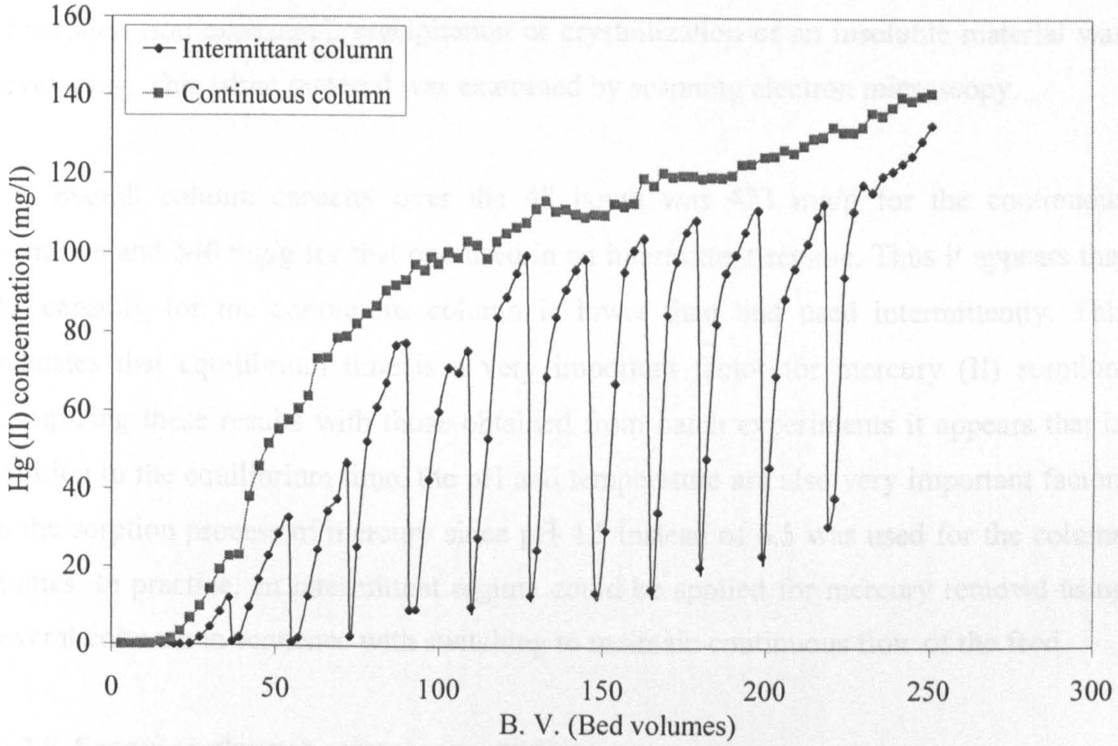

Figure 6.18. Column studies for mercury (II) on wet C160.

Thus after 17 bed volumes the ion exchange sites seems to be virtually exhausted and other processes became more important. The pattern of the breakthrough curve seems to be increasing but not as sharply as for cadmium (II), figure 5.25. Another similar column was prepared and operated in an intermittent regime such that the column is fed with solution for only 4 hours (~17 B. V.). Four hours was chosen as this was the breakthrough time for the continuous column. After this time the flow was stopped and the liquid in the column was allowed to equilibrate for 8 hours. On restarting the flow the initial samples of eluate have very low mercury concentrations which increase with time until the next shut-down period. During the shut-down period reduction of the sorbed mercury occurs and the succeeding eluate concentration again falls. Data are presented in appendix III, table 6.10 and 6.11. This experiment was followed for 250 bed volumes reaching 48 working hours similar to the time for the continuous column (figure 6.18). The saw-tooth pattern is repeated but with a general slow increase in the initial eluate concentration and higher mercury concentration at the end of the flow regime indicating a general reduction in the number of ion exchange sites available. During the rest periods small gas bubbles were observed on the carbon surface, presumably carbon dioxide from surface oxidation. Also, throughout the experiment a white precipitate developed on the carbon surface. In the column, the white precipitate (small crystals) developed into distinct zones along the column showing that following the initial stages of sorption (ion exchange), precipitation or crystallization of an insoluble material was developing. This white material was examined by scanning electron microscopy.

The overall column capacity over the 48 hours was 423 mg/g for the continuous operation and 540 mg/g for that one used in an intermittent regime. Thus it appears that the capacity for the continuous column is lower than that used intermittently. This indicates that equilibrium time is a very important factor for mercury (II) sorption. Comparing these results with those obtained from batch experiments it appears that in addition to the equilibrium time, the pH and temperature are also very important factors in the sorption process of mercury since pH 4.5 instead of 6.5 was used for the column studies. In practice, an intermittent regime could be applied for mercury removal using several columns in sequence with switching to maintain continuous flow of the feed.

6.2.9. Scanning electron microscope studies

The carbon particles covered with the white crystals that observed during the above experiments were removed from the column and examined by scanning electron microscopy which clearly identified needle-like crystals and, in addition, round micro-droplets were also found on the carbon surface and within the pores, figures 6.19 and 6.20.

These crystals and droplets were examined by electron microprobe elemental analysis and even though the analysis was carried out in the standard-less mode an estimate of the elemental composition could be made. Only mercury could be identified in the round microdroplets confirming them as elemental mercury. The white crystals showed a mercury: chlorine ratio of about 1:1 suggesting mercury (I) chloride precipitation.

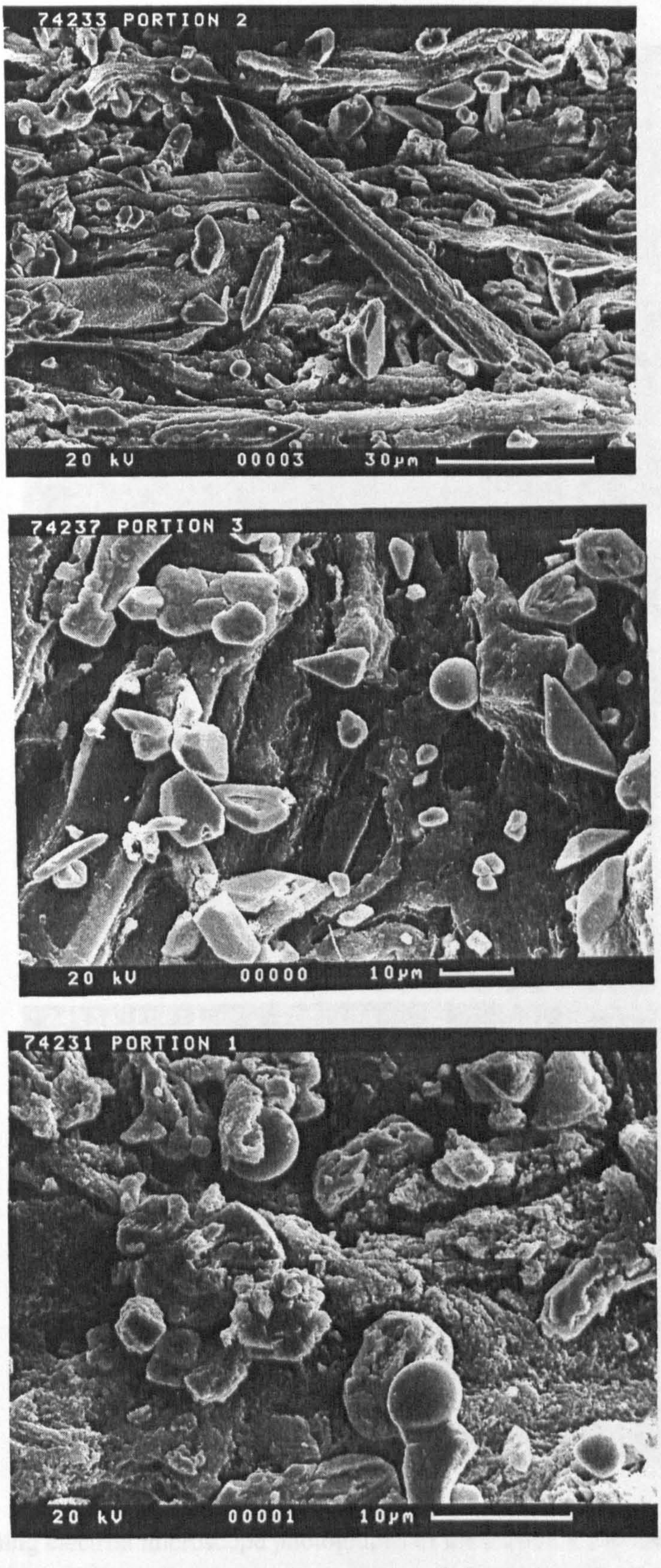

Figure 6.19. Scanning electron microscope photographs of the carbon C160 after mercury (II) chloride sorption; exterior. (Crystals of mercury (I) chloride and microdroplets of mercury metal).

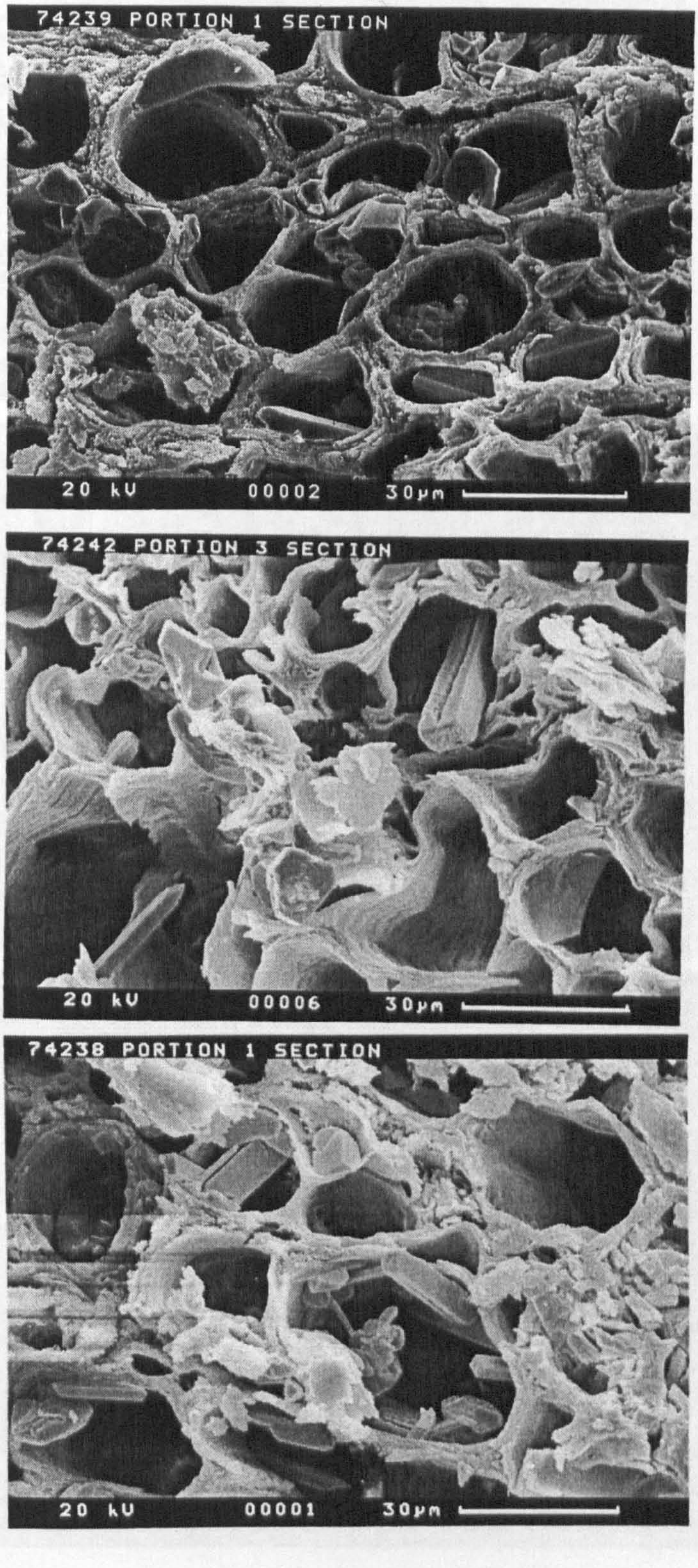

Figure 6.20. Scanning electron microscope photographs of the carbon C160 after mercury (II) chloride sorption; cross section.

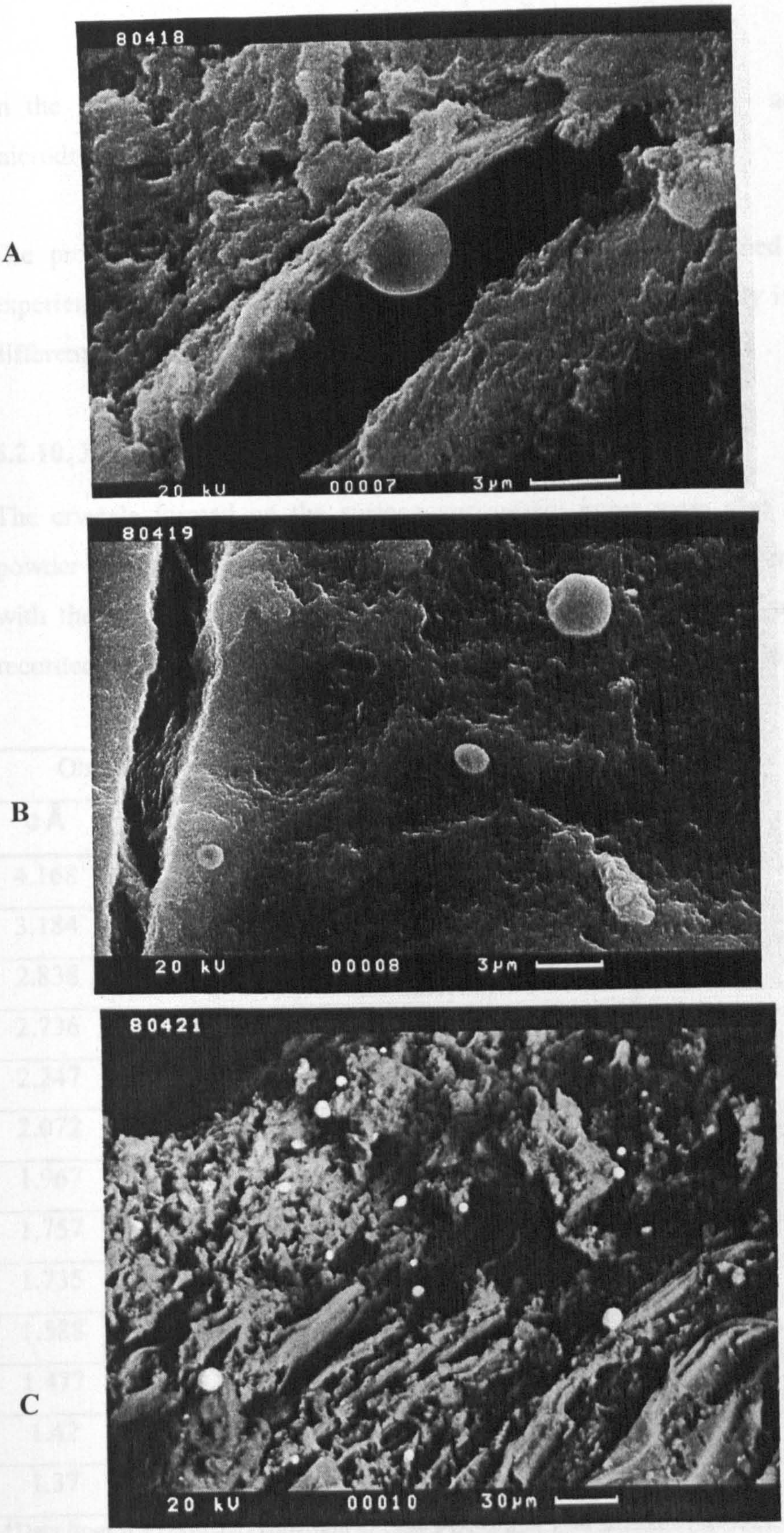

Figure 6.21. Scanning Electron microscope photographs of carbon C160 after the sorption of mercury (II) nitrate. (Elemental mercury microdroplets), A & B) by second electrons, C) by back scattered electrons.

In the case of removal of mercury from a nitrate solution - as expected - only microdroplets of mercury could be identified, figure 6.21.

The production of mercury and mercury (I) chloride confirmed that mercury (II) experiences redox reactions on the carbon surface and this mainly is the reason for the different behaviour of mercury compared to cadmium (II).

6.2.10. X-ray powder diffraction

The crystals formed on the surface and within pores were also analyzed by X-ray powder diffraction. The analysis confirmed the identification of mercury (I) chloride with the interplanar spacing (d) and relative line intensities (I) agreeing with those recorded, table 6.4. X-ray diffraction pattern is presented in figure 6.22.

Observed		Literature	
d Å	Intensity (I)	d Å*	Intensity (I)*
4.168	75	4.15	75
3.184	100	3.17	100
2.838	12	2.824	12
2.736	40	2.727	30
2.247	14	2.240	14
2.072	36	2.067	40
1.967	30	1.97	16
1.757	3.4	1.756	4
1.735	8.8	1.732	12
1.588	5.4	1.5841	6
1.477	8.8	1.4755	10
1.42	2.9	1.4164	3
1.37	3.9	1.3696	6

*Data from JCPDS-ICDD copyright © 1994 PDF-2 Sets 1-44 database (26-312)

Table 6.4 X-ray powder diffraction after mercury (II) chloride loading confirming that the crystals formed are of mercury (I) chloride.

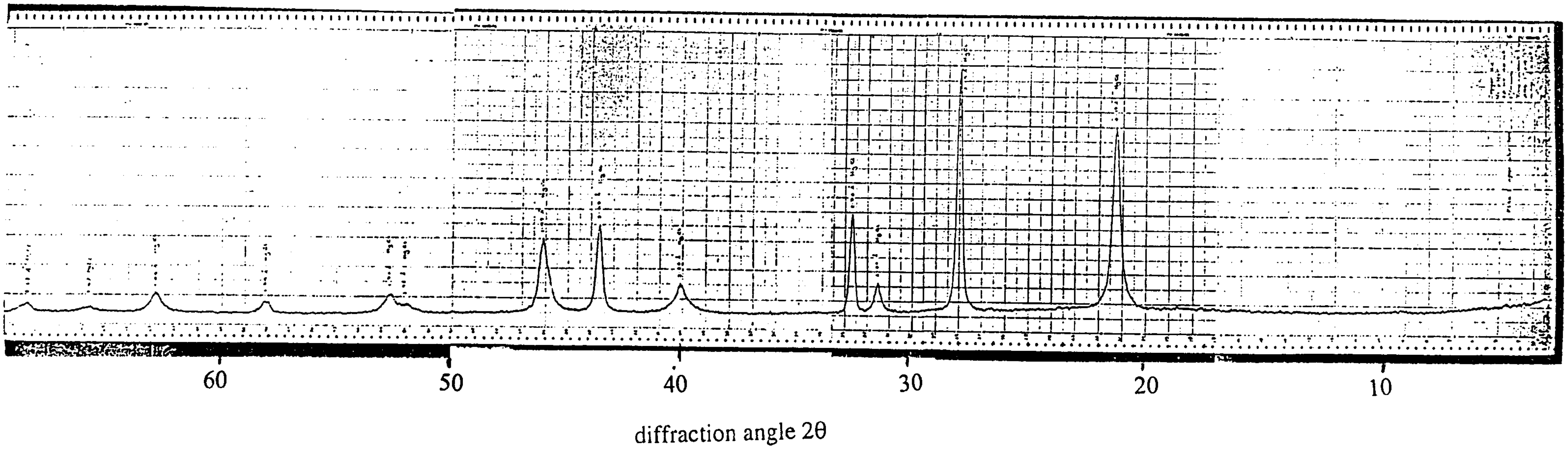

Figure 6.22. X-ray diffraction pattern of C160 after being loaded with Hg (II) chloride. The diffraction pattern shows the formation of Hg_2Cl_2.

6.2.11. FTIR studies

Another parameter which can provide information on changes to the carbon sorbent following mercury uptake is infra-red analysis, and in this work the infra-red spectra of the carbon after mercury (II) sorption showed a change in the surface functional groups, when compared to the initial material, figure 6.23. These spectra were recorded as KBr discs of the dried sorbent and therefore any deduction must be considered tentative, as accurate quantitative measurements could not be made. However with these limitations some useful collaborative evidence can be obtained.

Thus comparing these spectra the bands at around 3400 cm^{-1}, which are connected with the O-H stretching vibrations, become relatively more intense and broader after sorption, indicating the formation of more OH groups by mercury (II) reduction. On the other hand bands at around 1700 cm^{-1} related to C=O stretching vibrations showed an obvious decrease after mercury sorption, which probably reflects the process of decarboxylation accompanying the oxidation process with evolution of CO_2. The band around 1600 cm^{-1} became more intense after the mercury (II) sorption onto the carbon. This band is connected to skeletal C=C aromatic vibrations (129) and thus probably reflects a dehydrogenation process (179) accompanying the redox processes. An observed increase in the intensity of the bands and shoulders in the range between 1300 and 900 cm^{-1} which may be ascribed to the C-O vibrations associated with hydroxyl groups and ether type structures (129) reflects the increase in carbon-oxygen groups on the surface after mercury sorption as a result of oxidation.

6.2.12. Mechanism of the sorption process of mercury (II)

Previous workers (186, 166) have found that mercury (II) chloride can be reduced to mercury (I) on an activated carbon surface and on carbon fibres (173, 176), and to mercury metal (62). Fulvic acid also was found to reduce mercury (II) to mercury metal (183). This has led to the suggestion that the adsorption process involves a sequence of ion exchange, complex formation, redox reactions and precipitation (187). Experimental results obtained during this investigation, e.g. infra-red spectra, suggest that the carbon sorbent possesses abundant functional groups on the surface. As a result of the preparation conditions the carbon material also includes some lignin, an important component in the structure of most humic materials (190). The latter are also formed during hydrolysis of carbohydrates by concentrated acids (114).

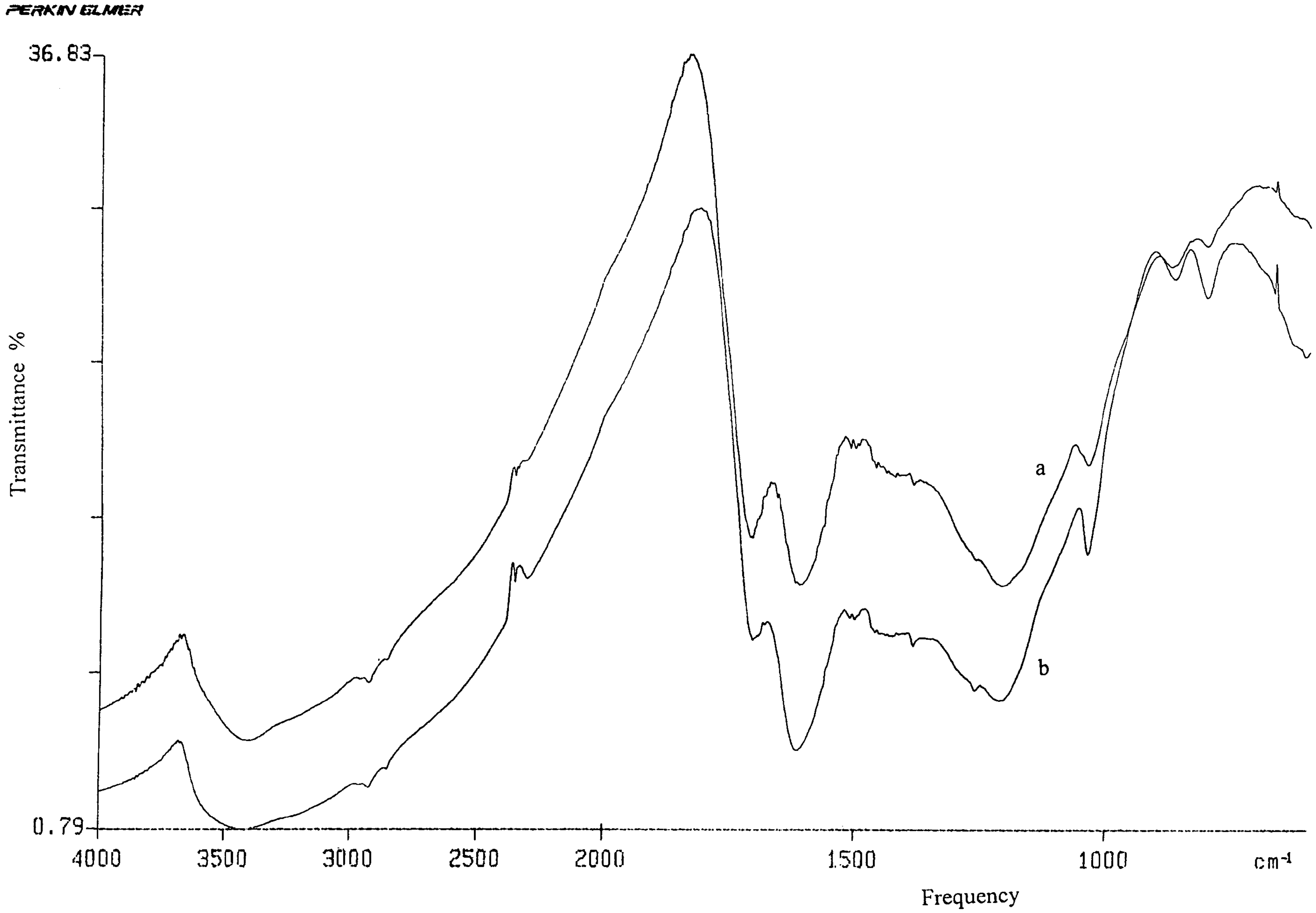

Figure 6.23. FTIR spectra of the Carbon. a) before Hg (II) sorption b) after Hg (II) sorption.

Such materials are known to adsorb metal ions and also can act as a reducing agent for some metal ions (190). Therefore it is suggested that the sorption of mercury consists of at least two processes: ion exchange and reduction in the following way. Initially the mercury (II) ions are sorbed onto the carbon by an ion exchange mechanism similar to cadmium (II) sorption following which there are a series of concurrent or sequential redox reactions. Possible redox reactions which may be involved are as follows:

a. Mercury (II) reduction

The reduction potentials of the various mercury couples are very close (equations 6.3 - 6.5) so that, depending on the precise experimental conditions, either the mercury (I) ion or metallic mercury can be produced.

$$2Hg^{2+} + 2e = Hg_2^{2+} \quad (E^o = +0.905\ V) \qquad (6.3)$$

$$Hg^{2+} + 2e = Hg^o \quad (E^o = +0.851\ V) \qquad (6.4)$$

$$Hg_2^{2+} + 2e = 2Hg^o \quad (E^o = +0.796\ V) \qquad (6.5)$$

Thus in the system under investigation the mercury (I) ions from the reduction, equation 6.3, can either gain more electrons to be reduced to metallic mercury, equation 6.5, or interact with the chloride ions available in the solution to give mercury (I) chloride, equation 6.6, which is sparingly soluble in water, table 6.5.

$$Hg_2^{2+} + 2\,Cl^- = Hg_2Cl_2 \qquad (6.6)$$

Then the mercury (I) chloride crystallites precipitate onto the carbon surface and also within the pores, migrating from the reduction site towards earlier deposited crystallites for crystal growth, so in time crystals develop as shown in figures 6.20 and 6.21. In the case of mercury (II) nitrate solution, only elemental mercury was produced on carbon surface, equations 6.4 and 6.5.

Compound	Solubility (g/dm^3)	
	Cold water	Warm/Hot water
Hg_2Cl_2	0.0020 (25 °C)	0.01 (43 °C)
$HgCl_2$	69 (20 °C)	480 (100 °C)

Table 6.5 Solubilities of mercury compounds (191)

b. Surface oxidation and carbon dioxide evolution

The process of mercury (II) reduction is accompanied by oxidation of the carbon surface, equations 6.7-6.11. Evolution of carbon dioxide was confirmed by the precipitation of barium carbonate, section 6.2.6. Also, small bubbles were observed in the sorption column during rest times. However, the amount of carbon dioxide evolved was less than the amount of mercury (II) sorbed onto the surface which suggests the presence of other surface oxidation processes, which is supported by the infrared spectra of the sorbent before and after reduction had occurred, figure 6.23.

Possible reactions at the carbon surface which may be involved are:

- oxidation of carbon in the presence of water and mercury ions:

$$C + 2H_2O + 4\,Hg^{2+} = CO_2 + 2\,Hg_2^{2+} + 4H^+ \qquad (6.7)$$

$$C + 2H_2O + 2\,Hg^{2+} = CO_2 + 2\,Hg^o + 4H^+ \qquad (6.8)$$

- Surface oxidation reaction:

In addition to the above reaction which removes carbon from the surface, partial oxidation can also occur to carbon compounds giving rise to the formation of hydroxyl (or phenolic) groups, carbonyl groups or carboxylic acids.

$$\sim C\text{-}H + Hg\,(\text{oxidized}) + H_2O = \sim C\text{-}OH + Hg\,(\text{reduced}) + H^+ \qquad (6.9)$$

$$\sim C\text{-}H\ /\ {>}C\text{-}OH + Hg\,(\text{oxidized}) + H_2O = \sim C{=}O + Hg\,(\text{reduced}) + H^+ \qquad (6.10)$$

$$\sim C\text{-}H\ /\ {>}C\text{-}OH + Hg\,(\text{oxidized}) + H_2O = \sim COOH + Hg\,(\text{reduced}) + H^+ \qquad (6.11)$$

From the infra-red spectra it was found that the band associated with the carbonyl group decreases after sorption at high temperature (60 °C) which suggests that the concentration of carbonyl groups decreases as a result of decarboxylation to CO_2. The infra-red band at 1600 cm^{-1} may be assigned to $-COO^-$ or aromatic -C=C- vibrational modes (129). As the intensity of the –C=O vibrations has decreased it suggests that the increase in 1600 cm^{-1} band is associated with the formation of -C=C- bands. This can be explained by a dehydrogenation reaction as postulated for the reduction of gold (III) onto lignite (179). ~~Thus~~ This reaction could be:

~CH-CH~ + Hg (oxidized) = ~C=C~ + $2H^+$ + Hg (reduced) (6.12)

At lower pH values (1.5-2) perhaps the sorption is lower, not only because of the high concentration of protons which compete with the mercury (II) ions for the ion exchange sites, but also because of the possible formation of $HgCl_4^{2-}$ (2). At such lower pH values (1.5-2) being adjusted using HCl, the molar concentration of Cl^- ($>10^{-2}$ mol/dm^3) was more than 4 times higher than that of Hg^{2+} up to 300 ppm. Reduction of Hg (II) from the complex form $HgCl_4^{2-}$ to elemental mercury has the following reduction potential:

$HgCl_4^{2-} + 4H^+ + 2e^- = Hg + 4HCl$ ($E^o = 0.48$ V) (from 165) (6.13)

and perhaps this reduction potential is lower than (or in the same range as) that of the carbon sorbent.

6.2.13. Discussion

The experimental results of mercury sorption can be summarized as follows;

The sorption of mercury (II) onto the carbon sorbent is faster and has higher uptake when samples which have been maintained in a wet condition are used. The kinetics of mercury (II) sorption were found to follow a first order reaction process, which depends mainly on the diffusion of the mercury ions through the carbon pores.

The sorption of mercury (II) is found to be dependent on the pH of the mercury (II) solution. The most suitable range for high mercury (II) uptake is from pH 6-7. The ratio of protons evolved and the mercury (II) sorbed was found to lie between 1 and 1.4 with a computed slope of 1.17. This indicates that the process is a mixture of ion exchange and reduction.

The higher mercury capacity for the wet sorbent is probably related to changes in the pore structure with the pores becoming narrower on drying with a resulting decrease in surface area. Swelling of the dried material by immersion in water is limited indicating the process is not completely reversible.

The presence of high concentrations of light metal ions such as Na^+, K^+, Mg^{2+} and Ca^{2+} showed a large decrease in mercury (II) uptake indicating competition for the ion exchange sites available on the carbon surface. However the uptake of mercury is not significantly affected by the presence of such metal ions at the concentration found in natural waters.

The sorption process is dependent on temperature with the mercury (II) uptake increasing with increase in temperature. Such changes in temperature may cause an increase in swelling of the adsorbent allowing more active sites to become available, but it is more likely to arise from the increase in the rate of reduction of mercury with temperature.

The overall sorption process is complex and includes both ion exchange and reduction steps. Precipitation of mercury (I) chloride on the surface and within the pores has been observed together with the formation of micro-droplets of elemental mercury. These results have been confirmed by X-ray powder diffraction and scanning electron microscopy.

The reduction properties of the carbon sorbent is related to the functional groups present on the surface and probably also to the matrix of the carbon which contains lignin, and probably humic acids.

With the mercury sorption mechanism including both reduction and ion exchange, the following conceptual picture of the overall process is proposed:

- mercury (II) cations first approach the sorbent as a result of electrostatic interaction with the ion exchange centers on the carbon surface replacing the protons on these functional groups;
- the sorbed mercury ions either migrate from these ion exchange groups to be reduced at another site on the surface leaving the ion exchange centre active or are reduced at the same functional group, e.g. $-COO^-$ by decarboxylation to carbon dioxide;
- reduction can occur either directly to elemental mercury or to mercury (I) cations which combine with chloride ions to form mercury (I) chloride crystallites;
- subsequent mercury (II) cations behave in a similar way to form a new crystallite of mercury (I) chloride which migrates to aggregate with previous formed crystallite to build up a crystal form.

- In the case of mercury removal from nitrate solution as expected only droplets of elemental mercury are observed.

According to the above mechanism, the kinetics, semi- continuous batch experiment and the column work can be explained as follows:
Redox processes are considered to be the main reason for mercury sorption being slow. The question which arises is: are the two processes simultaneous or sequential. The process is a first order process similar to that group of metals which does not experience reduction such as cadmium but with much longer periods of time. Indeed both experiments have been shown to be first order reactions depending on metal concentration. But in case of mercury sorption, two processes are involved namely ion exchange and reduction. Ion exchange is a fast process as in cadmium but reduction followed by crystal growth (for mercurous chloride) and mercury agglomeration (mercury microdroplets), are apparently slow processes, i.e. the overall rate determining step. The process of reduction is accompanied by oxidation on the surface enriching the surface with ion exchange sites which participate in further sorption but at the same time, some carboxylic groups may be oxidized to carbon dioxide which means that the surface can also lose some ion exchange sites.

Considering the effect of light metal ions, which do severely compete with cadmium, in the case of mercury, competition decreases sorption but not to the degree of excluding mercury which means that perhaps the reduction step is not directly sequential with ion exchange so light metal ions still can replace mercury (II) on ion exchange sites. On the other hand, the saw-tooth pattern of the intermittent column shows that by providing a resting period sufficient time is provided for the reduction and migration to occur and the ion exchange sites to be regenerated. However in general it is difficult to separate the ion exchange process from the reduction process in the kinetic experiments and this requires more work in the future.

6.3. Chromium (VI) Sorption

6.3.1. Introduction

Pollution of chromium is of considerable concern as the metal has found widespread use in electroplating, leather tanning, alloys, paints, pigments, wood preservatives, etc. which provide many causes for environmental pollution (192).

Chromium, in general, occurs in aqueous systems in both trivalent and hexavalent forms. The maximum levels permitted in waste-water are 5 mg/dm^3 for trivalent and 0.05 mg/dm^3 for hexavalent chromium (193). When emitted at low levels in the environment, trivalent chromium apparently plays an essential role in plant and animal metabolism, while hexavalent chromium is directly toxic to bacteria, plants and animals (194).

Chromium (VI) is readily hydrolysed in water (195). The dominant chromium (VI) species at total chromium concentrations below 500 ppm (0.01 mol/dm^3) are the oxyanions $HCrO_4^-$ and CrO_4^{2-}. The equilibrium between the two species depends on the pH of the chromium solution. $HCrO_4^-$ is dominant species at low pH while CrO_4^{2-} predominates at a higher pH environment such as natural waters (195). The dichromate ion $Cr_2O_7^{2-}$ predominates in acidic environments at concentrations higher than 500 ppm (195).

Among the various treatment techniques available, the most commonly used are chemical reduction and precipitation, adsorption and ion exchange (196). Reduction followed by precipitation is probably the most commonly used technique for the treatment of industrial effluents containing chromium (193). However, it is a process which can give incomplete chromium removal. Also, it has a high chemical requirement and produces a voluminous, toxic sludge which may pose disposal problems. Because of this the techniques of adsorption and ion exchange have been evaluated.

Adsorption of chromium (VI) on carbonaceous sorbents has been studied (61,66,67,94) and also using low cost sorbents such as saw-dust, sugar-cane bagasse, sugar beet pulp and maize cob (197), and onion skins (84). Chromium (VI) sorption was found to be pH dependent showing reduction to chromium (III) on the carbon surface (67, 198, 199).

In addition, Raji and Anirudhan (94) prepared carbon by treating saw-dust with concentrated sulphuric acid at 150 °C for 12 hours. The carbon product has been used for the removal of chromium (VI) and the adsorption was found to be pH and temperature dependent.

Huang and Wu (66) also found that chromium (VI) sorption on the surface of activated carbon was reduced into chromium (III) at low pH values (< pH 6) suggesting two processes were taking place on the carbon surface named as reduction and adsorption reactions. Similar results were also found by Perez-Candela *et al* (67).

6.3.2. Kinetic studies

The kinetic studies of chromium (VI) removal was investigated using two different pH values for the wet and the dry sorbents.

Chromium removal at pH 4.5 was apparently slow unlike that for cadmium (II) and other metal ions, Chapter 5. Like mercury (II) sorption, equilibrium was attained in ~96 hours for the wet sorbent and ~120 hours for the dried samples, compared to chromium (III) which approaches equilibrium within approximately 3 hours (Chapter 5, section 5.2.2). Thus, chromium (VI) sorption is much slower than chromium (III) reflecting a different mechanism of sorption, figures 6.24 and 6.25. Sorption data are presented in appendix III, table 6.12.

Starting with an initial pH 4.5, the uptake of chromium (VI) was found to vary almost linearly with the half power of time, $t^{0.5}$ in the initial stages of sorption in a similar manner to the kinetics of mercury (II) sorption, figure 6.26. As noted before such behaviour is predicted when a large initial fraction of the reaction is controlled by intra-particle diffusion (161). Also, as for both cadmium and mercury, the rate constant of pore diffusion of chromium (VI) for wet carbon is higher (0.1131 mmol g^{-1} $hour^{-0.5}$) than that for the dry material (0.0868 mmol g^{-1} $hour^{-0.5}$) possibly indicating narrower pores in the latter.

Preliminary experiments show that chromium (VI) is reduced to its lower oxidation state, chromium (III), on the carbon surface. Reduction in this case cannot be carried out without the participation of protons from the reaction media. i.e. the sorption process will be accompanied by a rise in pH (equations 6.17 and 6.18, p189 &190). Kinetic data for the experiment at pH 4.5 does not fit a first order reaction equation, as with mercury (II), but instead fits a second order rate expression (equation 6.14) as shown in figure 6.27 (correlation coefficient = 0.998 for wet, 0.997 for dry). The order of sorption reaction was found to be 2 by both the differentiation and integration methods.

$$\frac{1}{C_t} = \frac{1}{C_o} + k_2 t \tag{6.14}$$

where,

k_2 is the rate constant for a second order reaction, C_o is the initial concentration of chromium (VI) and C_t is the concentration at time t.

Reduction of chromium (VI) to chromium (III) seems to be the main sorption process dominating the mechanism of sorption. This may indicate that the reaction rate depends mainly on two components at this pH value 4.5, possibly, the concentration of chromium (VI) and that of the protons available in the reaction solution. The protons are consumed through a reduction process followed by ion exchange for chromium (III) in addition to the possible physical adsorption of chromium (VI). In this case, chromium (III) was not detected in solution which was believed to be sorbed via ion exchange.

Plotting $1/C_t$ against time t gives a straight line with a slope equals the rate constant k_2 (figure 6.27). Removal rate constant values of chromium (VI) are shown in table 6.6.

Starting with an initial pH 1.5, chromium (VI) shows faster removal than that at pH 4.5 for both of the sorbent samples C160 (wet and dry), approaching equilibrium within 50 hours as shown in figure 6.28. In these experiments, chromium (III) developed in solution with the progress of time. As the concentration of chromium (VI) decreases by time, chromium (III) concentration increases and at equilibrium, chromium (III) was the most abundant chromium species in solution, (figures 6.29, 6.30). Sorption data are presented in appendix III, table 6.13.

In this case, the sorption data with time do not show a linear variation with the half power of time in the first stages of adsorption showing no fit to equation 5.7. Removal data of chromium (VI) were found to fit a first order rate equation (eq. 5.8) as shown in

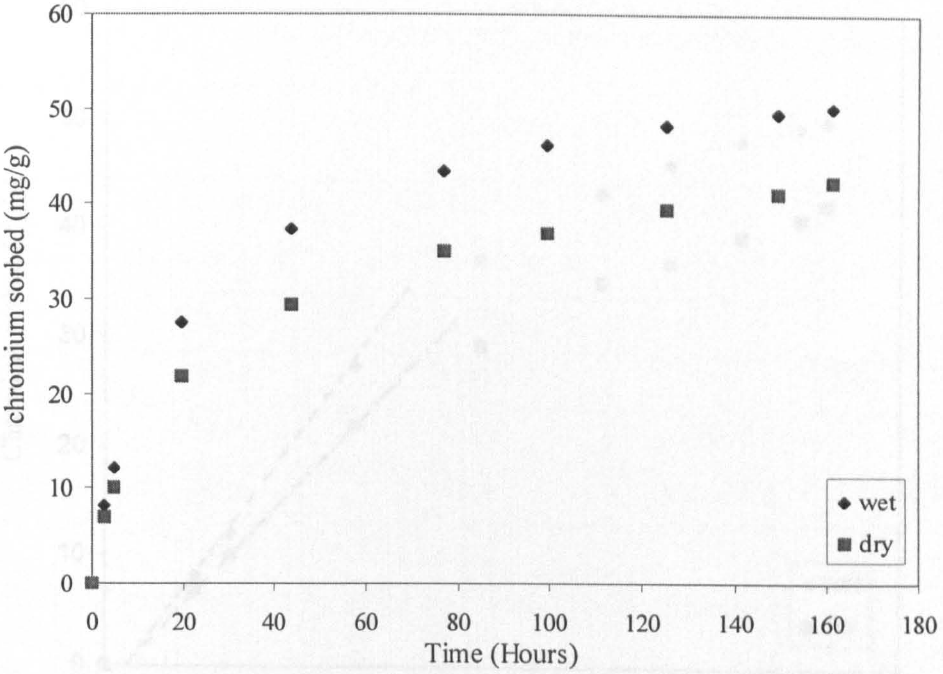

Figure 6.24. Kinetics of chromium (VI) sorption on wet and dry C160 at 25 °C. (Initial pH 4.5).

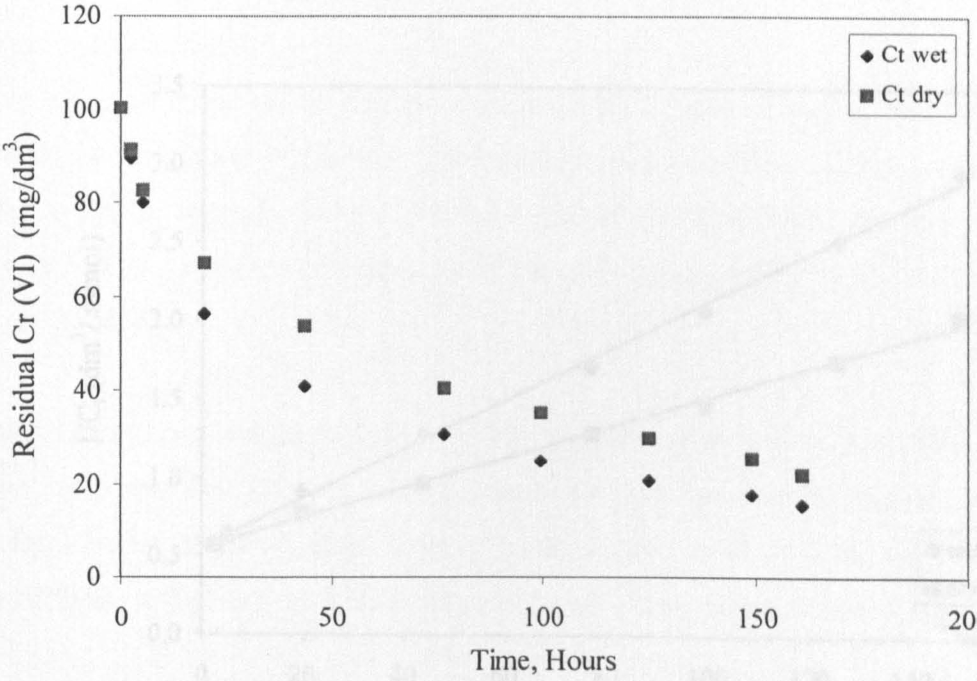

Figure 6.25. A Plot of the residual chromium (VI) concentration against time at 25 °C. (Initial pH 4.5, C_t = Cr (VI) concentration at time t, residual Cr (VI) was composing all chromium content at this pH).

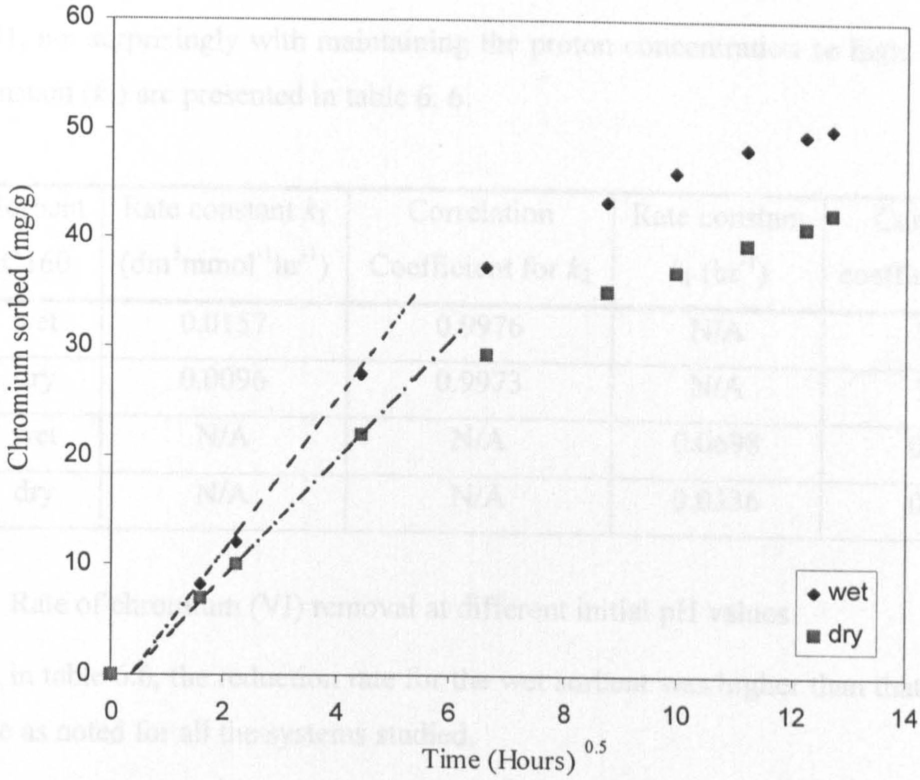

Figure 6.26. A plot of the rate of pore diffusion for chromium (VI) sorption on wet and dry C160 at 25 °C. (Initial pH 4.5).

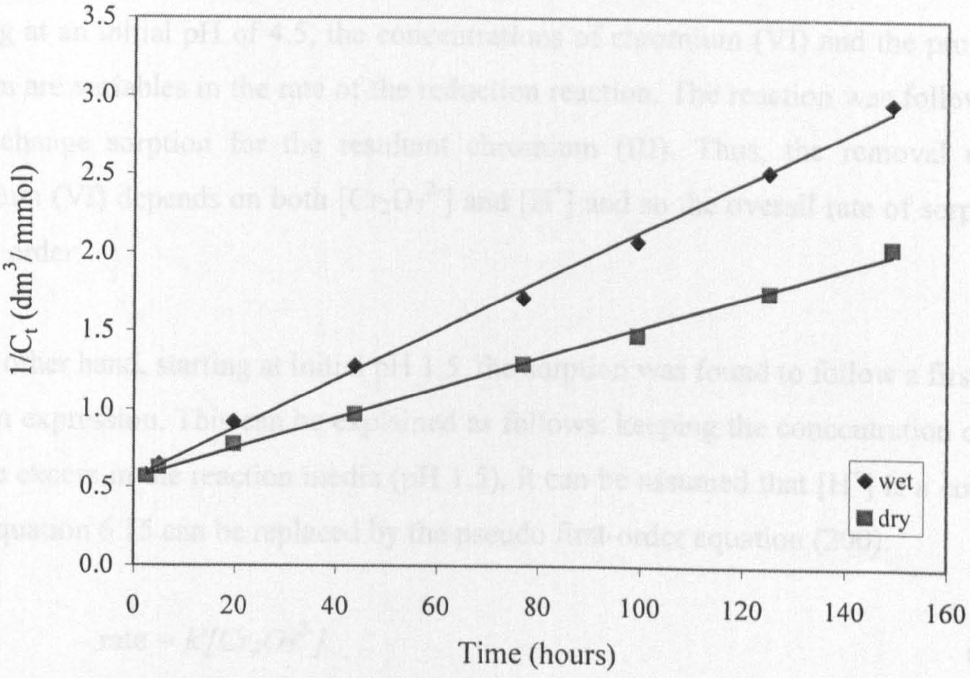

Figure 6.27. A plot of 1/C$_t$ against time for chromium (VI) sorption on C160 at 25 °C. (Initial pH 4.5).

figure 6.31, not surprisingly with maintaining the proton concentration so high. Values of rate constant (k_1) are presented in table 6. 6.

Initial pH	Sorbent C160	Rate constant k_2 ($dm^3mmol^{-1}hr^{-1}$)	Correlation Coefficient for k_2	Rate constant k_1 (hr^{-1})	Correlation coefficient for k_1
4.5	wet	0.0157	0.9976	N/A	N/A
	dry	0.0096	0.9973	N/A	N/A
1.5	wet	N/A	N/A	0.0698	0.993
	dry	N/A	N/A	0.0336	0.997

Table 6.6. Rate of chromium (VI) removal at different initial pH values.

As shown in table 6.6, the reduction rate for the wet sorbent was higher than that for the dry sample as noted for all the systems studied.

Considering the carbon concentration is constant since it is a solid material, the rate of chromium (VI) removal can be expressed as

$$\text{rate} = k[Cr_2O_7^{2-}][H^+] \tag{6.15}$$

where k is a constant.

Starting at an initial pH of 4.5, the concentrations of chromium (VI) and the protons in solution are variables in the rate of the reduction reaction. The reaction was followed by ion exchange sorption for the resultant chromium (III). Thus, the removal rate of chromium (VI) depends on both $[Cr_2O_7^{2-}]$ and $[H^+]$ and so the overall rate of sorption is second order.

On the other hand, starting at initial pH 1.5, the sorption was found to follow a first order reaction expression. This can be explained as follows: keeping the concentration of $[H^+]$ in large excess in the reaction media (pH 1.5), it can be assumed that $[H^+]$ is a constant. Thus equation 6.15 can be replaced by the pseudo first-order equation (200):

$$\text{rate} = k'[Cr_2O_7^{2-}] \tag{6.16}$$

k' is a constant (200). This makes the concentration of the protons very critical for the sorption / reduction behaviour of chromium (VI) on carbon C160 in solution with protons a full partner in the reduction reaction.

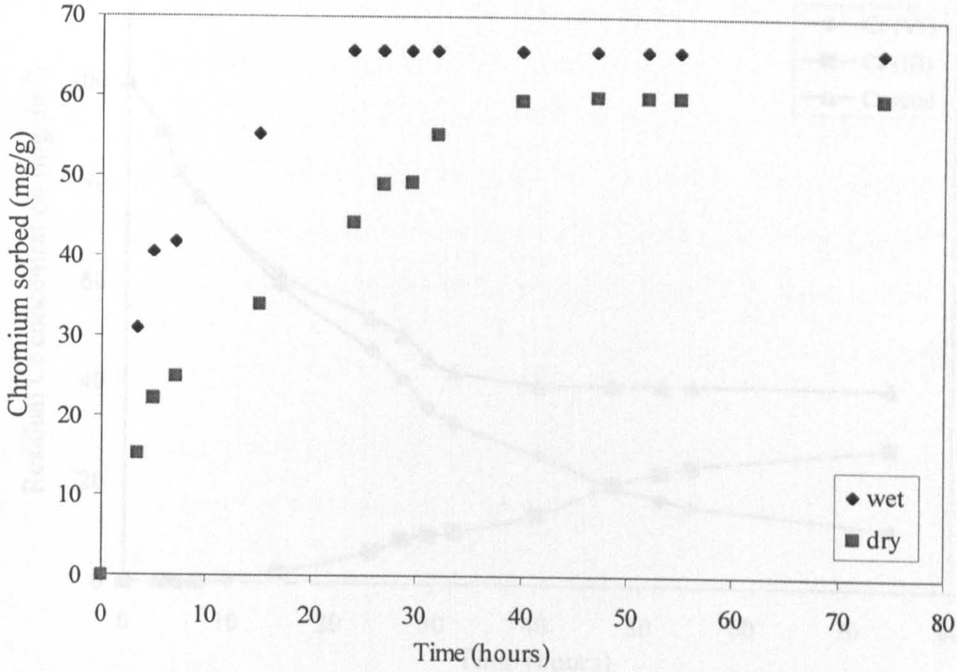

Figure 6.28. Kinetics of chromium sorption on wet and dry C160 at 25 °C. (Initial pH 1.5).

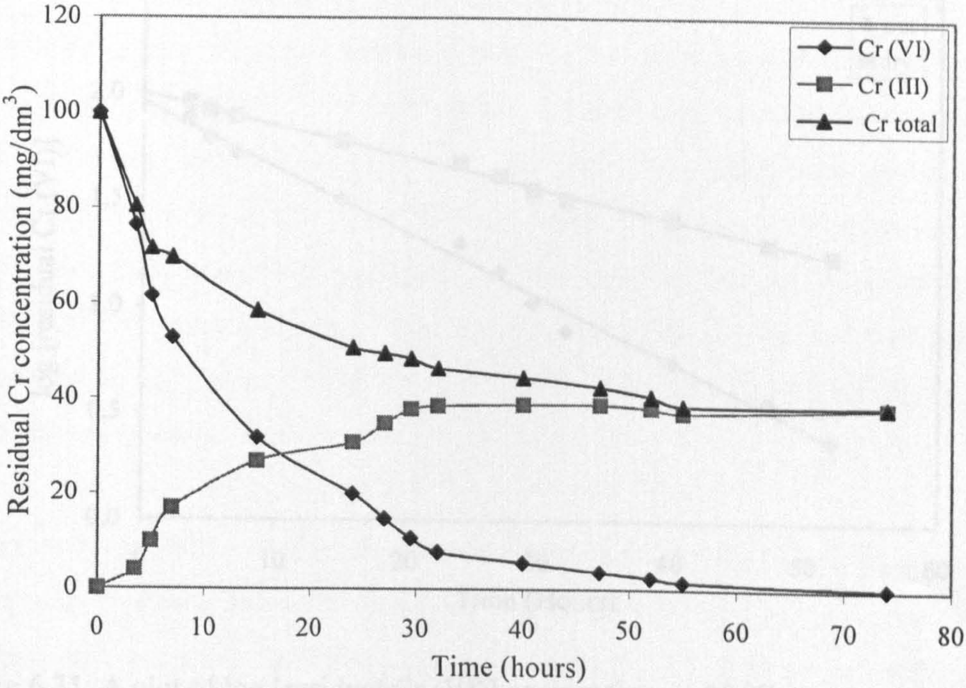

Figure 6.29. A plot of the residual chromium concentration against time at 25 °C using wet C160. (Initial pH 1.5).

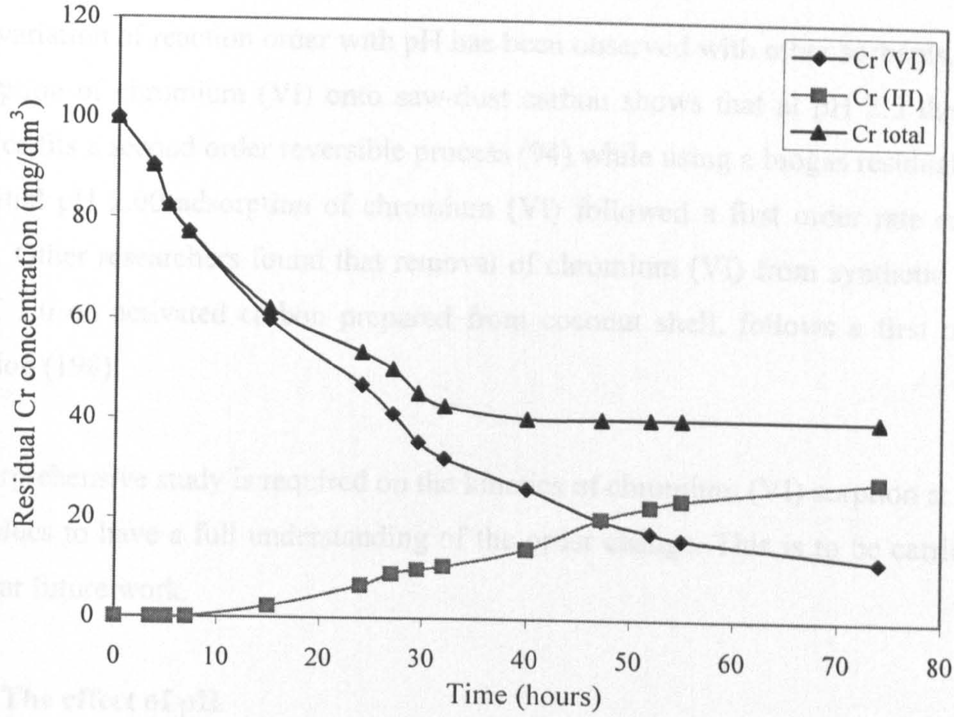

Figure 6.30. A plot of the residual chromium concentration against time at 25 °C using dry C160. (Initial pH 1.5).

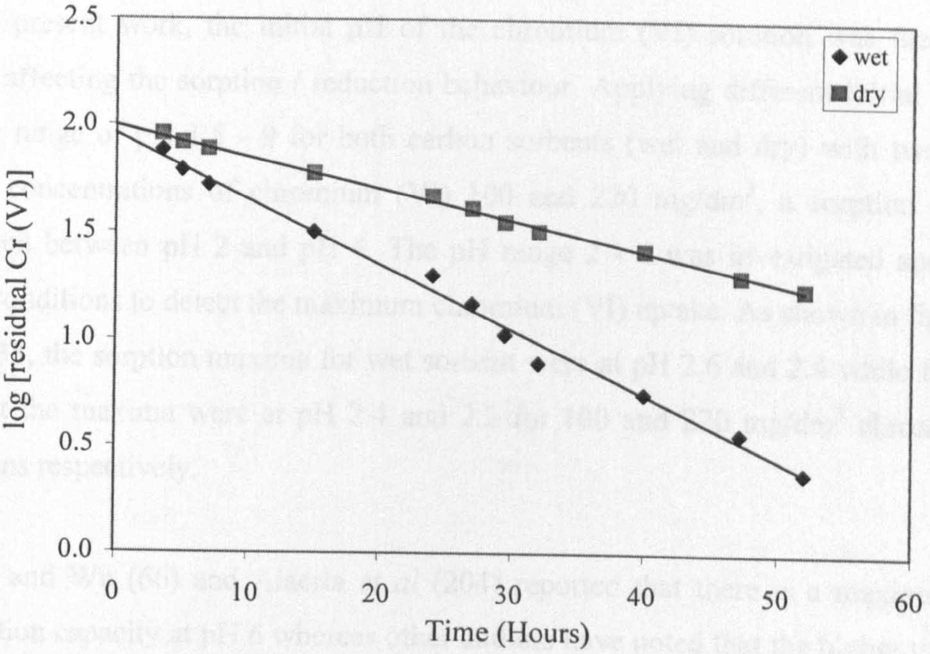

Figure 6.31. A plot of log [residual Cr (VI)] against time at 25 °C. (Initial pH 1.5, Chromium concentration is expressed as mg/dm^3).

This variation of reaction order with pH has been observed with other sorbents. Thus the adsorption of chromium (VI) onto saw-dust carbon shows that at pH 2.5 the sorption kinetics fits a second order reversible process (94) while using a biogas residual slurry at an initial pH 2.00 adsorption of chromium (VI) followed a first order rate expression (201). Other researchers found that removal of chromium (VI) from synthetic solutions at pH 1.0 on activated carbon prepared from coconut shell, follows a first order rate equation (198).

A comprehensive study is required on the kinetics of chromium (VI) sorption at different pH values to have a full understanding of the order change. This is to be carried out in the near future work.

6.3.3. The effect of pH

The adsorption of chromium (VI) on activated carbon and other adsorbents has been the subject of various studies (61, 67, 92, 193, 196-199, 201-203). However the results which have been reported are very variable, particularly in terms of the optimum pH for chromium removal.

In the present work, the initial pH of the chromium (VI) solution was the dominant factor affecting the sorption / reduction behaviour. Applying different initial pH values over a range of pH 1.5 - 9 for both carbon sorbents (wet and dry) with two different initial concentrations of chromium (VI) 100 and 220 mg/dm^3, a sorption maximum appeared between pH 2 and pH 4. The pH range 2 - 4 was investigated applying the same conditions to detect the maximum chromium (VI) uptake. As shown in figures 6.32 and 6.33, the sorption maxima for wet sorbent were at pH 2.6 and 2.4 while for the dry sorbent the maxima were at pH 2.4 and 2.2 for 100 and 220 mg/dm^3 chromium (VI) solutions respectively.

Huang and Wu (66) and Alaerta *et al* (204) reported that there is a maximum in the adsorption capacity at pH 6 whereas other authors have noted that the higher uptake was achieved at lower values e.g. pH $\leq$ 2.5 (203) and pH 2 (61). Sharma and Forster (197) found that removal of chromium (VI) was improved with decreasing pH. Using saw dust the authors (197) found that an almost complete removal of chromium (VI) at pH 1.5 for an initial concentration up to 40 mg/dm^3 and using concentrations up to 10 mg/dm^3

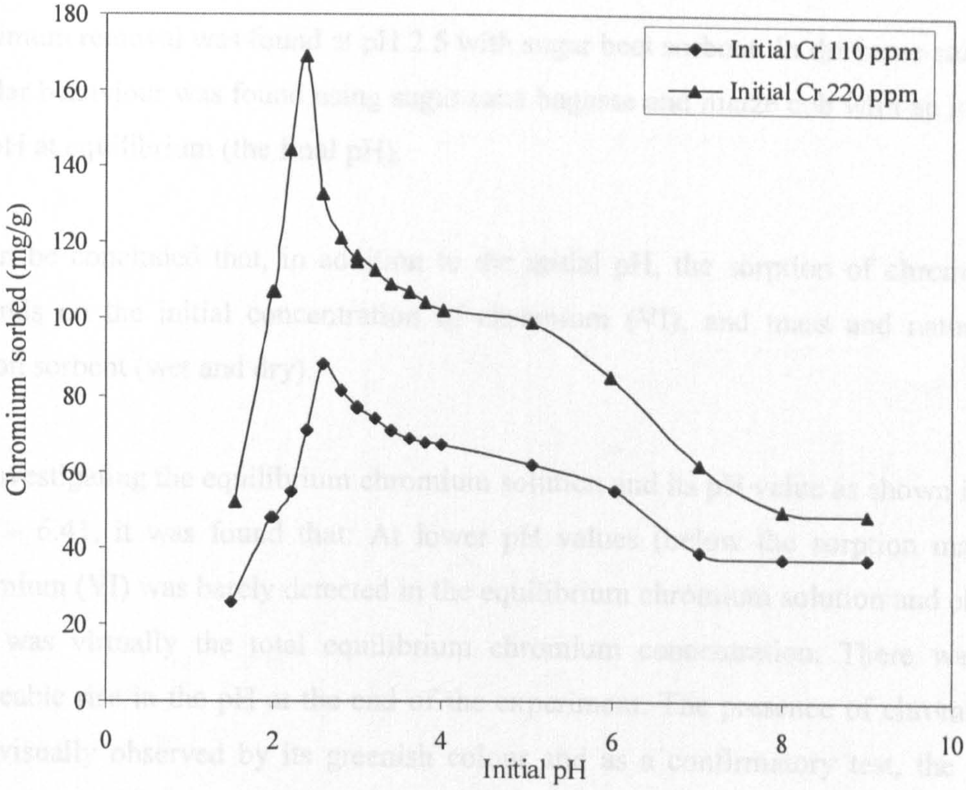

Figure 6.32. Sorption of chromium (VI) on wet C160 at different pH values at 25 °C.

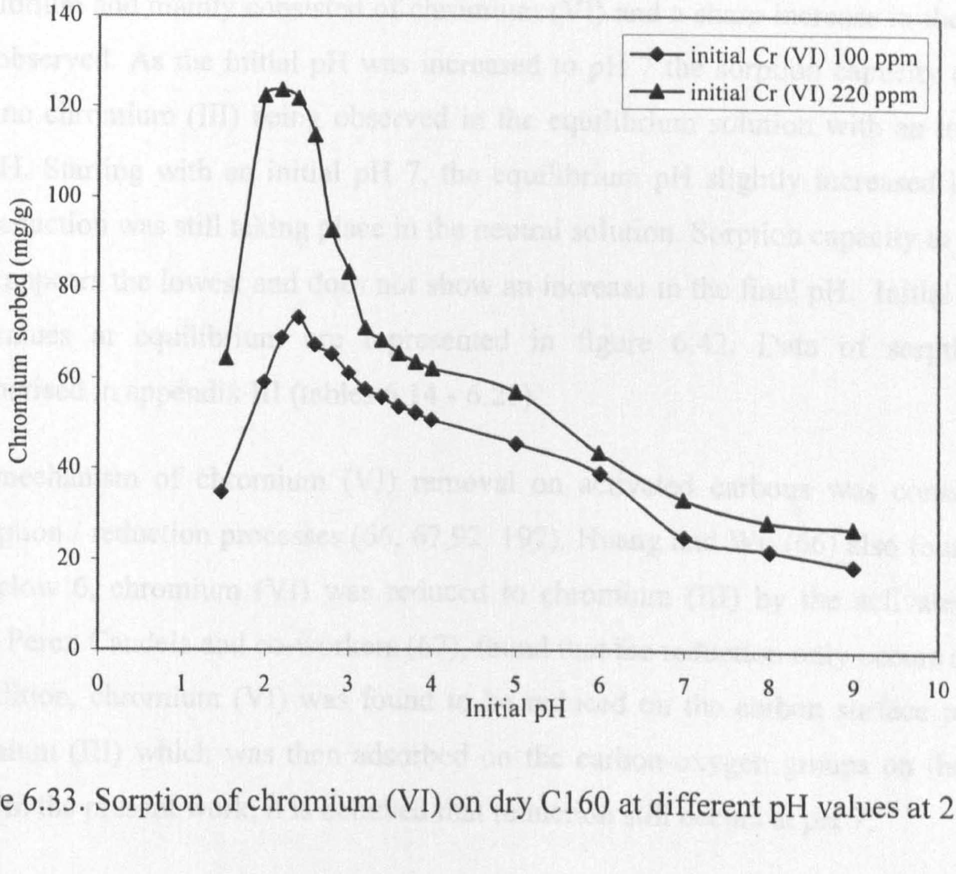

Figure 6.33. Sorption of chromium (VI) on dry C160 at different pH values at 25 °C.

maximum removal was found at pH 2.5 with sugar beet sorbent. In the same study (197), similar behaviour was found using sugar cane bagasse and maize cob with an increase in the pH at equilibrium (the final pH).

It can be concluded that, in addition to the initial pH, the sorption of chromium (VI) depends on the initial concentration of chromium (VI), and mass and nature of the carbon sorbent (wet and dry).

By investigating the equilibrium chromium solution and its pH value as shown in figures 6.34 – 6.41, it was found that: At lower pH values (below the sorption maximum), chromium (VI) was barely detected in the equilibrium chromium solution and chromium (III) was virtually the total equilibrium chromium concentration. There was also a noticeable rise in the pH at the end of the experiment. The presence of chromium (III) was visually observed by its greenish colour and as a confirmatory test, the resultant chromium (III) solution after adjusting the pH 2 - 4, was mixed with EDTA and then boiled for few minutes, when it gave a purple colour of λ_{max} at 538 mμ (205).

At the maximum sorption point, minimal chromium was detected in the solution at equilibrium and mainly consisted of chromium (VI) and a sharp increase in the final pH was observed. As the initial pH was increased to pH 7 the sorption capacity decreased with no chromium (III) being observed in the equilibrium solution with an increase in the pH. Starting with an initial pH 7, the equilibrium pH slightly increased indicating that reduction was still taking place in the neutral solution. Sorption capacity at pH 8 and pH 9 appears the lowest and does not show an increase in the final pH. Initial and final pH values at equilibrium are represented in figure 6.42. Data of sorption were summarised in appendix III (tables 6.14 - 6.21).

The mechanism of chromium (VI) removal on activated carbons was considered as adsorption / reduction processes (66, 67,92, 197). Huang and Wu (66) also found that at pH below 6, chromium (VI) was reduced to chromium (III) by the activated carbon while Perez-Candela and co-workers (67), found that the reduction only occurs at pH <3. In addition, chromium (VI) was found to be reduced on the carbon surface producing chromium (III) which was then adsorbed on the carbon-oxygen groups on the surface (92). In the present work, it is believed that reduction still occurs at pH 7.

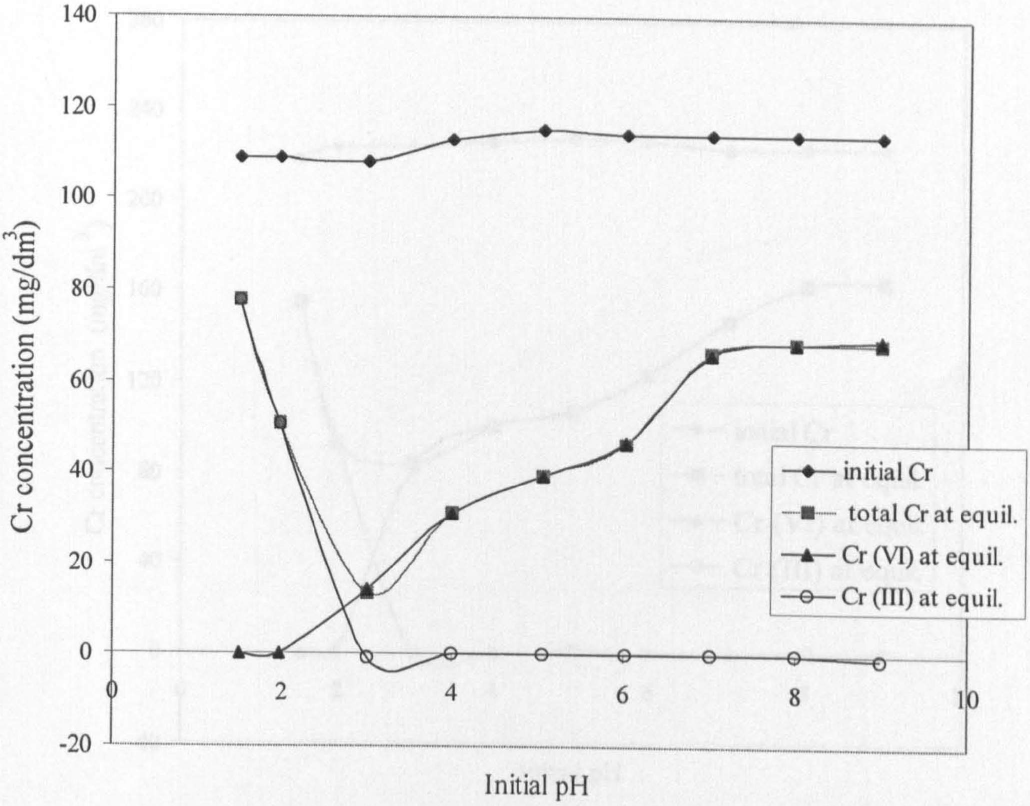

Figure 6.34. A Plot of chromium concentration before and after sorption on wet C160 at different initial pH values (Initial concentration 100 mg/dm^3).

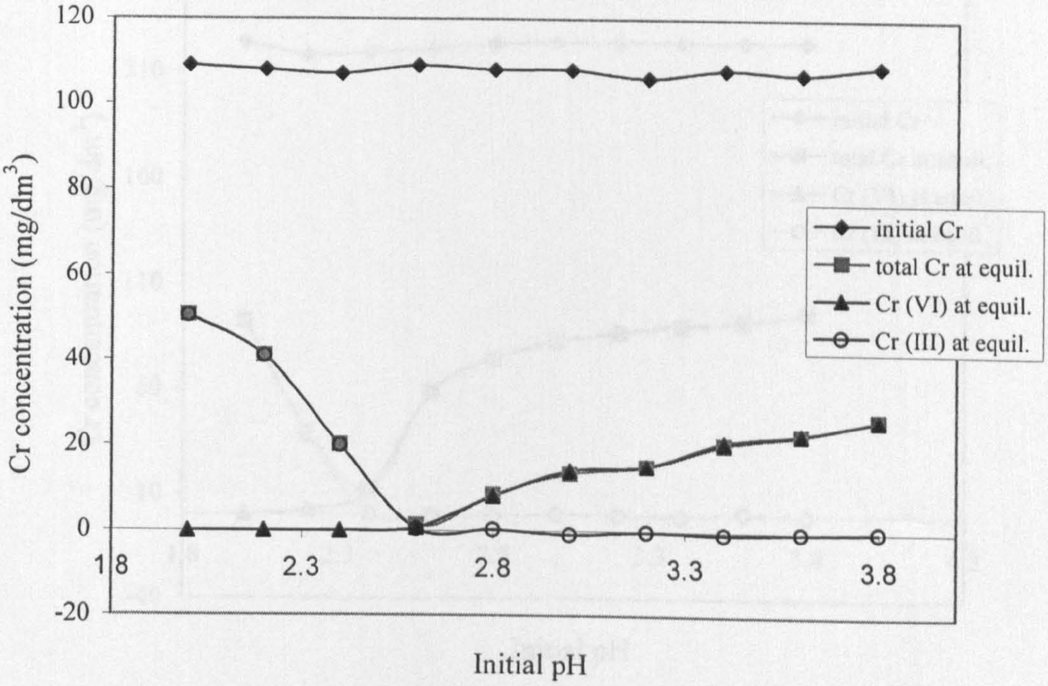

Figure 6.35. A Plot of chromium concentration before and after sorption on wet C160 at different initial pH values (Initial concentration 100 mg/dm^3).

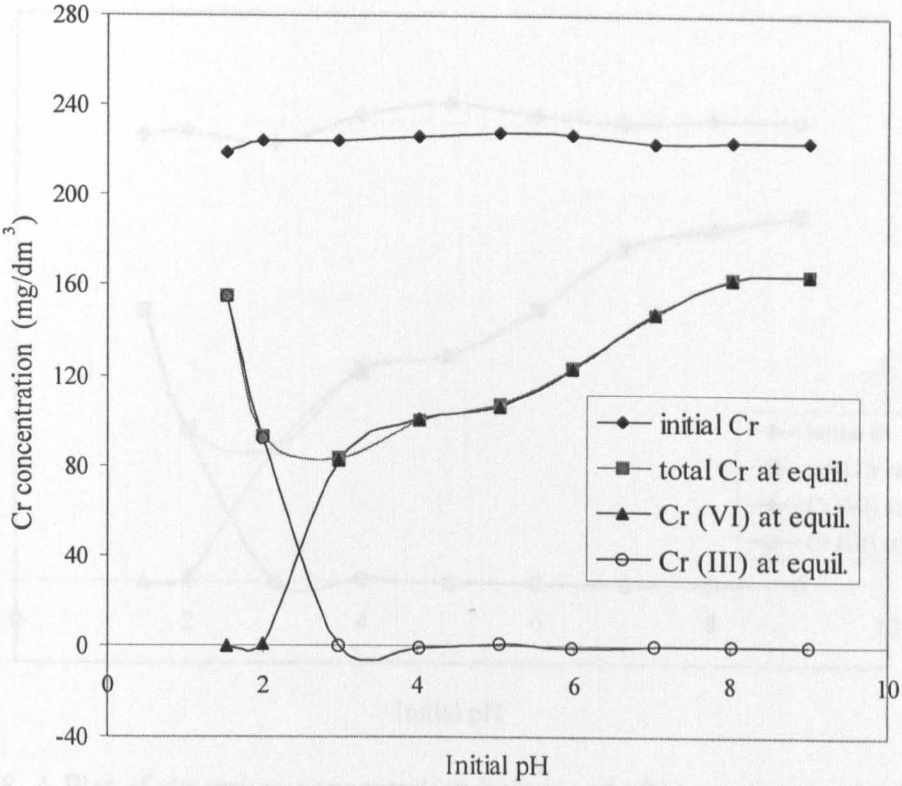

Figure 6.36. A Plot of chromium concentration before and after sorption on wet C160 at different initial pH values (Initial concentration 220 mg/dm^3).

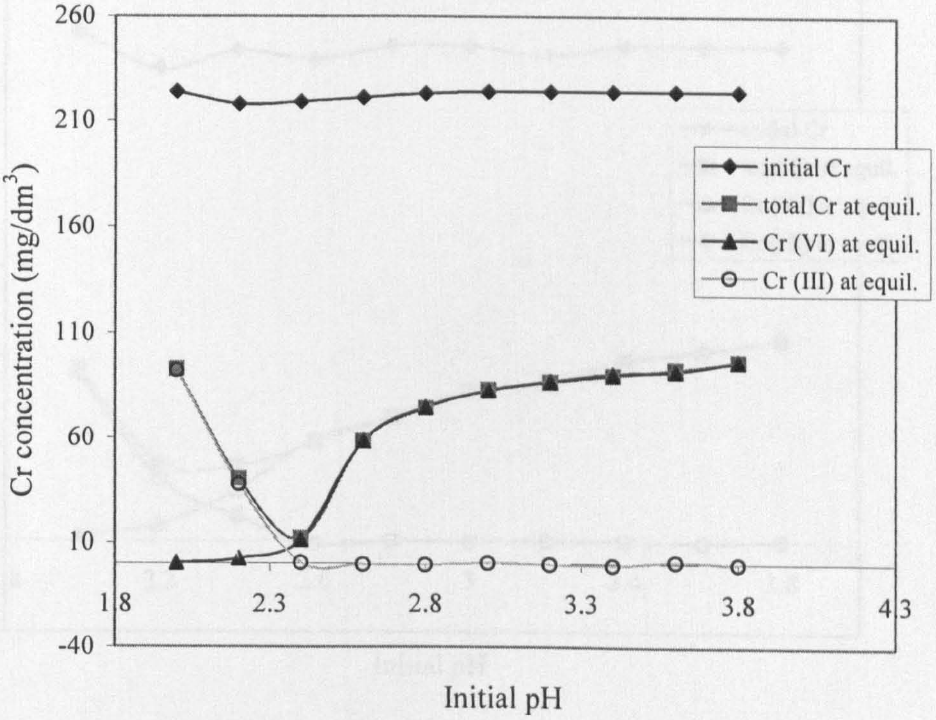

Figure 6.37. A Plot of chromium concentration before and after sorption on wet C160 at different initial pH values (Initial concentration 220 mg/dm^3).

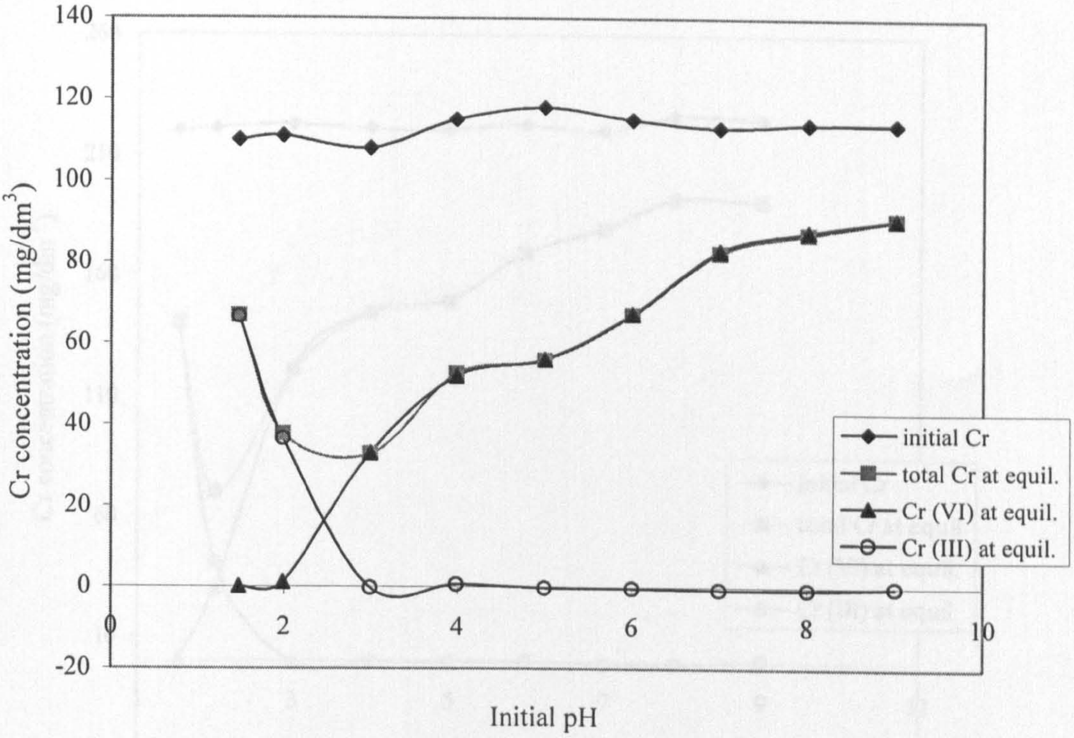

Figure 6.38. A Plot of chromium concentration before and after sorption on dry C160 at different initial pH values (Initial concentration 100 mg/dm^3).

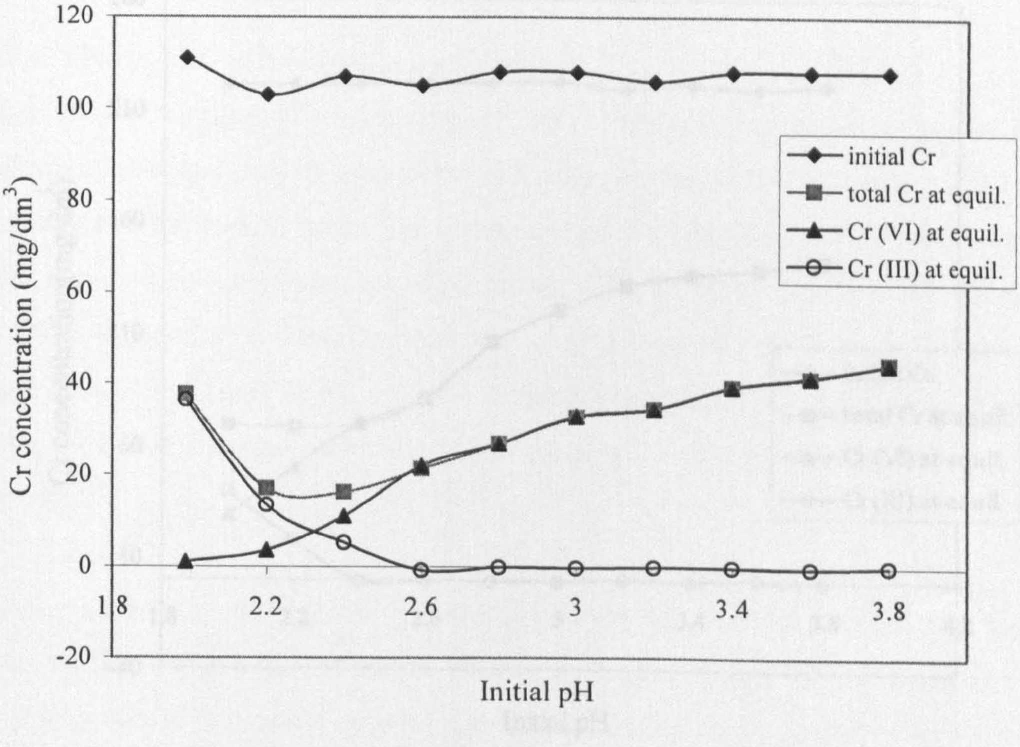

Figure 6.39. A Plot of chromium concentration before and after sorption on dry C160 at different initial pH values (Initial concentration 100 mg/dm^3).

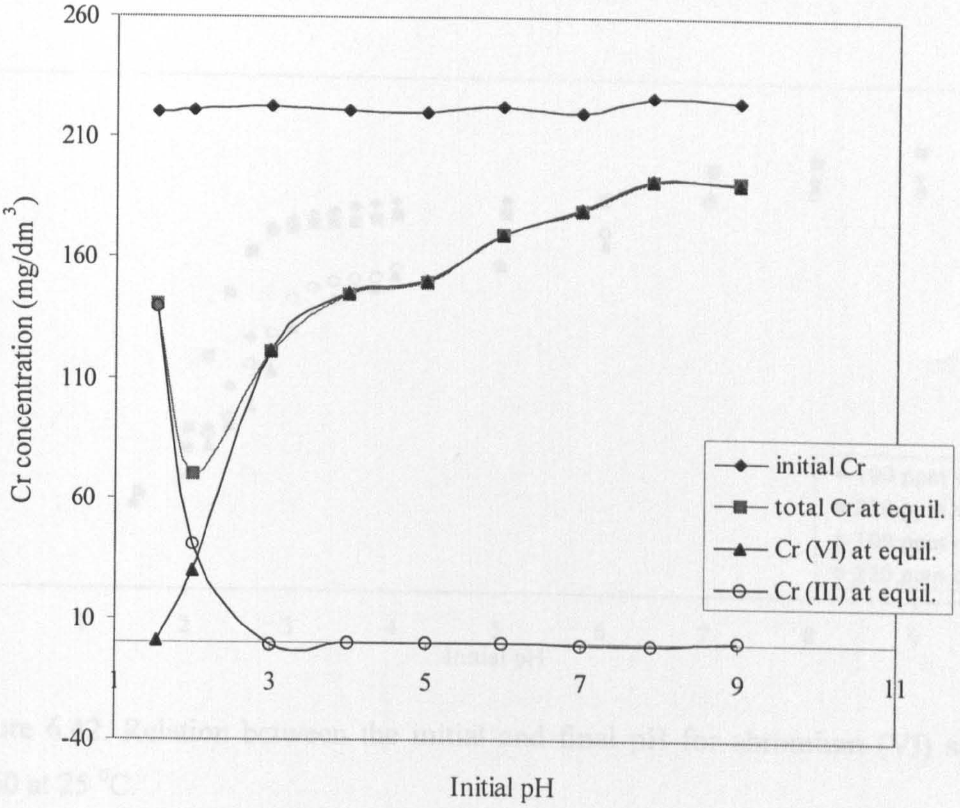

Figure 6.40. A Plot of chromium concentration before and after sorption on dry C160 at different initial pH values (Initial concentration 220 mg/dm^3).

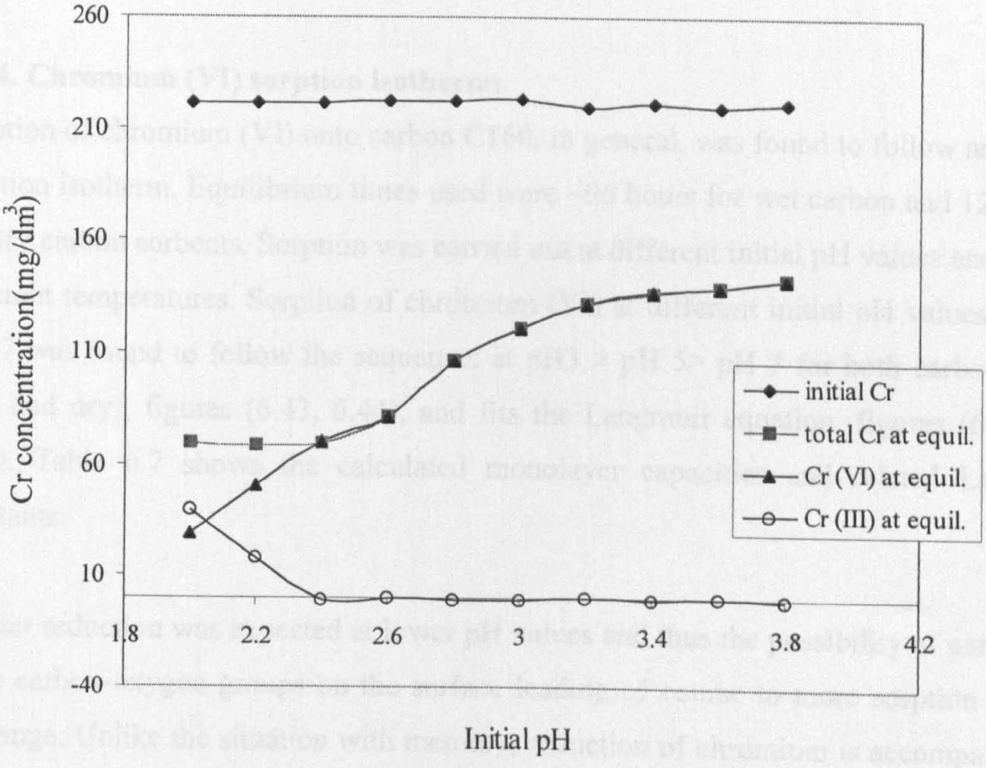

Figure 6.41. A Plot of chromium concentration before and after sorption on dry C160 at different initial pH values (Initial concentration 220 mg/dm^3).

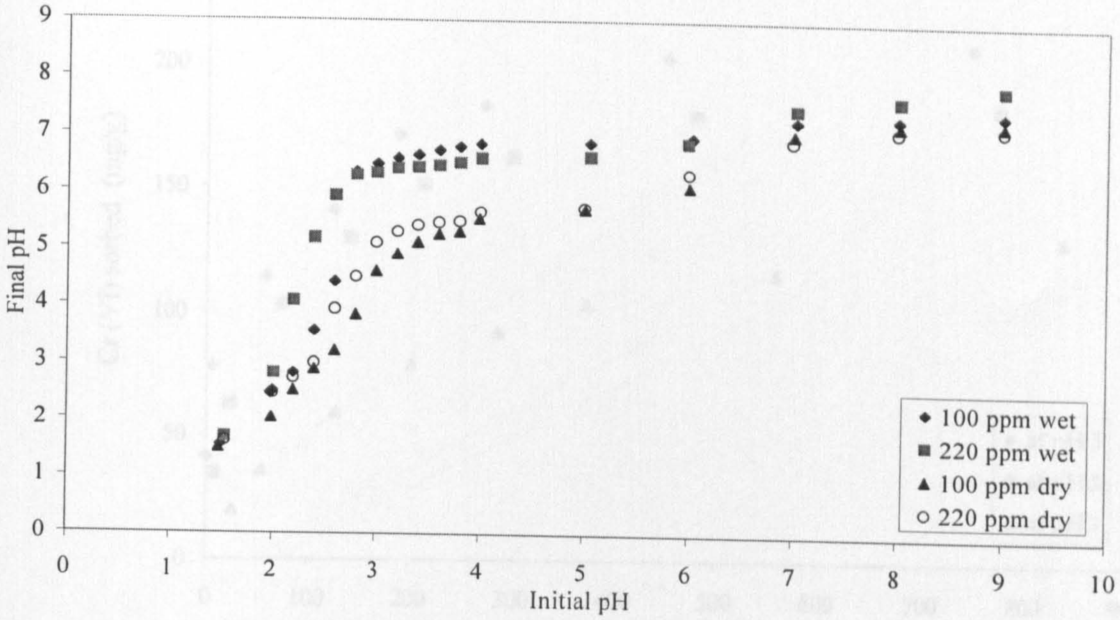

Figure 6.42. Relation between the initial and final pH for chromium (VI) sorption on C160 at 25 °C.

Sharma and Forster (197) noticed an increase in pH at equilibrium for chromium (VI) sorption on sawdust, sugar beet, maize cob and sugar cane bagasse.

6.3.4. Chromium (VI) sorption isotherms

Sorption of chromium (VI) onto carbon C160, in general, was found to follow an L-type sorption isotherm. Equilibrium times used were ~96 hours for wet carbon and 120 hours for dry carbon sorbents. Sorption was carried out at different initial pH values and also at different temperatures. Sorption of chromium (VI) at different initial pH values of 3, 5 and 7 was found to follow the sequence: at pH3 > pH 5> pH 7 for both carbon forms (wet and dry), figures (6.43, 6.44), and fits the Langmuir equation, figures (6.45 and 6.46). Table 6.7 shows the calculated monolayer capacities and related Langmuir constants.

Greater reduction was expected at lower pH values and thus the possibility of generating more carbon-oxygen groups on the surface leading of course to more sorption via ion exchange. Unlike the situation with mercury, reduction of chromium is accompanied by an increase in pH of solution therefore favouring the sorption of metal ions.

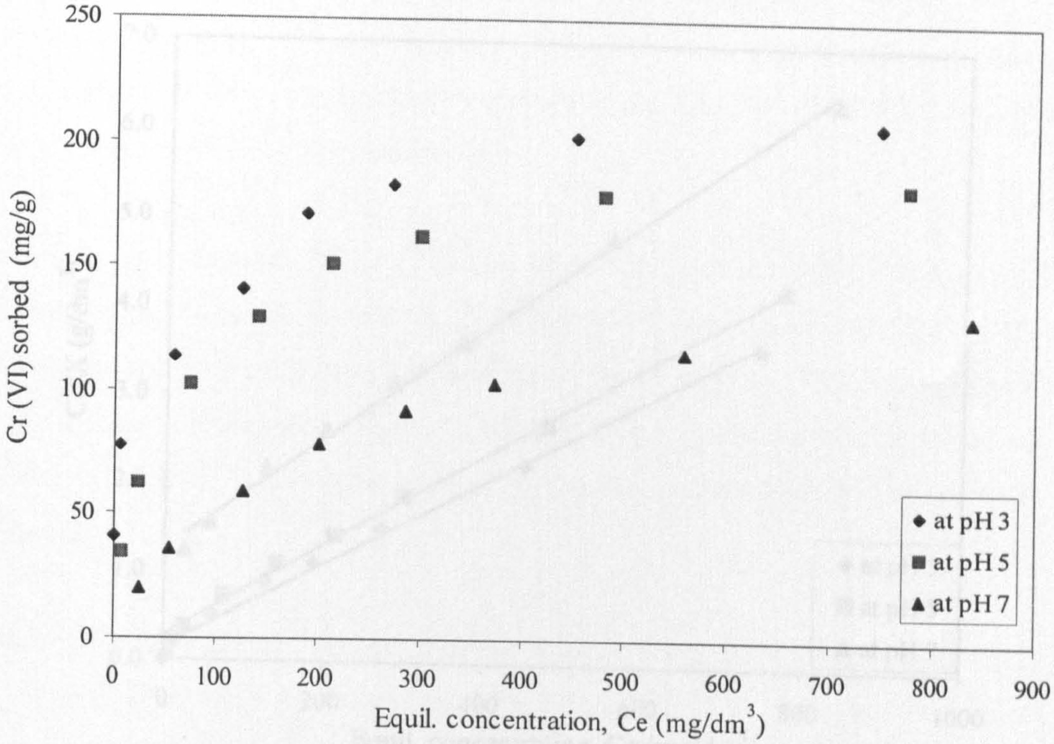

Figure 6.43. Sorption isotherms of chromium (VI) on wet C160 at different pH values at 25 °C.

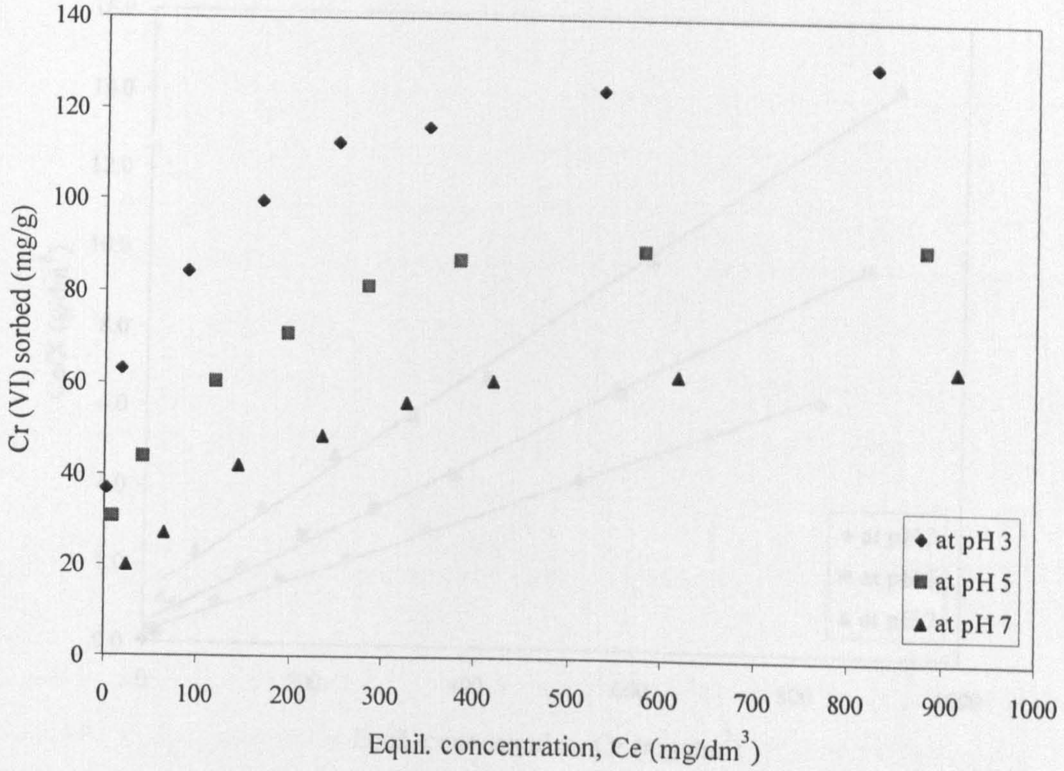

Figure 6.44. Sorption isotherms of chromium (VI) on dry C160 at different pH values at 25 °C.

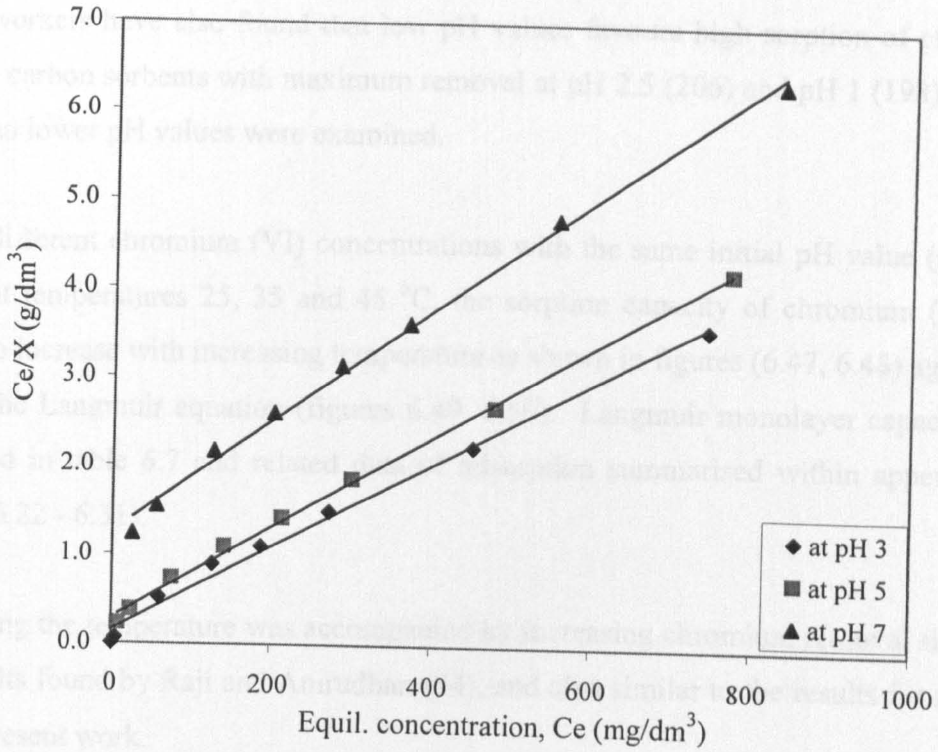

Figure 6.45. Langmuir isotherms for chromium (VI) sorption on wet C160 at different pH values at 25 °C.

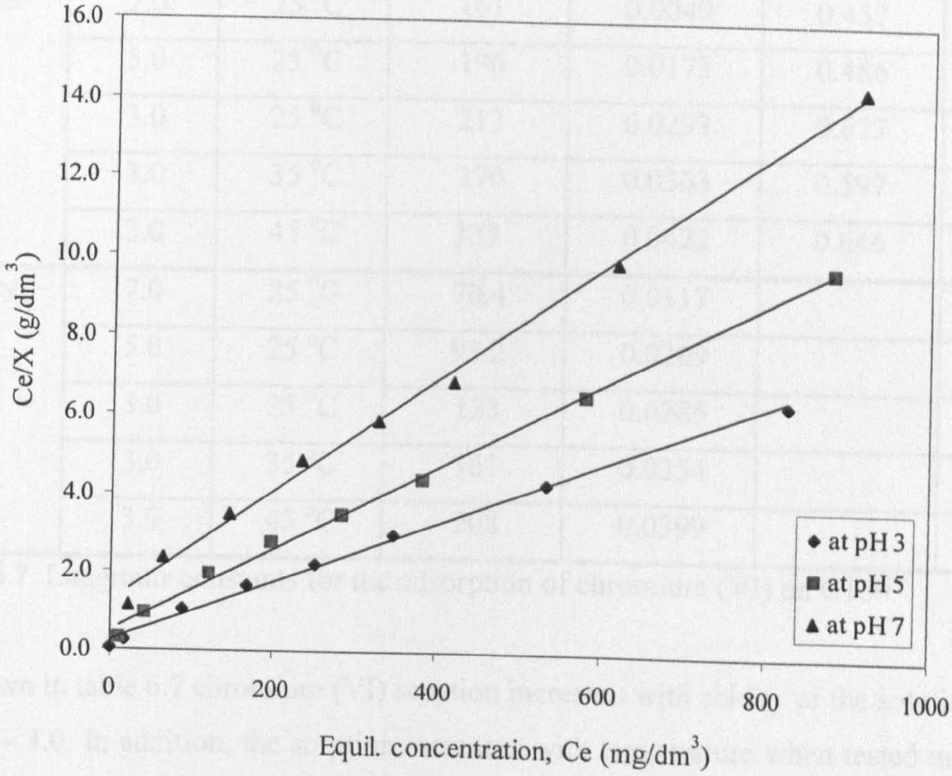

Figure 6.46. Langmuir isotherms for chromium (VI) sorption on dry C160 at different pH values at 25 °C.

Other workers have also found that low pH values favours high sorption of chromium (VI) on carbon sorbents with maximum removal at pH 2.5 (206) and pH 1 (198). In both cases, no lower pH values were examined.

Using different chromium (VI) concentrations with the same initial pH value (pH 3) at different temperatures 25, 35 and 45 °C, the sorption capacity of chromium (VI) was found to increase with increasing temperature as shown in figures (6.47, 6.48) again both fitting the Langmuir equation (figures 6.49, 6.50). Langmuir monolayer capacities are tabulated in table 6.7 and related data of adsorption summarised within appendix III, (tables 6.22 - 6.31).

Increasing the temperature was accompanied by increasing chromium removal similar to the results found by Raji and Anirudhan (94), and also similar to the results for mercury in the present work.

Carbon (C160)	Initial pH	Sorption Temp. °C	Langmuir constants		$\frac{X_m dry}{X_m wet}$	correlation coefficient for X_m
			X_m (mg/g)	b (dm^3 /mg)		
Wet	7.0	25 °C	161	0.0049	0.437	0.996
	5.0	25 °C	196	0.0173	0.486	0.998
	3.0	25 °C	213	0.0293	0.627	0.992
	3.0	35 °C	270	0.0363	0.597	0.993
	3.0	45 °C	323	0.0422	0.646	0.994
Dry	7.0	25 °C	70.4	0.0117		0.997
	5.0	25 °C	95.2	0.0209		0.997
	3.0	25 °C	133	0.0286		0.996
	3.0	35 °C	161	0.0354		0.997
	3.0	45 °C	208	0.0399		0.997

Table 6.7. Langmuir constants for the adsorption of chromium (VI) on C160.

As shown in table 6.7 chromium (VI) sorption increases with acidity of the solution from pH 7.0 - 3.0. In addition, the sorption increases with temperature when tested under the same pH conditions (pH 3). The values of $\frac{X_m dry}{X_m wet}$ show a large variation with pH but

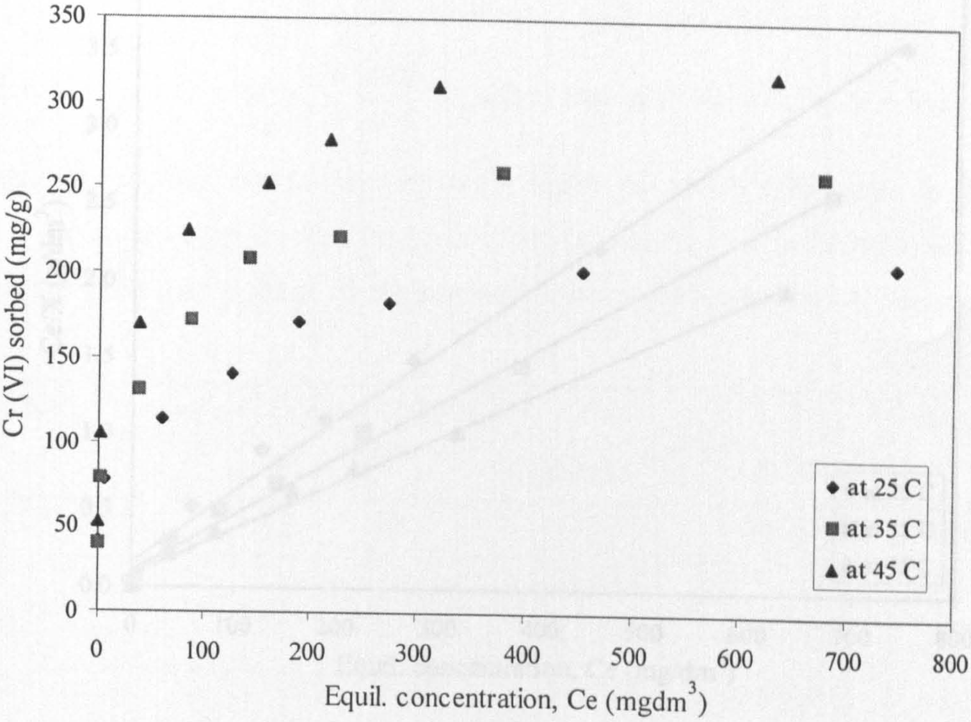

Figure 6.47. Sorption isotherms of chromium (VI) on wet C160 at different temperatures. (Initial pH 3).

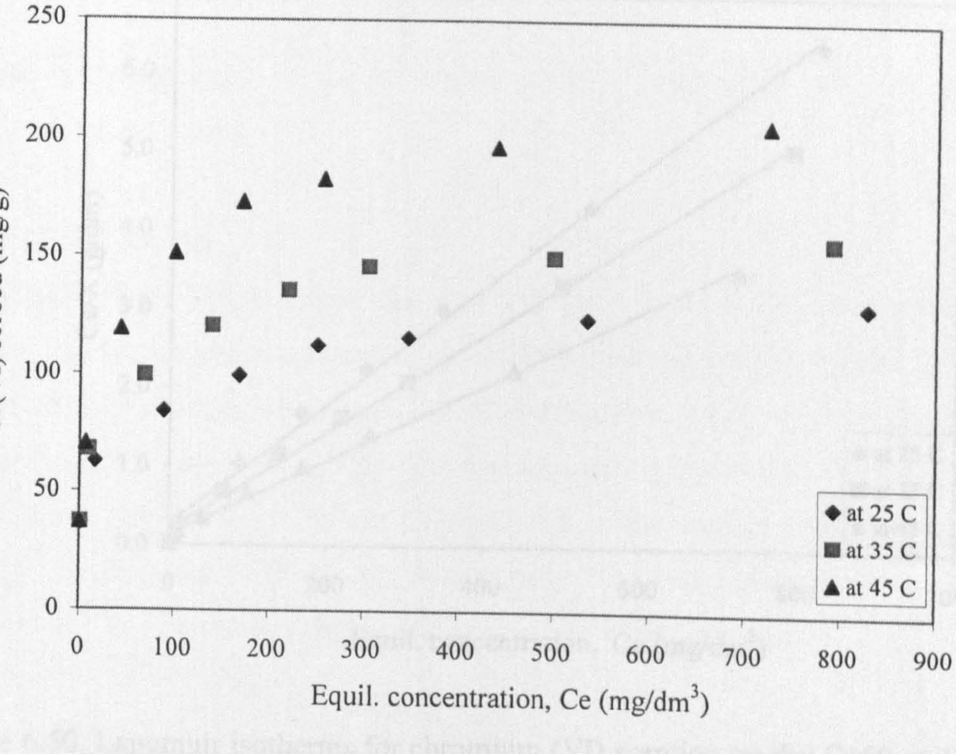

Figure 6.48. Sorption isotherms of chromium (VI) on dry C160 at different temperatures. (Initial pH 3).

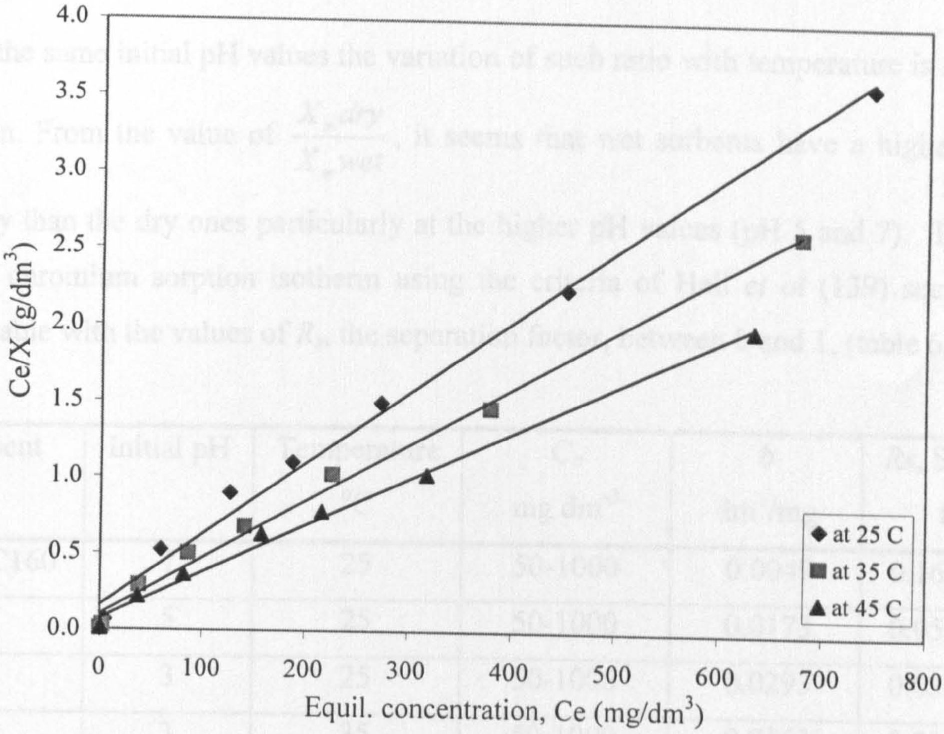

Figure 6.49. Langmuir isotherms for chromium (VI) sorption on wet C160 at different temperatures. (Initial pH 3).

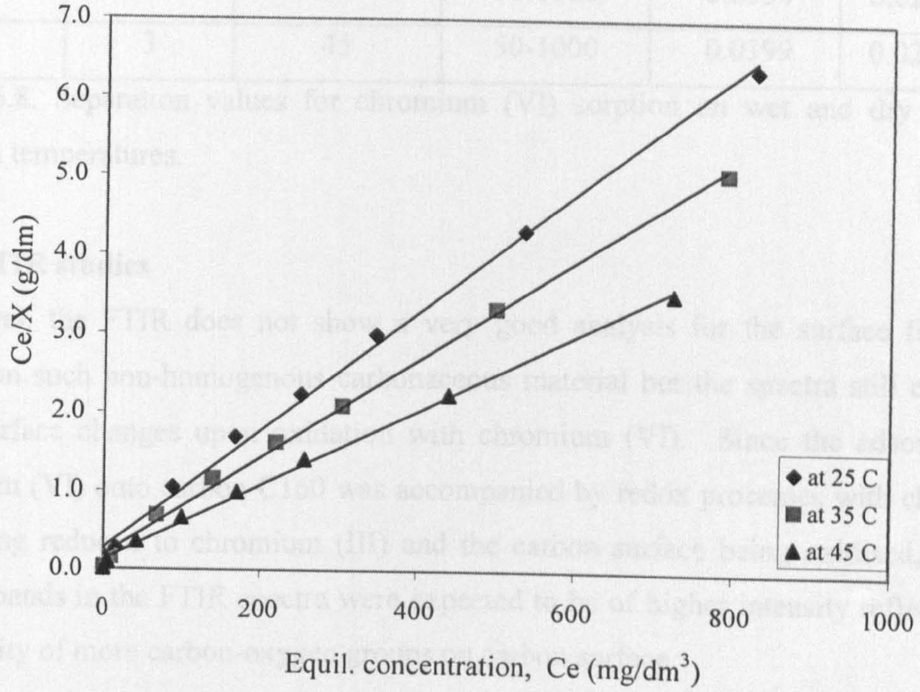

Figure 6.50. Langmuir isotherms for chromium (VI) sorption on dry C160 at different temperatures. (Initial pH 3).

using the same initial pH values the variation of such ratio with temperature is small and random. From the value of $\frac{X_m dry}{X_m wet}$, it seems that wet sorbents have a higher surface activity than the dry ones particularly at the higher pH values (pH 5 and 7). The shape of the chromium sorption isotherm using the criteria of Hall *et al* (139) seems to be favourable with the values of R_s, the separation factor, between 0 and 1, (table 6.8).

Sorbent	Initial pH	Temperature °C	C_o mg dm^{-3}	*b* dm^3/mg	*Rs*, Separation factor
Wet C160	7	25	50-1000	0.0049	0.1690-0.803
	5	25	50-1000	0.0173	0.0547-0.536
	3	25	50-1000	0.0293	0.0330-0.406
	3	35	50-1000	0.0363	0.0268-0.355
	3	45	50-1000	0.0422	0.0232-0.322
Dry C160	7	25	50-1000	0.0117	0.0790-0.632
	5	25	50-1000	0.0209	0.0457-0.489
	3	25	50-1000	0.0286	0.0338-0.412
	3	35	50-1000	0.0354	0.0274-0.361
	3	45	50-1000	0.0399	0.0245-0.334

Table 6.8. Separation values for chromium (VI) sorption on wet and dry C160 at different temperatures.

6.3.5. FTIR studies

In general, the FTIR does not show a very good analysis for the surface functional groups on such non-homogenous carbonaceous material but the spectra still can show some surface changes upon oxidation with chromium (VI). Since the adsorption of chromium (VI) onto carbon C160 was accompanied by redox processes with chromium (VI) being reduced to chromium (III) and the carbon surface being oxidised, carbon-oxygen bands in the FTIR spectra were expected to be of higher intensity reflecting the availability of more carbon-oxygen groups on carbon surface.

The spectra were obtained as summarised in Chapter 3, section 3.2.8 and the FTIR spectra are shown in figure 6.51. Comparing these spectra shows that the bands at around 3350 – 3400 cm^{-1}, which are connected with the O-H stretching vibrations,

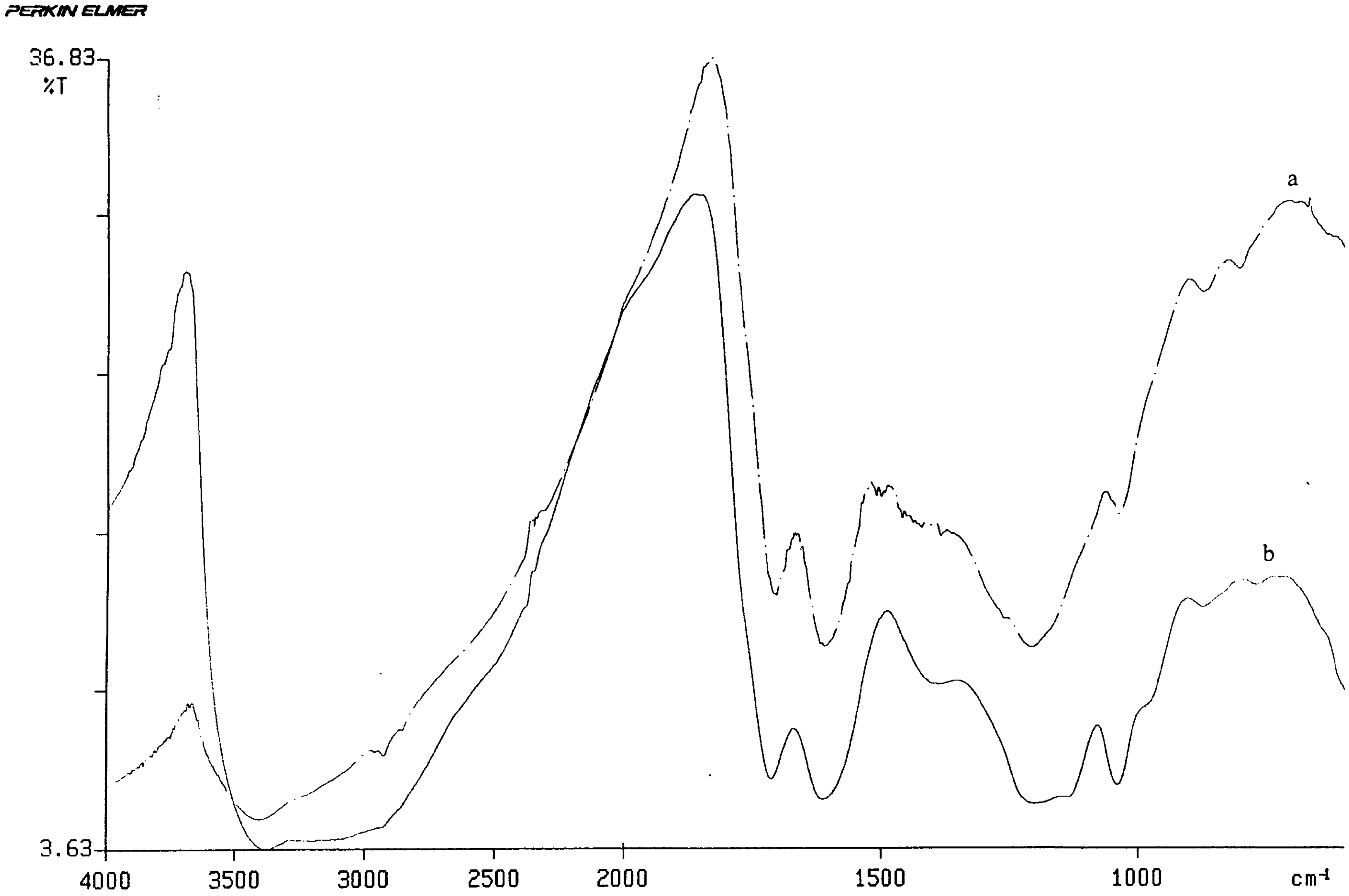

Figure 6.51. FTIR spectra of C160 before and after chromium (VI) sorption.
a. before sorption.
b. after sorption.

become relatively more intense and broader after sorption, indicating the formation of more OH groups by chromium (VI) reduction. In addition, an obvious change was obtained in the bands around 1700 cm^{-1} related to C=O stretching vibrations. Both carboxylation and decarboxylation accompanying the oxidation process are expected. The bands around 1700 and 1600 cm^{-1} seem to be more intense after chromium (VI) sorption indicating an increase in these groups.

An increase in the intensity of the bands and shoulders in the range between 1300 and 900 cm^{-1} which may be ascribed to the C-O vibrations associated with hydroxyl groups and ether type structures (129) reflects the increase of carbon-oxygen groups on the surface after chromium sorption as a result of oxidation.

FTIR measurements following the adsorption of chromium (VI) on activated carbon were examined by Bautista-Toledo *et al* (92). Their results supported the reduction of chromium (VI) to chromium (III) with the formation of both MO-Cr (VI) and MO-Cr (III) bands, where MO indicates the oxidised carbon surface.

6.3.6. Mechanism of chromium (VI) sorption

There are two processes taking place within chromium (VI) sorption:

1. Redox reaction with accompanying change of pH.
2. Sorption.

At low pH values (≤ 7), redox processes takes place producing chromium (III). Equations 6.17 and 6.18 show the redox processes involved in the reduction of chromium (VI) which are accompanied by a pH change since the protons are involved in the redox processes. Sorption of the reduced form, chromium (III), depends on the pH of the solution.

Chromium reduction

Chromium (VI) is available in solution as $Cr_2O_7^{2-}$ or CrO_4^{2-} depending on the concentration and pH (195). Chromium (VI) is reduced according to the following equations:

$Cr_2O_7^{2-} + 14\,H^+ + 6\,e^- \;=\; 2Cr^{3+} + 7\,H_2O$ (+1.232 V) (6.17)

or

$CrO_4^{2-} + 8\,H^+ + 3e^- \;=\; Cr^{3+} + 4\,H_2O$ (+1.350 V) (6.18)

Carbon oxidation

Carbon experiences oxidation similar to that experienced through mercury (II) reduction to produce carbon dioxide and surface carbon oxygen species which can be summarised as follows:

- oxidation of carbon to produce carbon dioxide in the presence of protons and chromium ions

  $3C + 2\,Cr_2O_7^{2-} + 16H^+ = 3CO_2 + 4Cr^{3+} + 8H_2O$ (6.19)

  $3C + 4\,CrO_4^{2-} + 20\,H^+ = 3\,CO_2 + 4\,Cr^{3+} + 10\,H_2O$ (6.20)

- surface oxidation reaction

  In addition to the above reaction which removes carbon from the surface, partial oxidation can also occur to carbon compounds giving rise to the formation of hydroxyl (or phenolic) groups, carbonyl groups or carboxylic acids.

$\sim$C-H + Cr (oxidized) + H^+ = $\sim$C-OH + Cr (reduced) + H_2O (6.21)

$\sim$C-H / $\sim$C-OH + Cr (oxidized) + H^+ = $\sim$C=O + Cr (reduced) + H_2O (6.22)

$\sim$C-H / $\sim$C-OH + Cr (oxidized) + H^+ = $\sim$COOH + Cr (reduced) + H_2O (6.23)

Chromium (III) produced in the solution was sorbed onto the ion exchange sites (carbon oxygen groups) available or generated via the redox processes and this sorption depends on the change of pH accompanied.

At higher pH values, chromium (VI) sorption is believed to be via physico-chemical adsorption especially above neutrality in which reduction does not seem to occur. Sharma and Forster (197), Huang and Wu (203) and Alaerts *et al* (204) considered that when oxo groups (C_xO and C_xO_2) are present on the carbonaceous material in contact with water, they hydrolyse water molecules as shown in equation 6.24:

$$C_xO + 2H_2O \;=\; C_xOH_2^{2+} + 2OH^- \qquad (6.24)$$

when chromium (VI) ions are introduced into the system, they are adsorbed onto the positively charged surface as in equation 6.25.

$$C_xOH_2^{2+} + HCrO_4^- \quad = \quad C_xO_2H_3CrO_3^+ \qquad (6.25)$$

Summation of equations 6.24 and 6.25 , gives equation 6.26

$$C_xO + 2H_2O \ + HCrO_4^- = \ C_xO_2H_3CrO_3^+ + 2OH^- \qquad (6.26)$$

6.3.7. Discussion

Sorption of chromium (VI) is very dependent on the pH of solution. As shown in equations (6.19 - 6.23), protons are involved in all the reactions with carbon as well as being consumed in the chromium (VI) reduction process and thus a rise in pH is expected during sorption. In the kinetic experiments, starting with the initial pH 4.5, sorption was slow and followed a second order rate equation, while with initial pH 1.5, the chromium (VI) reduction followed a pseudo first-order rate equation as the $[H^+]$ could be assumed constant.

Equilibrium studies at different initial pH values showed a maximum value of sorption within a particular pH range.

Starting with conditions of lower pH (≤2 for concentrations up to 220 mg/dm^3) complete reduction to chromium (III) was observed with a slight rise in the pH at equilibrium indicating consumption of protons in the reduction process (equations 6.17, 6.18). At such low pH conditions, the protons compete with the resulting chromium (III) for ion exchange sites giving low metal sorption since the rise in pH that accompanies reduction is not sufficient to allow complete removal of the chromium (III) via ion exchange.

Approaching the maximum point for chromium sorption, the equilibrium pH starts increasing as a result of reduction allowing more chromium (III) to be sorbed. At the maximum point, reduction of chromium (VI) was accompanied with a large increase in the equilibrium pH allowing most of the reduced form of chromium to be sorbed via ion exchange since very little or no chromium (III) was detected in the equilibrium solution.

Starting with initial pH values higher than that of the maximum uptake, sorption was still accompanied with an increase in the final pH, even starting with initial pH as 7, indicating most probably that reduction of chromium (VI) at such relatively higher pH to chromium (III) is still present which are sorbed via ion exchange. However reduction is less extensive as shown by the decrease in amount of chromium removed from solution.

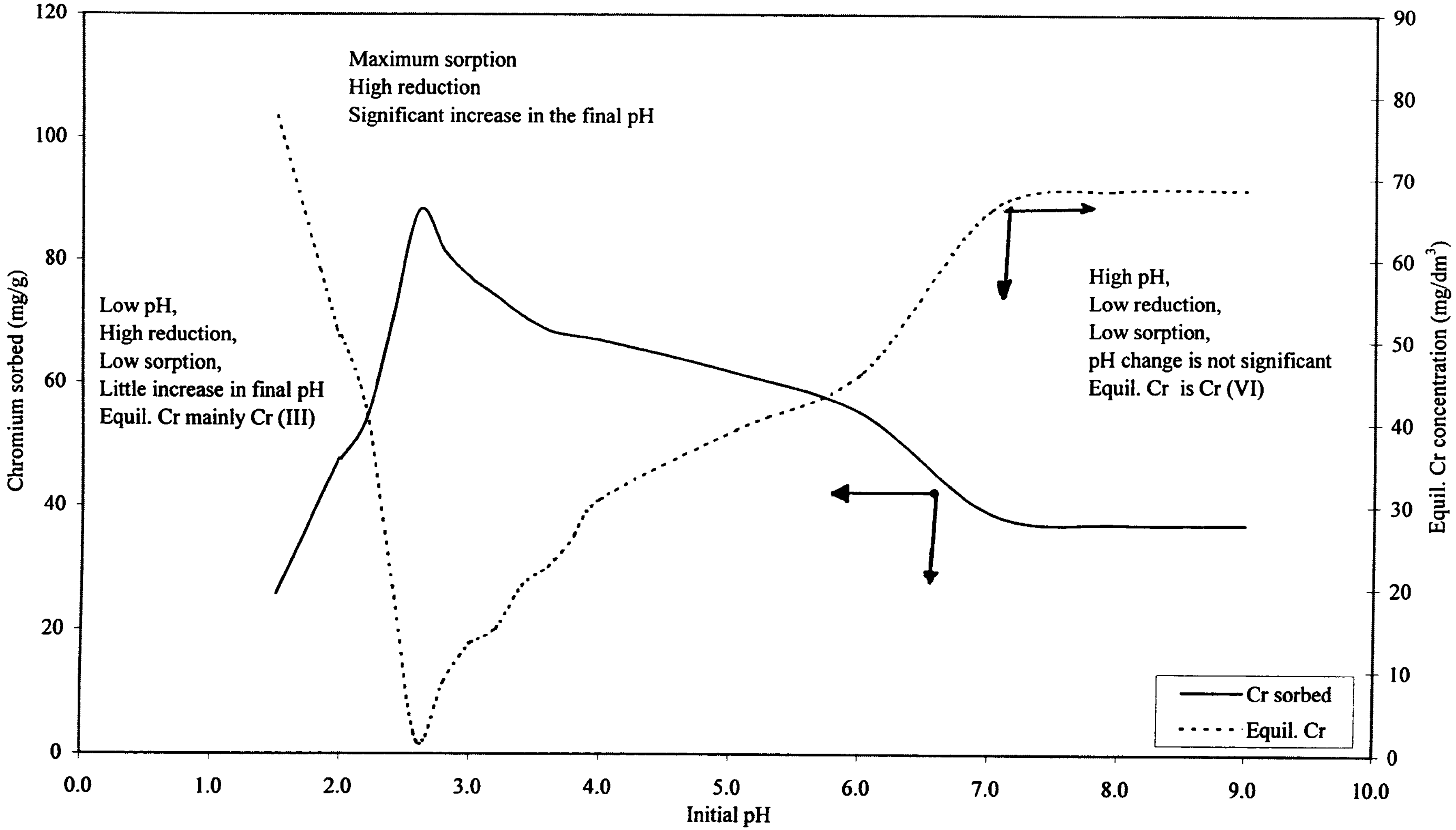

Figure 6.52 Relation between sorbed chromium and equilibrium chromium for using wet C160
(Initial Cr (VI) concentration 100 mg/dm^3).

For pH values above pH 7 a lower chromium removal was obtained with no significant changes in the pH. At such high pH values, reduction is not expected and chromium removal is then related to the physico-chemical adsorption of chromium (VI) as noted above. A representation of the relation between the amount sorbed and the equilibrium chromium concentrations at different initial pH values is shown in figure 6.52.

Temperature variation also has an effect on the sorption of chromium which was found to increase with increase in temperature under the same initial pH conditions.

The sorption-reduction of chromium (VI) depends on:
carbon mass and surface reactivity since carbon is the reducing agent in addition to providing some protons for the reduction reaction via surface ionisation;
the nature of the carbon since wet C160 has more surface activity than the dry sample;
the concentration of chromium (VI);
the initial pH value and the temperature of the sorption reaction.

The choice of the appropriate pH of sorption is the one where two conditions are being fulfilled:
1- reasonable reduction of chromium (VI) and, of course, the generation of more ion exchange functional groups on the carbon surface as a result.
2- Significant pH increase which allows the metal ions, Cr (III), to be sorbed via ion exchange.

6.4. Sorption of Precious Metals

6.4.1. Introduction

Gold, silver, palladium and platinum, in general, are known as precious metals and because of their value, concentration, recovery and smelting is a major subject of scientific research and industrial development.

"In 1915, Rose commented that the chlorination process, which was used largely to treat gold ores and gravity concentrates in the late nineteenth and early twentieth centuries, was mostly replaced by cyanidation except in a few mills (207)" (169). However the chlorination process for gold has been reappraised in the last decades due to the following factors (169): 1) the faster dissolution rate of gold compared to other lixiviants; 2) the less environmental sensitivity; 3) amenability to refractory ores, such as carbonaceous ores; 4) chlorine is less expensive than cyanide. The methods used for gold recovery from chloride solutions include: solvent extraction, reduction to elemental gold by reagents such as sulphur dioxide, replacement by zinc metal, electrolysis, adsorption by activated carbon and ion exchange (169). All these methods, except the adsorption process, require a solid - liquid separation to produce a clear solution before they can be used. Such filtration processes add expense to the flow-sheet and thus render carbon sorption process more attractive (169).

Gold reduction on a charcoal surface was reported by Henry (208) early in 1801 and later by others (209, 210) as reported by Sun and Yen (169). Recent research of gold sorption on activated carbon from chloride solution showed reduction to the element on the surface (59,169,171). In addition to activated carbon, lignite (179), humic substances derived from peat (180) and activated carbon fibres (173,175) also showed reducing properties capable of producing gold metal from its chloride solution.

Silver is an important metal in industry for many purposes. The primary use of silver is in photographic films and chemicals. Other products include electric and electronic products, alloys, batteries, catalysts, electroplating, jewellery, coins, dental and medical applications (211). In solution, ionic silver is toxic to aquatic plants and animals (48). In humans it also causes blue-grey discolouration of skin, mucous membranes and eyes (48).

The concentration of silver and its recovery from solutions is a target for researchers not only from the environmental aspects but also for an economic asset. Silver recovery by adsorption on several materials such as activated carbon (167), activated carbon fibres (175), lignite (178), manganese dioxide (212) and biomass (213) has been studied. Precipitation of silver metal from silver nitrate solution was observed on activated carbon (167), activated carbon fibre (175) and lignite (178).

The main uses of palladium are in the electronics and electrical industries, in circuitry and in dental alloys. It also finds many catalytic applications in industry (214). Jewellery and catalysts are the main uses of platinum which fulfils a wide range of roles in the chemical industry. Platinum catalysts are used for minimising exhaust emissions from petrol engines producing complete combustion of hydrocarbons, conversion of CO to CO_2 and the removal of nitrogen dioxide as N_2 (214).

Several processes have been used for the recovery of platinum from synthetic and industrial effluents such as sorption (215, 216), ion exchange (217) liquid-liquid extraction and membrane processes (218). Chloroplatinate (II) ions can be reduced to platinum metal on the surface of activated carbon (171, 219). Other researchers found that activated carbon fibres reduced platinum (IV) as H_2PtCl_6 to its metallic form (174, 175, 220).

Palladium (II) has been recovered on some sorbents such as hydrated zirconium oxide (221), Amberlite IRA-93 (217) and nitrogen-containing fibrous sorbents (222). Palladium (II) can be reduced to its metallic form on lignite (178) and activated carbon (171).

Thus it was interesting to study the adsorption of these metallic species onto the sorbent from flax shive because of its significant CEC and reduction properties. Also its low cost will allow recovery of the elements by combustion of the loaded material.

6.4.2. Sorption kinetics

Figures 6.53 and 6.54 show the rate of removal of these metals on wet and dry samples of C160. In all cases, as expected from the early studies presented in Chapters 4 and 5, the wet sample showed the faster rates. Considering the individual elements gold (III) was fastest, reaching equilibrium in about 30 hours (wet) and 70 hours (dry). This was followed by palladium (II): 70 hours (wet) 120 (dry); silver (I): 160 hours (wet) and 185 hours (dry) and lastly platinum (II) which has both the lowest kinetics (~200 hours) and lowest uptake.

The uptake of precious metal ions was found to vary almost linearly with the half power of time, $t^{0.5}$, in the initial stages of sorption as shown in figures 6.55 and 6.56. The relation was expressed by equation 5.7 and as noted earlier this approximately linear variation is predicted for a large initial fraction of reaction controlled by intraparticle diffusion (161). The extent of linearity varies with the metal ions showing a correlation to the rate of pore diffusion, the slower the rate of pore diffusion, the longer the period that shows linearity. The calculated values for k_d show a significant increase for wet sorbents over that for the dry sorbents, table 6.9. However, the linear plots do not pass through the origin. Similar results were found in other systems and have been interpreted as pore diffusion being not the only rate controlling step (160, 188).

Preliminary experiments show that this group of precious metals experience reduction on the carbon surface. For the residual metal ion concentrations in solution with time, it was found that gold (III), palladium (II), silver (I) and platinum (II) sorption follows a first order reaction process expressed by equation 5.8, figures 6.57 and 6.58. Rate constants are presented in table 6.9 and kinetics data are shown in appendix III, table 6.32 - 6.35.

It is believed that the ion exchange step is fast and the reduction step is slow and thus is considered as the rate determining step. The reduction step, as will be discussed later, depends only on the metal ions and thus, overall, the reaction follows first order kinetics. In some other studies, gold sorption was reported to follow a first order reduction process on lignite (179) and activated carbon (169).

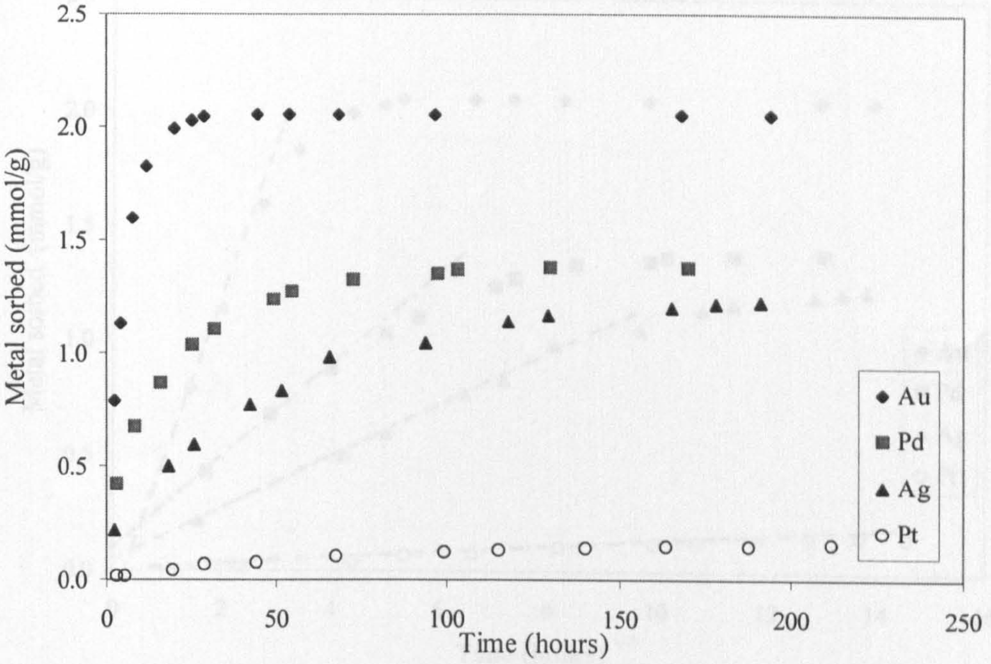

Figure 6.53. Kinetics of sorption of precious metals on wet C160 at 25 °C.

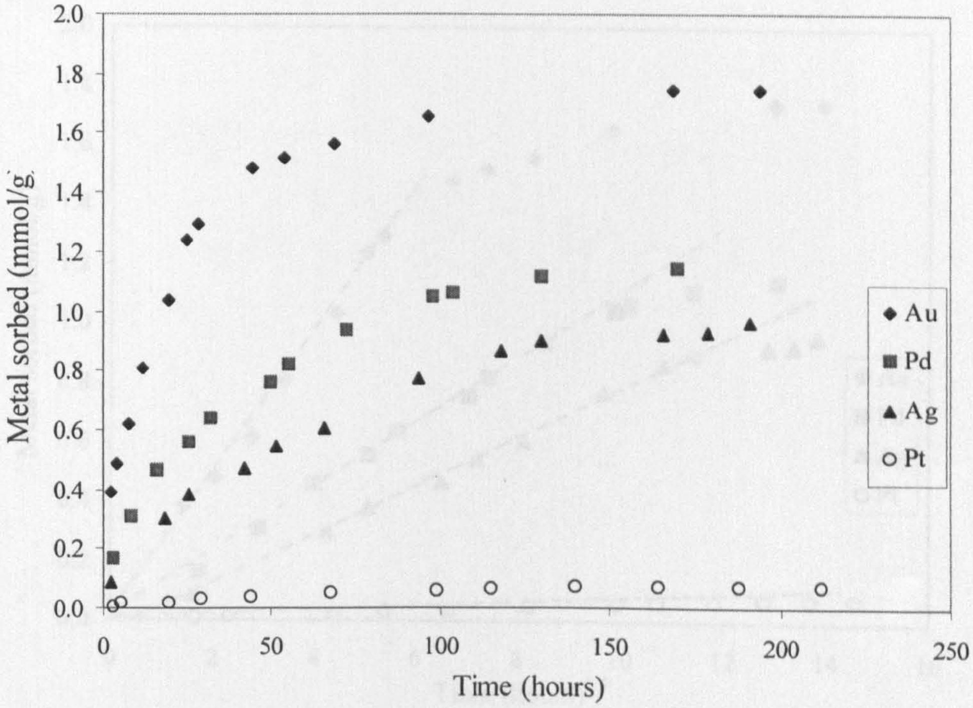

Figure 6.54. Kinetics of sorption of precious metals on dry C160 at 25 °C.

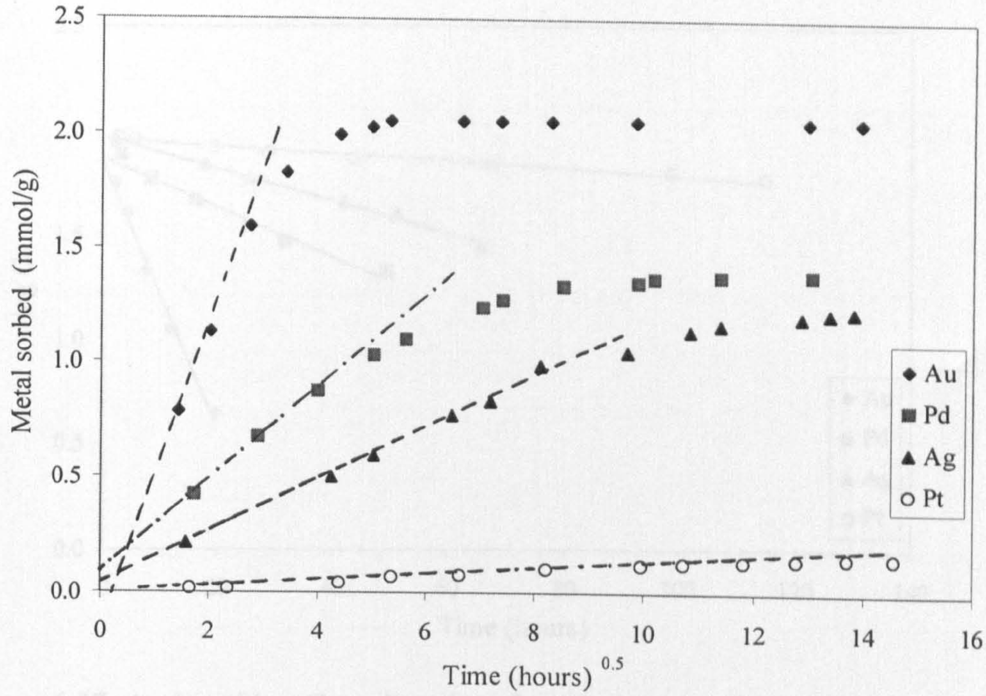

Figure 6.55. A plot of the rate of pore diffusion of precious metals on wet C160 at 25 °C.

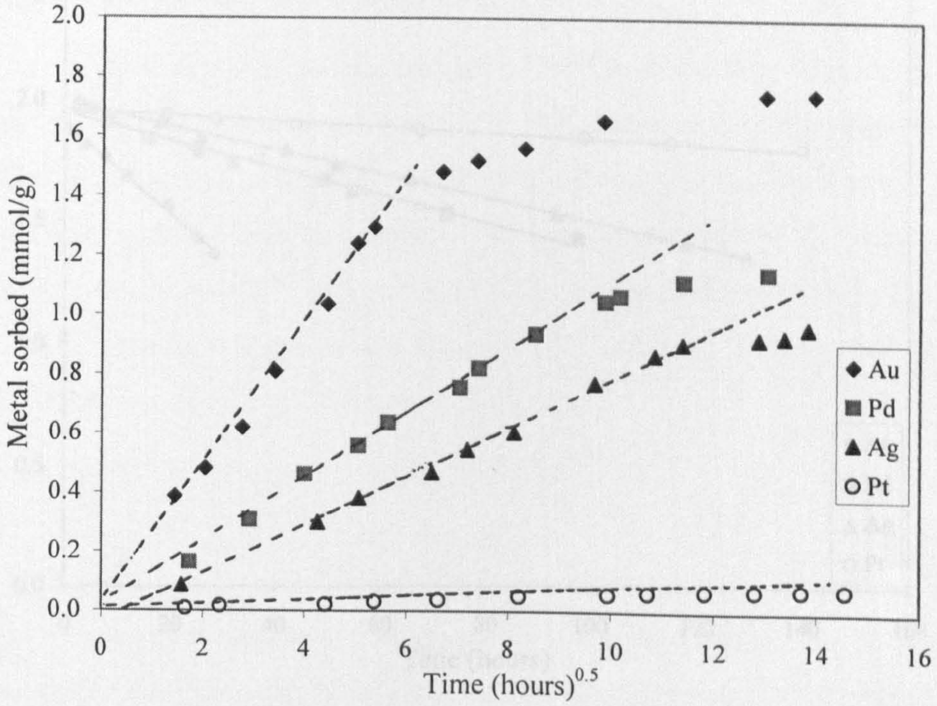

Figure 6.56. A plot of the rate of pore diffusion of precious metals on dry C160 at 25 °C.

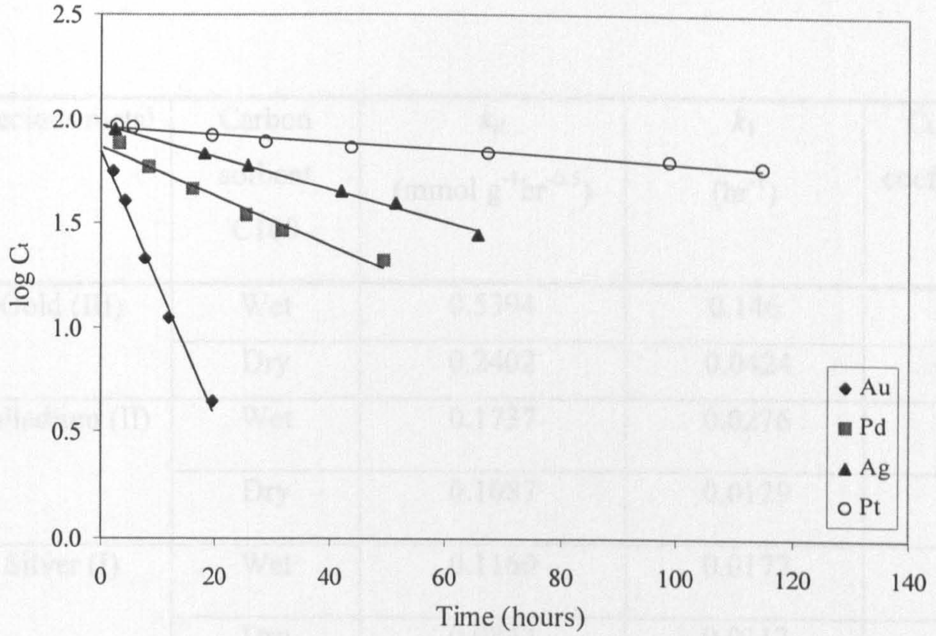

Figure 6.57. A plot of log C_t against time for precious metal sorption on wet C160 at 25 °C. (C_t is expressed as mg/dm^3).

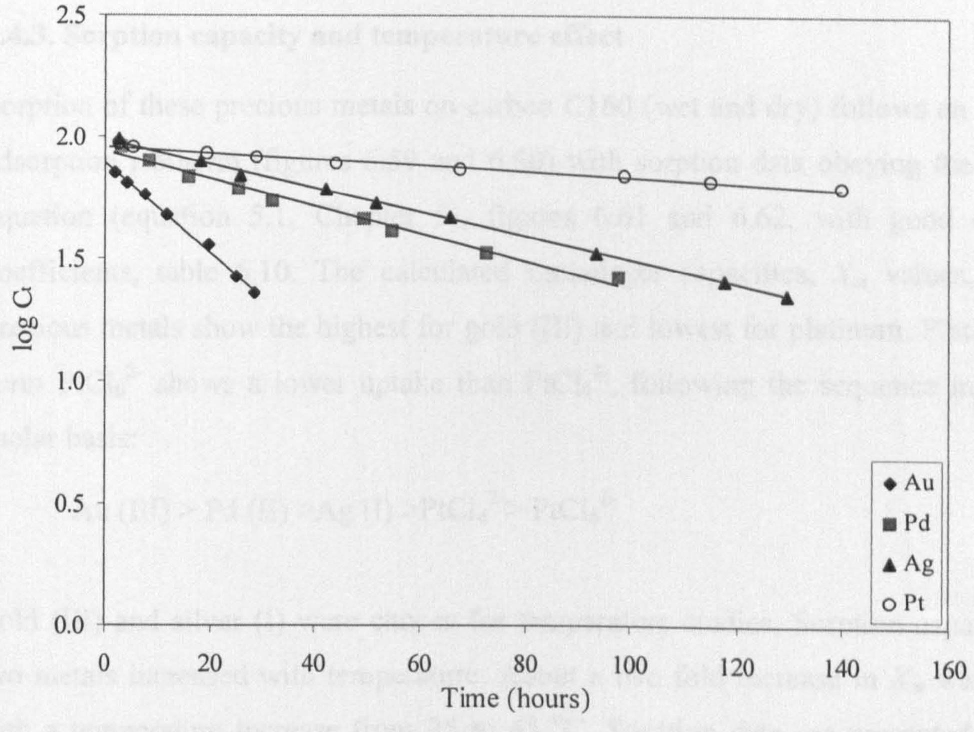

Figure 6.58. A plot of log C_t against time for precious metal sorption on dry C160 at 25 °C. (C_t is expressed as mg/dm^3).

Precious metal	Carbon sorbent C160	k_d (mmol $g^{-1}hr^{-0.5}$)	k_1 (hr^{-1})	Correlation coefficient (for k_1)
Gold (III)	Wet	0.5394	0.146	0.989
	Dry	0.2402	0.0424	0.996
Palladium (II)	Wet	0.1737	0.0276	0.976
	Dry	0.1087	0.0129	0.986
Silver (I)	Wet	0.1160	0.0177	0.994
	Dry	0.0842	0.0113	0.998
Platinum (II)	Wet	0.013	3.915×10^{-3}	0.972
	Dry	0.0059	2.764×10^{-3}	0.977

Table 6.9. Pore-diffusion rate constants, and rate constants of adsorption for precious metals on carbon C160 at 25 °C.

6.4.3. Sorption capacity and temperature effect

Sorption of these precious metals on carbon C160 (wet and dry) follows an "L - type" adsorption isotherm (figures 6.59 and 6.60) with sorption data obeying the Langmuir equation (equation 5.1, Chapter 5), figures 6.61 and 6.62, with good correlation coefficients, table 6.10. The calculated monolayer capacities, X_m values, for these precious metals show the highest for gold (III) and lowest for platinum. Platinum in its form $PtCl_6^{2-}$ shows a lower uptake than $PtCl_4^{2-}$, following the sequence in mass and molar basis:

$$Au (III) > Pd (II) > Ag (I) > PtCl_4^{2-} > PtCl_6^{2-}$$

Gold (III) and silver (I) were chosen for temperature studies. Sorption capacity of the two metals increased with temperature. About a two fold increase in X_m was achieved with a temperature increase from 25 to 45 °C. Sorption data are presented in figures 6.63-6.66 and appendix III (tables 6.36 - 6.39). Equilibrium sorption of platinum (IV) is presented in figure 6.67 showing an L-type isotherm and also fitting the Langmuir equation with a monolayer capacity lower than that of platinum (II), table 6.10.

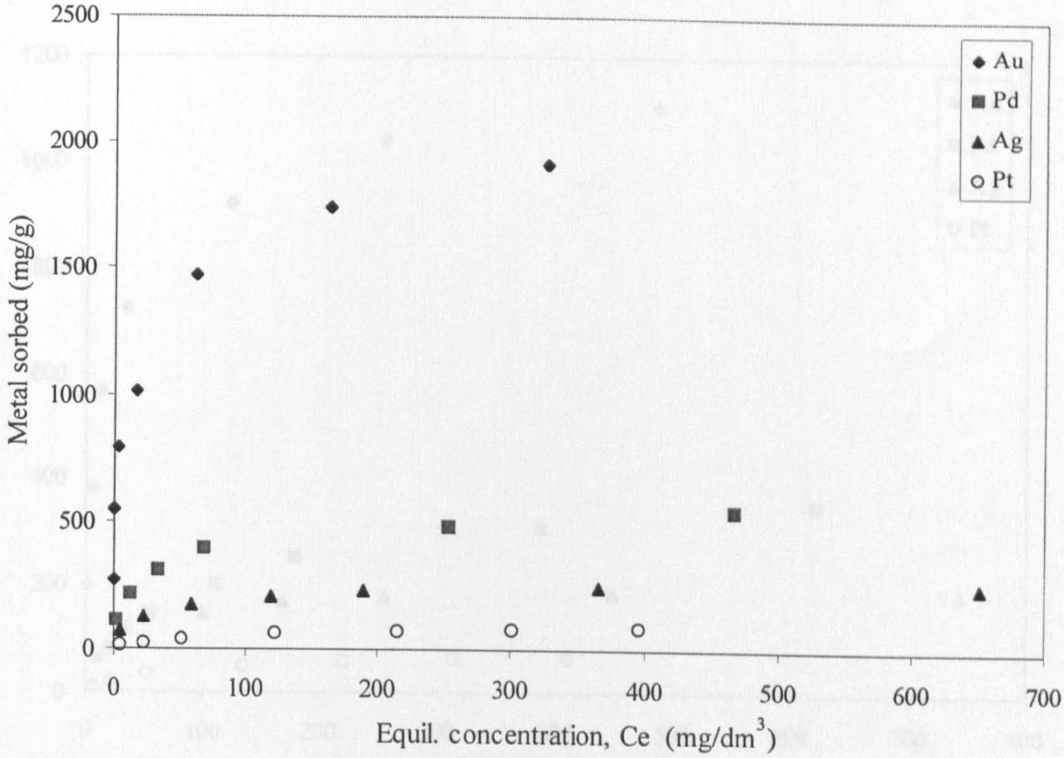

Figure 6.59a. Sorption isotherms of precious metals on wet C160 at 25 °C.

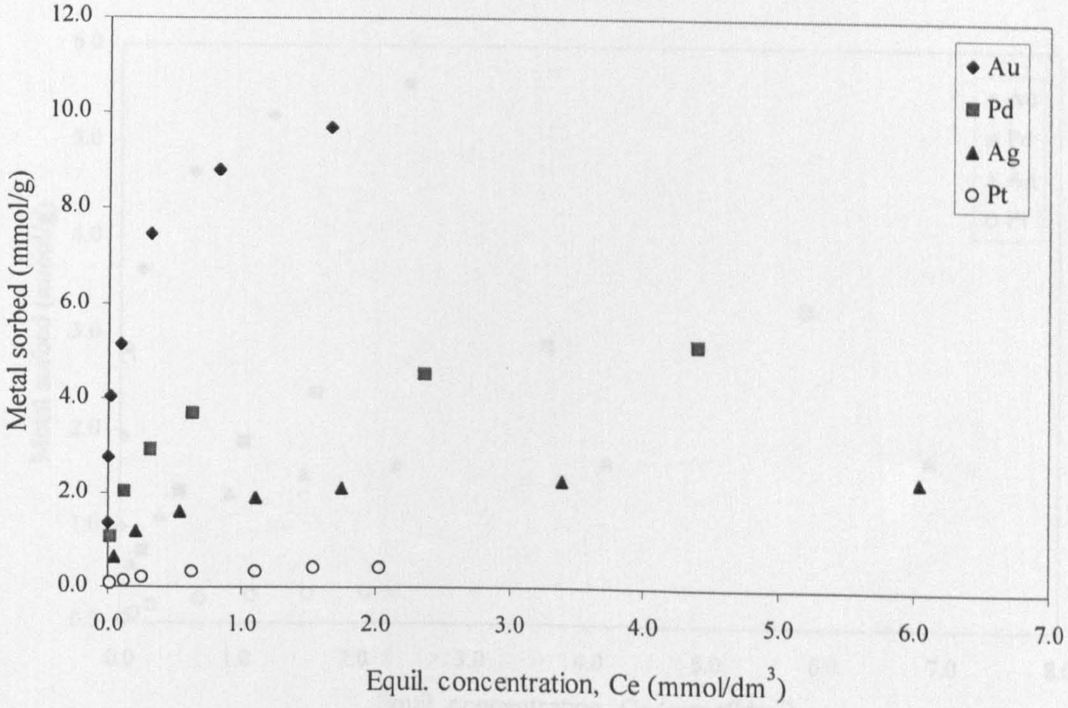

Figure 6.59b. Sorption isotherms of precious metals on wet C160 at 25 °C.

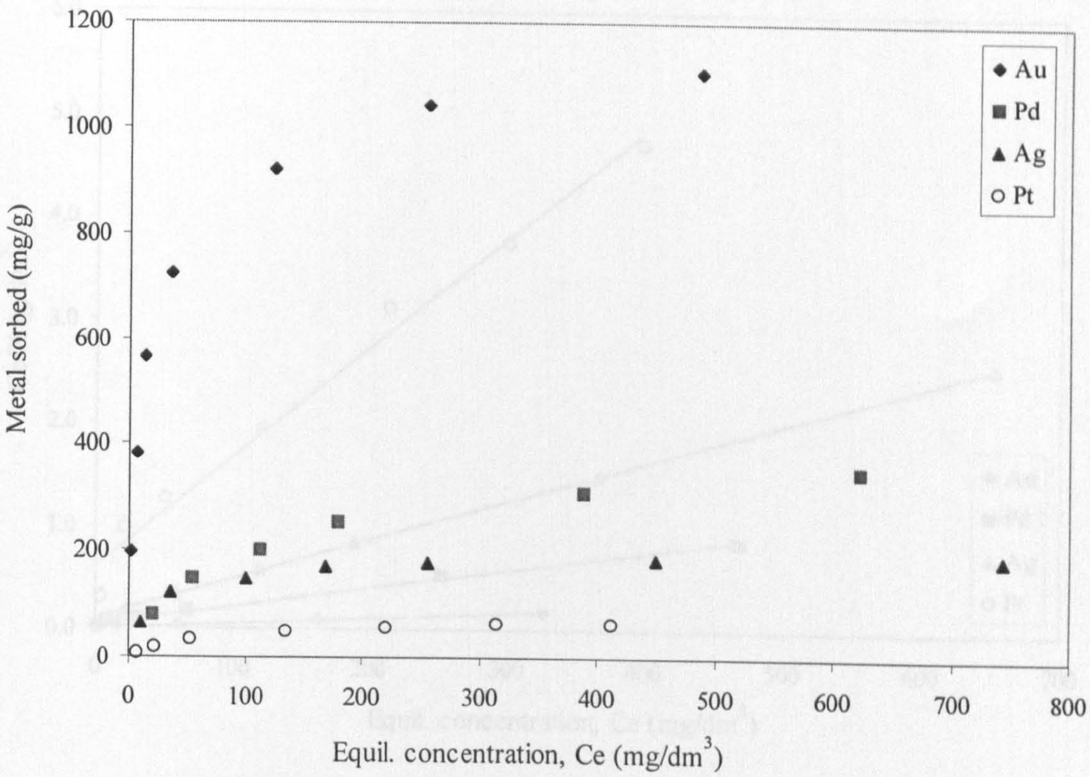

Figure 6.60a. Sorption isotherms of precious metals on dry C160 at 25 °C.

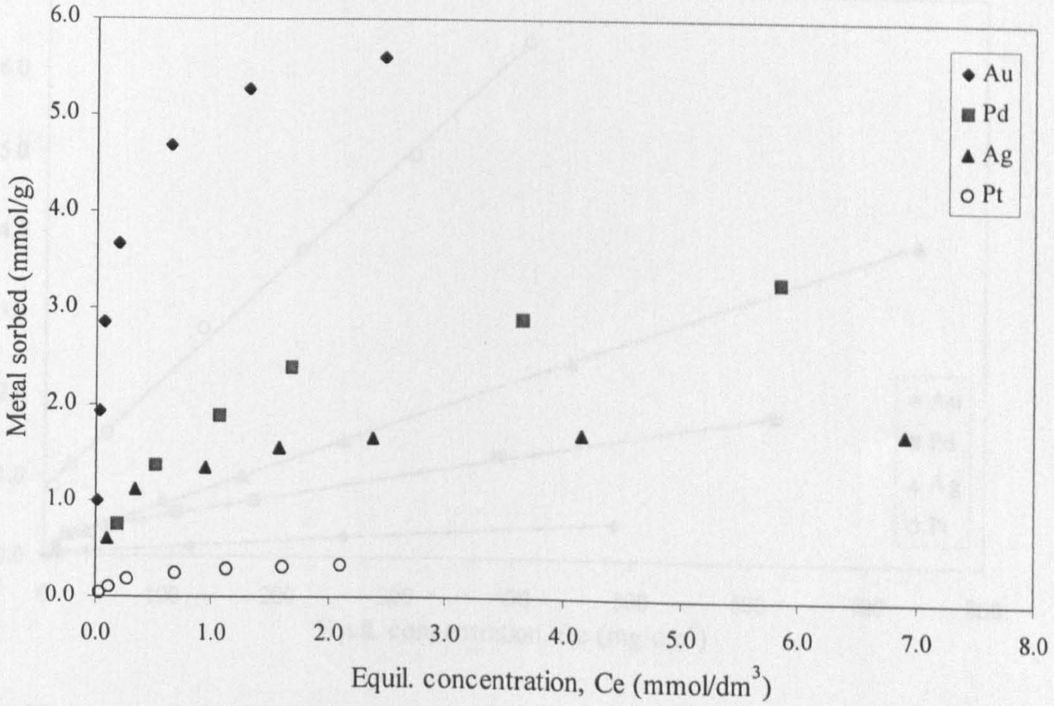

Figure 6.60b. Sorption isotherms of precious metals on dry C160 at 25 °C.

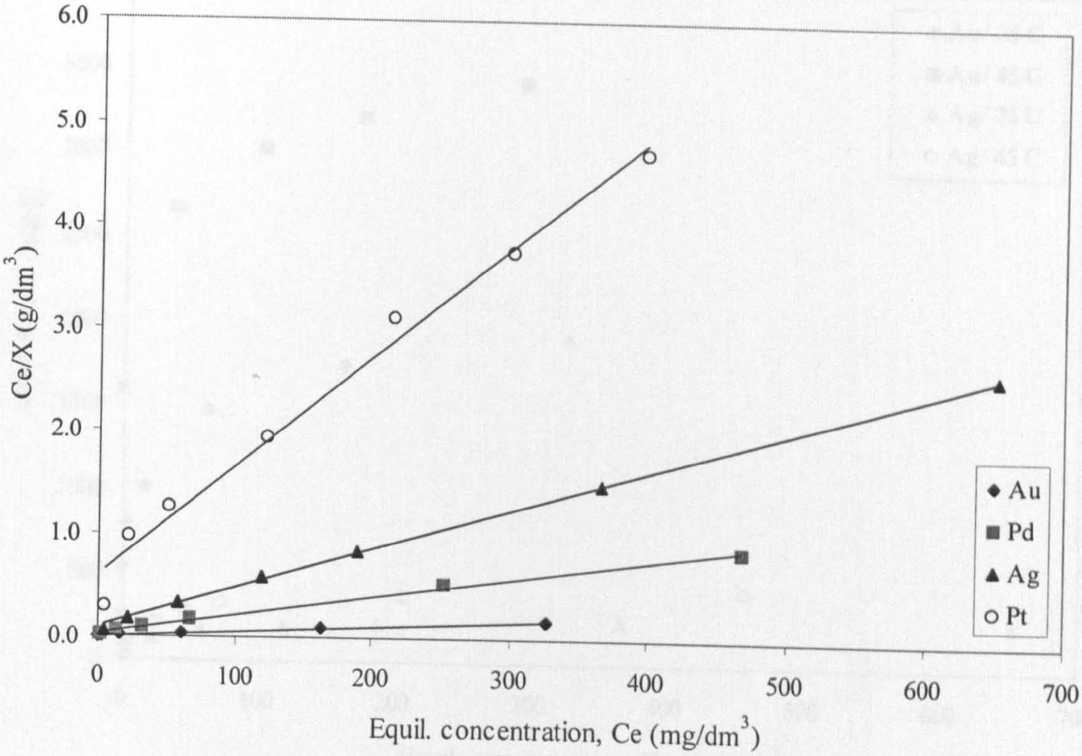

Figure 6.61. Langmuir isotherms for the sorption of precious metals on wet C160 at 25 °C.

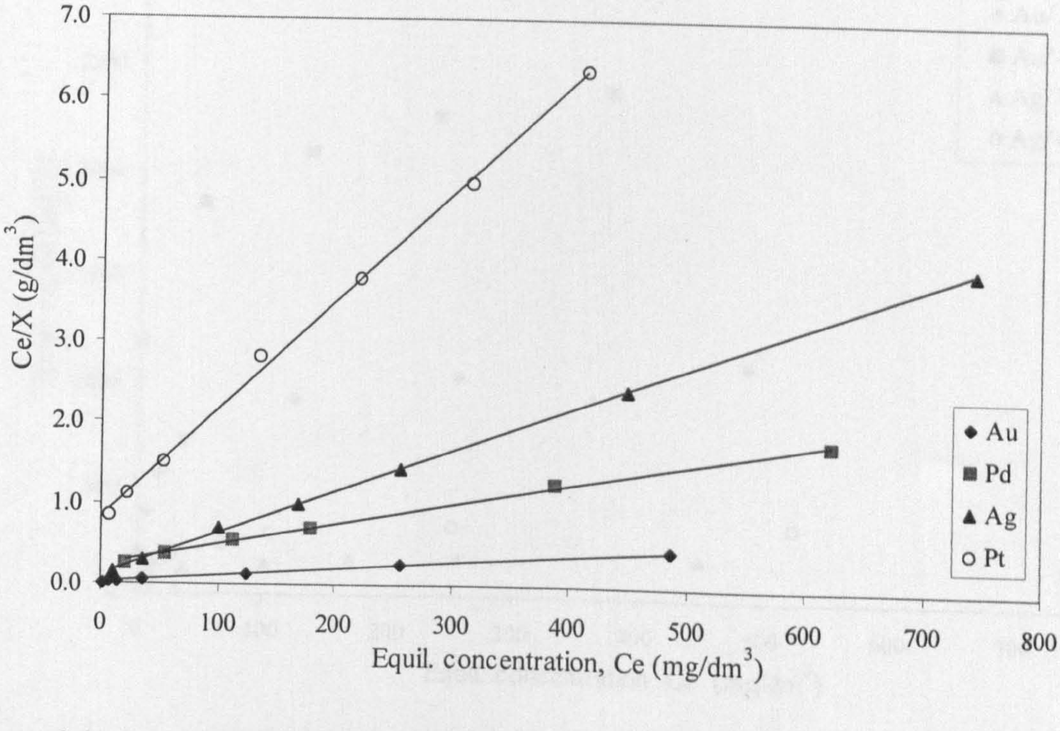

Figure 6.62. Langmuir isotherms for the sorption of precious metals on dry C160 at 25 °C.

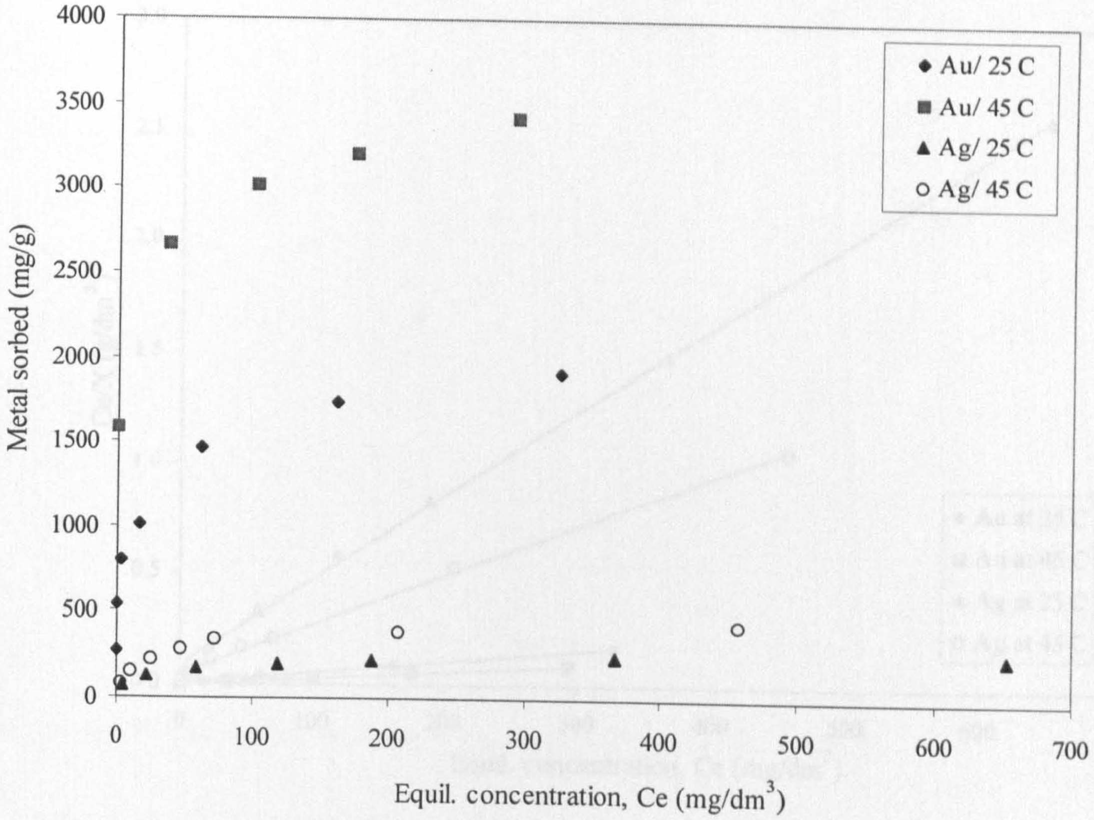

Figure 6.63. Sorption isotherms of gold and silver on wet C160 at 25 and 45 °C.

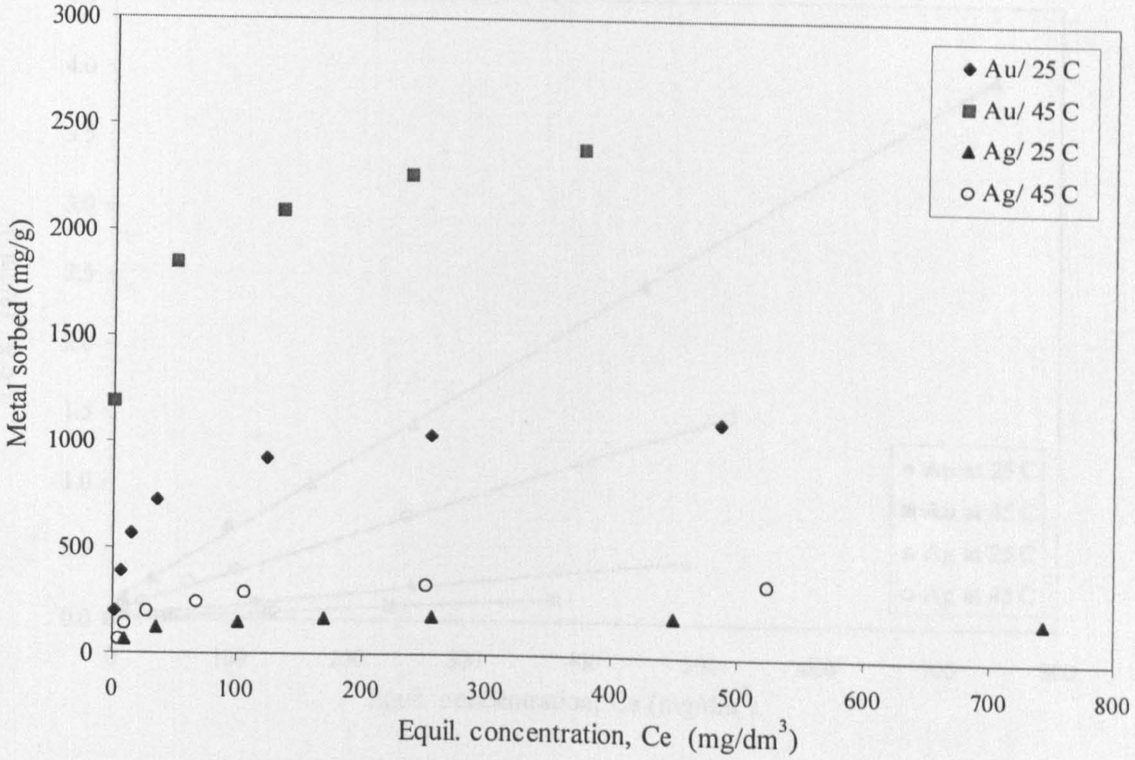

Figure 6.64. Sorption isotherms of gold and silver on dry C160 at 25 and 45 °C.

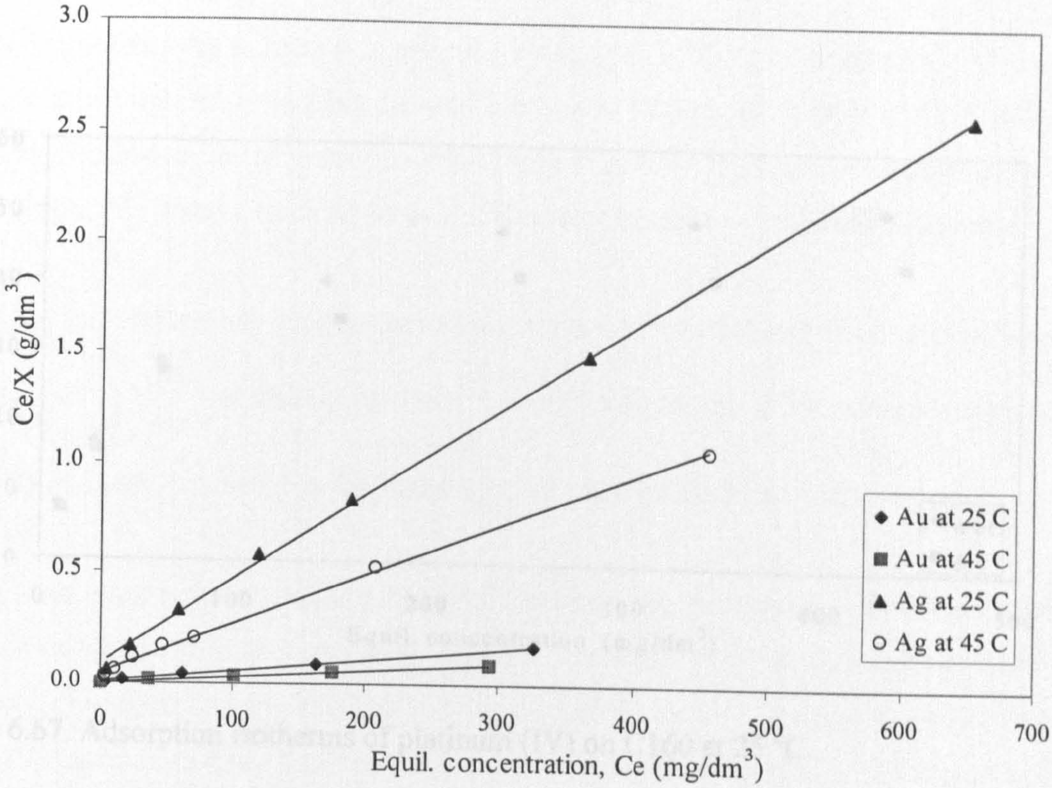

Figure 6.65. Langmuir isotherms for gold and silver sorption on wet C160 at 25 and 45 °C.

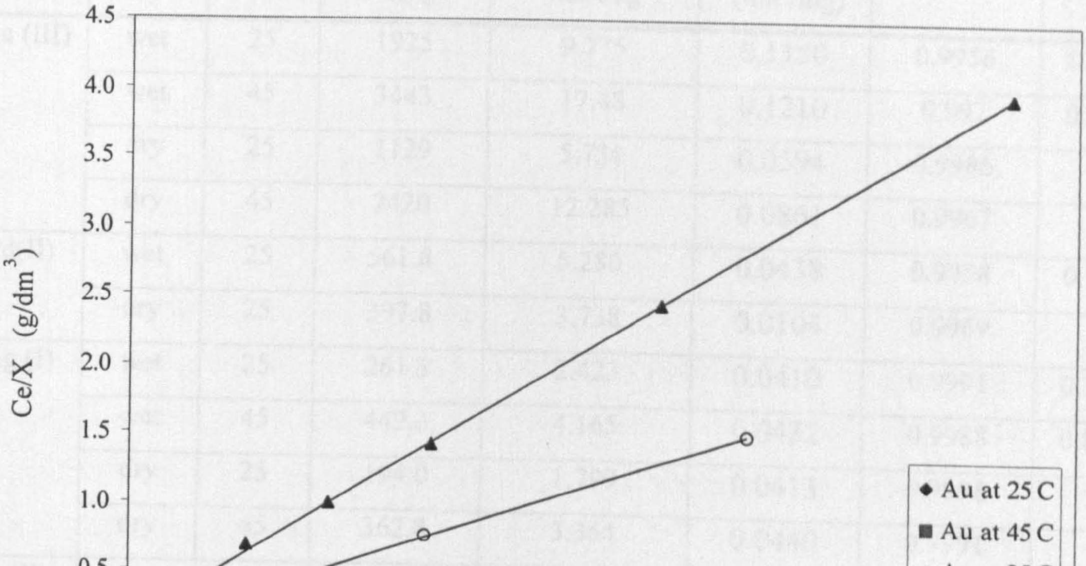

Figure 6.66. Langmuir isotherms for gold and silver sorption on dry C160 at 25 and 45 °C.

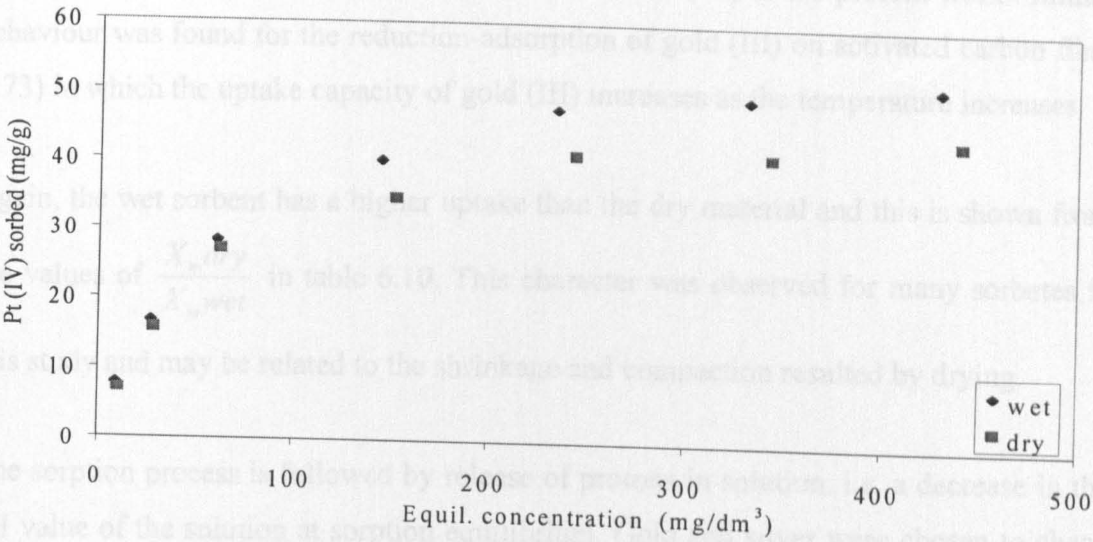

Figure 6.67. Adsorption isotherms of platinum (IV) on C160 at 25 °C

Metal	Carbon C160	Temp. °C	Langmuir constants			Correlation coefficient for (X_m)	$\frac{X_m dry}{X_m wet}$
			X_m (monolayer capacity)		b constant		
			mg/g	mmol/g	(dm^3/mg)		
Au (III)	wet	25	1925	9.775	0.1150	0.9956	0.5866
	wet	45	3443	17.48	0.1210	0.997	0.7027
	dry	25	1129	5.734	0.0594	0.9986	
	dry	45	2420	12.285	0.0861	0.9967	
Pd(II)	wet	25	561.8	5.280	0.0438	0.9958	0.7080
	dry	25	397.8	3.738	0.0104	0.9969	
Ag (I)	wet	25	261.3	2.423	0.0410	0.9991	0.7424
	wet	45	449.3	4.165	0.0432	0.9988	0.8076
	dry	25	194.0	1.799	0.0413	0.9998	
	dry	45	362.8	3.364	0.0440	0.9991	
Pt (II)	wet	25	93.93	0.481	0.0177	0.9865	0.7876
	dry	25	73.98	0.379	0.0165	0.9983	
Pt (IV)	wet	25	59.53	0.305	0.0152	0.9992	0.8275
	dry	25	49.26	0.253	0.0171	0.9984	

Table 6.10. Langmuir constants of precious metals' sorption onto the wet and dry C160.

The surface activity for reduction is believed to increase with rising temperature similar to the increased uptake of mercury (II) and chromium (VI) in the present work. Similar behaviour was found for the reduction-adsorption of gold (III) on activated carbon fibre (173) in which the uptake capacity of gold (III) increases as the temperature increases.

Again, the wet sorbent has a higher uptake than the dry material and this is shown from the values of $\frac{X_m dry}{X_m wet}$ in table 6.10. This character was observed for many sorbates in this study and may be related to the shrinkage and compaction resulted by drying.

The sorption process is followed by release of protons in solution. i.e. a decrease in the pH value of the solution at sorption equilibrium. Gold and silver were chosen to check the ratio [H^+]/[Metal sorbed]. A linear relationship of the molar concentration of protons released in solution to that of sorbed metals was found with a slope of 3.07 for gold and 1.02 for silver sorption at 25 °C, figures 6.68 and 6.69. In a similar study (179), the release of protons accompanying gold (III) reduction on lignite showed a ratio, [H^+]/[Au sorbed], 3:1.

According to equation 5.4 (Chapter 5), R_s, the separation factor, for different precious metal ions and at different temperatures was calculated and tabulated in table 6.11. Sorption of the precious metals on the carbon C160 follows the favourable type of adsorption isotherms since the values of R_s were found to be between 0.0 and 1.0 (139).

6.4.4. Scanning electron microscopy

A golden precipitate was observed on carbon samples loaded from gold (III) chloride while a white silver precipitate was also observed on sorbent samples loaded from silver (I) nitrate. The SEM photographs clarified the presence of elemental forms of gold, silver, palladium and platinum (figures 6.70-6.73) and this was confirmed by the X-ray powder diffraction as shown later.

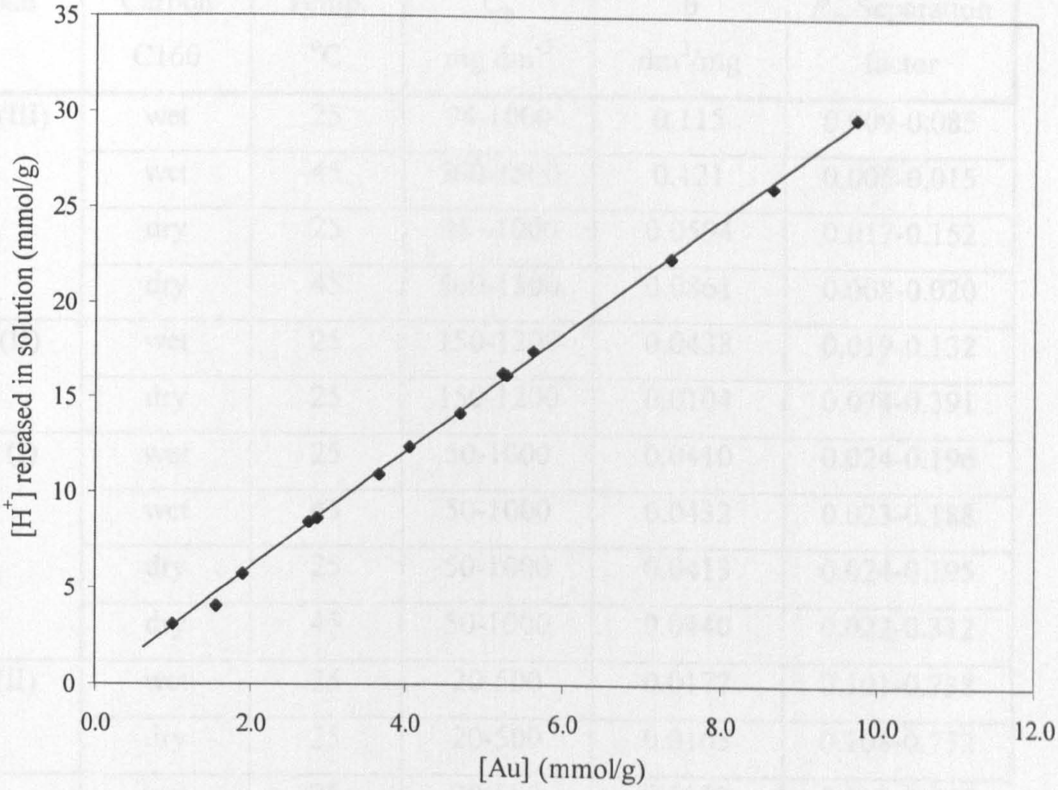

Figure 6.68. Relation between the protons released in solution and gold sorbed.

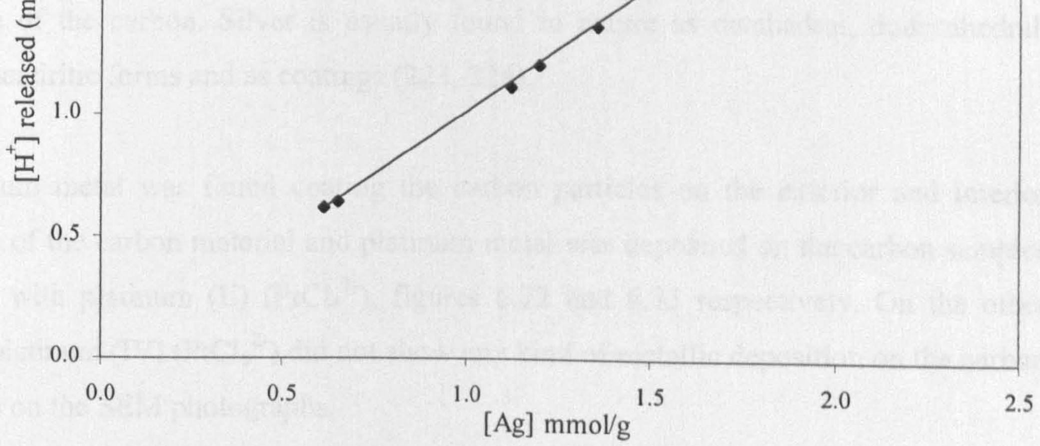

Figure 6.69. Relation between the protons released in solution and silver sorbed.

Metal	Carbon C160	Temp. °C	C_o mg dm^{-3}	b dm^3/mg	R_s, Separation factor
Au (III)	wet	25	94-1000	0.115	0.009-0.085
	wet	45	560-1500	0.121	0.005-0.015
	dry	25	94 -1000	0.0594	0.017-0.152
	dry	45	560-1500	0.0861	0.008-0.020
Pd (II)	wet	25	150-1200	0.0438	0.019-0.132
	dry	25	150-1200	0.0104	0.074-0.391
Ag (I)	wet	25	50-1000	0.0410	0.024-0.196
	wet	45	50-1000	0.0432	0.023-0.188
	dry	25	50-1000	0.0413	0.024-0.195
	dry	45	50-1000	0.0440	0.022-0.312
Pt (II)	wet	25	20-500	0.0177	0.101-0.738
	dry	25	20-500	0.0165	0.108-0.752
	wet	25	20-500	0.0152	0.116-0.767
	dry	25	20-500	0.0171	0.104-0.745

Table 6.11. Separation values for precious metals sorption on wet and dry C160 at different temperatures.

Elemental gold was deposited on the carbon surface in microcrystals that grew to cover approximately all the surface, figure 6.70. SEM photographs of carbon samples loaded with silver (I) showed the presence of crystals of silver metal growing in a tree-like form (dendrite), figure 6.71. In addition, silver was found as coatings in the interior surface of the carbon. Silver is usually found in nature as octahedral, dodecahedral, wiry, dendritic forms and as coatings (223, 224).

Palladium metal was found coating the carbon particles on the exterior and interior surface of the carbon material and platinum metal was deposited on the carbon samples loaded with platinum (II) ($PtCl_4^{2-}$), figures 6.72 and 6.73 respectively. On the other hand, platinum (IV) ($PtCl_6^{2-}$) did not show any kind of metallic deposition on the carbon surface on the SEM photographs.

Generally, the precipitation of gold, silver, palladium and platinum (II) inside the sorbent particles was less than that found on the exterior surface.

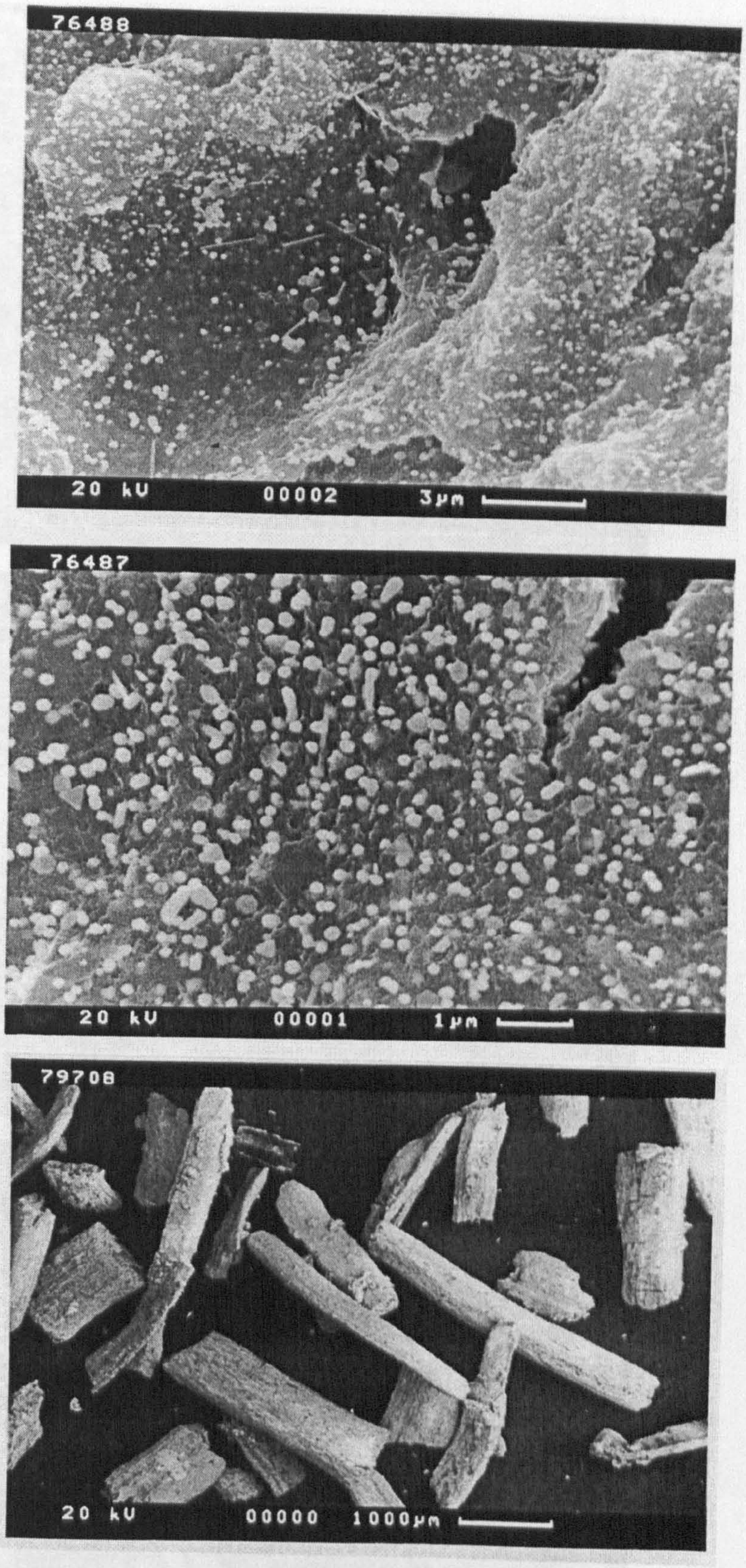

Figure 6.70. SEM Photographs of precipitated gold metal over C160.

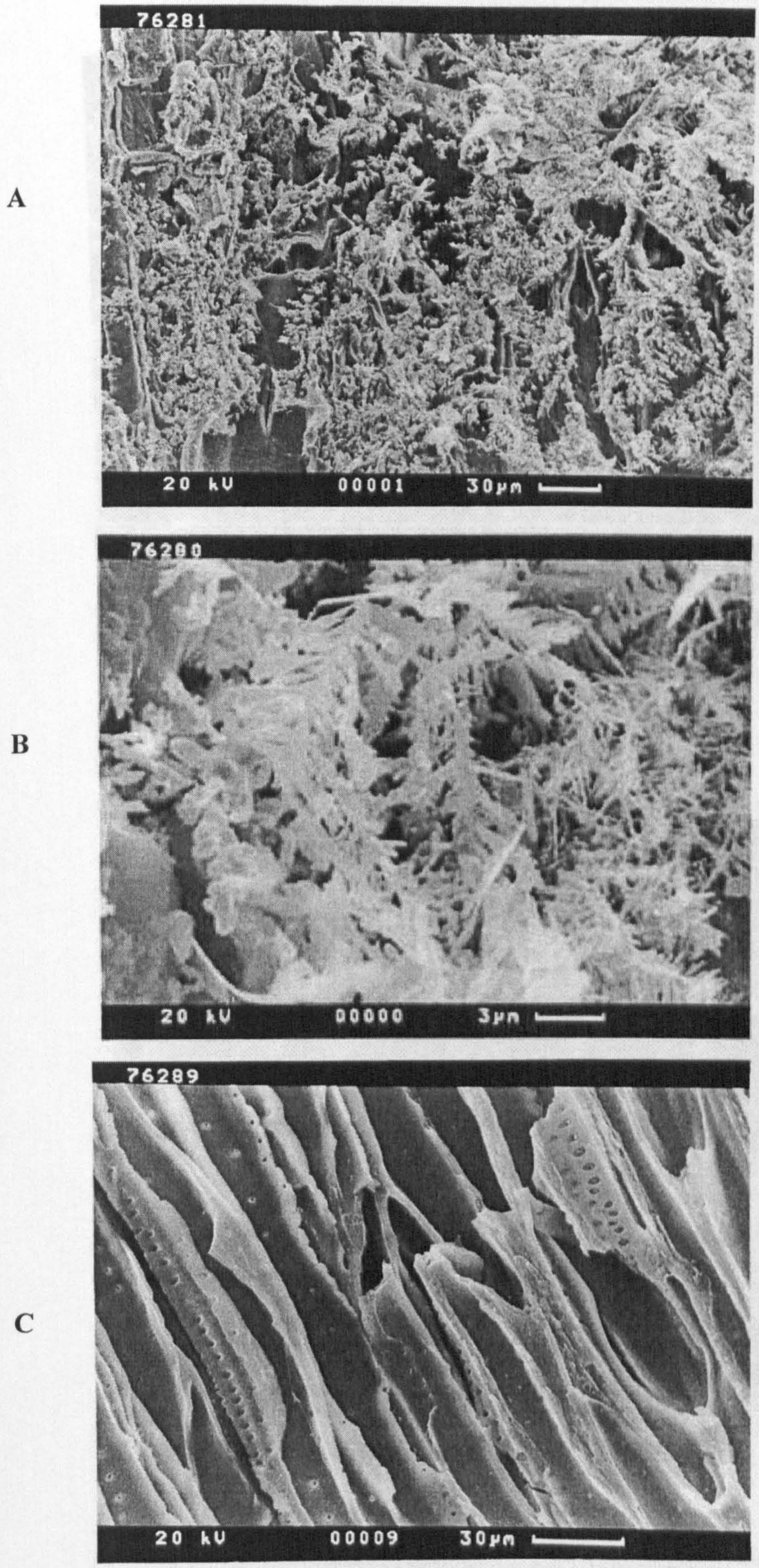

Figure 6.71. SEM photographs of precipitated silver on C160. A & B) exterior (dendritic form), C) cross section (coating).

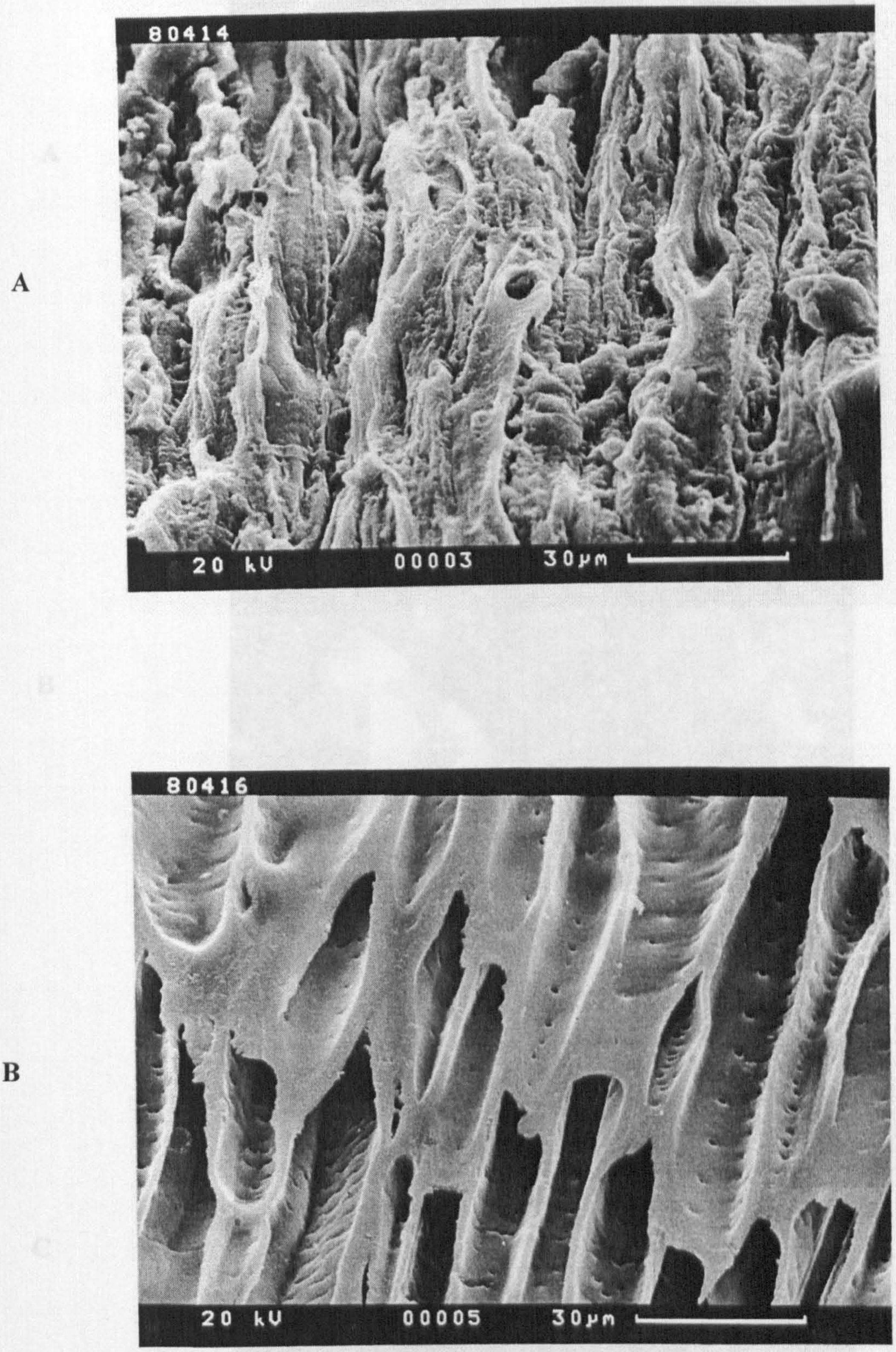

Figure 6.72. SEM Photographs of precipitated palladium metal on C160. A) exterior, B) cross section.

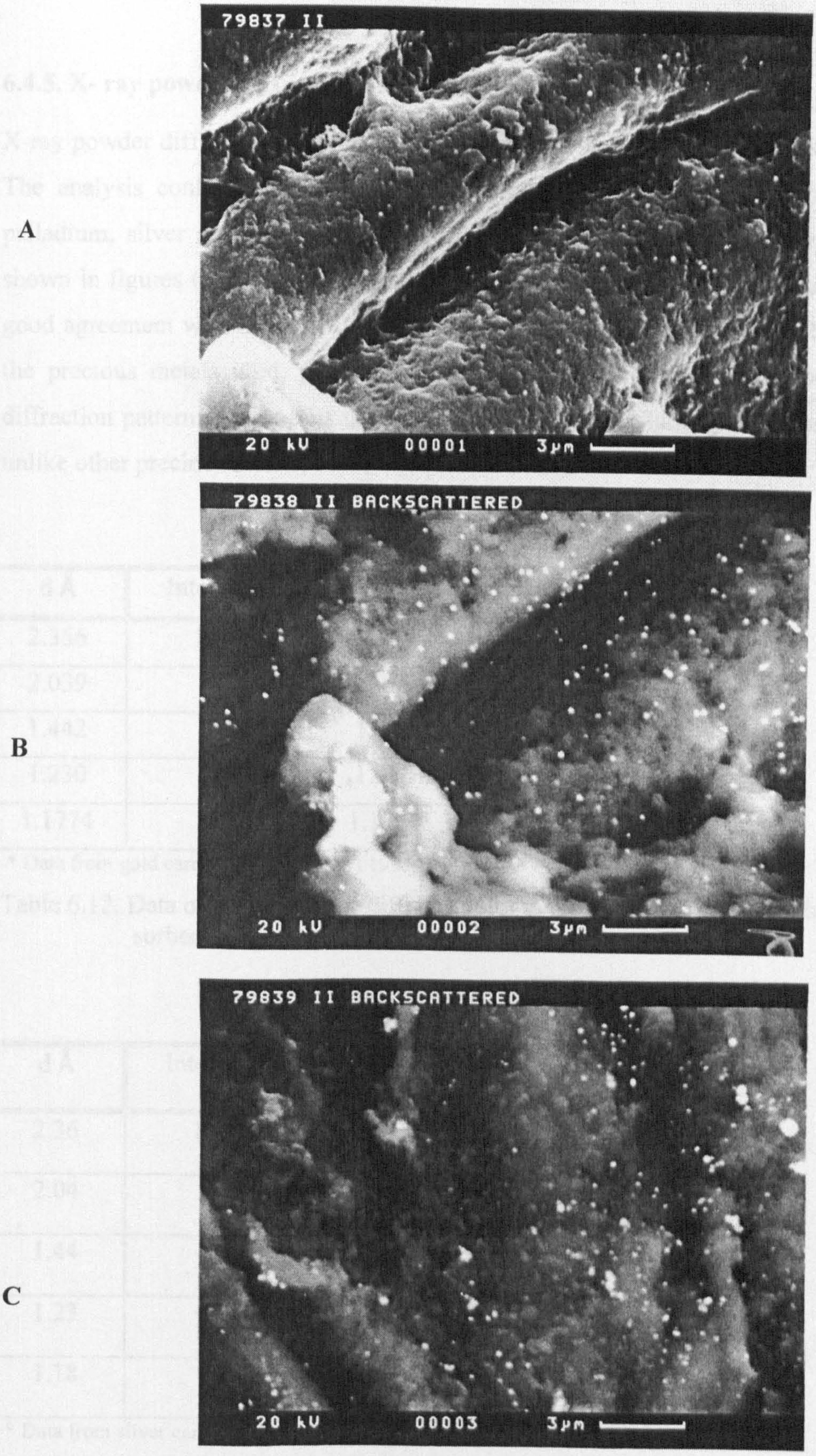

Figure 6.73. SEM Photographs of precipitated platinum metal on C160.
A) secondary electron image, B & C) backscattered electrons image.

6.4.5. X- ray powder diffraction

X-ray powder diffraction for carbon samples loaded with these metals was carried out. The analysis confirmed that the crystals formed are the elemental forms of gold, palladium, silver and platinum. X-ray diffraction patterns of the precious metals are shown in figures 6.74 - 6.77. Interplanar spacing (d) and relative intensities (I) show a good agreement with those recorded for those precious metals, tables 6.12-15. Among the precious metals used, platinum (IV) did not show any identified peaks on the diffraction pattern. This means that platinum (IV) is not reduced on the carbon surface unlike other precious metals.

d Å	Intensity	d Å *	Intensity*
2.356	100	2.355	100
2.039	44	2.039	52
1.442	24	1.442	32
1.230	27	1.230	36
1.1774	6	1.1774	12

* Data from gold card (JCPDS – ICDD) 1994, PDF-2 Sets 1-44 database.

Table 6.12. Data of X-ray powder diffraction for gold precipitate on the carbon sorbent.

d Å	Intensity	d Å *	Intensity*
2.36	100	2.359	100
2.04	26	2.044	40
1.44	19	1.445	25
1.23	20	1.231	26
1.18	7	1.1796	12

* Data from silver card (JCPDS – ICDD) 1994, PDF-2 Sets 1-44 database.

Table 6.13. Data of X-ray powder diffraction for silver precipitate on the carbon sorbent.

d Å	Intensity	d Å *	Intensity*
2.252	100	2.246	100
1.951	42	1.945	42
1.377	20	1.376	25
1.174	18	1.173	24
1.1252	5	1.1232	8

* Data from palladium card (JCPDS – ICDD) 1994, PDF-2 Sets 1-44 database.

Table 6.14. Data of X-ray powder diffraction for palladium precipitate on the carbon sorbent.

d Å	Intensity	d Å *	Intensity*
2.252	100	2.265	100
1.9513	50	1.9616	53
1.381	24	1.3873	31

* Data from Platinum card (JCPDS – ICDD) 1994, PDF-2 Sets 1-44 database.

Table 6.15. Data of X-ray powder diffraction for platinum precipitate on the carbon sorbent.

6.4.6. Mechanism of precious metals sorption

SEM photographs showed the production of the elemental forms of gold, silver palladium and platinum on the sorbent surface and this was confirmed by X-ray analysis. The mechanism of sorption is the reduction to the elemental form by an oxidation-reduction reaction with the sorbent material. The carbon material showed, as mentioned earlier, its reducing character for mercury (II) and chromium (VI). The reduction processes taking place for the metals are accompanied by surface oxidation of the carbon.

Reduction of gold (III), palladium (II), silver and platinum (II) on the carbon can be postulated as:

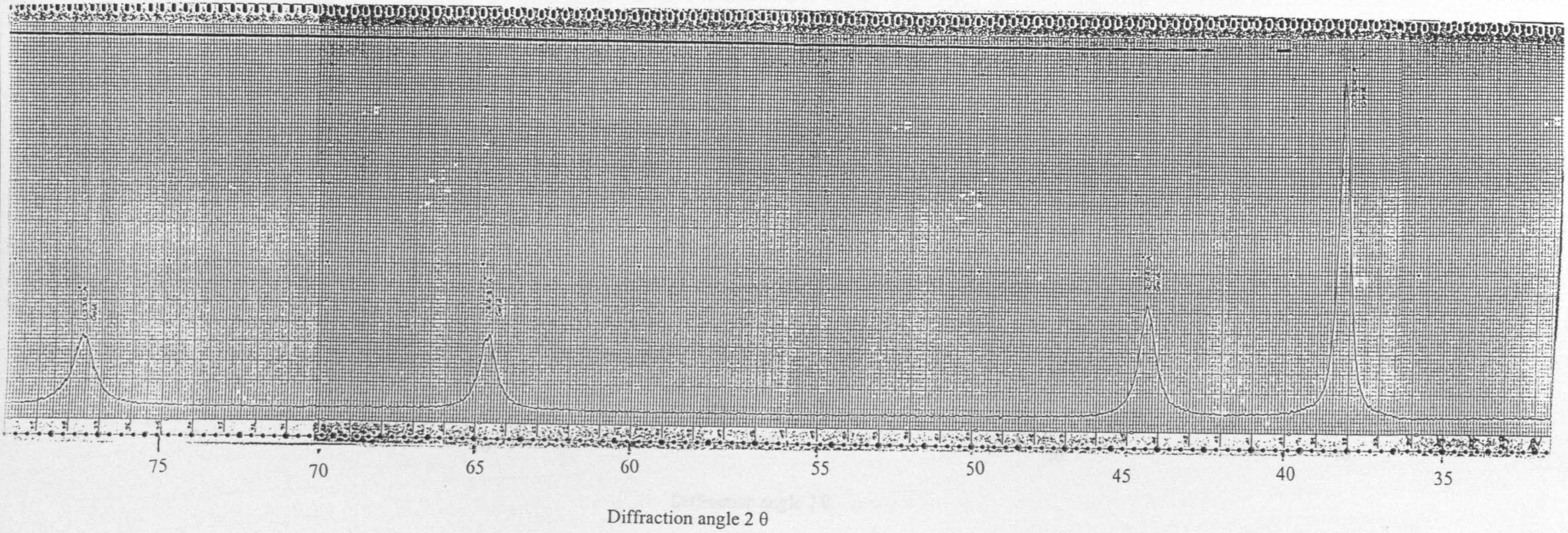

Figure 6.74. X-ray diffraction pattern after Au (III) sorption on C160 sorbent. The diffraction pattern shows the formation of gold metal.

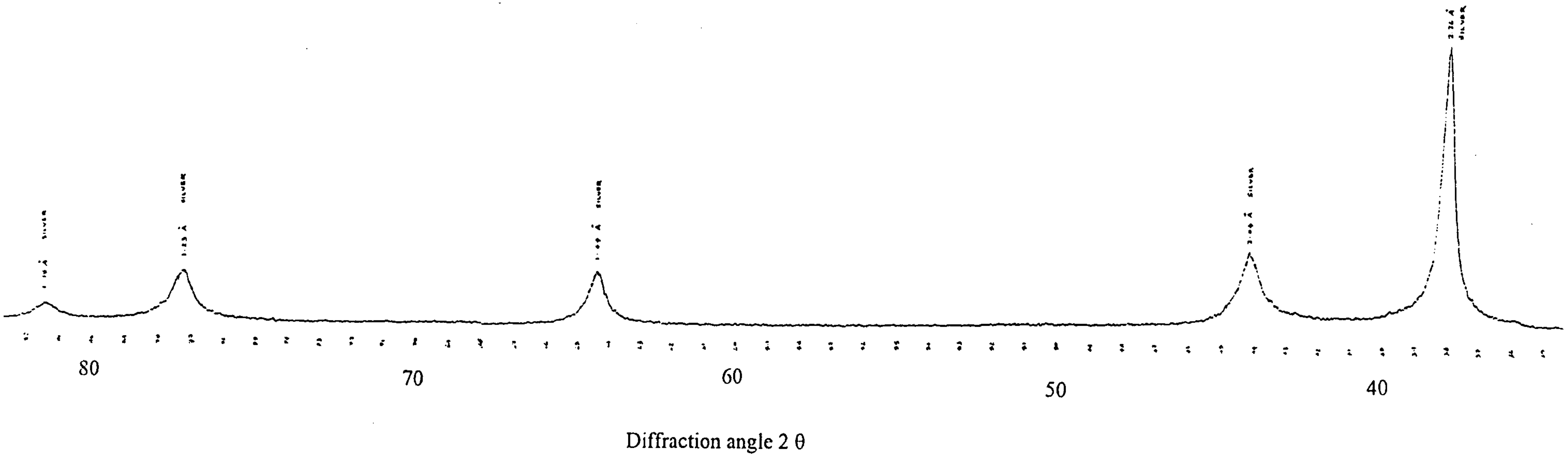

Figure 6.75. X-ray diffraction pattern after Ag (I) sorption on C160 sorbent. The diffraction pattern shows the formation of silver metal.

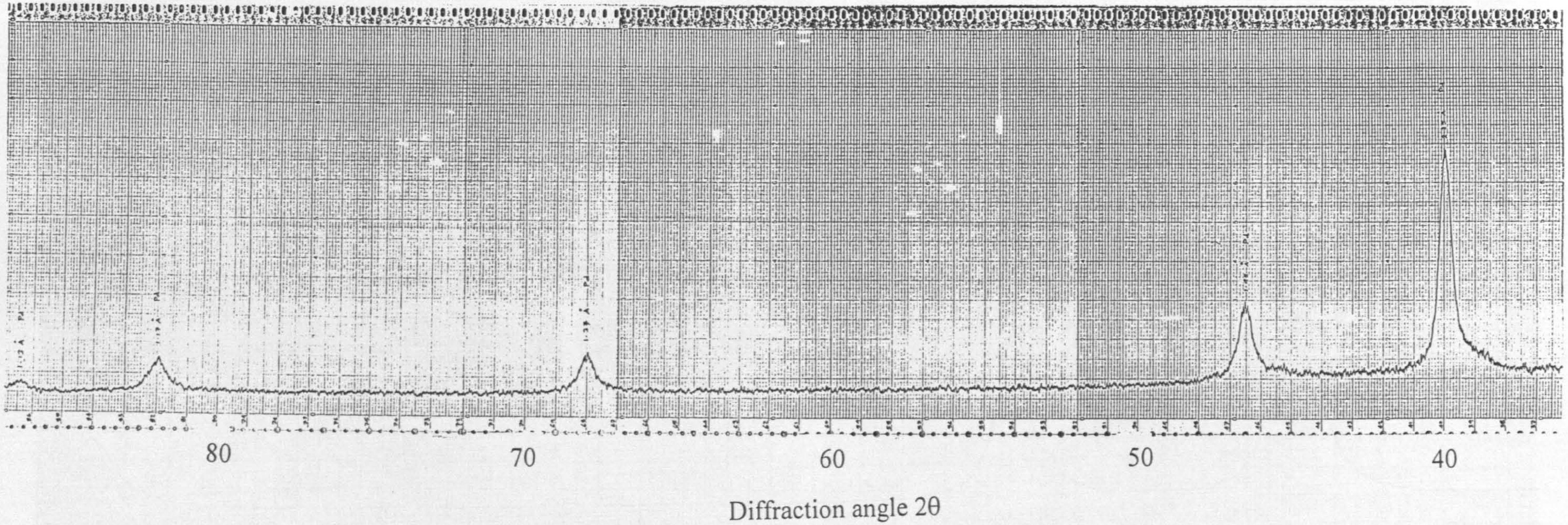

Figure 6.76. X-ray diffraction pattern after Pd (II) sorption on C160 sorbent. The diffraction pattern shows the formation of palladium metal.

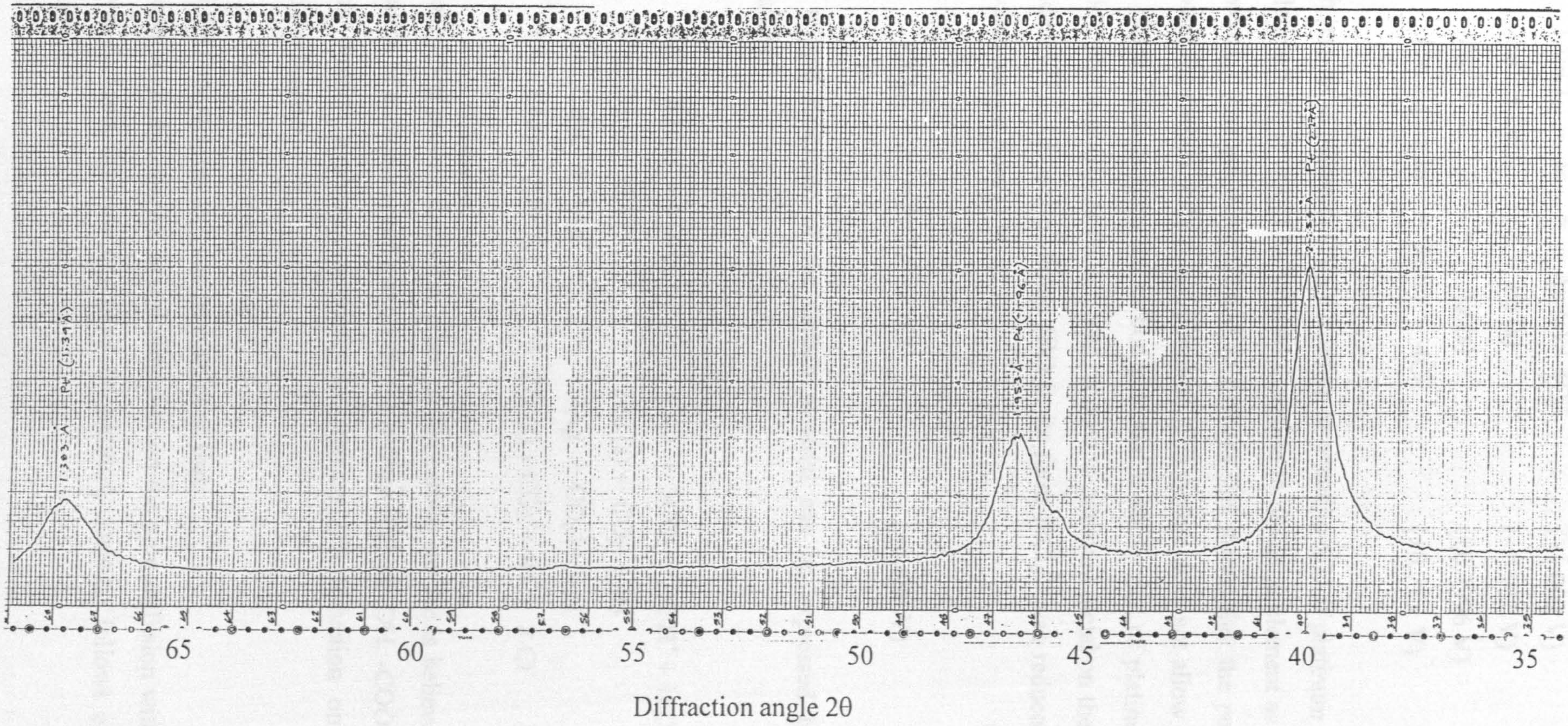

Figure 6.77. X-ray diffraction pattern after Pt (II) sorption on C160 sorbent. The diffraction pattern shows the formation of platinum metal.

$$[AuCl_4]^- + 3e^- = Au\,(s) + 4Cl^- \qquad (+1.002\ V) \qquad (6.27)$$

$$Pd^{2+} + 2e^- = Pd\,(s) \qquad (+0.951\ V) \qquad (6.28)$$

$$Ag^+ + e^- = Ag\,(s) \qquad (+0.7996\ V) \qquad (6.29)$$

$$[PtCl_4]^{2-} + 2e^- = Pt\,(s) + 4Cl^- \qquad (+0.755\ V) \qquad (6.30)$$

With respect to platinum (IV), according to equation 6.31 if platinum (IV) was reduced to platinum (II) it would be reduced therefore to platinum element as in equation 6.30. However, it has not occurred and so perhaps this means that the potential difference between the carbon sorbent and platinum (IV) system does not allow such reduction to take place. Thus perhaps the carbon potential is above that of platinum (IV). In other studies, platinum (II), as $PtCl_4^{2-}$, was reduced to platinum metal on the activated carbon surface (171, 219) and platinum (IV) in its form $PtCl_6^{2-}$ was reduced to platinum on activated carbon fibre (174, 175).

$$PtCl_6^{2-} + 2e^- = PtCl_4^{2-} + 2Cl^- \qquad (+0.680\ V) \qquad (6.31)$$

The related oxidation of the carbon material can be expressed by the following equations:

$$3C + 6\,H_2O + 4\,[AuCl_4]^- = 4\,Au + 3CO_2 + 12\,H^+ + 16Cl^- \qquad (6.32)$$

$$C + 2H_2O + 2Pd^{2+} = 2Pd\,(s) + CO_2 + 4H^+ \qquad (6.33)$$

$$C + 2H_2O + 4Ag^+ = 4Ag + CO_2 + 4\,H^+ \qquad (6.34)$$

$$C + 2H_2O + 2[PtCl_4]^{2-} = 2Pt\,(s) + CO_2 + 4H^+ + 8\,Cl^- \qquad (6.35)$$

The oxidation process that takes place on the carbon surface is believed to include the formation of carbon-oxygen groups on the surface such as -OH, -COOH, in addition to carbon dioxide evolution, similarly to mercury (II) reduction on the carbon as mentioned earlier.

From the previous results it can be concluded that:

1. Sorption kinetics shows their dependence on the pore diffusion with higher rate for the wet sorbents than the dry ones. In addition, sorption follows a first order rate equation.

2. Sorption of these metals fits the Langmuir equation, with sorption capacity following the order gold (III) > palladium (II) > silver (I) > platinum (II). The metal uptake increased with temperature for gold (III) and silver (I).

3. SEM photographs shows the presence of the metallic form of gold, silver, palladium and platinum. These results were confirmed using the X-ray powder diffraction.

4. Platinum (II) was found to be reduced to platinum metal while platinum (IV) was not reduced. This could mean that the potential of the carbon material might be within the range of platinum (IV) reduction potential and platinum (IV) was sorbed via adsorption.

5. The carbon, C160, is an efficient sorbent for the precious metals, gold (III), palladium (II), silver (I) and platinum (II) where they can be extracted on the carbon in their elemental form followed by carbon combustion to recover the metals.

6.5. Sorption of manganese (VI)

6.5.1. Sorption-reduction capacity

Potassium permanganate, $KMnO_4$, is a strong oxidising agent especially under acidic conditions (105). Preliminary experiments show that potassium permanganate is reduced on the carbon surface in acidic, neutral and basic media. Reduction to MnO_2 and Mn (II) was observed. It was clear that reduction to such lower oxidation states was higher under acidic conditions than neutral or basic solutions.

Under acidic conditions, the reaction of potassium permanganate leads to the formation of not only manganese dioxide but also Mn (II). Similar reduction to manganese dioxide and manganese (II) was found by the reaction of potassium permanganate with activated carbon fibres (175). The process was accompanied with carbon-oxygen group formation as well as carbon dioxide evolution (176).

A sorption experiment (repeated 3 times) was carried out under acidic conditions starting with an initial pH of 1.3. The sorption experiment was carried out for 72 hours ending with a final pH of 1.5. After being filtered through a Millipore cellulose ester filter (0.22μm), the equilibrium solution was analysed by ICP for total manganese and the non-reacted potassium permanganate was determined via back titration with sodium thiosulphate solution as detailed in section 3.3.2.2.4.

After the first 10-15 minutes of the experiment, manganese dioxide precipitate starts to develop in the solution and over the carbon particles which could be clearly observed. At the end of the experiment the equilibrium solution was found to contain manganese (II) which may be obtained by the reduction of either permanganate or manganese dioxide.

Carbon	wt (g)	Initial $KMnO_4$ (mg/dm^3)	Ce total Mn (mg/dm^3)	Ce Mn (II) (mg/dm^3)	Ce $KMnO_4$ (mg/dm^3)	sorbed/reduced to MnO_2 (mg/dm^3)	Sorbed (mg/g)
Wet	0.0194*	1000	52.5	51.47	1.03	947.5	2442
Dry	0.0335	1000	35.00	34.28	0.72	965	1440

* weight on dry basis

Table 6.16. Sorption-reduction data of Mn (VII) using wet and dry C160 at 25 °C and initial pH 1.3. (Initial pH 1.3, final pH 1.5).

Sorption reduction data are summarised in table 6.16. The sorption-reduction capacity was measured by applying the Langmuir equation (eq. 5.1).

The residue that contains manganese dioxide and the carbon particles were investigated using the scanning electron microscope. SEM photographs shows the presence of the dark brownish precipitate of MnO_2 (figure 6.78). The precipitate of manganese dioxide seems to be amorphous since it did not show identified peaks in the X-ray powder diffraction. Under acidic conditions, sorption-reduction capacity of $KMnO_4$ was found to be high reaching about 2.4 g/g using the wet sorbent and about 1.4 g/g for the dry.

6.5.2. FTIR

Starting with such a strong oxidising agent, such as potassium permanganate in acidic solution, more oxidation to the carbon surface was expected, appearing as carbon-oxygen groups in addition to carbon dioxide evolution. Infrared spectra of the carbon before and after the reaction with potassium permanganate are presented in figure 6.79.

The FTIR spectra show the changes occurring on the carbon surface as a result of the permanganate reaction. The bands at around 3350 – 3400 cm^{-1}, which are connected with the O-H stretching vibrations, become relatively more intense and broader after permanganate reaction, indicating the formation of more OH groups. A change was also obtained in the bands around 1700 cm^{-1} related to C=O stretching vibrations and after the reaction, this band is reduced to almost a shoulder. This could be related to decarboxylation to carbon dioxide which is believed to accompany the oxidation process. The band around 1600 cm^{-1} became more intense after the permanganate reaction. This band is connected to skeletal C=C aromatic vibrations (129) and thus probably reflects a dehydrogenation process (179) occurring among the redox processes. In addition, a change is shown in the intensity of the bands and shoulders in the range between 1300 and 900 cm^{-1} which may be ascribed to the C-O vibrations associated with hydroxyl groups and ether type structures (129). As shown in figure 6.79 some bands approximately disappear after the reaction with permanganate, this is mainly related to the carbon dioxide formation. Carbon dioxide formation seems to be the most important oxidation process on the carbon surface.

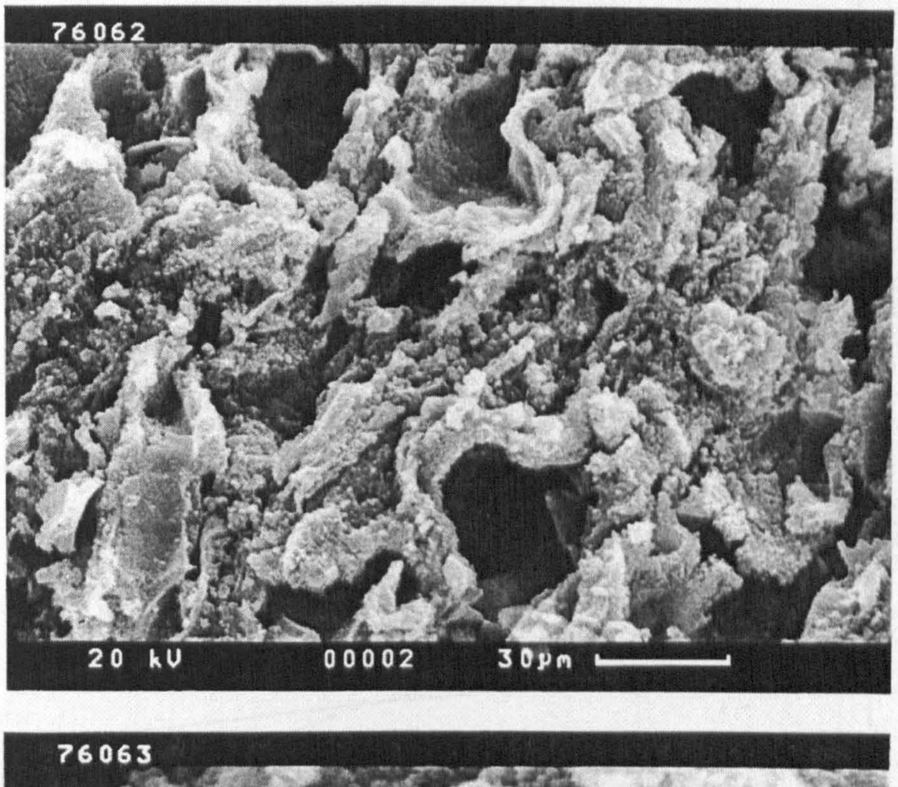

Figure 6.78. SEM Photographs of precipitated manganese dioxide over C160 out of potassium permanganate solution.

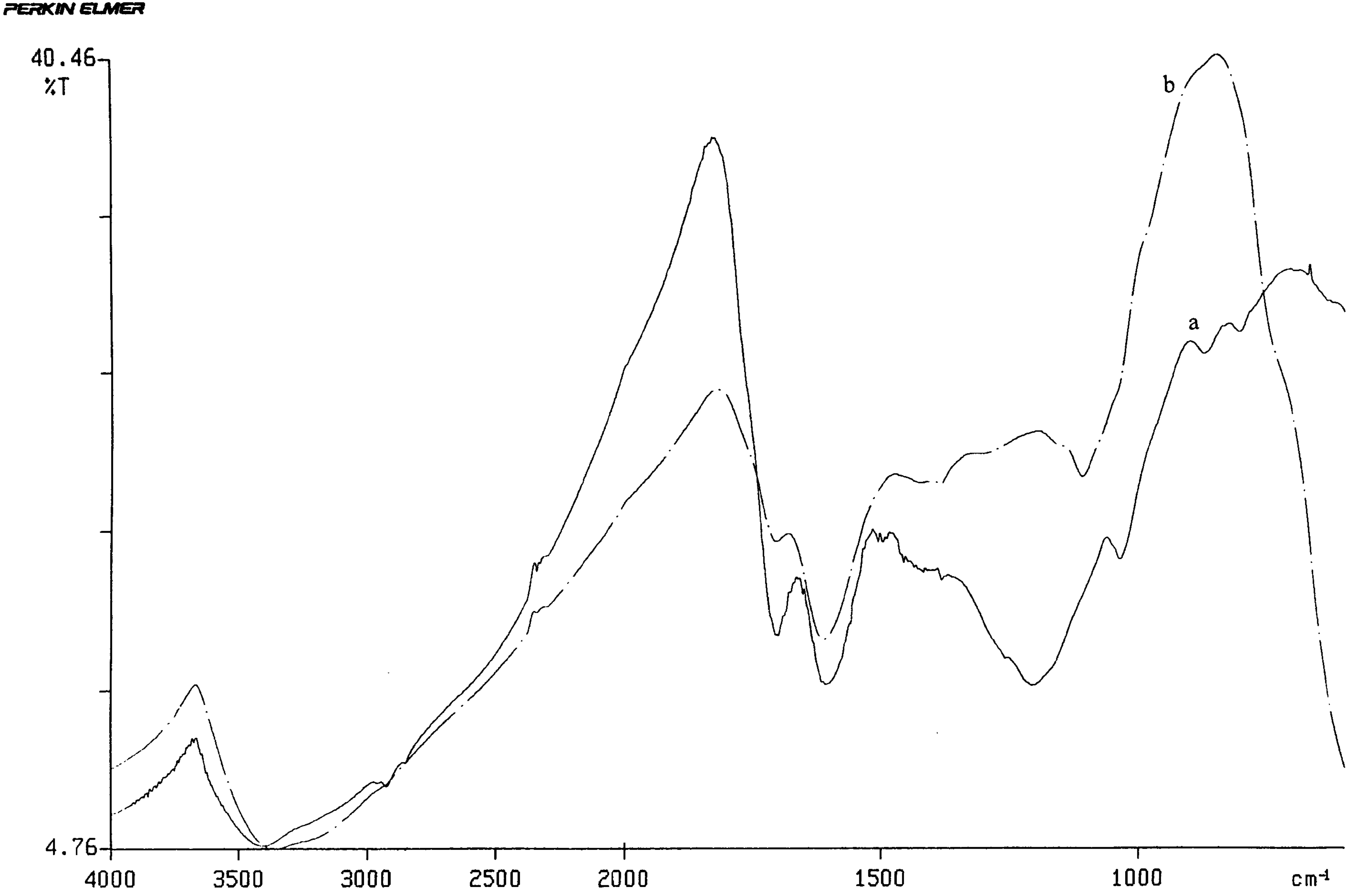

Figure 6.79. FTIR spectra of C160 before and after potassium permanganate reaction. a. before reaction b. after reaction

6.5.3. Mechanism of sorption reduction of $KMnO_4$

Manganese dioxide as a result of the permanganate reduction on the carbon surface was produced in significant amounts covering the carbon particles and precipitating in the bottom of the reaction vessel.

In addition, SEM photographs (figure 6.78) shows the precipitate of manganese dioxide, and manganese (II) was chemically measured in the equilibrium solution. FTIR shows a variation in the carbon-oxygen groups on the surface after the reaction. These facts confirms the oxidation reduction reactions taking place.

From the preliminary experiments, under acidic conditions, allowing the reaction to proceed for longer periods, manganese dioxide dissolves resulting in manganese (II) as the only component in the reaction solution. Similar behaviour was found for permanganate reduction onto activated carbon fibres (175).

Reduction of permanganate to manganese dioxide and manganese (II) can be expressed as follows:

$$MnO_4^- + 4H^+ + 3e^- = MnO_2 + 2H_2O \quad (+1.695V) \quad (141) \qquad (6.36)$$

$$MnO_4^- + 8H^+ + 5e^- = Mn^{2+} + 4H_2O \quad (+1.51V) \quad (141) \qquad (6.37)$$

$$MnO_2\,(s) + 4H^+ + 2e^- = Mn^{2+} + 2H_2O \quad (+1.23V) \quad (141) \qquad (6.38)$$

With the reduction of potassium permanganate, carbon was oxidised to produce more carbon-oxygen groups and carbon dioxide. Redox reaction can be expressed as:

$$3C + 4MnO_4^- + 4H^+ = 4MnO_2 + 2H_2O + 3CO_2 \qquad (6.39)$$

$$5C + 4MnO_4^- + 12H^+ = 5CO_2 + 4Mn^{2+} + 6H_2O \qquad (6.40)$$

$$C + 2MnO_2 + 4H^+ = CO_2 + 2Mn^{2+} + 2H_2O \qquad (6.41)$$

$$\sim CH\text{-}CH \sim + Mn\,(VII) = \sim C{=}C \sim + 2H^+ + Mn\,(\text{reduced}) \qquad (6.42)$$

Manganese (II) can be obtained either directly from the reduction of potassium permanganate as in equation 6.37 or by further reduction of manganese dioxide, Mn (IV), in acidic conditions as shown in equation 6.38. Sorption of Mn (VII) seems to be mainly related to the reduction to MnO_2.

6.6. Sorption of Iron (III)

6.6.1. Sorption-reduction capacity

Reduction of iron (III), $FeCl_3$, to iron (II) on the surface of the carbon was expected. Experimental conditions are summarised in section 3.3.2.2.4. Iron (II) was developed as a result of the reduction on the carbon surface during the experiment which was allowed to progress for ~ 260 hours with continuous shaking.

Carbon C160	Wt (g)	Initial Fe^{3+} (mg/dm^3)	Total Ce (Fe^{2+} +Fe^{3+}) (mg/dm^3)	Ce reduced (Fe^{2+}) (mg/dm^3)	Ce (Fe^{3+}) (mg/dm^3)	Sorbed X (mg/g)
Wet	0.0925*	1021	855	404	451	89.7
Dry	0.1222	1021	842	353	489	73.1

* weight on dry basis.

Table 6.17. Sorption-reduction data for iron (III) on C160 at 25 °C. (Initial pH 2.4, final pH 2.17).

Starting with an initial pH 2.4, iron (II) was found in the equilibrium solution. As shown in table 6.17, iron sorption seems to be small compared to the concentration of reduced iron which stays in equilibrium solution and this could be related to the decrease in pH (pH final 2.17) in the final solution as a result of carbon oxidation, eq. 6.44.

In other studies, iron (III) was found to be reduced to iron (II) on the surface of activated carbon fibres (175) and also by using fulvic acid (183).

6.6.2. FTIR

It was expected that iron (III), a weak oxidising agent, to make little oxidation on the carbon surface. FTIR spectra of the carbon before and after the reaction were almost incapable of showing a significant change as shown in figure 6.80.

6.6.3 Mechanism of sorption reduction of iron (III)

Iron (III) is reduced to iron (II) on the carbon surface as expressed in the following equation:

$$Fe^{3+} + e^- = Fe^{2+} \qquad +0.77V \qquad (6.43)$$

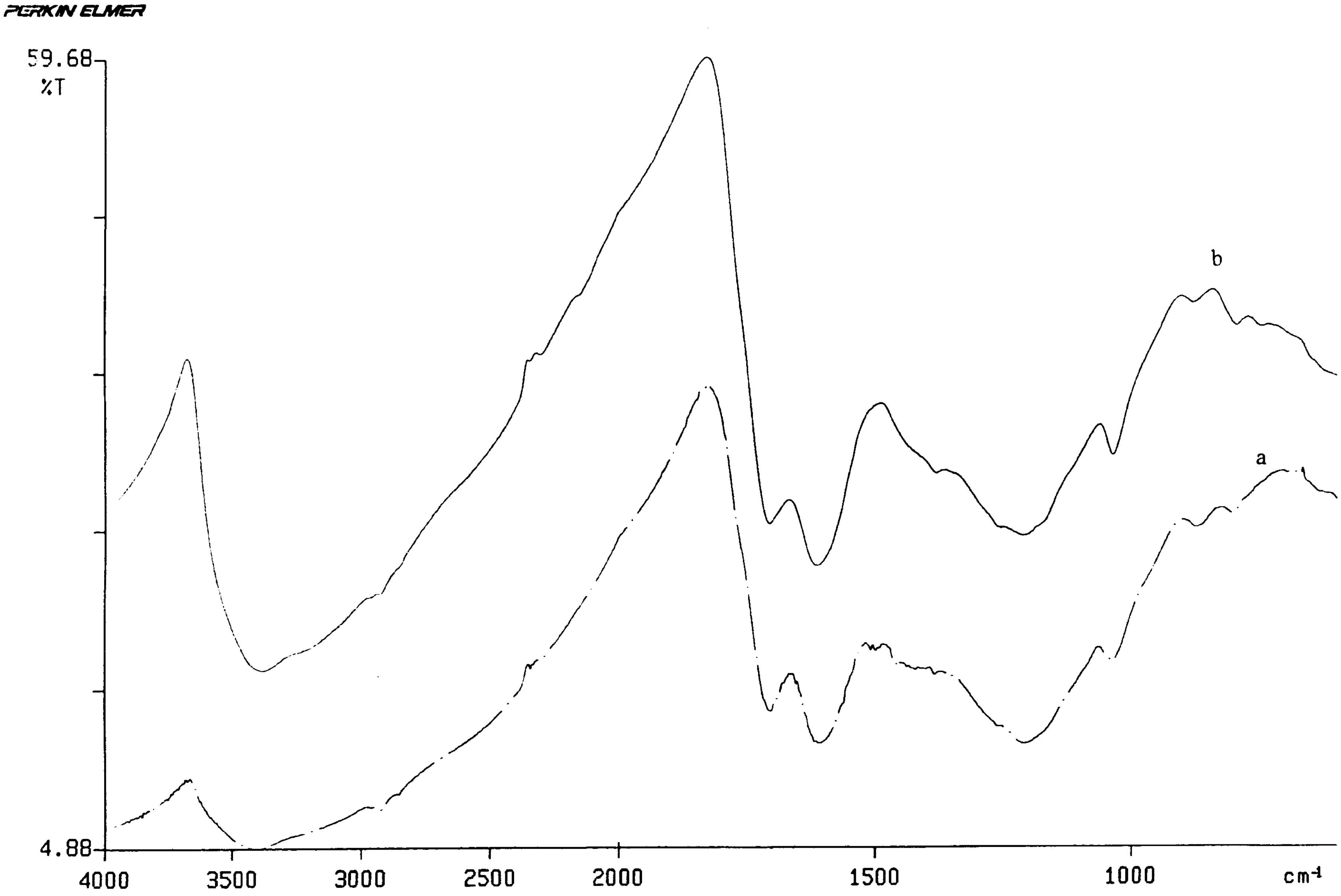

Figure 6.80. FTIR spectra of C160 before and after iron (III) sorption..
a. before reaction
b. after reaction

Iron (III) and/or iron (II) can be sorbed via ion exchange on the carbon surface, and carbon-oxygen functional groups are increased by the end of the sorption process as shown from the FTIR spectra.

$$C + 4Fe^{3+} + 2H_2O = CO_2 + 4\,Fe^{2+} + 4H^+ \qquad (6.44)$$

Dehydrogenation can also take place as:

$$\sim CH\text{-}CH\sim + Fe^{3+} = \sim C{=}C\sim + 2H^+ + Fe^{2+} \qquad (6.45)$$

6.7. Reduction property of carbon by dehydration with sulphuric acid treatment

As an agricultural by-product, flax shive composes mainly polysaccharides (cellulose, hemicellulose) and lignin as main components and being treated with sulphuric acid a carbonaceous material was produced. During hydrolysis, the decomposition of sugars by concentrated acids is accompanied by the formation of humic substances (114). The carbon product contains lignin, as discussed in Chapter 4, which is an important component in the structure of most humic materials (190). Accordingly treatment of this agricultural by-product with sulphuric acid would produce a carbonaceous material which is probably full of humic substances. Such materials are known to adsorb metal ions and also can act as a reducing agent for some metal ions (181,190, 225, 226).

In addition, there is a number of carbon-oxygen functional groups and species on the carbon surface which can participate in the oxidation reduction processes. e.g. the transformation of hydroxyl or aldehydic groups to carboxylic groups the latter which can also be oxidised to carbon dioxide.

Oxidation of the carbon to produce carbon dioxide, equation 6.46, was chosen to represent the oxidation processes of carbon coupled with metal reduction.

$$C + 2H_2O = CO_2 + 4H^+ + 4e^- \qquad (6.46)$$

The possible oxidation reactions of the organic functional groups on the carbon material can be summarised as (180, 227):

$$\mathrm{RCH_3 + H_2O = R\text{-}CH_2OH + 2H^+ + 2e^-} \tag{6.47}$$

$$\mathrm{RCH{=}CH_2 + H_2O = R\text{-}CO\text{-}CH_3 + 2H^+ + 2e^-} \tag{6.48}$$

$$\mathrm{Ph\text{-}H + H_2O = Ph\text{-}OH + 2H^+ + 2e^-} \tag{6.49}$$

$$\mathrm{R\text{-}CH_2OH = RCHO + 2H^+ + 2e^-} \tag{6.50}$$

$$\mathrm{R\text{-}CHOH\text{-}CH_3 = R\text{-}CO\text{-}CH_3 + 2H^+ + 2e^-} \tag{6.51}$$

$$\mathrm{Ph\text{-}OH = Ph{=}O + H^+ + e^-} \tag{6.52}$$

$$\mathrm{R\text{-}CHO + H_2O = RCOOH + 2H^+ + 2e^-} \tag{6.53}$$

$$\mathrm{R\text{-}CO\text{-}CH_3 + 2H_2O = RCOOH + CH_3OH + 2H^+ + 2e^-} \tag{6.54}$$

$$\mathrm{Ph{=}O + H_2O = O{=}Ph{=}O + 2H^+ + 2e^-} \tag{6.55}$$

$$\mathrm{RCOOH + H_2O = CO_2 + ROH + 2H^+ + 2e^-} \tag{6.56}$$

$$\mathrm{Ph\text{-}O^{\cdot} = Ph{=}O + e^-}\ \text{(free radical depletion).} \tag{6.57}$$

(Ph = phenyl group)

Another reaction which can take place during oxidation is dehydrogenation:

$$\mathrm{{\sim}CH\text{-}CH{\sim} \;=\; {\sim}C{=}C{\sim} + H_2}\quad (180) \tag{6.58}$$

Metallic species such as Hg^{2+}, Au^{3+}, Cr^{6+}, Pd^{2+}, Ag^{+}, Pt^{2+}, Mn^{7+} and Fe^{3+} are considered as oxidising agents that experienced reduction on the surface of the carbon sorbent, table 6.18.

Metal ions	Formula	Reduced forms		
		Lower oxidation states		Elemental
		Soluble	Insoluble	
Hg (II)	$HgCl_2$		Hg_2Cl_2	Hg^0
Hg (II)	$Hg(NO_3)_2$	Hg (I)		Hg^0
Cr (VI)	$K_2Cr_2O_7$	Cr (III)		
Mn (VII)	$KMnO_4$	Mn (II)	MnO_2	
Fe (III)	$FeCl_3$	Fe (II)		
Au (III)	$AuCl_4^-$			Au^0
Pd (II)	$PdCl_2$			Pd^0
Ag (I)	$AgNO_3$			Ag^0
Pt (II)	$PtCl_4^{2-}$			Pt^0

Table 6.18. Reduced forms of the metal ions on the carbon sorbent.

6.7.1. Factors affecting the sorption reduction of metal ions

The sorption results, in this study, are referenced to the standard reduction potentials, but because the solution of metal ions (oxidising agents) have different initial pH values, different concentrations and different additions of carbon materials (reducing agent) the standard reduction potential is strictly not applicable, however they do provide a convenient reference point for comparison.

The factors that can affect the sorption-reduction of metal ions on the carbon material include temperature and pH of the sorption media as noted below.

6.7.1.1. Effect of temperature

Sorption-reduction capacity seems to increase with temperature for chromium (VI), gold (III) mercury (II) and silver (I). Such phenomenon seems to be opposing the physical adsorption capacity that usually decreases with temperature increase (175). Similar results were found for gold (III), mercury (II) and silver (I) on activated carbon fibres (173, 175) showing a sorption increase with temperature.

6.7.1.2. Effect of pH

Sorption was found to increase with pH for metal ions such as mercury (II) with maximum sorption at pH 7 and precipitation takes place above such pH value. However, chromium (VI) shows a maximum sorption at low pH (2.2-2.6) and it decreases with pH increase showing the lowest sorption at pH 8 and 9. Mercury reduction does not involve protons and protons were produced in the reaction solution as a result of carbon oxidation and so a pH decrease was obtained at equilibrium. On the other hand, reduction of chromium (VI) does require protons and so a pH rise at equilibrium was obtained. Maximum sorption was related to an increased reduction with sufficient change in the final pH allowing sorption of chromium (III) via ion exchange.

Similar results (175) showed that with pH increase an increase in sorption for mercury (II) was obtained while a sorption decrease with potassium permanganate was found. This was related to a decrease in the standard potential of MnO_4^- with increasing pH and consequently the sorption - reduction decreased (175).

Thus, it can be concluded that a change in the pH of the solution of the sorbent may make a change in the potential difference between the oxidants (metal ions) and the reductant (carbon material).

6.7.3. Prediction of the reduction potential of the carbon by dehydration

As mentioned earlier, $HgCl_2$, $AuCl_4^-$, $Cr_2O_7^{2-}$, $PdCl_2$, $AgNO_3$, MnO_4^- and $FeCl_3$ show reduction on the carbon surface. In addition, $PtCl_4^{2-}$ showed reduction to platinum metal while $PtCl_6^{2-}$ did not show such reduction.

According to equations 6.31 and 6.30, if $PtCl_6^{2-}$ was reduced to $PtCl_4^{2-}$, it would consequently be reduced to platinum metal. This did not occur and so could be related to the difference in their standard reduction potentials $PtCl_6^{2-}$/ $PtCl_4^{2-}$ (+0.68 V) and $PtCl_4^{2-}/Pt^o$ (+0.755 V). This means that the potential difference between the carbon material and $PtCl_6^{2-}$/ $PtCl_4^{2-}$ does not allow the reduction of platinum (IV) to platinum (II) to occur. Therefore, the reduction potential of the carbon material could be similar or close to +0.68 V.

In other studies, activated carbon was found to reduce $PtCl_4^{2-}$ to metallic platinum (171, 219) while activated carbon fibre (174, 175, 220) was capable of reducing $PtCl_6^{2-}$ to platinum metal. It can be concluded that the potential difference between $PtCl_6^{2-}/PtCl_4^{2-}$ and activated carbon fibre is sufficient to such reduction to take place followed by a further reduction to platinum metal, which is not the case with C160. Accordingly, the reduction potential of the carbon material, C160, is expected to be higher than that of activated carbon fibre.

In the case of other metal ions studied including copper (II), cadmium (II), cobalt (II), chromium (III), lead (II), nickel (II) and zinc (II) that possess lower standard reduction potentials, no reduction was identified, confirming that their reduction potentials are expected to be lower than that of the carbon material.

Previous studies have estimated reduction potentials for humic substances to be 0.5 - 0.7 V at pH 0 with values decreasing at ~25 mV/pH unit as pH increases (180, 181, 182) while fulvic acid shows a reduction potential ~ 0.5V at pH 2 (183). For activated carbon, "The reduction potential of activated carbons have been found (172) to be between 0.40 and 0.08 V."(167). In another study, considering the reduction potential of activated carbon was 0.24 V, Adams found that this allowed $HgCl_2$ to be reduced to Hg_2Cl_2 but not the cyanide species of mercury (II), $Hg(CN)_2$ or $Hg(CN)_4^{2-}$ which did not undergo any kind of reduction on the carbon surface (166) because of their much lower standard reduction potentials, table 6.1.

Half cell reaction	Standard reduction potential (V)	ref.
$MnO_4^- + 4H^+ + 3e^- = MnO_2 + 2H_2O$	+1.695	141
$MnO_4^- + 8H^+ + 5e^- = Mn^{2+} + 4H_2O$	+1.51	141
$MnO_2 (s) + 4H^+ + 2e^- = Mn^{2+} + 2H_2O$	+ 1. 23	141
$CrO_4^{2-} + 8 H^+ + 6e^- = Cr^{3+} + 4 H_2O$	+1.350	168
$Cr_2O_7^{2-} + 14 H^+ + 6 e^- = 2Cr^{3+} + 7 H_2O$	+1.232	168
$[AuCl_4]^- + 3e^- = Au (s) + 4Cl^-$	+1.002	168
$Pd^{2+} + 2e^- = Pd (s)$	+0.951	168
$2Hg^{2+} + 2e = Hg_2^{2+}$	+ 0.905	168
$Hg^{2+} + 2e = Hg^{o}$	+ 0.851	168
$Hg_2^{2+} + 2e = 2Hg^{o}$	+0.796	168
$Ag^+ + e^- = Ag (s)$	+0.7996	168
$Fe^{3+} + e^- = Fe^{2+}$	+ 0.77	168
$[PtCl_4]^{2-} + 2e^- = Pt (s) + 4Cl^-$	+0.755	168
Humic acid	+0.7	181,183,225
------------	The estimated potential of the carbon, C160	----------
$PtCl_6^{2-} + 2e^- = PtCl_4^{2-} + 2Cl^-$	+0.680	168
Fulvic acid	+0.50	183
$Cu^{2+} + 2 e^- = Cu (s)$	+ 0.3419	168
Activated carbon	+ 0.24	166
$Pb^{2+} + 2e = Pb (s)$	-0.1262	168
$Co^{2+} + 2 e = Co (s)$	-0.28	168
$Ni^{2+} + 2e = Ni (s)$	-0.257	168
$Cd^{2+} + 2e = Cd (s)$	-0.403	168
$Cr^{3+} + 3e = Cr (s)$	-0.744	168
$Zn^{2+} + 2 e = Zn (s)$	- 0.7618	168

Table 6.19. Standard reduction potentials of selected half-cell reactions.

From this study, the reduction potential of carbon C160 is expected to be below the standard potential of $PtCl_4^{2-}/Pt^0$ (+0.755 V) and higher than the reduction potential of Cu^{2+}/Cu^0 (+0.342 V). It is most probably close to the value of the platinum (IV) reduction to platinum (II), (+0.680 V). Perhaps there is a good agreement of the reduction potential of humic acid extracted from peat and lignite and that of the carbon by dehydration. This will be comprehensively investigated in the future. As shown in table 6.19, the greater the potential difference between the metallic systems (oxidising agents) and the carbon material (reducing agent), the higher the sorption reduction capacity.

Table 6.19 presents the standard reduction potentials of metals investigated in this study in addition to fulvic and humic acids, and activated carbon. In this table, above the dotted line, reduction takes place to the lower oxidation states indicated in the half-cell reactions whilst below, no reduction takes place on the carbon surface.

6.8. Ageing effect of the carbons C160 and C200

Ageing of the carbon in different storage environments is an important factor. As shown in section 4.16, storing the carbon in the ambient air has a significant effect on the sorption of mercury (II), cadmium (II) and the cation exchange and base neutralisation capacities.

An increase in cadmium (II) sorption, cation exchange and base neutralisation capacities was obtained while mercury (II) sorption showed a decrease in its sorption capacity.

The wet sorbents, being stored in aqueous solution with few drops of sulphuric acid to prevent bacterial growth, seem to change little showing a slight decrease in mercury (II) sorption with a slight increase in the sorption of cadmium (II) and CEC in addition to base neutralisation capacity data.

Such a change in the properties of the carbon prepared with dehydration could be related to air oxidation and a possible surface reaction.

It seems that dry sorbents experience more oxidation on the carbon surface being continuously exposed to air while the wet sorbents have less exposure since they are kept under aqueous solution.

Oxidation taking place on the carbon surface increased the content of carbon-oxygen functional groups. This was noticed with the slight increase of cadmium (II) sorption, cation exchange and base neutralisation capacities, section 4.16. An increase in –OH and -COOH concentration was obtained, in addition to the possibility of the carbon being oxidised to carbon dioxide as expressed by equation 6.46. Redox reactions can be expressed as:

$$C + 2H_2O = CO_2 + 4\,H^+ + 4e^- \qquad (6.46)$$

$$O_2 + 4H^+ + 4e^- = 2H_2O \qquad (+1.229\ V)\ (165) \qquad (6.59)$$

On the other hand, storing the carbon, moistened with residual concentrated sulphuric acid, sealed as a wet sample for ~30 months, seems to preserve the carbon from ageing. This could be related to the lack of oxygen in addition to the presence of a high concentration of protons which perhaps makes the reaction expressed by equation 6.59 to shift to right, and also making a shift of the reaction expressed by equation 6.46 to the left retarding the oxidation process.

Since cadmium (II) sorption increases with time together with the cation exchange and base neutralisation capacity data, there is an increase in the carbon-oxygen content, such as -COOH and -OH, as a result of air-oxidation. Mercury (II) sorption decreases with time which means that reduction sites decreases. The increase in the carbon-oxygen groups as a result of oxidation is not compensating for the decrease of some reduction sites which could mean that oxidation of carbon to carbon dioxide is perhaps a significant process involved.

Storing the carbon wet in highly acidic conditions seems to be an effective and cheap way of preserving the carbon for long periods of time.

6.9. Conclusion

1.The carbon prepared by dehydration with sulphuric acid possesses ion exchange properties. In addition, it has reducing properties capable of concentrating some metal ions on the carbon surface in their metallic forms. Reducing nature of the carbon may be related to the presence of easily oxidised components or species within the carbonaceous product such as humic substances. C160 was chosen for these studies because of the higher product yield and more environmentally friendly preparation and because there was very little difference from C200 in behaviour for mercury removal.

2. Various metal ions experience reduction to lower oxidation states and metallic forms on the carbon surface such as $AuCl_4^-$, $PdCl_2$, $Cr_2O_7^{2-}$, MnO_4^-, $AgNO_3$, $FeCl_3$ and $PtCl_4^{2-}$.

3. Compared to those in Chapter 5, metal ions in this Chapter have generally slower kinetics with a variety of equilibrium periods, the shortest with gold (III) and the longest for platinum (II). This could be related to the different nature of these metal ions (as oxidising agents) and their chemistry in solution.

4. As with mercury (II), the sorption of gold (III), palladium (II), silver (I) and platinum (II) shows a linear relation with the half power of time ($t^{0.5}$) in the initial stages of sorption. This means that a large fraction of the reaction of these metals with the sorbent C160 is controlled by intra-particle diffusion. In addition their sorption fits a first order rate equation showing the dependence of the rate of sorption on the concentration of metal ions. Sorption kinetics of chromium (VI) was found to depend on the initial pH. Starting at pH 4.5, chromium removal shows a linear relation with the half-power of time in the initial stages of sorption, and in addition, it fits a second order rate equation. While starting at pH 1.5, the sorption kinetics do not show such a linear relation with the half power of time in the initial stages of sorption and chromium reduction to chromium (III) was found to follow a first order rate equation.

5. Equilibrium studies with different values of pH have been studied for mercury (II) and chromium (VI). Mercury (II) sorption is extremely low at low pH values (pH 1.5 - 2). The sorption starts increasing with the increase in pH reaching the best sorption from pH 6 - 7 while chromium (VI), at pH values ≤ 2, sorption was found low with approximately complete reduction to chromium (III), passing through a maximum

sorption at a range of pH values (2.2 - 2.6). With further increase in pH chromium sorption starts to decrease reaching the lowest value at pH 8-9. The reason for such difference in behaviour is related to the fact that chromium (VI) reduction requires the presence of protons and the maximum sorption was related to an increased reduction with a sufficient rise in the final pH allowing chromium (III) to be sorbed via ion exchange.

6. Light metal ions such as potassium, sodium, calcium and magnesium compete with mercury sorption on ion exchange sites decreasing its uptake on the carbon sorbent.

7. Sorption of metal ions which follows the Langmuir equation shows a much more significant increase with temperature than recorded for the metal ions, Chapter 5, which are sorbed via ion exchange with no identified reduction. Sorption capacity follows the sequence on equivalence basis:

$$MnO_4^- > Au\,(III) \approx Cr_2O_7^{2-} > Pd^{2+} > Hg^{2+} > Ag^+ > Fe^{3+} > Pt^{2+}$$

This almost agrees with the sequence of their standard reduction potential except in the case of chromium (VI) where, because of its high dependence on pH, pH 3 was used for the capacity experiment.

8. The cumulative sorption capacity was tested for mercury (II) showing that sorption equilibrium is not really related to the filling of adsorption sites but is related to the solution pH being low enough to allow mercury to be sorbed. The sorption capacity exceeds 1g Hg/g carbon and efficient removal of mercury was obtained from tap water showing that the competing light metal ions has little effect.

9. The study of mercury (II) using a fixed bed column shows the possibility of removing mercury from effluents with a high mercury content by using the column intermittently allowing the sorption sites to be reactivated during the rest periods with precipitation of mercury.

10. SEM photographs shows clearly the production of elemental forms and compounds which are water insoluble. Gold (III), palladium (II), silver (I), platinum (II) and mercury (II) show their reduction to metallic states. Mercury also shows reduction to mercury (I) which interacts with the chloride ions in solution to give mercury (I)

chloride which is water insoluble. Potassium permanganate shows reduction to manganese dioxide which was precipitated over the carbon particles and in the reaction solution.

11. Mercury (I) chloride and all the elemental forms were examined by X-ray powder diffraction which confirms their presence on the carbon surface while manganese dioxide appears to be amorphous.

12. During the reduction of the metallic species the carbon material was oxidised producing carbon dioxide and creating more carbon-oxygen groups which act as additional ion exchange sites.

13. The carbon sorbent is able to reduce $PtCl_4^{2-}$ into platinum metal, while platinum (IV) in the form of $PtCl_6^{2-}$ could not be reduced. The reduction potential of the carbon material could be about 0.7V.

14. The factors that affect the sorption of such reducible metallic systems include temperature, pH and the presence of other metal ions.

15. The reducing properties of this carbon product enable the concentration and the production of metals in their elemental forms on the carbon surface. This allows the recovery of the metal by combustion of the loaded material.

CHAPTER 7. CONCLUSIONS AND FUTURE WORK

7.1. Conclusions

Flax shive is a woody by-product which is produced from flax processing in huge quantities (2.5 tonnes per every ton of flax fibre). The material is considered to be a waste product and a problem in itself. Currently, flax receives a subsidy from the European Commission so that the acreage devoted to the cultivation of flax is increasing. This means that the by-product, flax shive, is also produced in large quantities and there is no ready market for this material.

Natural cellulosic materials used for the removal of heavy metals show low removal capacities. This thesis discusses the production of a carbonaceous sorbent from flax shive by reaction with sulphuric acid, and its application for the recovery of heavy metals from aqueous environments.

Carbon is a well known sorbent used for water treatment. Activated carbon is usually prepared thermally via carbonisation. The carbon can be activated either chemically prior to the carbonisation process or physically following carbonisation. In general, this way of preparation is costly and also the carbon has little capacity for heavy metal removal from aqueous solution. For this purpose the carbon requires a modification process such as oxidation either thermally by air-oxidation, or by treatment with strong oxidising agents such as nitric acid, to increase the number of carbon-oxygen groups on the carbon surface capable of acting as cation exchange sites for the removal of heavy metals. Other modifications include sulfurisation and impregnation with extractants such as EDTA. These procedures improve the active carbon capacity but also these additional preparation steps increase the cost and so application of such carbons is limited. Above all, the recovery of heavy metals after sorption on activated carbons is not efficient.

7.1.1. Preparation and characterisation of the carbonaceous sorbents

The carbon sorbent prepared from flax shive by reaction with sulphuric acid in a one step process seems to be more efficient when compared to active carbon with the additional advantage of low cost.

Flax shive, during treatment with sulphuric acid, undergoes the following processes: swelling and fragmentation, carbonisation and partial oxidation. As a result, a charred mass with a high content of carbon-oxygen groups capable of behaving as cation exchange sites is produced while retaining the hydrophilic nature of the carbon.

The carbon produced contains a high organic content and a low nitrogen surface area (~20 m^2/g), similar to non-activated carbons. The carbon product still retains the fibrous woody texture with no identified peaks by the X-ray powder diffraction confirming a lack of carbon crystallites within the structure. As prepared the carbon also possesses a high moisture content (84-88%) with the advantage of a higher sorption capacity for heavy metals than samples that have been previously dried.

There are at least four variables to be considered in the preparation of the carbon: reaction time, temperature, weight: volume ratio (flax shive: acid) and the concentration of the sulphuric acid. To prepare a suitable sorbent for heavy metals, the conditions were optimised considering the following parameters: yield of sorbent; consumption of acid and energy applied; and the removal capacity of two different metal ions, cadmium (II) and mercury (II). Based on these criteria, two sorbents have been produced C160 and C200. Preparation was processed as follows: clean dry flax shive is added to sulphuric acid (12 molar) in a ratio of 1:9 (wt: volume) for 25 - 30 minutes at 160°C and 200°C to produce C160 and C200 respectively. Cadmium (II) and mercury (II), were chosen to optimise the preparation conditions, as the behaviour of the carbon sorbent with these elements was different.

The sorbent, C160, shows better yield, lower cation exchange capacity, a higher pH value and lower cadmium sorption than C200, but both carbons show similar uptake for mercury (II). Apparently C200 experiences more oxidation during preparation than C160, being produced at a higher temperature (200°C). This was confirmed by elemental analysis with a higher oxygen content for C200 and also the FTIR spectra showed more intense peaks for -OH, -COOH and carbon-oxygen bands. In addition, base neutralisation capacity data confirmed the presence of more -OH, and -COOH groups on C200.

Cadmium (II) sorption behaves similar to the cation exchange capacity on both sorbents showing ~ 2 fold increase for C200 over C160, this indicates that cadmium was mainly sorbed via ion exchange. On the other hand, similar experiments for mercury (II) sorption on C160 and C200, indicate a different mechanism for mercury not as simple as that for cadmium. Thus the kinetic experiments for cadmium (II) reached equilibrium after approximately 3 hours, while mercury (II) required about 120 hours for equilibrium.

Such differences between these two metals towards the carbon material suggests the possibility of a number of metals behaving similarly to cadmium and another category behaving like mercury (II). Based on this, the two sorbents were produced, C200 being more suitable to cadmium and other similar metal ions because of the higher ion exchange capacity, and C160, is more suitable for mercury and other similar metals because of the better yield and less acid and energy consumed.

7.1.2. Sorption via ion exchange

Investigating the sorption of a variety of metal ions, a group of metals were found to behave similar to the cadmium (II) sorption behaviour. This group of metals includes chromium (III), copper (II), cobalt (II), nickel (II), lead (II) and zinc (II).

Carbon C160 carbon shows similar fast kinetics to C200 sorbing cadmium from aqueous solution in which equilibrium was attained within the first three hours. In addition C200 shows higher removal capacity than C160. Wet forms of the carbon sorbent shows insignificant increase in sorption capacity to those that had been previously dried.

Kinetics of sorption for other metal ions such as chromium (III), copper (II), cobalt (II), nickel (II), zinc (II) and lead (II) on the carbon C200, is fast reaching equilibrium within the first three hours similar to cadmium (II).

There is a linear relation between the amount sorbed and the half power of time in the early stages of sorption and this indicates that a large fraction of metal sorption is controlled by intra-particle diffusion during the early stages of sorption. The sorption kinetics also fit a first order rate equation showing the dependence on the concentration of metal ions.

Among this category of metals, cadmium was chosen for extensive study of the effect of parameters such as pH, temperature and presence of metal ions.

At low pH values (< 3), sorption was dramatically low. At pH 3 and higher, sorption increases with similar capacities up to pH 7. The molar ratio of the protons released in solution to the cadmium sorbed was recorded as 2.03 indicating that ion exchange is the main process by which cadmium sorption is taking place.

Sorption of these metal ions, in general, follows the Langmuir isotherm with capacity of cadmium on C160 lower than that on C200 with an insignificant increase for sorption on wet sorbents and this could be related to more swelling and more ion exchange sites being available.

Sorption capacity seems to be higher for copper (II) and lead (II) and smaller for cadmium (II) and chromium (III). This could be related to their different chemistry in solution. For the metals discussed within Chapter 5 the relation of the monolayer capacity of C160 and that of C200 in their dry forms, $\frac{X_m C160}{X_m C200}$, was found to be within a range between 0.54-0.61 which is close to that of the cation exchange capacity of both carbons in their dry state, $\frac{CEC\ C160}{CEC\ C200}$, (0.62). This suggests that, ion exchange process is considered to be main or perhaps the only process occurring for this group of metals.

The presence of metal ions in cadmium (II) solution such as K^+, Na^+, Ca^{2+} and Mg^{2+}, was found to compete strongly with cadmium ions for sorption on the ion exchange sites on the carbon surface. Presence of these metals in such a high concentration can completely prohibit cadmium (II) sorption.

Successive loading shows about 3 fold increase in cadmium sorption after seven cycles (109 mg/g) and this was related to the fact that the equilibrium attained was due to the pH change being lower enough to prevent any more cadmium being sorbed.

The fast kinetics shows the advantage of using the carbon for cadmium dynamic sorption. A sharp S-shape curve was shown on loading cadmium (II) on the carbon with a capacity higher than that obtained from the equilibrium studies. Breakthrough was obtained after 60-70 bed volumes. Stripping of cadmium (II) was also studied with 0.5 mol/dm^3 sulphuric acid proving to be a good stripping solution with high efficiency for up to 7 runs.

7.1.3. Sorption-reduction of heavy metals

For the sorption studies of mercury (II) and similar metal ions, C160 was chosen for its better yield and the lower energy consumed in its preparation. In addition, it has similar sorption capacity for mercury to that of C200 which is prepared at higher temperature.

From the preliminary investigations of mercury (II) sorption, it was found out that mercury (II) experiences reduction on the carbon surface to lower oxidation states and this is considered as the main reason for mercury (II) behaving differently from cadmium (II) and other non-reducible metal ions, Chapter 5.

A group of metals showing slow kinetics was found to undergo reduction on the carbon surface. Those metals, in addition to mercury (II), include chromium (VI), gold (III), silver (I), palladium (II), platinum (II), iron (III) and manganese (VII) in the form of $HgCl_2$, $Cr_2O_7^{2-}$, $AuCl_4^-$, $AgNO_3$, $PdCl_2$, $PtCl_4^{2-}$, $FeCl_3$ and MnO_4^- respectively.

The time required for approximate equilibrium was found to be different from one metal to another within this category showing the shortest equilibrium time for gold (III), $AuCl_3$, (30 hours for wet, 72 hours for dry) and the longest for platinum (II), $PtCl_4^{2-}$ (200 hours for both forms of C160). This could be related to the different nature of these metal ions and their chemistry in solution.

The wet sorbent, C160, shows shorter equilibrium time than that required for the dry ones. Sorption kinetics for this group of metals shows a linear relationship between the amount sorbed and the half power of time ($t^{0.5}$) in the early stages of adsorption except for chromium (VI) at pH 1.5. This means that a large fraction of the reaction of these metals with the sorbent C160 was controlled by intra-particle diffusion.

Sorption kinetics were also found to fit a first order rate equation showing the dependence of sorption on the concentration of metal ions. This phenomenon was observed for gold (III), palladium (II), mercury (II), silver (I) and platinum (II). Chromium (VI) has a different behaviour, which depends on the initial pH as it requires protons to undergo reduction to chromium (III). The rate of removal of chromium (VI) at pH 4.5 fits a second order rate equation, while at pH at 1.5, reduction rate of chromium (VI) follows a first order rate equation. Among this group of metals, mercury (II) and chromium (VI) were studied extensively.

Equilibrium studies using different pH values were studied for mercury (II) and chromium (VI). Similar to the effect of pH on cadmium (II) sorption, mercury (II) sorption was extremely low at low pH values and then increases with pH reaching maximum sorption at pH 6-7. On the other hand, chromium (VI) sorption shows maximum sorption at pH 2.2-2.6 with lower sorption before and after this range. This was related to the fact that chromium (VI) reduction does require protons to undergo reduction, and at low initial pH (< 2.2); reduction is extensive and the resultant pH is low enough to retard chromium (III) sorption. At pH 2.2-2.6, reduction again is extensive but now the rise in pH allows chromium (III), the reduced form, to be sorbed via ion exchange. Sorption decreases at higher pH values (> 2.6) due to the lack of protons and hence a decrease in reduction occurs with resulting decrease in sorption of chromium (III).

Light metal ions such as potassium, sodium, calcium and magnesium have a competitive effect on mercury sorption. These metals compete with mercury ions for the ion exchange sites and so decrease its sorption and the related reduction processes.

Sorption of these reducible metal ions follows the Langmuir equation with a much more significant increase with temperature than those recorded for the non-reducible metals such as cadmium (II) which are sorbed via ion exchange. Increasing the temperature could increase the surface activity towards reduction processes. Sorption capacity was found to follow the following sequence on equivalence basis with both carbon states (wet and dry):

$$MnO_4^- > Au\ (III) \approx Cr_2O_7^{2-} > Pd^{2+} > Hg^{2+} > Ag^+ > Fe^{3+} > Pt^{2+}$$

This agrees with their reduction potential sequence except in the case of chromium (VI). In this case, sorption is highly dependent on pH and an initial pH 3.0 was chosen for capacity experiments in this case.

Successive loading shows about 5 fold increase in mercury (II) sorption from a synthetic water exceeding 1 g/g by the twelfth cycle and efficient removal of mercury was obtained from tap water showing that the competing light metal ions have little effect. This was related to the fact that equilibrium attained was due to pH change being low enough to prevent mercury being sorbed and not to fully occupied sorption sites.

Column studies have also been carried out for mercury (II) from aqueous solution. Mercury (II) sorption shows a smooth break-through after 21 bed volumes. However, an intermittent column study performed for the same number of bed volumes showed a saw-tooth pattern. This pattern is a result of reduction of the mercury occurring during the resting time of the column. This resting allowed the mercury (II) ions to migrate from ion exchange sites to a reduction site forming mercury (I) ions which interact with the chloride ions available in solution precipitating as mercury (I) chloride, or after further reduction, as elemental mercury that can accumulate to form a mercury microdroplet. The process releases the ion exchange sites and also creates new ones. Thus eventually the carbon would be completely oxidised leaving a residue of mercury (I) chloride or elemental mercury. In practical applications several columns could be operated in series allowing the effluent to be directed to another column whilst the first was "resting".

SEM photographs show the presence of elemental metals as a result of surface reduction, with gold, palladium, silver, platinum and mercury being observed. For mercury (II) sorption from chloride media, mercury (I) chloride crystals in addition to microdroplets of mercury were developed while from nitrate media, only mercury microdroplets were obtained. X-ray powder diffraction confirmed the presence of these species. A precipitate of manganese dioxide was observed on the carbon surface but it seems to be amorphous.

The carbon prepared by dehydration is able to reduce $PtCl_4^{2-}$ to platinum metal, but in contrast $PtCl_6^{2-}$ was not reduced. The standard potential of platinum (IV) as $PtCl_6^{2-}$

could be very close to the reduction potential of the carbonaceous material. Metal ions having lower reduction potentials do not show any reduction on the carbon surface. It is estimated that the standard potential of the sorbent is around that for the reduction of $PtCl_6^{2-}$ (+0.68V) or close to that of humic acid (+0.7V).

Unlike activated carbons, carbon prepared by dehydration experiences oxidation in open air over longer periods of storing. Reduction sites decrease creating more ion exchange sites on the carbon surface. Storing the carbon under acidic conditions for long periods seems to preserve the carbon from oxidation.

The factors that can affect the sorption of the group of metal ions which experience reduction on the C160 surface include pH, temperature, presence of other metal ions and the different nature of the oxidizing metallic species.

Finally it can be concluded that the carbon prepared by dehydration with sulphuric acid possesses both ion exchange properties and reducing properties capable of concentrating some metal ions on the carbon surface to their metallic forms. The reducing nature of the carbon may be related to the presence of easily oxidized components or species within the carbonaceous product e.g. humic substances. Such carbon material has many advantages:

- easily prepared;
- cheap;
- can be used several times for metals sorbed via ion exchange;
- can concentrate precious metals such as gold, silver, palladium and platinum in their metallic form which allows the recovery of the metals by combustion of the loaded material.
- concentrates other toxic metals such as mercury which it converts into solids such as mercury metal and mercury (I) chloride;
- can be used also to sorb and to reduce chromium (VI) to chromium (III) which is less toxic than chromium (VI);
- can be used environmentally and industrially.

7.2. Recommendations for Future Work

This work has opened a wide area for research on the recovery of metal ions from waste waters and industrial effluents using such a cheap sorbent with reduction properties which enable the precipitation of some metal ions to their elemental state. In addition, this material could be tested in barriers for water treatment and landfill leachates. Industrial effluent streams could also be tested.

Accordingly the work could be continued as follows:

- changing the preparation conditions to find more economic methods of saving acid and energy consistent with the preparation of the best sorbent for different metals.
- more studies are required on recycling of sulphuric acid used in the preparation and possible reuse in the preparation of further batches of adsorbent.
- the sorbent was not fully characterised in this present work and further characterisation is required.
- expanding the number of metals and metallic mixtures synthetically prepared and naturally available varying the conditions of pH, temperature, in the presence of various counter anions.
- further extensive column studies to optimise design and operating parameters and modelling to produce the most efficient multi-column use, to meet the appropriate discharge and other environmental limits.
- application of the carbon to natural and industrial sites such as mine drainage and landfill leachates with a contactor design in a trial to find the application area of such carbonaceous material within the realm of sorbents.
- the removal of organic compounds such as phenol and dyes has not been considered in this project and a full investigation of their sorption is required.

- finally the application of different isotherm equations and a more complete study of the process kinetics to try to understand the underlying physical chemistry of the process.

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APPENDIX I

CHAPTER 4. PREPARATION AND CHARACTERISATION OF CARBON BY REACTION WITH SULPHURIC ACID AND ITS OPTIMISATION FOR HEAVY METALS SORPTION FROM AQUEOUS SOLUTIONS

Experimental Results

Appendix I.

Reaction Time (min.) [a,b,c]	Yield %	Reaction Temp. (°C) [a,b,d]	Yield %	Ratio of flax shive : H_2SO_4 (wt : v) [a,c,d]	Yield %	H_2SO_4 concn. (mol dm^{-3}) [b,c,d]	Yield %
10	60.2	100	50.4	1:5	57.3	10.0	46.7
20	59.0	120	54.8	1:7	58.2	12.0	58.3
30	58.5	140	57.0	1:9	58.3	14.0	56.9
45	58.2	160	58.3	1:12	57.6	16.0	53.4
60	58.0	180	54.2			18.2	51.3
		200	50.2				

St. dev. for yield results are in the range of (0.1414 - 1.13).

a. sulphuric acid concentration 12 mol dm^{-3}; b. flax shive: H_2SO_4 ratio 1:9; c. reaction temperature 160°C; d. reaction time 25 minutes.

Table 4.1. Yield of carbon sorbents as a function of preparation conditions.

Reaction Time (min.) [a,b,c]	CEC (meq/g)	Reaction Temp. (°C) [a,b,d]	CEC (meq/g)	Ratio of flax shive : H_2SO_4 (wt : v) [a,c,d]	CEC (meq/g)	H_2SO_4 concn. (mol dm^{-3}) [b,c,d]	CEC (meq/g)
10	1.47	100	1.00	1:5	1.43	10.0	1.18
20	1.50	120	1.19	1:7	1.65	12.0	1.72
30	1.71	140	1.35	1:9	1.71	14.0	2.42
45	2.03	160	1.71	1:12	1.69	16.0	2.77
60	2.12	180	2.31			18.2	2.94
		200	2.78				

St. dev. for CEC results are in the range of (0.0141 - 0.1414).

a. sulphuric acid concentration 12 mol dm^{-3}; b. flax shive: H_2SO_4 ratio 1:9; c. reaction temperature 160°C; d. reaction time 25 minutes.

Table 4.2. Cation exchange capacity of the carbon sorbents as a function of preparation conditions.

Appendix I.

Reaction Time (min.) [a,b,c]	pH	Reaction Temp. (°C) [a,b,d]	pH	Ratio of flax shive : H_2SO_4 (wt : v) [a,c,d]	pH	H_2SO_4 concn. (mol dm^{-3}) [b,c,d]	pH
10	3.18	100	3.35	1:5	3.10	10.0	3.24
20	3.11	120	3.26	1:7	3.05	12.0	3.06
30	3.03	140	3.11	1:9	3.05	14.0	3.02
45	3.01	160	3.05	1:12	3.05	16.0	3.00
60	2.95	180	3.01			18.2	2.79
		200	2.85				

a. sulphuric acid concentration 12 mol dm^{-3}; b. flax shive: H_2SO_4 ratio 1:9; c. reaction temperature 160°C; d. reaction time 25 minutes.
St. dev. for the pH values are in the range of (0.0035-0.4243).

Table 4.3. pH values of the carbon sorbents as a function of preparation conditions.

Reaction Time (min.) [a,b,c]	Moisture %	Reaction Temp. (°C) [a,b,d]	Moisture %	Ratio of flax shive : H_2SO_4 (wt : v) [a,c,d]	Moisture %	H_2SO_4 concn. (mol dm^{-3}) [b,c,d]	Moisture %
10	84.2	100	85.0	1:5	83.2	10.0	84.2
20	86.1	120	84.8	1:7	87.0	12.0	86.6
30	86.7	140	86.4	1:9	86.7	14.0	86.7
45	86.4	160	86.9	1:12	87.6	16.0	86.4
60	84.9	180	85.2			18.2	84.9
		200	85.3				

a. sulphuric acid concentration 12 mol dm^{-3}; b. flax shive: H_2SO_4 ratio 1:9; c. reaction temperature 160°C; d. reaction time 25 minutes.
St. dev. for moisture data are in the range of (0.085-1.018).

Table 4.4. Moisture content of carbon sorbents as a function of preparation conditions.

Appendix I.

Reaction Time (minutes)^{a,b,c}	Ce (equil. concn.) (mg/dm^3)	X (sorbed) (mg/g)	Final pH	Reaction Temp.(^{o}C) ^{a,b,d}	Ce (equil. concn.) (mg/dm^3)	X (sorbed) (mg/g)	Final pH
10	67.6	16.1	3.45	100	77.2	11.3	3.46
20	67.2	16.3	3.45	120	74.4	12.7	3.45
30	65.7	17.1	3.37	140	71.4	14.2	3.42
45	60.7	19.2	3.35	160	64.6	17.7	3.39
60	60.2	19.8	3.29	180	54.7	22.5	3.34
				200	41.8	29.0	3.3

ratio of flax shive : sulphuric acid (wt: V) ^{a,c,d}	Ce (equil. concn.) (mg/dm^3)	X (sorbed) (mg/g)	Final pH	H_2SO_4 Concn. (mol dm^{-3}) ^{b,c,d}	Ce (equil. concn.) (mg/dm^3)	X (sorbed) (mg/g)	Final pH
1:5	73.0	13.5	3.43	10.0	74.8	12.5	3.54
1:7	66.0	16.9	3.41	12.0	64.7	17.6	3.36
1:9	64.7	17.6	3.39	14.0	52.6	23.6	3.24
1:12	65.4	17.2	3.42	16.0	44.0	27.9	3.22
				18.2	38.1	30.9	3.06

a. sulphuric acid concentration 12 mol dm^{-3} ; b. flax shive : sulphuric acid ratio 1:9; c. reaction temperature 160°C; d. reaction time 25 minutes.
St. dev. for Ce (0.028-1.202) and Cd (II) sorbed , X, (0.007-1.273).

Table 4.5. Sorption of cadmium (II) onto carbon sorbents as a function of preparation conditions.
(Initial concentration of Cd (II) = 100 mg/dm^3, initial pH = 6.0).

Appendix I.

Reaction Time (minutes)[a,b,c]	Ce (equil. concn.) (mg/dm^3)	X (sorbed) (mg/g)	Final pH	Reaction Temp.(°C) [a,b,d.]	Ce (equil. concn.) (mg/dm^3)	X (sorbed) (mg/g)	Final pH
10	63.2	96.9	3.10	100	102.0	69.3	3.12
20	39.6	115	3.09	120	76.2	88.0	3.12
30	39.8	115	3.08	140	64.7	96.7	3.11
45	37.1	117	3.06	160	39.4	114	3.07
60	38.0	116	3.03	180	40.0	115	3.07
				200	38.9	115	3.07

Ratio of flax shive : sulphuric acid (wt: V) [a,c,d]	Ce (equil. concn.) (mg/dm^3)	X (sorbed) (mg/g)	Final pH	H_2SO_4 Concn. (mol dm^{-3}) [b,c,d]	Ce (equil. concn.) (mg/dm^3)	X (sorbed) (mg/g)	Final pH
1:5	47.0	109	3.10	10.0	70.3	91.3	3.19
1:7	39.4	114	3.09	12.0	39.8	114	3.08
1:9	40.0	115	3.08	14.0	39.2	115	3.02
1:12	49.2	108	3.11	16.0	38.1	117	3.02
				18.2	38.9	116	3.01

a. sulphuric acid concentration 12 mol dm^{-3} ; b. flax shive : sulphuric acid ratio 1:9, c. reaction temperature 160°C; d. reaction time 25 minutes.

St. dev. of Ce (0.071- 1.838) and of Hg (II) sorbed, X, (0.212-1.980).

Table 4.6. Sorption of mercury (II) from chloride media onto carbon sorbents as a function of preparation conditions.
(Initial concentration of Hg (II) = 194 mg/dm^3, initial pH = 5.05).

Appendix I.

Time, days	Time, months	C160 w	C200 w	C160 d	C200 d
2	0.07	16.97	28.50	16.90	29.75
17	0.57	17.22	28.87	17.20	29.87
41	1.37	17.89	29.70	18.90	31.83
78	2.60	18.34	31.00	19.59	32.14
130	4.33	19.01	31.42	20.49	32.29
159	5.30	19.57	31.25	20.89	33.23
207	6.90	19.89	31.89	21.23	33.61
274	9.13	20.23	32.00	21.50	34.48
365	12.17	20.33	32.20	22.02	35.12
*900	30.00	16.58	NA	17.04	NA

(*) refers to the sample, C160, stored moistened with residual sulphuric acid , sealed for 30 months.
St.dev. for Cd (II) sorbed wet and dry for wet sorbents (0.0027-0.8557) and dry sorbents (0.0195-0.4837).

Table 4.7. Cadmium (II) sorption data (mg/g) on carbons C160 and C200 with ageing in ambient air. (Initial Cd (II) concentration 100 mg/dm^3, pH = 6.2).

Time, days	Time, months	C160 w	C200 w	C160 d	C200 d
2	0.07	1.68	2.77	1.67	2.78
17	0.57	1.74	2.76	1.70	2.89
41	1.37	1.73	2.79	1.75	3.05
78	2.60	1.85	2.88	1.91	3.13
130	4.33	1.90	3.00	1.95	3.21
159	5.30	1.90	3.06	2.00	3.37
207	6.90	1.96	3.07	2.04	3.46
274	9.13	2.12	3.21	2.30	3.61
365	12.17	2.21	3.39	2.38	3.76
(*) 900	30.00	1.72	NA	1.69	NA

(*) refers to the sample, C160, stored moistened with residual sulphuric acid , sealed for 30 months.
St. dev. for Cd (II) sorbed wet and dry for wet (0.0057 - 0.014088) and dry sorbents (0.00037 - 0.01131).

Table 4.8. Cation exchange capacity data (meq/g) of carbons C160 and C200 with ageing in ambient air.

Appendix I.

Time, days	Time, months	C160 w	C200 w	C160 d	C200 d
2	0.07	137.7	142.2	116.2	118.2
17	0.57	130.0	128.7	111.3	113.7
41	1.37	121.2	116.7	92.5	101.4
78	2.60	116.3	111.1	70.7	78.6
130	4.33	106.9	103.3	58.6	66.2
159	5.30	103.1	97.0	56.0	62.9
207	6.90	95.1	93.1	53.0	61.1
274	9.130	92.7	92.1	52.3	59.4
365	12.17	89.2	87.7	48.4	55.3
(*) 900	30.00	134.6	NA	108.5	NA

(*) refers to the sample, C160, stored (sealed) moistened with residual sulphuric acid for 30 months.
St. dev. for Hg (II) sorbed for both sorbents wet (0.0071-1.8775) and dry sorbents (0.0026 - 1.5329).

Table 4.9. Mercury (II) sorption data (mg/g) on carbons C160 and C200 with ageing in ambient air. (Initial Hg (II) concentration 200 mg/dm^3, pH 5.00).

APPENDIX II

CHAPTER 5. APPLICATION OF CARBON BY DEHYDRATION FOR METAL REMOVAL FROM AQUEOUS SOLUTION VIA ION EXCHANGE

Experimental Results

Appendix II.

Time (minutes)	C_t (mg/dm^3)	Cd (II) sorbed (mg/g)	Cd (II) sorbed (mmol/g)
3	39.06	4.63	0.04
6	34.85	7.66	0.07
12	30.35	10.54	0.09
24	25.78	13.76	0.12
45	20.79	17.76	0.16
60	18.46	19.39	0.17
90	16.25	20.98	0.19
114	14.21	22.43	0.20
144	13.21	22.96	0.20
200	12.03	23.66	0.21
300	11.31	23.96	0.21
500	10.71	24.16	0.21

Table 5.1. Kinetics of sorption of cadmium (II) on wet C200 at 25°C.

(Initial concentration =44.0 mg/dm^3, initial pH = 6.00, vol.:200 ml Cd (II) solution, wt of carbon = 1.4552 g (wet) = 0.2134 g (on dry basis), moisture % = 85.34%).

Time (minutes)	C_t (mg/dm^3)	Cd (II) sorbed mg/g	Cd (II) sorbed mmol/g
3	40.46	3.38	0.03
6	36.97	5.75	0.05
12	33.53	7.58	0.07
24	29.47	10.27	0.09
45	24.85	13.90	0.12
60	21.88	16.05	0.14
90	19.04	18.15	0.16
114	17.23	19.33	0.17
144	15.33	19.82	0.18
200	14.64	20.00	0.18
300	13.99	20.15	0.18
500	13.43	20.23	0.18

Table 5.2. Kinetics of sorption of cadmium (II) on dry C200 at 25°C.

(Initial concentration =44.0 mg/dm^3, initial pH = 6.00, vol.: 200ml Cd (II) solution, wt of carbon = 0.2094 g).

Appendix II.

Time (minutes)	C_t (mg/dm^3)	Cd (II) sorbed (mg/g)	Cd (II) sorbed (mmol/g)
3	40.46	3.29	0.03
6	37.28	5.30	0.05
12	33.60	7.30	0.06
24	29.92	9.56	0.09
45	25.64	12.70	0.11
60	23.41	14.16	0.13
90	21.05	15.71	0.14
114	19.85	16.23	0.14
144	19.11	16.35	0.15
200	18.41	16.42	0.15
300	17.86	16.36	0.15
500	17.19	16.41	0.15

Table 5.3. Kinetics of sorption of cadmium (II) on wet C160 at 25°C.
(Initial concentration =44.0 mg/dm^3, initial pH = 6.00, vol. : 200 ml Cd (II) solution, wt used = 1.5018 g (wet) = 0.2151 g (on dry basis), Moisture % = 85.68 %).

Time (minutes)	C_t (mg/dm^3)	Cd (II) sorbed mg/g	Cd (II) sorbed mmol/g
3	41.32	1.53	0.01
6	38.53	3.12	0.03
12	35.25	4.67	0.04
24	31.61	6.78	0.06
45	26.69	10.46	0.09
60	23.21	12.93	0.12
90	21.42	13.94	0.12
114	20.10	14.55	0.13
144	19.13	14.86	0.13
200	18.35	15.01	0.13
300	17.53	15.20	0.14
500	16.95	15.17	0.13

Table 5.4. Kinetics of sorption of cadmium (II) on dry C160 at 25°C.
(Initial concentration =43.0 mg/dm^3, initial pH = 6.00, vol. : 200 ml Cd (II) solution, wt of carbom = 0.2199 g).

Appendix II.

Time (minutes)	C_t (mg/dm^3)	sorbed (mg/g)	sorbed (mmol/g)
3	42.68	4.29	0.07
6	38.79	7.10	0.12
10	34.64	10.24	0.17
15	32.08	11.88	0.20
20	28.91	14.17	0.24
30	26.92	15.35	0.26
50	24.51	16.97	0.29
80	23.03	17.73	0.30
120	22.02	18.04	0.31
200	20.77	18.60	0.32
300	19.79	18.91	0.32
500	18.88	19.16	0.32

Table 5.5. Kinetics data for cobalt (II) sorption on dry C200 at 25 °C.

(Wt of carbon = 0.2012 g, vol. : 200 ml Co (II) solution, initial concentration = 47 mg/dm^3, Initial pH = 5.56).

Time (minutes)	C_t (mg/dm^3)	sorbed (mg/g)	sorbed (mmol/g)
3	40.04	9.95	0.16
6	34.42	14.57	0.23
10	29.77	18.33	0.29
15	25.94	21.84	0.34
20	22.77	23.84	0.38
30	20.39	25.59	0.40
45	18.48	26.91	0.42
75	16.22	28.63	0.45
135	14.59	29.76	0.47
200	13.97	29.93	0.47
300	13.47	29.98	0.47
400	13.05	29.95	0.47
500	12.53	30.02	0.47

Table 5.6. Kinetics data for copper (II) sorption on dry C200 at 25°C.

(Wt of carbon = 0.2002 g, vol. : 200 ml Cu (II) solution, initial concentration = 50 mg/dm^3, Initial pH = 4.50).

Appendix II.

Time (minutes)	C_t (mg/dm^3)	sorbed (mg/g)	sorbed (mmol/g)
4	37.56	4.45	0.07
6	33.99	7.09	0.11
10	30.44	9.78	0.15
15	27.51	11.91	0.18
20	24.57	14.12	0.22
30	22.09	15.93	0.24
45	19.92	17.46	0.27
60	18.74	18.62	0.28
90	16.74	19.52	0.30
120	15.30	20.43	0.31
180	14.18	21.07	0.32
240	13.05	21.72	0.33
300	12.14	22.18	0.34
400	11.38	22.51	0.34
500	10.66	22.81	0.35

Table 5.7. Kinetics data for zinc (II) sorption on dry C200 at 25°C.

(Wt of carbon = 0.1994 g, vol. : 200 ml Zn (II) solution, initial concentration = 42 mg/dm^3, Initial pH = 5.00).

Time (minutes)	C_t (mg/dm^3)	sorbed (mg/g)	sorbed (mmol/g)
3	39.00	7.00	0.12
6	34.83	10.19	0.17
12	30.86	13.27	0.23
15	27.79	15.53	0.26
20	25.58	17.31	0.29
30	23.75	18.43	0.31
45	21.73	19.77	0.34
80	19.82	21.04	0.36
120	18.27	21.98	0.37
170	16.99	22.69	0.39
230	16.17	22.96	0.39
300	15.53	23.07	0.39
400	14.95	23.11	0.39
500	14.45	23.08	0.39

Table 5.8. Kinetics data for nickel (II) sorption on dry C200 at 25 °C.

(Wt of carbon = 0.2024 g, vol. : 200 ml Ni (II) solution, initial concentration = 46 mg/dm^3, Initial pH = 5.00).

Appendix II.

Time (minutes)	C_t (mg/dm^3)	sorbed (mg/g)	sorbed (mmol/g)
4	42.64	2.83	0.05
6	40.48	3.91	0.08
10	38.02	5.31	0.10
15	35.61	6.70	0.13
20	33.57	7.77	0.15
30	31.26	9.14	0.18
45	27.23	10.55	0.20
60	24.95	12.01	0.23
80	23.30	12.90	0.25
110	21.72	13.74	0.26
140	20.51	14.25	0.27
200	19.34	14.72	0.28
300	18.20	15.19	0.29
400	17.52	15.22	0.29
500	16.85	15.24	0.29

Table 5. 9. Kinetics data for chromium (III) sorption on dry C200 at 25°C.

(Wt of carbon = 0.2024 g, vol. : 200 ml Cr (III) solution, initial concentration = 45.5 mg/dm^3 Initial pH = 3.25).

Time (minutes)	C_t (mg/dm^3)	sorbed (mg/g)	sorbed (mmol/g)
3	40.06	9.90	0.05
6	34.38	18.45	0.09
10	27.38	24.09	0.12
15	22.00	29.17	0.14
20	17.21	33.35	0.16
30	14.42	35.65	0.17
45	12.44	37.21	0.18
60	10.64	38.64	0.19
90	8.88	40.07	0.19
120	7.36	41.31	0.20
200	6.53	41.90	0.20
300	5.81	42.39	0.20
400	5.42	42.59	0.21
500	5.10	42.71	0.21

Table 5. 10. Kinetics data for lead (II) sorption on dry C200 at 25 °C.

(Wt of carbon = 0.2008 g, vol: : 200 ml Pb (II) solution, initial concentration = 50.0 mg/dm^3 Initial pH = 5.00).

Appendix II.

Initial concn (mg/dm^3)	Ce, (Equil. Concn.) (mg/dm^3)	X, Cd (II) sorbed (mg/g)	Initial pH	Final pH
22	17.89	1.88	2.01	2.00
	1.13	9.43	3.01	2.87
	0.66	9.80	4.03	3.36
	0.68	9.80	5.03	3.39
	0.73	9.80	6.00	3.40
	0.73	9.79	7.00	3.42
40	32.10	3.60	2.00	2.00
	6.13	15.58	3.02	2.82
	2.77	17.01	4.02	3.14
	2.72	17.15	5.01	3.20
	2.56	17.14	6.10	3.20
	1.36	17.70	6.96	3.19
60	45.83	6.52	2.01	2.00
	19.40	20.30	3.00	2.76
	9.17	23.33	4.00	3.03
	8.88	23.20	5.00	3.08
	8.35	23.41	6.00	3.08
	8.74	23.54	6.95	3.07

St. dev. for Ce (0.021-0.141)

St. dev. for X (0.004-0.277)

Table 5.11. Effect of initial pH on the cadmium sorption on wet C200 at 25°C.

Appendix II.

Initial concn (mg/dm^3)	Ce, (Equil. Concn) (mg/dm^3)	X, Cd (II) sorbed (mg/g)	Initial pH	Final pH
20	17.98	1.99	2.01	2.00
	5.99	8.00	3.01	2.70
	3.00	9.49	4.03	3.38
	3.02	9.48	5.03	3.40
	2.94	9.51	6.00	3.40
	2.96	9.51	6.89	3.45
40	32.41	3.73	2.00	1.99
	11.81	13.91	3.01	2.83
	7.62	15.95	4.03	3.17
	7.97	15.93	5.03	3.20
	7.38	15.90	6.00	3.22
	7.25	15.94	6.88	3.26
60	48.00	5.86	2.00	1.99
	21.94	19.03	3.01	2.78
	17.43	21.64	4.03	3.05
	15.49	22.21	5.03	3.09
	14.98	22.42	6.00	3.10
	15.10	22.34	6.90	3.10

St. dev. for Ce (0.007-0.488)

St. dev. for X (0.003-0.240)

Table 5. 12. Effect of initial pH on the cadmium sorption on dry C200 at 25°C.

Appendix II.

A

Metal concn. (mg/dm^3)	X, Cd (II) sorbed (mg/g)			
	K$^+$	Na$^+$	Ca^{++}	Mg^{++}
0	39.20	39.20	39.20	39.20
100	30.45	25.42	23.30	15.44
200	20.46	11.38	15.94	0.79
300	9.75	0.00	5.40	0.00

B

Metal concn. (mg/dm^3)	X, Cd (II) sorbed (mg/g)			
	K$^+$	Na$^+$	Ca^{++}	Mg^{++}
0	35.70	35.70	35.70	35.70
100	28.56	24.31	22.07	14.11
200	18.85	9.94	14.17	0.24
300	8.47	0.00	4.83	0.00

St. dev. for X (0.0127-0.4497).

Table 5.13. Effect of light metal ions on cadmium (II) sorption.
A) wet C200, B) dry C200.

Appendix II.

A

Ce (mg/dm^3)	X, sorbed (mg/g)
1.53	4.20
4.65	7.65
17.42	11.21
49.21	15.63
83.24	18.36
119.9	19.99
158.2	20.87
256.4	21.76
356.1	21.87

St. dev. of Ce (0.018- 1.172)

St. dev. of X, (0.006- 0.311)

C

Ce (mg/dm^3)	X, sorbed (mg/g)
1.50	4.27
4.25	8.10
15.41	13.30
42.02	17.90
77.25	20.87
112.1	22.24
148.2	22.96
246.3	23.88
340.9	24.60

St. dev. of Ce (0.0113-0.433)

St. dev. of X, (0.030- 0.495)

B

Ce (mg/dm^3)	X, sorbed (mg/g)
1.50	4.26
4.45	7.90
16.21	12.30
45.02	17.02
80.10	19.87
116.7	21.47
152.1	22.16
248.9	22.98
345.2	23.23

St. dev. of Ce (0.014- 1.131)

St. dev. of X, (0.006- 0.311)

D

Ce (mg/dm^3)	X, sorbed (mg/g)
1.57	4.18
5.98	7.00
20.23	10.93
53.18	14.98
86.00	17.35
123.2	18.62
162.3	19.53
261.8	20.12
361.8	20.23

St. dev. of Ce (0.004- 0.512)

St. dev. of X, (0.052- 0.132)

Table 5.14. Cadmium (II) sorption on C160 at different temperatures.

A) wet C160 at 25 °C, B) wet C160 at 35°C, C) wet C160 at 45°C and D) dry C160 at 25°C.

Appendix II.

A

Equil. Concn (mg/dm^3)	X,Cd (II) sorbed (mg/g)
0.42	9.15
6.39	20.32
20.44	27.91
46.69	34.29
76.09	38.99
110.00	41.26
208.71	42.70
306.65	43.82

St. dev. of Ce (0.010- 0.458), St. dev. of X, (0.116- 0.834)

B

Equil. Concn (mg/dm^3)	X,Cd (II) sorbed (mg/g)
0.35	9.21
4.46	21.30
18.21	29.12
42.69	35.83
74.16	40.15
108.45	42.01
205.79	43.98
304.06	44.79

St. dev. of Ce (0.146- 0.554),St. dev. of X, (0.013- 0.782)

C

Equil. Concn (mg/dm^3)	X,Cd (II) sorbed (mg/g)
0.059	9.31
1.546	22.26
15.976	30.1
40.481	37.02
69.826	41.98
105.88	44.02
203.329	45.3
300.26	46.52

St. dev. of Ce (0.021-0.724),St. dev. of X, (0.099- 0.354)

Table 5.15. Sorption data of cadmium (II) on wet C200 at different temperatures. A) at 25°C, B) at 35°C, C) at 45°C.

Appendix II.

A

Equil. Concn (mg/dm^3)	X,Cd (II) sorbed (mg/g)
3.435	8.12
12.198	18.769
28.203	25.54
59.425	31.764
91.782	34.507
128.395	35.695
225.075	36.764
324.297	37.588

St. dev. of Ce (0.157- 0.861),St. dev. of X, (0.047- 0.552).

B

Equil. Concn (mg/dm^3)	X,Cd (II) sorbed (mg/g)
3.148	8.301
11.475	19.339
27.128	26.33
55.14	32.014
88.222	35.569
124.727	36.982
220.58	38.179
320.25	38.994

St. dev. of Ce (0.006- 1.471), St. dev. of X, (0.057- 0.583).

C

Equil. Concn (mg/dm^3)	X,Cd (II) sorbed (mg/g)
3.114	8.451
9.681	20.2
25.986	26.98
52.732	33.5
87.073	37.4
122.837	38.62
219.94	39.99
318.757	40.5

St. dev. of Ce (0.100-0.963), St. dev. of X, (0.006- 0.311).

Table 5.16. Sorption data of cadmium (II) on dry C200 at different temperatures. A) at 25°C, B) at 35°C, C) at 45°C.

Appendix II.

Co (II) on C160

Ce (mg/dm^3)	X, Co Sorbed (mg/g)
12.03	4.94
37.43	8.27
65.50	10.76
103.80	13.23
145.10	14.46
187.33	15.29
294.33	15.80
403.08	15.72

Initial pH = 5.56

St. dev. of Ce (0.130-1.226)

St. dev. of X (0.083- 1.224)

Cr (III) on C160

Ce (mg/dm^3)	X,Cr Sorbed (mg/g)
9.98	5.48
35.83	8.58
64.30	10.25
103.70	11.66
144.15	12.38
185.25	12.81
290.58	13.13
395.50	13.63

Initial pH = 3.15

St. dev. of Ce (0.100-0.618)

St. dev. of X (0.109- 0.361)

Cu (II) on C160

Ce (mg/dm^3)	X, Cu Sorbed (mg/g)
7.75	6.07
23.63	13.11
45.20	17.26
76.25	21.81
110.65	24.72
145.42	26.94
244.17	27.78
342.42	28.71

Initial pH = 3.54

St. dev. of Ce (0.106-0.655)

St. dev. of X (0.091- 0.407)

Co (II) on C200

Ce (mg/dm^3)	X, Co Sorbed (mg/g)
8.18	6.91
26.33	13.78
50.50	18.21
87.10	21.62
126.15	23.78
167.33	25.18
269.67	27.92
377.17	28.77

Initial pH = 5.56

St. dev. of Ce (0.071-1.651)

St. dev. of X (0.0259- 0.4203)

Cr (III) on C200

Ce (mg/dm^3)	X, Cr Sorbed (mg/g)
7.43	6.77
26.95	13.03
50.60	17.23
85.60	20.50
124.45	22.30
164.27	23.41
269.42	23.56
374.50	24.01

Initial pH = 3.15

St. dev. of Ce (0.134-0.853)

St. dev. of X (0.150- 0.487)

Cu (II) on C200

Ce (mg/dm^3)	X, Cu Sorbed (mg/g)
6.05	6.95
16.60	16.67
34.45	22.82
59.95	29.88
89.85	34.83
123.83	38.16
213.00	43.15
307.00	46.41

Initial pH = 3.54

St. dev. of Ce (0.167-0.998)

St. dev. of X (0.035- 0.383)

Table 5. 17. Equilibrium data for sorption of metal ions onto C160 and C200 at 25°C: cobalt (II), chromium (III) and copper (II) .

Appendix II., Table 5.17 continued.

Ni (II) on C160

Ce (mg/dm^3)	X, Ni Sorbed (mg/g)
9.88	6.03
37.03	11.96
59.35	13.81
98.90	15.57
140.55	16.67
183.08	17.44
291.33	17.80
399.50	18.16

Initial pH = 4.00

St. dev of Ce (0.139-1.020),

St. dev of X (0.016- 0.377)

Ni (II) on C200

Ce (mg/dm^3)	X, Ni Sorbed (mg/g)
7.13	7.44
26.33	17.30
42.80	22.03
77.25	26.43
116.60	28.59
158.08	29.66
263.75	31.53
373.00	31.19

Initial pH = 4.00

St. dev. of Ce (0.139- 1.000)

St. dev. of X, (0.136- 0.513)

Zn (II) on C160

Ce (mg/dm^3)	Zn Sorbed (mg/g)
8.13	4.12
26.08	7.42
46.15	9.70
74.85	11.75
105.10	13.01
135.42	14.25
215.00	15.56
295.42	16.35

Initial pH = 4.20

St. dev of Ce (0.105-1.150)

St. dev of X, (0.121- 0.324)

Zn (II) on C200

Ce (mg/dm^3)	X, Zn Sorbed (mg/g)
3.55	6.44
18.10	11.39
33.95	15.75
58.70	19.85
85.70	22.73
113.92	25.00
190.75	27.66
268.58	29.68

Initial pH = 4.20

St. dev. of Ce (0.057-1.202)

St. dev. of X, (0.0166- 0.764)

Pb (II) on C160

Ce (mg/dm^3)	X, Pb Sorbed (mg/g)
3.55	8.68
11.15	20.88
23.40	30.68
42.85	42.49
65.60	52.10
92.67	59.93
173.60	72.93
274.80	75.89

Initial pH = 4.75

St. dev of Ce (0.311- 0.566)

St. dev of X, (0.134- 0.890)

Pb (II) on C200

Ce (mg/dm^3)	X, Pb Sorbed (mg/g)
2.55	8.93
7.25	22.08
12.60	34.88
20.90	51.40
30.80	67.17
46.92	80.04
97.25	105.85
174.67	118.67

Initial pH = 4.75

St. dev. of Ce (0.158- 670)

St. dev. of X, (0.061- 1.047)

Table 5. 17. Equilibrium data for sorption of metal ions onto C160 and C200 at 25°C: nickel (II), zinc (III) andlead (II) .

Appendix II.

Cycle number	Ce (mg/dm^3)	Cd (II) sorbed X, (mg/g)	Cd (II) sorbed cumulatively X, (mg/g)
1	35.67	31.27	31.27
2	56.87	20.97	52.24
3	67.10	26.00	68.24
4	71.52	13.85	82.09
5	78.23	10.59	92.67
6	85.00	7.29	99.96
7	93.72	3.05	103.02

St dev. of Ce (0.118 - 1.381).
St dev. of X cumulative (0.081 - 1.567).

Table 5.18. Sorption data for cadmium (II) onto dry C200 carbon for seven cycles. Initial Cadmium concentration 100 mg/dm^3, initial pH 6.

Appendix II.

Column 1

Time minutes	B. V.	Cd concn. (mg/dm^3)
21	6.74	0.02
42	13.48	0.01
56	17.98	0.01
70	22.47	0.02
84	26.96	0.01
105	33.70	0.01
119	38.19	0.02
133	42.69	0.03
147	47.19	0.05
168	53.93	0.12
175	56.17	0.16
189	60.67	0.29
203	65.16	0.50
222	71.26	1.06
234	75.11	1.71
246	78.96	2.68
258	82.82	3.88
270	86.67	5.46
282	90.52	7.80
294	94.37	10.62
306	98.22	13.99
318	102.07	16.96
330	105.93	21.04
342	109.78	24.97
354	113.63	29.21
372	119.40	34.63
390	125.19	40.74
408	130.96	44.24
426	136.74	47.41
444	142.52	51.63
468	150.22	54.89
486	156.00	58.97
504	161.78	61.39
516	165.63	63.21
534	171.41	63.28
552	177.19	67.32
570	182.96	70.32
588	188.74	71.23
606	194.52	72.09
624	200.30	72.35

column capacity = 61.8 mg/g

Column 2

Time minutes	B. V.	Cd concn. (mg/dm^3)
21	6.74	0.01
42	13.48	0.02
56	17.98	0.01
63	20.22	0.01
84	26.96	0.01
105	33.70	0.02
126	40.44	0.03
133	42.69	0.08
147	47.19	0.15
168	53.93	0.20
189	60.67	0.52
210	67.41	1.26
222	71.26	2.13
234	75.11	3.32
246	78.96	4.92
258	82.81	7.03
270	86.67	9.56
282	90.52	12.73
294	94.37	16.53
306	98.22	20.38
318	102.07	24.50
330	105.93	28.72
332	106.57	33.18
350	112.35	37.93
368	118.12	43.40
392	125.83	49.15
410	131.60	53.95
428	137.38	56.87
446	143.16	59.68
464	148.94	63.59
482	154.72	64.87
500	160.49	66.84
518	166.27	68.94
536	172.05	70.40
554	177.83	73.00
572	183.60	73.97
590	189.38	74.69
602	193.23	75.52
614	197.09	74.88

column capacity = 57.2 mg/g

Table 5.19. Column studies for cadmium (II) onto C200, run 1 and run 2.
wt of carbon (dry) 1.5g, initial Cd (II) concentration 85 mg/dm^3,initial pH 6.00.

Appendix II.

Table 5.19 continued

Column 3

Time minutes	B. V.	Cd concn. (mg/dm^3)
21	6.74	0.01
42	13.48	0.01
63	20.22	0.01
84	26.96	0.01
105	33.70	0.02
126	40.44	0.03
147	47.19	0.07
168	53.93	0.14
189	60.67	0.19
210	67.41	0.48
222	71.26	1.10
234	75.11	2.00
246	78.96	3.12
258	82.81	4.45
270	86.67	6.65
282	90.52	9.23
294	94.37	12.12
306	98.22	16.12
318	102.07	20.10
330	105.93	24.23
332	106.57	27.34
350	112.35	32.03
368	118.12	36.12
392	125.83	42.08
410	131.60	48.98
428	137.38	52.89
446	143.16	55.23
464	148.94	58.89
482	154.72	62.54
500	160.49	64.00
518	166.27	65.78
536	172.05	68.87
554	177.83	70.23
572	183.60	71.02
590	189.38	72.04
602	193.23	72.87
614	197.09	73.02

column capacity = 59.8 mg/g

Column 4

Time minutes	B. V.	Cd concn. (mg/dm^3)
21	6.74	0.01
42	13.48	0.01
63	20.22	0.02
84	26.96	0.07
105	33.70	0.20
126	40.44	0.47
147	47.19	0.89
168	53.93	1.55
189	60.67	2.51
210	67.41	3.84
228	73.19	5.33
246	78.96	7.32
258	82.81	8.80
270	86.67	10.54
282	90.52	12.92
294	94.37	15.32
306	98.22	18.30
318	102.07	20.85
330	105.93	24.41
342	109.78	27.96
354	113.63	31.70
372	119.41	37.98
390	125.19	43.12
408	130.96	48.35
426	136.74	53.66
444	142.52	59.01
462	148.30	61.75
480	154.07	65.23
498	159.85	68.17
516	165.63	70.27
534	171.41	72.54
552	177.19	75.91
570	182.96	75.64
588	188.74	76.73
606	194.52	77.23
618	198.37	80.92
630	202.22	81.06

column capacity = 57.5 mg/g

Table 5.19. Column studies for cadmium (II) onto C200, run 3 and run 4. wt of carbon (dry) 1.5g, initial Cd (II) concentration 85 mg/dm^3,initial pH 6.00.

Appendix II.

Table 5.19 continued

Column 5

Time minutes	B. V.	Cd concn. (mg/dm^3)
18	5.78	0.01
36	11.56	0.02
54	17.33	0.01
72	23.11	0.06
90	28.89	0.11
108	34.67	0.16
126	40.44	0.35
144	46.22	0.67
162	52.00	1.18
180	57.78	1.84
192	61.63	2.51
204	65.48	3.25
216	69.33	4.02
228	73.19	4.86
240	77.04	6.15
252	80.89	7.31
264	84.74	8.83
276	88.59	10.84
288	92.44	12.51
300	96.30	15.10
312	100.15	17.66
324	104.00	20.83
342	109.78	25.19
360	115.56	30.54
378	121.33	35.81
396	127.11	40.88
414	132.89	46.21
432	138.67	51.15
450	144.44	54.73
468	150.22	57.38
486	156.00	62.72
504	161.78	63.15
522	167.56	65.56
540	173.33	67.79
558	179.11	69.71
576	184.89	73.76
594	190.67	74.56
612	196.44	75.98
630	202.22	76.87

column capacity = 60.0 mg/g

Column 6

Time minutes	B. V.	Cd concn. (mg/dm^3)
18	5.78	0.01
36	11.56	0.02
54	17.33	0.03
72	23.11	0.05
90	28.89	0.07
108	34.67	0.18
126	40.44	0.38
144	46.22	0.62
162	52.00	1.11
180	57.78	1.74
192	61.63	2.33
204	65.48	2.98
216	69.33	3.83
228	73.19	4.64
240	77.04	5.84
252	80.89	6.95
264	84.74	8.74
276	88.59	10.54
288	92.44	12.35
300	96.30	14.36
312	100.15	17.01
324	104.00	20.47
342	109.78	24.31
360	115.56	30.36
378	121.33	36.15
396	127.11	40.13
414	132.89	45.39
432	138.67	49.79
450	144.44	54.61
468	150.22	58.10
486	156.00	60.97
504	161.78	66.31
522	167.56	69.34
540	173.33	72.06
558	179.11	73.87
576	184.89	75.02
594	190.67	76.34
612	196.44	76.78
630	202.22	77.34
648	208.00	78.23
666	213.78	77.68
686	220.20	78.56
702	225.33	79.05

column capacity = 60.4 mg/g

Table 5.19. Column studies for cadmium (II) onto C200, run 5 and run 6. wt of carbon (dry) 1.5g, initial Cd (II) concentration 85 mg/dm^3,initial pH 6.00.

Table 5.19 continued

Column 7

Time minutes	B. V.	Cd concn. (mg/dm^3)
21	6.74	0.01
42	13.48	0.02
63	20.22	0.10
84	26.96	0.04
105	33.70	0.13
126	40.44	1.14
147	47.19	1.15
168	53.93	1.25
189	60.67	1.92
210	67.41	3.05
224	71.90	4.89
238	76.40	5.67
252	80.89	6.94
266	85.38	8.64
280	89.88	10.79
294	94.37	13.72
308	98.86	16.58
322	103.36	19.03
336	107.85	23.89
350	112.35	28.07
364	116.84	31.96
378	121.33	36.64
399	128.07	42.58
420	134.81	47.50
441	141.56	52.29
462	148.30	56.98
483	155.04	62.80
504	161.78	64.94
525	168.52	68.55
546	175.26	69.96
567	182.00	71.51
588	188.74	72.50
609	195.48	74.36
630	202.22	76.11
651	208.96	76.96
672	215.70	77.28
686	220.20	78.12
700	224.69	77.70

column capacity = 60.7 mg/g

Table 5.19. Column studies for cadmium (II) onto C200, run 7.
wt of carbon (dry) 1.5g, initial Cd (II) concentration 85 mg/dm^3,initial pH 6.00.

Appendix II.

Time (Minutes)	B. V.	Column 1	Column 2	Column 3	Column 4	Column 5	Column 6	Column 7
		Cd concn. (mg/dm^3)	Cd concn. (mg/dm^3)	Cd concn. (mg/dm^3)	Cd concn. (mg/dm^3)	Cd concn. (mg/dm^3)	Cd concn. (mg/dm^3)	Cd concn. (mg/dm^3)
3.0	0.963	658	577	454	532	622	456	481
6.0	1.926	1998	2000	1977	1899	1989	2004	1924
9.0	2.889	2250	2109	2266	2103	2050	2089	2110
12.0	3.852	2176	1979	1781	1563	1933	1787	1786
15.0	4.815	1325	1234	1055	1155	1022	1187	1191
20.0	6.420	678	667	786	756	667	702	767
25.0	8.025	345	304	345	457	420	436	468
30.0	9.630	155	166	189	289	257	260	220
35.0	11.235	88.2	93.7	101	168	163	133	120
40.0	12.840	56.34	45.30	66.80	98.90	88.23	87.45	66.30
45.0	14.444	33.77	25.40	45.20	55.80	33.67	42.80	56.80
50.0	16.049	22.23	26.70	33.20	33.30	16.45	14.28	23.80
55.0	17.654	17.23	15.56	19.20	19.45	13.56	11.47	15.30
60.0	19.259	14.24	12.20	13.50	14.23	10.11	8.94	10.32
65.0	20.864	10.23	10.40	8.78	10.30	7.34	7.06	8.25
70.0	22.469	7.89	8.99	7.88	4.30	6.56	6.26	6.35
75.0	24.074	5.45	5.67	6.45	3.32	4.56	4.87	5.26
80.0	25.679	3.30	3.34	5.54	2.89	3.55	3.60	3.57

Table 5.20. Stripping data for cadmium (II) for 7 runs

APPENDIX III

CHAPTER 6. SORPTION-REDUCTION OF METAL IONS ON CARBON BY DEHYDRATION WITH SULPHURIC ACID.

Experimental Results

Appendix III

A

Time (Hours)	C_t (mg/dm^3)	Hg (II) sorbed (mg/g)
3.00	72.5	36.60
10.25	51.4	68.00
19.00	33.9	94.20
27.00	25.5	105.00
51.00	10.9	126.40
75.00	5.3	134.50
99.00	3.4	137.00
123.00	2.8	137.70
147.00	3.3	138.20
171.00	1.9	138.50

B

Time (Hours)	C_t (mg/dm^3)	Hg (II) sorbed (mg/g)
3.00	88.5	10.50
19.00	66.0	40.00
27.00	56.5	49.80
51.00	39.3	72.70
75.00	27.3	88.30
99.00	21.6	95.00
123.00	15.6	102.30
147.00	12.6	105.30
171.00	10.2	107.70

Initial pH 5.00, total volume 200 ml, Initial conc. = 95 mg/dm^3,
Moisture content of wet sorbent = 87.7%, wt on the dary basis = 0.123g

Table 6.1. Kinetics of mercury (II) sorption on carbon C160 at 25°C.
A: wet, B: dry

Appendix III.

A

Initial Concn, C_o (mg/dm^3)	Ce (mg/dm^3)	X, sorbed (mg/g)	pH initial	pH final
99	0.75	73.20	7.01	3.23
97	0.73	73.00	5.99	3.25
98	1.07	72.60	5.01	3.14
97	0.96	72.40	4.01	3.00
100	7.67	69.90	3.00	2.77
100	81.10	14.20	2.01	2.01
105	93.40	8.75	1.21	1.21

St. dev. for Ce (0.199 - 0.947).
St. dev. for X (0.243 - 1.153).

B

Initial Concn, C_o (mg/dm^3)	Ce (mg/dm^3)	X, sorbed (mg/g)	pH initial	pH final
195	0.92	148.30	7.00	2.97
201	8.21	144.30	6.01	2.95
198	8.37	143.67	5.00	2.91
204	20.17	137.67	3.99	2.88
204	42.73	121.67	3.00	2.66
205	171.67	25.57	2.01	2.00
210	191.67	13.97	1.22	1.21

St. dev. for Ce (0.577 - 2.318).
St. dev. for X (0.577 - 1.527525).

C

Initial Concn, C_o (mg/dm^3)	Ce (mg/dm^3)	X, sorbed (mg/g)	pH initial	pH final
298	14.33	204.67	7.00	2.80
299	41.67	186.00	6.01	2.88
301	56.77	175.30	5.01	2.87
307	88.57	158.67	4.00	2.85
310	120.96	136.00	3.00	2.64
318	275.33	30.70	2.01	1.98
330	299.33	22.07	1.21	1.21

St. dev. for Ce (0.064 - 1.528).
St. dev. for X (0.153 - 1.528).

Table 6.2. Effect of pH on mercury (II) sorption on wet C160.

A. Moisture content = 86.86%., Initial Concn. = ~100 mg/dm^3.

B. Moisture content = 86.86%., Initial Concn. = ~200 mg/dm^3.

C. Moisture content = 86.26%., Initial Concn. = ~300 mg/dm^3.

Appendix III.

A

Initial Concn, C_o (mg/dm^3)	Ce, Hg (mg/dm^3)	X, sorbed (mg/g)	pH initial	pH final
100	14.90	64.30	7.01	3.32
100	23.50	57.63	6.00	3.30
100	27.70	54.50	5.01	3.26
101	34.67	50.10	4.01	3.25
104	56.43	35.90	3.01	2.91
103	87.60	11.63	2.02	2.01
103	92.70	7.75	1.21	1.21

St. dev. for Ce (0.0173 - 0.252).

St. dev. for X (0.0577 - 0.173).

B

Initial Concn, C_o (mg/dm^3)	Ce, Hg (mg/dm^3)	X, sorbed (mg/g)	pH initial	pH final
200	40.07	120.67	7.00	3.08
199	45.60	115.95	6.01	3.08
199	47.80	113.88	5.00	3.07
198	65.67	99.93	4.00	3.01
198	106.30	69.10	3.01	2.79
195	172.67	16.83	2.02	2.01
196	182.67	10.17	1.20	1.20

St. dev. for Ce (0.0577 - 2.122).

St. dev. for X (0.081 - 1.922).

C

Initial Concn, C_o (mg/dm^3)	Ce, Hg (mg/dm^3)	X, sorbed (mg/g)	pH initial	pH final
295	68.70	169.30	7.00	2.93
297	104.30	144.00	6.03	2.96
300	126.67	130.33	5.03	3.00
301	148.30	114.33	4.01	2.96
300	185.33	85.90	3.00	2.76
300	265.96	25.23	2.03	2.01
302.00	283.07	14.43	1.21	1.20

St. dev. for Ce (0.0751 - 1.473).

St. dev. for X (0.0577 - 1.155).

Table 6.3. Effect of pH on mercury (II) sorption on dry C160.

A. Initial Concn. = ~100 mg/dm^3.

B. Initial Concn. = ~200 mg/dm^3.

C. Initial Concn. = ~300 mg/dm^3.

Appendix III.

A

Ce, Equil. Concn (mg/dm^3)	Hg sorbed (X) (mg/g)
0.97	71.0
7.68	136.9
4.20	184.6
85.1	255.4
129.0	265.5
260.0	312.9
514.0	337.0

St. dev. for Ce (0.021 -2.121).
St. dev. for X (0.00.283 - 2.121).

C

Ce, Equil. Concn (mg/dm^3)	Hg sorbed (X) (mg/g)
0.83	76.3
1.04	152.7
1.67	228.5
6.40	299.9
29.30	352.3
113.0	444.9
291.0	529.6

St. dev. for Ce (0.007 - 1.414).
St. dev. for X (0.071 - 2.12).

B

Ce, Equil. Concn (mg/dm^3)	Hg sorbed (X) (mg/g)
1.02	75.3
1.21	151.1
15.6	216.8
45.4	268
81.3	317
206	373
449	410

St. dev. for Ce (0.0001 - 1.414).
St. dev. for X (0.0141 - 0.849).

D

Ce, Equil. Concn (mg/dm^3)	Hg sorbed (X) (mg/g)
0.75	74.32
4.45	147.6
25.87	224.3
65.23	279.2
166.5	335.7
309	368.8
500	376.5

St. dev. for Ce (0.0141 - 0.763).
St. dev. for X (0.679 - 1.386).

Table 6.4. Sorption data for mercury (II) on wet C160.

A. Chloride media, Initial pH 6.5, at 25°C.
B. Chloride media, Initial pH 6.5, at 35°C.
C. Chloride media, Initial pH 6.5, at 45°C.
D. Nitrate media, initial pH 3.2, at 25°C.

Appendix III.

A

Ce, Equil. Concn (mg/dm^3)	Hg sorbed (X) (mg/g)
1.6	27.4
14	61.5
37.2	116.5
70	165.1
115	204
172	233
333	259.2
594	283.8

St. dev. for Ce (0.016 - 2.83).
St. dev. for X (0.071 - 1.414).

B

Ce, Equil. Concn (mg/dm^3)	Hg sorbed (X) (mg/g)
1.5	27.7
4.08	68.6
13.6	134
26.3	194.3
82.8	242.3
113	277.1
163	307.3
531	329.9

St. dev. for Ce (0.0212 - 2.83).
St. dev. for X (0.071 - 2.121).

C

Ce, Equil. Concn (mg/dm^3)	Hg sorbed (X) (mg/g)
0.88	27.8
2.29	69.8
8.02	136.6
13.1	205
23.8	271.1
64.9	308.9
202	351.7
465	374.3

St. dev. for Ce (0.028 -2.828).
St. dev. for X (0.071 - 2.12).

D

Ce, Equil. Concn (mg/dm^3)	Hg sorbed (X) (mg/g)
6.17	70.7617
29.9	127.895
66.445	175.60526
124.35	208.8257
255.65	257.3617
428.75	280.4003
610.75	294.44

St. dev. for Ce (0.023 - 0.778).
St. dev. for X (0.134 - 0.1.131).

Table 6.5. Sorption data for mercury (II) on dry C160.

A. Chloride media, Initial pH 6.5, at 25°C.
B. Chloride media, Initial pH 6.5, at 35°C.
C. Chloride media, Initial pH 6.5, at 45°C.
D. Nitrate media, initial pH 3.2, at 25°C.

Appendix III.

A

Equil. concn. Ce (mg/dm^3)	X, sorbed (mg/g)	Metal ion	Concn. of light metal ion (mg/dm^3)
68.20	180.0	none	none
145.3	125.9	K	100.0
172.0	106.9		200.0
187.0	97.4		300.0
166.3	111.2	Na	100.0
196.7	89.4		200.0
215.3	77.1		300.0
190.9	94.1	Ca	100.0
205.3	84.8		200.0
219.3	74.6		300.0
207.7	82.3	Mg	100.0
227.3	69.5		200.0
234.3	64.3		300.0

St. dev. for Ce (0.078 - 2.082).

St. dev. for X (0.071 - 1.540).

B

Equil.concn. Ce (mg/dm^3)	X, sorbed (mg/g)	Metal ion	Concn. of light metal ion (mg/dm^3)
130.0	123.3	none	none
175.0	91.3	K	100.0
189.3	81.2		200.0
208.0	67.4		300.0
183.0	85.9	Na	100.0
197.7	75.0		200.0
219.3	58.9		300.0
188.7	81.7	Ca	100.0
200.3	73.0		200.0
219.9	58.3		300.0
199.3	73.8	Mg	100.0
210.3	65.8		200.0
231.0	50.7		300.0

St. dev. for Ce (0.078 - 2.082).

St. dev. for X (0.071 - 1.540).

Table 6.6. Effect of light metal ions on mercury (II) removal on carbon C160.

A. Wet, moisture content 85.5%, initial concentration of Hg (II) 328 mg/dm^3.

B. Dry, initial concentration of Hg (II) 300 mg/dm^3.

Appendix III.

Hg (II) sorbed X (mg/g)	Average of X (mg/g)	Wt of barium carbonate produced, mg (mg)	mean value of barium carbonate ppt. (mg)
895	895	17.9	17.9
895		18	
894		17.8	

St. dev. of X = 0.577, St. dev. of carbonate weight = 0.1

Initial mercury concentration = 6000 mg/dm^3, pH = 5-6, temperature 60 ± 2°C.

Table 6.7. Results of carbon dioxide evolution during the mercury (II) sorption on wet carbon C160 at ~60° C.

Appendix III.

A

Ce, equil. Concn. mg/dm^3	X sorbed, Separate mg/g	X sorbed cumulativel mg/g	Cycles no.
117.50	181.97	181.97	1
212.73	136.67	318.64	2
291.35	99.27	417.91	3
316.60	87.25	505.16	4
330.70	80.55	585.71	5
340.23	76.01	661.72	6
355.00	68.98	730.71	7
356.70	68.18	798.88	8
370.53	61.60	860.48	9
374.50	59.71	920.19	10
389.98	52.34	972.53	11
406.58	44.45	1016.98	12

St. dev. for Ce (0.0354 - 3.384).
St. dev. for X (0.510 - 3.230).

B

Ce, equil. Concn. mg/dm^3	X sorbed, Separate mg/g	X sorbed cumulativel mg/g	Cycles no.
202.7	144.5	144.5	1
272.6	110.6	255.1	2
320.1	87.4	342.5	3
342.5	76.6	419.1	4
353.5	71.2	490.4	5
372.0	62.2	552.6	6
386.5	55.2	607.8	7
399.2	49.0	656.8	8
417.4	41.0	696.9	9
431.8	33.2	730.1	10
440.0	29.2	759.2	11
450.0	24.3	783.5	12

St dev of Ce (0.247 - 3.323).
St dev. of X cumulative (0.115 - 2.159).

Table 6.8. Successive sorption of mercury (II) on carbon C160 at 25 °C : A) wet B) dry
Synthetic water , pH 4.5, initial Hg concentration 500 mg/dm^3.

Ce, equil. Concn. mg/dm^3	X sorbed, Separate mg/g	X sorbed cumulativel mg/g	Cycles no.
2.8	185.3	185.3	1
10.2	182.1	367.4	2
14.3	180.3	548	3
18.2	178.6	726	4
20.2	177.8	904	5
30.0	173.5	1078	6
48.2	165.6	1243	7

St dev. of Ce (0.0424 - 0.240).
St dev. of X cumulative (0.509 - 1.534).

Table 6.9. Successive sorption of mercury (II) on wet carbon C160 at 25 °C.
Natural water,
(initial concentrations: Hg (II): 430, K: 5.35, Na: 27.0, Ca: 11.3 and Mg : 6.6 mg/dm^3, Initial pH 6.6).

Appendix III.

Continuous column

Time, min	B. V.	Hg Concn. mg/dm^3
42	3	0.05
84	6	0
126	9	0.04
168	12	0.14
210	15	0.56
252	18	1.58
294	21	3.52
336	24	6.9
378	27	10.01
420	30	14.55
462	33	19.59
504	36	23.17
546	39	23.55
588	42	38.61
630	45	46.47
672	48	52.16
714	51	55.97
756	54	58.2
798	57	61.12
840	60	64.3
882	63	73.69
924	66	73.94
966	69	78.9
1008	72	79.3
1050	75	82.5
1092	78	85.06
1134	81	87.06
1176	84	90.86
1218	87	92.16
1260	90	93.65
1302	93	97.49
1344	96	96.1
1372	98	99.26
1400	100	97.64
1442	103	100.58
1484	106	99.22
1526	109	103.24
1568	112	102.29
1610	115	99.02
1652	118	103.31
1694	121	105.4
1736	124	106.87
1778	127	108.1
1820	130	111.56
1862	133	113.59
1904	136	110.93
1946	139	111.41
1988	142	110.25
2030	145	109.58
2072	148	110.16
2114	151	110.02
2156	154	112.95
2198	157	112.27
2240	160	113.13
2282	163	119.31
2324	166	117.55
2366	169	120.73
2408	172	119.71
2450	175	120.01
2492	178	120
2534	181	119.25
2576	184	119.65
2618	187	119.51
2660	190	120.18
2702	193	122.85
2744	196	123.09
2800	200	124.82
2842	203	125.03
2884	206	126.7
2926	209	125.8
2968	212	127.65
3010	215	129.54
3052	218	130
3094	221	132.34
3136	224	131.03
3178	227	131.04
3220	230	132.4
3262	233	135.9
3304	236	135.2
3346	239	137.3
3388	242	140
3430	245	139.1
3472	248	140.2
3514	251	141

Table 6.10. Sorption data of Hg (II) on a fixed bed (continuous regime).
wt of carbon =1.004 g, Initial pH = 4.5.

Appendix III

Intermittent column

Time, min	B. V.	Hg Concn. mg/dm^3
42	3	0.03
84	6	0.11
126	9	0.1
168	12	0.13
210	15	0.21
252	18	0.57
266	19	0.09
294	21	0.12
336	24	0.32
378	27	1.94
420	30	4.79
462	33	8.7
504	36	12.4
518	37	1.02
546	39	2.09
588	42	9.96
630	45	17.27
672	48	23.47
714	51	29.15
756	54	33.49
770	55	1.04
798	57	2.14
840	60	12.89
882	63	25.23
924	66	35.17
966	69	38.3
1008	72	47.48
1022	73	2.5
1050	75	25.98
1092	78	52.91
1134	81	61.62
1176	84	67.84
1218	87	77.19
1260	90	77.8
1274	91	9.54
1302	93	9.67
1358	97	43.23
1400	100	60.6
1442	103	71.6
1484	106	70.37
1526	109	75.93
1540	110	10.4
1568	112	28.45
1610	115	53.9
1652	118	84.3
1694	121	89.48
1736	124	95.48
1778	127	99.89
1792	128	13.45
1820	130	25.34
1862	133	69.6
1904	136	84.51
1946	139	91.46
1988	142	96.52
2030	145	99.04
2072	148	14.25
2114	151	30.46
2156	154	67.98
2198	157	96.09
2240	160	101.34
2282	163	104.34
2310	165	15.23
2338	167	35.32
2380	170	85.24
2422	173	98.68
2464	176	105.98
2506	179	108.98
2520	180	21.065
2548	182	49.02
2590	185	83.09
2632	188	95.98
2674	191	100.35
2716	194	106.09
2772	198	111.56
2786	199	24.09
2814	201	46.96
2842	203	70.13
2884	206	89.5
2926	209	97.09
2982	213	103.23
3024	216	109.98
3052	218	113.09
3066	219	31.83
3094	221	39.17
3136	224	95.06
3178	227	111.34
3220	230	117.94
3262	233	116.08
3304	236	120.04
3346	239	121.38
3388	242	123.23
3430	245	125.17
3472	248	129.04
3514	251	132.87

* The double line shows working periods which was for ~4 hours followed by 8 hours rest, and it shows the saw-pattern.

Table 6.11. Sorption data of Hg (II) on a fixed bed (intermittent regime).
wt of carbon =1.004 g, Initial pH = 4.5.

Appndix III.

A

Time (Hours)	C_t (mg/dm^3)	X, sorbed (mg/g)
2.50	89.44	8.23
5.00	80.01	12.10
19.75	56.39	27.46
43.75	40.71	37.25
76.92	30.38	43.43
99.42	25.11	46.07
125.25	20.63	48.26
149.25	17.55	49.50
161.25	15.46	50.09

wt on dry basis = 0.2564 g, volume = 200 ml,
Initial concentration of Cr (VI) 100 mg/dm^3.

B

Time (Hours)	C_t (mg/dm3)	X, sorbed (mg/g)
2.50	91.27	6.98
5.00	82.71	10.14
19.75	66.97	21.91
43.75	53.55	29.29
76.92	40.32	35.04
99.42	35.28	37.03
125.25	29.75	39.54
149.25	25.49	41.22
161.25	22.00	42.43

wt = 0.2533 g, volume = 200 ml,
Initial concentration of Cr (VI) 100 mg/dm^3.

Table 6.12. Kinetcs data for sorption of Chromium (VI) on C160 at 25° C with Initial pH 4.5. (A: Wet, B: dry).

Appendix III.

A

Time (Hours)	C_t, Cr total (mg/dm^3)	C_t, Cr (VI) (mg/dm^3)	C_t, Cr (III) (mg/dm^3)	log Cr (VI)	Sorbed (mg/g)
3.50	80.4	76.4	4.0	1.883	31.0
5.00	71.5	61.7	9.9	1.790	40.6
7.00	69.7	52.8	16.8	1.723	41.8
15.00	58.6	31.8	26.7	1.503	55.3
24.00	50.7	20.0	30.7	1.301	65.7
27.00	49.6	14.8	34.8	1.169	65.7
29.50	48.5	10.6	37.8	1.027	65.8
32.00	46.5	7.8	38.6	0.893	65.7
40.00	44.5	5.6	38.8	0.750	65.8
47.25	42.5	3.7	38.8	0.563	65.8
52.00	40.5	2.4	38.1	0.383	65.8
55.00	38.5	1.6	37.0		65.7
74.00	38.5	0.3	38.2		65.8

wt wet = 1.1 g , wt on dry basis =0.1263 g, volume 200 ml, initial Cr (VI) concn 100 mg/dm^3.

B

Time (Hours)	C_t, Cr total (mg/dm^3)	C_t, Cr (VI) (mg/dm^3)	C_t, Cr (III) (mg/dm^3)	log Cr (VI)	Sorbed (mg/g)
3.50	90.44	90.44	0.00	1.956	15.23
5.00	82.44	82.44	0.00	1.916	22.16
7.00	77.16	77.16	0.00	1.887	25.10
15.00	61.97	59.69	2.28	1.776	33.93
24.00	53.33	46.81	6.52	1.670	44.28
27.00	50.02	41.10	8.92	1.614	49.07
29.50	45.27	35.45	9.82	1.550	49.33
32.00	42.67	32.17	10.51	1.507	55.32
40.00	40.29	26.25	14.04	1.419	59.39
47.25	40.29	20.00	20.29	1.301	60.03
52.00	40.28	17.50	22.79	1.243	60.04
55.00	40.28	16.16	24.12	1.209	60.04
74.00	40.28	12.05	28.23	1.081	60.03

wt = 0.13 g, volume = 200 ml, initial Cr (VI) concn 100 mg/dm^3.

Table 6.13. Kinetics of chromium (VI) removal on C160 at 25°C.
with initial pH = 1.5. A. wet, B. dry.

Appendix III.

A

Initial pH	Initial Cr (VI) (mg/dm^3)	Cr total (equil.) (mg/dm^3)	Eq Cr (VI) (mg/dm^3)	Eq Cr (III) (mg/dm^3)
1.50	109	77.60	0.02	77.58
1.98	109	50.67	0.03	50.64
3.00	108	13.42	14.22	-0.80
4.00	113	30.90	30.91	-0.01
5.05	115	39.35	39.33	0.02
6.03	114	46.37	46.42	-0.05
7.02	114	66.22	66.13	0.09
8.00	114	68.58	68.56	0.02
8.99	114	68.63	69.21	-0.58

B

Initial pH	Initial Cr (VI) (mg/dm^3)	Cr total (equil.) (mg/dm^3)	Eq Cr (VI) (mg/dm^3)	Eq Cr (III) (mg/dm^3)
2.00	109	50.67	0.03	50.65
2.20	108	41.26	0.05	41.21
2.40	107	20.23	0.07	20.16
2.60	109	1.44	0.84	0.61
2.80	108	8.65	8.29	0.36
3.00	108	13.42	14.22	-0.80
3.20	106	15.12	15.28	-0.16
3.40	108	20.32	20.90	-0.59
3.60	107	22.69	22.90	-0.21
3.80	109	26.41	26.36	0.05

(A &B) St. dev. for equil. Cr (t) (0.0557-1.291), St. dev. for equil. Cr (VI) (0.0001- 0.726).

Table 6.14. Chromium Equilibrium data of chromium (VI) sorption on wet C160 at 25°C. Initial Cr (VI) concentration ~100 mg/dm^3. A) pH range 1-9. B) pH range 2- 3.8.

Initial pH	Final pH	Sorbed (mg/g)
1.50	1.563	25.74
1.98	2.266	47.64
2.01	2.5005	47.64
2.20	2.8195	54.39
2.40	3.5775	70.76
2.60	4.44	88.16
2.80	6.355	81.45
3.00	6.669	77.08
3.20	6.699	74.13
3.40	6.719	70.92
3.60	6.735	68.60
3.80	6.815	67.70
4.00	6.844	66.96
5.05	6.866	61.67
6.03	7.008	54.96
7.02	7.288	38.84
8.00	7.33	37.17
8.99	7.44	37.09

St. dev. for final pH values (0.0007-0.0651).

St. dev. for sorbed Cr (X) (0.002 - 1.025).

Table 6.15. Chromium (VI) sorption on wet C160 at 25° C at different pH values at 25°C. Initial Cr (VI) concentration ~100 mg/dm^3.

Appendix III.

A

Initial pH	Initial Cr(VI) (mg/dm^3)	Cr total (equil.) (mg/dm^3)	Cr (VI) (mg/dm^3)	Cr (III) (mg/dm^3)
1.54	219	155.14	0.11	155.03
2.01	224	92.70	0.41	92.29
3.00	224	82.98	82.67	0.31
4.01	226	100.17	101.03	-0.86
5.06	228	106.80	106.10	0.70
5.99	227	122.84	123.52	-0.68
7.02	223	147.13	147.59	-0.46
8.01	224	162.63	162.80	-0.16
9.00	224	164.32	164.33	-0.01

B

Initial pH	Initial Cr(VI) (mg/dm^3)	Cr total (equil.) (mg/dm^3)	Cr (VI) (mg/dm^3)	Cr (III) (mg/dm^3)
2.00	224	92.70	0.41	92.29
2.20	218	40.40	2.43	37.97
2.40	219	11.90	11.45	0.45
2.60	221	58.20	58.63	-0.43
2.80	223	74.23	74.75	-0.51
3.00	224	82.98	82.67	0.31
3.20	224	86.42	86.78	-0.36
3.40	224	89.36	90.27	-0.90
3.60	224	92.42	91.53	0.89
3.80	224	96.03	96.28	-0.25

(A&B) St dev. for equil. Cr (t) (0.0518-1.247), St. dev. for equil. Cr (VI) (0.0003-0.896).

Table 6.16 Chromium Equilibrium data of chromium (VI) sorption on wet C160 at 25°C. Initial Cr (VI) concentration ~220mg/dm^3. A) pH range 1-9 B) pH rage 2 - 3.8.

Initial pH	Final pH	Sorbed (mg/g)
1.54	1.697	52.15
2.01	2.82	107.03
2.20	4.079	144.51
2.40	5.185	168.86
2.60	5.927	132.79
2.80	6.2865	121.34
2.99	6.33	115.15
3.00	6.34	116.51
3.20	6.415	112.63
3.40	6.4345	109.33
3.60	6.465	107.09
3.80	6.5165	104.46
4.01	6.598	102.46
5.06	6.63	99.29
5.99	6.876	85.19
7.02	7.4915	61.78
8.01	7.659	50.06
9.00	7.891	48.88

St. dev. for final pH values (0.0014 - 0.0749).
St. dev. for sorbed Cr (X) (0.0947-1.130).

Table 6.17. Chromium (VI) sorption on wet C160 at 25° C at different pH values. Initial Cr (VI) concentration ~220 mg/dm^3.

Appendix III.

A

Initial pH	Initial Cr(VI) (mg/dm^3)	Cr total (equil.) (mg/dm^3)	Cr (VI) (mg/dm^3)	Cr (III) (mg/dm^3)
1.48	110	66.86	0.06	66.80
1.99	111	37.71	1.06	36.65
3.00	108	32.78	33.02	-0.24
3.99	115	52.47	51.88	0.59
5.01	118	55.83	56.06	-0.23
6.01	115	67.05	67.40	-0.34
7.00	113	82.32	82.94	-0.62
8.01	114	87.05	87.73	-0.68
9.00	114	90.76	90.90	-0.14

B

Initial pH	Initial Cr(VI) (mg/dm^3)	Cr total (equil.) (mg/dm^3)	Cr (VI) (mg/dm^3)	Cr (III) (mg/dm^3)
1.99	111	37.71	1.06	36.65
2.20	103	17.05	3.55	13.50
2.40	107	16.28	11.02	5.26
2.60	105	21.41	22.17	-0.76
2.80	108	26.92	26.98	-0.07
3.00	108	32.78	33.02	-0.24
3.20	106	34.51	34.59	-0.08
3.40	108	39.28	39.40	-0.12
3.60	108	41.27	41.55	-0.29
3.80	108	44.59	44.47	0.12

(A&B) St. dev. for equil. Cr (t) (0.0509-1.444), St. dev. for equil. Cr (VI) (0.0006-0.713).

Table 6.18. Chromium Equilibrium data of chromium (VI) sorption on dry C160 at 25°C. Initial Cr (VI) concentration ~100 mg/dm^3. A) pH range 1-9 B) pH range 2-3.8.

Initial pH	Final pH	Sorbed (mg/g)
1.48	1.506	34.902
1.99	2.037	59.264
2.2	2.52	68.976
2.4	2.889	73.455
2.6	3.216	67.46
2.8	3.847	65.39
3	4.606	61.221
3.2	4.91	57.56
3.4	5.1195	55.87
3.6	5.26	53.818
3.8	5.305	52.49
3.989	5.53	50.915
5.005	5.705	45.62
6.005	6.111	38.918
7.003	7.05	25.029
8.007	7.23	22.015
9	7.275	18.83

St. dev. for sorbed values (0.0424-1.448).
St. dev. for final pH values (0.006-0.071).

Table 6.19. Chromium (VI) sorption on dry C160 at 25° C at different pH values. Initial Cr (VI) concentration ~100 mg/dm^3.

Appendix III.

A

Initial pH	Initial Cr(VI) (mg/dm^3)	Cr total equil. (mg/dm^3)	Cr VI (mg/dm^3)	Cr III (mg/dm^3)
1.53	220	140.1	0.95	139.2
2.00	221	69.8	29.46	40.34
3.00	223	120.4	120.99	-0.58
4.00	221	144.6	144.93	-0.30
5.00	220	149.6	150.00	-0.37
6.00	223	169.3	169.76	-0.44
6.99	220	179.0	179.90	-0.91
7.90	227	192.0	192.57	-0.57
9.00	225	191.7	191.30	0.42

B

Initial pH	Initial Cr(VI) (mg/dm^3)	Cr total equil. (mg/dm^3)	Cr VI (mg/dm^3)	Cr III (mg/dm^3)
2.00	221	69.80	29.46	40.34
2.20	221	68.75	50.68	18.08
2.40	221	69.72	70.31	-0.60
2.60	222	81.49	81.39	0.10
2.80	222	106.37	106.73	-0.36
3.00	223	120.41	120.99	-0.58
3.20	220	131.88	131.12	0.76
3.40	221	136.44	136.82	-0.39
3.60	220	139.14	138.73	0.42
3.80	221	142.47	142.53	-0.06

(A&B) St. dev. for equil Cr (t) (0.0474-1.937), St. dev. for equil. Cr (VI) (0.0132-1.272).

Table 6.20. Chromium Equilibrium data of chromium (VI) sorption on dry C160 at 25° C. Initial Cr (VI) concentration ~100 mg/dm^3, A) pH 1-9 B) pH 2-3.8.

Initial pH	Final pH	Sorbed (mg/g)
1.54	1.63	64.53
2.00	2.47	122.5
2.20	2.74	123.7
2.40	3.00	121.8
2.60	3.94	113.7
2.80	4.50	92.72
3.00	5.11	83.50
3.20	5.30	71.12
3.40	5.41	68.53
3.60	5.47	65.51
3.80	5.49	63.64
4.00	5.65	62.24
5.00	5.73	56.99
5.99	6.34	43.55
6.99	6.93	33.34
7.98	7.12	28.41
9.00	7.18	27.10

St. dev. for sorbed values (0.0481-2.305).
St. dev. for final pH values (0.0042-0.087).

Table 6.21. Chromium (VI) sorption on dry C160 at 25° C at different pH values. Initial Cr (VI) concentration ~220 mg/dm^3.

Appendix III.

Ce, Equil. Concn. (mg/dm^3)	Cr sorbed (X) (mg/g)
25.05	20.28
55.75	36.01
127.35	58.80
203.23	78.18
287.59	91.70
372.40	103.08
557.80	115.89
836.70	131.33

St. dev. for Ce (0.1414- 1.697).
St. dev. for X (0.346- 1.722).
Table 6.22. Sorption of Chromium (VI) on wet C160 at 25°C. (Initial pH 7).

Ce, Equil. Concn. (mg/dm^3)	Cr sorbed (X) (mg/g)
7.80	34.42
23.51	62.09
75.07	101.90
141.30	129.03
214.38	151.16
301.35	161.77
479.59	178.54
774.59	182.96

St. dev. for Ce (0.195- 1.923).
St. dev. for X (0.117 - 1.543).
Table 6.23. Sorption of Chromium (VI) on wet C160 at 25°C. (Initial pH 5).

Ce, Equil. Concn. (mg/dm^3)	Cr sorbed (X) (mg/g)
0.25	40.45
4.93	77.23
59.51	113.67
126.44	140.88
187.93	170.75
273.10	182.69
452.79	202.30
745.75	207.70

St. dev. for Ce (0.023 -1.294).
St. dev. for X (0.321- 2.167).
Table 6.24. Sorption of Chromium (VI) on wet C160 at 25°C. (Initial pH 3).

Ce, Equil. Concn. (mg/dm^3)	Cr sorbed (X) (mg/g)
0.23	40.14
2.36	79.00
38.05	130.82
86.15	172.18
141.15	208.75
226.15	221.56
379.00	259.29
677.88	259.78

St. dev. for Ce (0.004- 1.72).
St. dev. for X (0.120- 2.166).
Table 6.25. Sorption of Chromium (VI) on wet C160 at 35°C. (Initial pH 3).

Ce, Equil. Concn. (mg/dm^3)	Cr sorbed (X) (mg/g)
0.51	53.21
1.23	105.67
37.22	169.97
82.00	224.88
157.89	252.34
216.15	278.39
317.81	310.32
633.23	318.54

St. dev. for Ce (0.016- 0.832).
St. dev. for X (0.161- 1.137).
Table 6.26. Sorption of Chromium (VI) on wet C160 at45°C. (Initial pH 3).

Appendix III.

Ce, Equil. Concn. (mg/dm^3)	Cr sorbed (X) (mg/g)
23.16	20.21
64.31	27.04
144.59	41.79
234.36	48.56
326.47	55.87
419.45	60.93
617.71	62.34
915.16	63.88

St. dev. for Ce (0.223 - 2.411).
St. dev. for X (0.198- 0.969).
Table 6.27., Sorption of Chromium (VI) on dry C160 at 25°C. (Initial pH 7).

Ce, Equil. Concn (mg/dm^3)	Cr sorbed (X) (mg/g)
9.44	30.68
41.87	43.84
119.69	60.39
197.02	70.79
283.72	81.28
382.78	87.09
581.58	89.45
881.08	90.23

St. dev. for Ce (0.141 - 1.704).
St. dev. for X (0.113- 0.638).
Table 6.28. Sorption of Chromium (VI) on dry C160 at 25 C. (Initial pH 5).

Ce, Equil. Concn (mg/dm^3)	Cr sorbed (X) (mg/g)
1.23	36.77
16.68	62.84
88.35	84.46
168.29	99.78
251.15	112.59
346.71	115.95
535.25	124.25
825.00	129.91

St. dev. for Ce (0.014- 1.739).
St. dev. for X (0.289- 1.52).
Table 6.29. Sorption of Chromium (VI) on dry C160 at 25 C. (Initial pH 3).

Ce, Equil. Concn (mg/dm^3)	Cr sorbed (X) (mg/g)
1.02	36.94
10.23	67.70
68.35	99.73
139.45	120.71
220.05	135.91
304.51	145.89
499.34	150.19
792.1	157.02

St. dev. for Ce (0.123 - 1.725).
St. dev. for X (0.232- 0.857).
Table 6.30. Sorption of Chromium (VI) on dry C160 at 35 C. (Initial pH 3).

Ce, Equil. Concn (mg/dm^3)	Cr sorbed (X) (mg/g)
0.23	37.36
6.40	70.38
42.58	119.26
100.10	151.44
170.90	173.04
256.50	182.81
439.50	196.46
725.08	206.08

St. dev. for Ce (0.064 - 1.556).
St. dev. for X (0.229 - 1.776).
Table 6.31. Sorption of Chromium (VI) on dry C160 at 45 C. (Initial pH 3).

Appendix III.

A

Time, hrs	C_t (mg/dm^3)	sorbed (mg/g)
2.08	55.95	155.26
4.17	40.75	222.84
7.67	21.20	314.30
11.67	11.14	360.06
19.67	4.39	391.36
25.17	2.73	398.62
28.67	1.68	403.18
44.67	1.49	403.71
54.17	1.39	403.84
68.67	1.30	403.85
96.67	1.23	403.84
168.67	1.13	403.93
194.17	1.08	403.97

wt used (wet) = 0.1668 g , moistrure % = 88%,

wt on dry basis = 0.0200, volume =100 ml, initialpH = 2.00.

Initial concentration = 87 mg/dm^3

B

Time, hrs	C_t (mg/dm^3)	sorbed (mg/g)
2.08	71.33	76.44
4.17	65.31	95.37
7.67	57.79	122.21
11.67	47.66	159.62
19.67	36.43	204.09
25.17	26.49	244.31
28.67	22.97	255.15
44.67	14.27	291.83
54.17	12.02	299.05
68.67	9.65	307.29
96.67	5.25	325.86
168.67	1.37	343.16
194.17	1.21	343.72

wt used = 0.0205, volume =100 ml., initialpH = 2.00.

Initial concentration = 87 mg/dm^3.

Table 6.32. Kinetics data for gold (III) on C160 at 25°C.
A) wet B) dry.

Appendix III.

A

Time, hours	C_t (mg/dm^3)	sorbed (mg/g)
3.00	75.85	45.14
8.50	58.77	72.11
16.00	45.66	92.62
25.50	34.73	109.8
31.75	29.37	117.3
49.50	20.75	131.2
54.83	17.50	135.6
72.50	13.88	141.4
97.50	12.10	143.8
103.5	10.62	145.8
130.0	9.94	146.4
170.0	9.28	147.0

wt used (wet) = 0.8425 g , moistrure % = 87.7%,
wt on dry basis = 0.1070 g, volume =200 ml, initialpH = 2.00.
Initial concentration = 100 mg/dm^3.

B

Time, hours	C_t (mg/dm^3)	sorbed (mg/g)
3.00	91.15	17.66
8.50	80.34	32.88
16.00	69.18	49.33
25.50	61.49	59.49
31.75	54.87	67.90
49.50	46.20	80.75
54.83	40.80	87.61
72.50	33.39	99.82
97.50	26.46	111.49
103.50	24.63	113.35
130.00	21.15	118.58
170.00	18.85	121.63

wt used = 0.1002 volume =100 ml, initialpH = 2.00.
Initial concentration = 100 mg/dm^3.

Table 6.33. Kinetics data for palladium(II) on C160 at 25°C.
A) wet B) dry.

Appendix III.

A

Time, hrs	C_t (mg/dm^3)	sorbed (mg/g)
2.50	89.63	23.63
18.17	68.15	53.77
25.67	59.46	63.99
42.17	45.35	83.50
51.67	39.63	89.99
65.67	28.04	106.38
93.67	23.23	112.89
117.67	16.30	123.10
129.67	14.07	125.89
165.67	11.22	129.82
178.66	9.67	131.72
191.17	8.61	132.89

wt used (wet) = 0.9734 g , moistrure % = 87.5%,
wt on dry basis = 0.1217, volume =200 ml., initialpH = 5.00.
C_o, the initial concentration = 104 mg/dm^3

B

Time, hrs	C_t (mg/dm^3)	sorbed (mg/g)
2.50	97.76	9.40
18.17	79.04	32.46
25.67	70.23	41.42
42.17	61.35	50.81
51.67	53.41	59.17
65.67	47.09	65.43
93.67	33.76	83.36
117.67	25.92	93.59
129.67	22.41	97.61
165.67	20.24	99.75
178.66	19.06	100.49
191.17	16.21	103.76

wt on dry basis = 0.1327, volume =200 ml., initialpH = 5.00.
Initial concentration = 104 mg/dm^3

Table 6.34. Kinetics data for silver (I) on C160 at 25°C.
A) wet B) dry.

Appendix III.

A

Time, hours	C_t (mg/dm^3)	sorbed (mg/g)
2.75	93.50	3.83
5.50	90.13	3.97
19.50	83.70	8.82
29.00	78.30	12.95
44.00	73.69	16.01
67.50	67.97	20.23
99.00	62.80	23.78
115.00	58.71	25.83
140.00	55.13	27.80
164.00	51.80	28.87
188.00	48.71	29.63
212.00	46.20	30.12

wt used (wet) = 0.8923 g , moistrure % = 86.7%,
wt on dry basis = 0.1307 g, volume =200 ml, initialpH = 5.00.
Initial concentration = 96 mg/dm^3.

B

Time, hours	C_t (mg/dm^3)	sorbed (mg/g)
2.75	94.75	1.91
5.5	90.52	3.31
19.5	86.44	4.51
29	82.44	6.36
44	78.95	7.49
67.5	74.11	10.04
99	69.96	11.63
115	66.17	12.74
140	62.84	13.86
164	59.43	14.50
188	56.13	15.01
212	53.53	15.10

wt on dry basis = 0.1311 g, volume =200 ml, initialpH = 5.00.
Initial concentration = 96 mg/dm^3.

Table 6.35. Kinetics data for platinum (II) on C160 at 25°C.
A) wet B) dry.

Appendix III.

A)

Equil. Concn. Ce (mg/dm^3)	X, sorbed (mg/g)
0.15	269.55
0.40	544.10
3.38	792.53
16.73	1010.72
61.25	1471.68
162.70	1740.84
326.08	1913.87

St. dev. for Ce (0.028-0.802).
St. dev. for X (0.0703- 3.147).

B)

Equil. Concn. Ce (mg/dm^3)	X, sorbed (mg/g)
1.85	196.06
7.22	382.51
13.90	562.32
35.44	722.50
124.25	921.58
256.00	1040.00
486.83	1103.50

St. dev. for Ce (0.007-0.711).
St. dev. for X (0.2305- 2.121).

C)

Equil. Concn. Ce (mg/dm^3)	X, sorbed (mg/g)
0.10	1579.41
36.30	2658.48
101.70	3009.04
176.10	3200.82
293.90	3409.47

St. dev. for Ce (0.028-1.272).
St. dev. for X (0.682-3.178).

D)

Equil. Concn. Ce (mg/dm^3)	X, sorbed (mg/g)
0.40	1190.63
50.25	1850.40
135.20	2095.00
237.80	2260.00
376.70	2390.00

St. dev. for Ce (0.113-1.414).
St. dev. for X (1.838- 3.069).

Table 6.36. Sorption of gold (III) on C160.

A) using wet sorbent at 25°C

B) using dry sorbent at 25°C

C) using wet sorbent at 45°C

D) using dry sorbent at 45°C

Appendix III.

A)

Equil. Concn. Ce (mg/dm^3)	X, sorbed (mg/g)
4.19	70.09
22.30	129.33
58.84	175.77
120.00	204.38
189.19	226.54
366.31	245.00
652.25	253.09

St. dev. for Ce (0.059-1.711).
St. dev. for X (0.0552- 1.713).

B)

Equil. Concn. Ce (mg/dm^3)	X, sorbed (mg/g)
10.24	65.91
36.10	121.05
100.76	146.50
169.95	169.15
256.75	178.73
449.38	184.01
744.28	188.03

St. dev. For Ce (0.160-1.520).
St. dev. For X (0.163-2.444).

C)

Equil. Concn. Ce (mg/dm^3)	X, sorbed (mg/g)
3.03	76.72
10.15	151.64
24.55	217.91
46.85	281.62
71.60	340.00
207.82	390.00
457.25	431.44

St. dev. For Ce (0.0212-1.386).
St. dev. For X (0.564- 1.683).

D)

Equil. Concn. Ce (mg/dm^3)	X, sorbed (mg/g)
4.43	69.97
9.50	140.86
27.35	201.07
66.79	245.73
106.25	289.52
251.63	330.17
523.88	349.57

St. dev. For Ce (0.066-1.945).
St. dev. For X (0.0703-1.079).

Table 6.37. Sorption of silver (I) on C160.

A) using wet sorbent at 25°C
B) using dry sorbent at 25°C
C) using wet sorbent at 45°C
D) using dry sorbent at 45°C

Appendix III.

A)

Equil. Concn. Ce (mg/dm^3)	X, sorbed (mg/g)
1.90	110.84
12.85	214.69
32.80	311.14
67.50	392.25
251.75	483.33
467.67	547.53

St. dev. for Ce (0.042-1.702).
St. dev. for X (0.471- 3.0648).

B)

Equil. Concn. Ce (mg/dm^3)	X, sorbed (mg/g)
19.80	78.91
54.77	147.07
112.50	202.10
178.97	255.17
387.50	308.73
622.08	350.25

St. dev. for Ce (0.5657-2.150).
St. dev. for X (0.588- 2.637).

Table 6.38. Sorption of Palladium (II) on C160

A) using wet sorbent at 25°C
B) using dry sorbent at 25°C

A)

Equil. Concn. Ce (mg/dm^3)	X, sorbed (mg/g)
3.94	13.10
22.18	22.74
50.65	40.38
122.70	63.16
215.10	69.30
301.00	80.32
396.17	83.99

St dev. for Ce (0.566 - 1.989).
St dev. for X (0.343- 2.062).

B)

Equil. Concn. Ce (mg/dm^3)	X, sorbed (mg/g)
7.59	9.02
22.55	20.12
52.25	34.75
134.75	47.70
220.10	57.98
313.75	62.86
411.17	64.47

St dev. for Ce (0.192 - 2.192).
St dev. For X (0.121- 1.308).

C)

Equil. Concn. Ce (mg/dm^3)	X, sorbed (mg/g)
9.18	7.88
27.20	16.74
61.00	28.30
145.15	40.10
234.50	47.74
332.17	49.51
429.17	51.63

St dev. for Ce (0.092-2.09).
St dev. for X (0.048-1.64).

D)

Equil. Concn. Ce (mg/dm^3)	X, sorbed (mg/g)
10.30	7.12
28.50	15.76
62.70	27.15
152.50	34.72
243.90	41.13
343.58	41.30
440.00	43.80

St dev. for Ce (0.113-1.471).
St dev. for X (0.006-0.769).

Table 6.39. Sorption data of platinum on C160 at 25 °C.

A) platinum (II) on wet sorbent
B) platinum (II) on dry sorbent
C) platinum (IV) on wet sorbent
D) platinum (IV) on dry sorbent

PUBLICATIONS

1. Cox M., El-Shafey E. I., Pichugin A. A. and Appleton Q. "Preparation and characterisation of a carbon sorbent from flax shive by dehydration with sulphuric acid", *J. Chem. Tech. Biotechnol.* **74**: 1-11 (1999).

2. Cox M., El-Shafey E. I., Pichugin A. A. and Appleton Q., "Removal of Mercury (II) From Aqueous solution on A Carbonaceous sorbent Prepared From Flax shive", *J. Chem. Tech. Biotechnol.* **75**: 1-9 (2000).

Journal of Chemical Technology and Biotechnology *J Chem Technol Biotechnol* 74:1019–1029 (1999)

Preparation and characterisation of a carbon adsorbent from flax shive by dehydration with sulfuric acid

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Abstract: A carbon adsorbent has been prepared from flax shive by treatment with sulfuric acid. Several factors have been considered in the preparation: reaction time, temperature, and the amount and concentration of sulfuric acid. The optimised conditions of preparation were based on the cation exchange capacity, yield and sorption performance for the metals cadmium and mercury(II). These two metals behave differently when adsorbed on the carbon. Thus cadmium sorption follows the cation exchange capacity data and the optimum conditions for preparing the carbon for this and other metals sorbed by an ion exchange mechanism were: 12 mol dm^{-3} sulfuric acid at a ratio of 1:9 (weight flax shive:volume acid), 25–30 min reaction time at 200 °C. Similar preparative conditions were found to give the optimum results for mercury sorption except that in this case, the temperature was 160 °C. The sorbent shows a much higher uptake for mercury than cadmium, which suggests that the sorption mechanism for mercury sorption is not only ion exchange. The sorbents retained a high level of moisture (>80%), and elemental analysis shows very low amounts of sulfur (~1%). Scanning electron microscopy shows that the carbon retains the fibrous texture of the original shive and X-ray diffraction shows that the carbons are amorphous. The presence of carboxyl, carbonyl and hydroxyl (or phenolic) groups is confirmed by infra-red spectroscopy.

Keywords: sorption; carbon; sulfuric acid; heavy metals; flax shive; environmental remediation

INTRODUCTION

The term 'activated carbon' is applied to group of materials that possess a highly developed internal surface area and porosity. They are extremely versatile adsorbents that are used in a wide range of applications for the removal of species from gases or liquids for purification or recovery of chemicals. They are generally manufactured from a wide range of carbonaceous materials of which wood, peat, lignite and coal are the most common. Other materials which result as a waste product from other manufacturing processes have also been used, the most common of these is coconut shell, but various fruit stones, eg apricot, plum; nut shells, and straw from cereal crops, eg wheat, cotton, have been also studied. Two general methods of preparation may be used, the first subjects the feed material to a temperature below 800 °C for a defined period of time to produce a char and remove volatile matter and tarry compounds which are formed as by-products. The carbon char can then be 'activated' to produce the required surface area and pore structure by heating at a higher temperature, between 800 and 1200 °C in an oxidising atmosphere. The alternative process involves chemical activation, where the feed material is impregnated with certain chemicals, eg zinc chloride or phosphoric acid prior to the carbonisation process at 400–600 °C in the absence of air. Carbonisation of agricultural materials can also be performed by dehydration with sulfuric acid and phosphoric acid at low temperature, resulting in a colloidal and porous active charcoal.[1–3] Few studies have been reported on this type of carbon which has been variously named collactivit,[4,5] colloidal carbon[6] and activated carbon.[7] Some Japanese researchers have used some other names for such carbon, thus Mizuno and Kato called this carbon first 'shitsujun kasseitan' (moistened active charcoal) and later 'suike kasseitan' (hydrated active charcoal),[2,8] terms also used by Hanzawa and Satonaka.[2,9] Komoto used the terms 'sulfuric acid-activated carbon' and 'ion exchange activated carbon'.[10]

These activated carbons prepared by sulfuric acid dehydration showed their highest activity in the moistened state and this decreases on drying.[9,10]

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Komoto[10] prepared an active material from saw-dust using sulfuric acid and studied the conditions of preparation and the properties of the resulting carbon. The product contained 72% moisture and possessed both decolourising and ion-exchange properties. The latter was related to the presence of carboxylic, sulfonic and hydroxyl groups found on the surface of the carbon.

Pichugin *et al*[11] prepared a carbon from flax shive using sulfuric acid and showed that the sorbent had a good sorption affinity for the removal of heavy metals from water. This paper extends the work by optimising the preparation, characterising the product and giving some results for the removal of cadmium and mercury(II) from aqueous solution.

Flax (*Linum usitatissimum*) is a versatile plant providing a fibre and also an oilseed, linseed, both of which have economic potential. During the processing of the flax plant for fibre, flax shive is separated as a woody by-product from the retted flax straw by scutching[12] and for every tonne of fibre, 2.5 tonnes of shive will be produced.[13] In its natural state shive has no nutritional value and if it is to be used as animal feed, has to be first upgraded[13] with a biological or a chemical treatment. Exploitation of the shive has been limited due to its chemical composition, consisting largely (90–98%) of three polymeric materials: cellulose, hemicellulose and lignin.

Flax currently receives a subsidy from the European Commission so that the acreage devoted to growing of flax is increasing. This means that the by-product, flax shive, is also produced in large quantities in Europe and as indicated above there is no ready market for this material. So this study was carried out to try to find a useful product from this waste in the form of a sorbent for heavy metals. This paper describes the preparation and characterisation of the sorbent and its performance in the removal of metals from aqueous solution. These studies concentrated on metals known to have an environmental significance, such as cadmium and mercury, as it was envisaged that the sorbent could provide a useful cheap method of purifying waste streams containing these metals.

EXPERIMENTAL

Materials

Mercury and cadmium stock solutions were prepared from Aldrich Chemicals Analar grade chemicals using distilled deionised water. Sulfuric acid (98%) was supplied by Breckland Scientific Supplies.

Flax shive was supplied by NFO[†] as chopped pieces with diameters ranging from ~1 to ~3 mm and length from ~0.5 cm to ~2 cm, having an apparent density of ~0.17 g/cm^{-3}. The shive had a composition of: cellulose 46.0%; hemicellulose 26.2%; lignin 23.1%; lipid 1.2%; nitrogen 0.2% and ash 3.1%, (Gilbertson, private communication).

Preparation of the carbon sorbents

Carbon sorbents were prepared by the dehydration of flax shive using the same general methods but varying the concentrations and relative amounts of sulfuric acid, temperatures and reaction times.

Details are given below of the preparation of one of the sorbents, carbon C160, as an example of the general method used.

Sulfuric acid (12 mol dm^{-3}) was added to clean air-dried flax shive (15.0 g) in a ratio of 1:9 (wt of shive: volume of sulfuric acid). The mixture was then heated to 155–160 °C for 15–20 min with occasional stirring. Following the addition of the acid, the temperature was kept in this range for the required reaction time, 25–30 min. The resulting black mixture was allowed to cool, and the spent sulfuric acid (black liquor) was filtered off under vacuum. The carbonised material was washed several times with distilled water until the pH of the filtrate was between 4 and 5.

For experiments with the wet sorbent the product was stored under distilled water which was replaced from time to time (twice a week) to avoid any possible bacterial growth. Before use, the wet sorbent was washed with a stream of distilled water between two mesh sieves, 1 mm and 212 µm, to remove fine particulates and to select a suitable size range for the sorption experiments. The sample was filtered and left under suction for 30 min to remove any surface water from the particles. Samples were then weighed to determine the moisture content, and for the sorption experiments.

For experiments with dry sorbent the product was dried in an oven at 120 °C overnight to constant weight, transferred to a desiccator to cool and finally stored in dry, clean and well sealed polyethylene flasks. The carbon was ground and passed between 1 mm and 212 µm sieves for use in the sorption experiments.

To optimise the preparation of the sorbent the concentration of sulfuric acid; reaction time; temperature and the ratio of shive to the amount of sulfuric acid in the above method were varied. The following series of experiments were performed:

(i) *Effect of reaction time*: ~15 g shive + 12 mol dm^{-3} sulfuric acid at a ratio of 1:9, wt/vol at 155–160 °C for 10, 20, 30, 45 and 60 min.

(ii) *Effect of reaction temperature*: ~15 g shive + 12 mol dm^{-3} sulfuric acid at a ratio of 1:9, wt/vol at 100, 120, 140, 160, 180 and 200 °C for 25 min.

(iii) *Effect of ratio of reactants*: ~15 g shive + 12 mol dm^{-3} sulfuric acid with relative ratios 1:3, 1:5, 1:7, 1:9 and 1:12 wt/vol at 155–160 °C for 25 min.

(iv) *Effect of sulfuric acid concentration*: ~15 g shive + 10, 12, 14, 16 and 18.2 mol dm^{-3}

[†] Natural Fibre Organisation, Church Court, Clewers Hill, Waltham Chase, Hampshire, SO32 2LN, UK

sulfuric acid at a ratio of 1:9 wt/vol at 155–160°C for 25 min.

The samples were washed, dried and stored as mentioned above. The samples used in the optimisation of the preparation conditions were all used in the dry state within 20 days from the preparation time.

Sorbent samples for the study of metal uptake, after preparation, washing and drying, were ground to a size between 1 mm and 212 μm and stored in a desiccator under vacuum prior to the following experiments being carried out.

Acidity of the sorbents

A sample of sorbent (0.100 g) was mixed with distilled decarbonated water (20 cm^3) and two drops of acetone, to facilitate wetting of the sample, and refluxed for 15 min. After cooling the pH of the sludge was obtained using a pH meter and combined pH electrode.[14,15]

Cation exchange capacity

The cation exchange capacity (CEC) of the carbon was measured using a standard ASTM method.[16]

An accurately weighed sample of the dried sorbent (0.6 g) was placed in a 100 cm^3 flask, hydrochloric acid, Analar grade (50.00 cm^3, 0.5 mol dm^{-3}) added and the mixture shaken for 1 h. (Controlled Environment Incubator Shaker, New Brunswick Scientific Co, Inc Edison, NJ USA). After filtration the solid was washed with distilled deionised water until a sample (10 cm^3) of the wash water showed no precipitate with 1% silver nitrate solution (3 cm^3). The moistened sorbent was then transferred to a clean 100 cm^3 flask and shaken again in the incubator for 1 h at room temperature with barium acetate solution (50 cm^3, 0.25 mol dm^{-3}). The sorbent was removed by vacuum filtration, washed with distilled deionised water (3×50 cm^3) and the filtrate and washings titrated with 0.1 mol dm^{-3} sodium hydroxide using phenolphthalein as indicator.

Sorption of mercury(II) and cadmium(II) from aqueous solution

Samples of the sorbents (~0.0660 g) were added to a mercury(II) chloride solution (50 cm^3 of 200 mg dm^{-3}) at an initial pH ~5.00. For the sorption of cadmium, the sorbent (0.1000 g) was added to a cadmium sulfate solution (50 cm^3 of 100 mg dm^{-3}) at an initial pH 6.0. The samples were shaken continuously in the incubator shaker at a shaking rate of 150 rpm at 25°C.

Preliminary kinetic experiments for the sorption of cadmium(II) and mercury(II) from solution using the dried carbon C160 showed that equilibrium was attained in about 3 h for cadmium(II) and about 120 h (5 days) for mercury(II). Subsequent experiments with mercury(II) sorption were left in the shaker incubator to attain equilibrium for 120 h, and cadmium samples were left for 10 h.

Once equilibrium had been attained the solution was sampled, approximately 1 cm^3 of 0.5 mol dm^{-3} nitric acid added to minimise metal adsorption losses on the glass and the samples diluted to give appropriate concentrations for analysis by ICP-AES. This was carried out using a Perkin-Elmer Plasma 40 Emission Spectrometer at wavelengths 253.652 nm and 214.438 nm for mercury and cadmium respectively. The final pH of the solution at equilibrium was also measured.

Characterisation of the carbon sorbent

Physical techniques used to characterise the sorbent included:

(i) X-ray powder diffraction using a Philips PW 1730 generator with a Philips 1050/25 powder goniometer, and Philips PW 1390 measuring electronics using Cu K_α as the incident radiation.

(ii) Scanning electron microscope analysis was carried out on the dried carbon sorbents using a Camscan CS44 scanning electron microscope to obtain textural and surface information before sorption and, after sorption, to check for any precipitation of metals or compounds as a result of the sorption process.

(iii) Electron microprobe elemental analysis was carried out on the Camscan CS44 using a Camscan Editor Energy Dispersive Analysis (EDAX) system in the standard-less mode (manufacture's calibrations).

(iv) Surface area determination of some carbon sorbents was measured in the laboratories of MCA Services.[†] The size of the carbon used was between 1 mm and 212 μm and the surface area was measured via nitrogen adsorption (volumetric technique/Sorptomatic). Activation and degassing were carried out at 120°C for 3 h under vacuum.

(v) Fourier transform infra-red spectrophotometry was used to determine the surface functional groups on the sorbents. The sorbent samples were dried in an oven overnight to remove any moisture retained from the atmosphere which could interfere with observation of hydroxyl groups on the surface. This was followed by encapsulation into dry potassium bromide (KBr) discs. The discs were scanned in transmission mode using a Perkin-Elmer Paragon 1000 FTIR from 800 to 4000 cm^{-1} with background subtraction and using a total of 16 scans.

Carbon, hydrogen, nitrogen and sulfur content of samples of C160 and C200 were analysed by MEDIC Ltd,[‡] using standard methods.

[†] MCA Services, Melbourn Science Park, Melbourn, S Cambridgeshire, SG8 6EJ, UK

[‡] MEDIC Ltd, Brunel Science Centre, Cooper's Hill Lane, Englefield Green, Egham, Surrey, TW20 0JZ, UK

Table 1. Yield of carbon sorbents as a function of preparation conditions

Reaction Time (min)^{a,b,c}	Yield (%)	Reaction Temp (°C)^{a,b,d}	Yield (%)	Ratio of flax shive: H_2SO_4 (wt: vol)^{a,c,d}	Yield (%)	H_2SO_4 concn (mol dm^{-3})^{b,c,d}	Yield (%)
10	60.2	100	50.4	1:5	57.3	10	46.7
20	59.0	120	54.8	1:7	58.2	12	58.3
30	58.5	140	57.0	1:9	58.3	14	56.9
45	58.2	160	58.3	1:12	57.6	16	53.4
60	58.0	180	54.2			18.2	51.3
		200	50.2				

[a] Sulfuric acid concentration 12 mol dm^{-3}; [b] flax shive: H_2SO_4 ratio 1:9, [c] reaction temperature 160°C, [d] reaction time 25 min

Table 2. Cation exchange capacity of the carbon sorbents as a function of preparation conditions

Reaction time (min)^{a,b,c}	CEC (meq g^{-1})	Reaction temp (°C)^{a,b,d}	CEC (meq g^{-1})	Ratio of flax shive: H_2SO_4 (wt:vol)^{a,c,d}	CEC (meq g^{-1})	H_2SO_4 concn (mol dm^{-3})^{b,c,d}	CEC (meq g^{-1})
10	1.47	100	1.00	1:5	1.43	10	1.18
20	1.50	120	1.19	1:7	1.65	12	1.72
30	1.71	140	1.35	1:9	1.71	14	2.42
45	2.03	160	1.71	1:12	1.69	16	2.77
60	2.12	180	2.31			18.2	2.94
		200	2.78				

[a] Sulfuric acid concentration 12 mol dm^{-3}; [b] flax shive: H_2SO_4 ratio 1:9, [c] reaction temperature 160°C, [d] reaction time 25 min

RESULTS

Optimisation of the sorbent preparation

Effect of changing variables on yield of sorbent

The effect of reaction time on the carbon reflects a slight decrease in yield as shown in Table 1. Changing the weight/volume ratio of reactants shows very little variation in the yield, although it was found that lower ratios such as 1:3 were not capable of carbonising some hard pieces of the flax shive. It also appears that with the ratio of 1:5 there was virtually no residual acid left and some hard pieces of shive were present which were not well carbonised.

Variation of concentration of acid and temperature both showed a significant and similar effect on the yield. While with 10 mol dm^{-3} sulfuric acid the yield was low, it reached a maximum at 12 mol dm^{-3} and then gradually decreased to 18.2 mol dm^{-3}, ie concentrated sulfuric acid. The filtrate in the case of 10 mol dm^{-3} sulfuric acid was darker than the other concentrations used. Using the optimal concentration of the acid (12 mol dm^{-3}) at different reaction temperatures, it was found that at 100°C a low yield was obtained and the filtrate was very black. The yield gradually increased with temperature until at 160°C the yield reached its maximum value. Further increase in temperature decreased the yield. It was also observed that the filtrate became lighter as the temperature increased.

Effect of variables on cation exchange capacity

Cation exchange capacity (CEC) studies were undertaken to obtain information about the total amount of exchangeable cations that can be bound by the sorbent. To measure this the relevant functional groups on the sorbent were first protonated with hydrochloric acid. Following filtration and washing free of acid with distilled water, the sorbent was placed in a barium acetate solution and the exchangeable protons replaced with barium ions. The released protons were then titrated with standard sodium hydroxide in the presence of an indicator.

The results, expressed as meq g^{-1}, are presented in Table 2 and Fig 1–4, and show that the CEC increases with reaction time while there is no significant change in CEC with the change of the ratio of sulfuric acid in the range 1:5–1:12. However a large increase in CEC occurs as the temperature increases, while maintaining the other factors constant, so that using 12 mol dm^{-3} sulfuric acid an approximate three-fold increase in CEC occurred for the carbon heated at 200°C over that for the sample prepared at 100°C.

Similar results were found when the effect of acid concentration was investigated. As the concentration of the sulfuric acid increased the CEC showed an approximate three-fold increase between 10 and the concentrated form of acid (18.2 mol dm^{-3}).

Acidity of the sorbents

The pH of the aqueous slurry of the carbon material provides a convenient indicator of the surface groups on carbon. The pH of the carbon slurry reflects the surface acidic groups which, in this case, are mainly carboxylate ions with only a very slight addition from

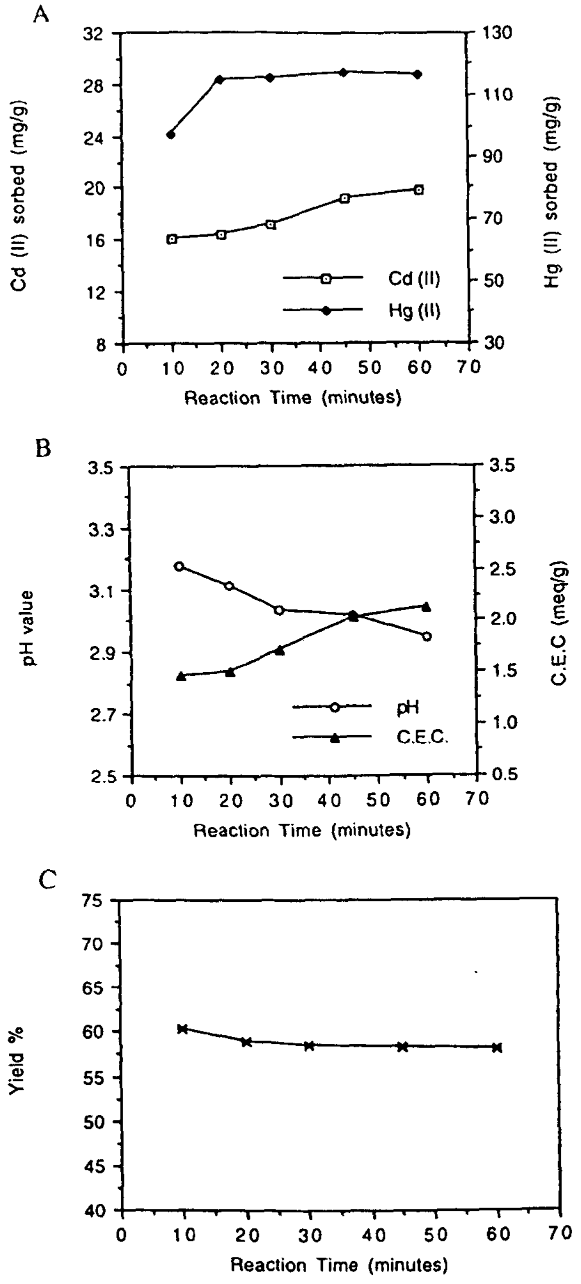

Figure 1. Effect of reaction time on the properties of carbon sorbents.

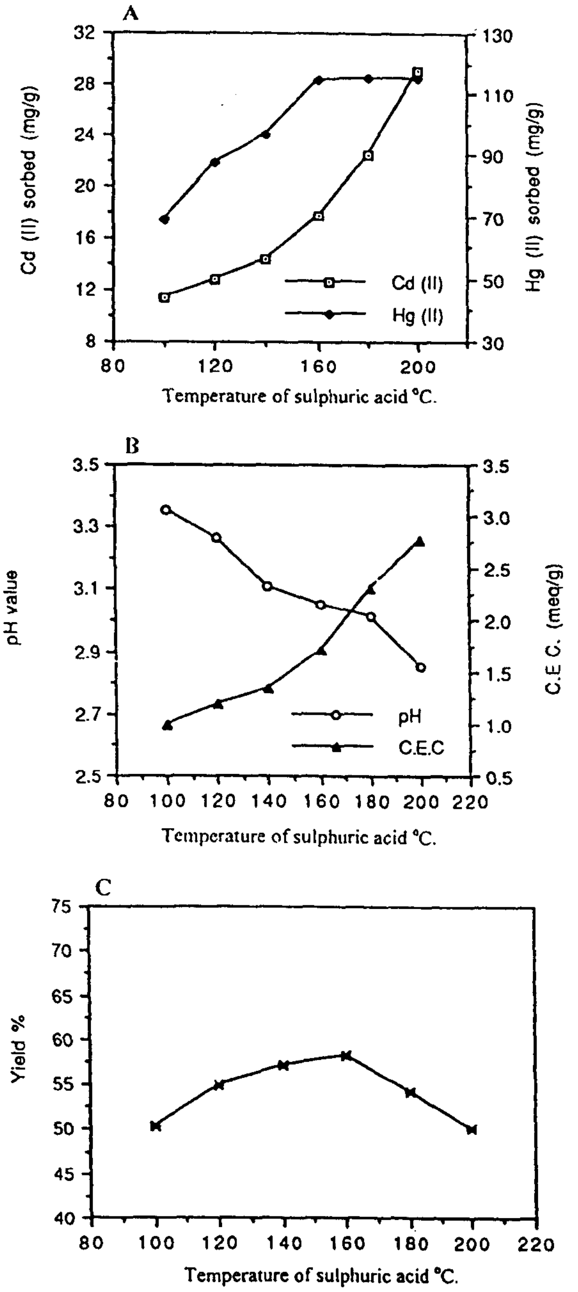

Figure 2. Effect of sulfuric acid temperature on the properties of the carbon sorbents.

sulfonic groups due to the low concentration of sulfur in the sorbent. As the concentration of such functional groups increases on the carbon surface, the pH of the carbon decreases.

Table 3 shows the pH values of the carbon sorbents. A slight decrease in the pH value is found as the reaction time increases, but there is no real significant change when different ratios of sulfuric acid are used. An obvious change in the pH was obtained by increasing the temperature and increasing the concentration of the sulfuric acid. These results are similar to those found for the cation exchange capacity, Figs 1–4.

Moisture content

The moisture content for the whole range of carbon sorbents is very similar with values ranging from ~83% to 88% (table 4). This moisture is present due to the swelling of the carbons during preparation and washing.

Sorption of cadmium (II)

Cadmium(II) sorption shows similar results to that of cation exchange capacity, Figs 1–4. Thus as the reaction time increases cadmium(II) uptake increases, and there is a slight decrease for the carbon prepared from the 1:5 weight/volume ratio while it is approximately the same for the other ratios. A large increase in uptake occurs as the reaction temperature increases, with a three-fold increase in uptake on to the carbon

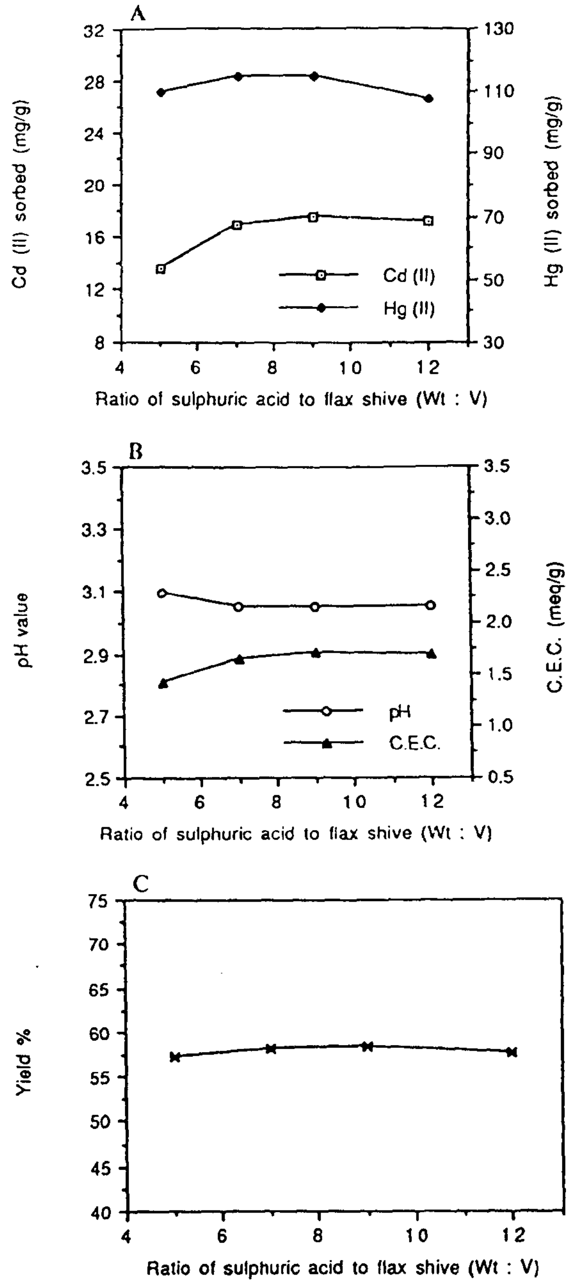

Figure 3. Effect of ratio of flax shive to sulfuric acid (12 mol dm^{-3}) on the properties of the carbon sorbents.

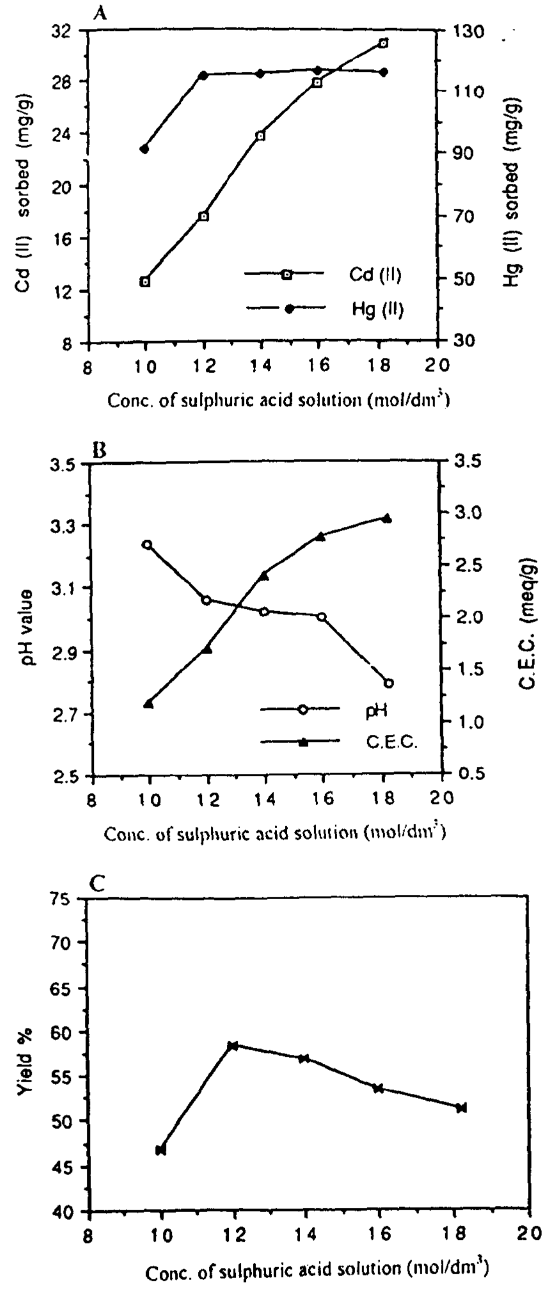

Figure 4. Effect of sulfuric acid concentration on the properties of the carbon sorbents.

prepared at 200 °C compared with that prepared at 100 °C. A similar three-fold increase was also found as the concentration of the sulfuric acid increases, from 10 to 18.2 mol dm^{-3}. Measurement of the solution pH after sorption showed a decrease that followed an inverse trend to the amount of cadmium(II) sorbed.

The relatively fast kinetics, the similarities to the cation exchange capacity results, and the pH of the final solutions indicate that the mechanism of sorption of cadmium(II) onto the carbon sorbents is most probably due to an ion exchange process.

Sorption of mercury(II)

Mercury(II) behaves in a different way to that found for cadmium(II) and the cation exchange capacity data, thus, for example, mercury takes 120 h to reach equilibrium compared with 3 h for cadmium. This indicates a different sorption mechanism for mercury(II) from cadmium(II).

The first feature to note in the metal sorption results (Figs 1(A), 2(A), 3(A), 4(A)) is that the uptake of mercury(II) is very much higher than cadmium(II) under the same conditions. Also although carbons prepared at the lowest reaction time, 10 min, show lower mercury(II) uptake, no significant increase in the mercury(II) uptake was observed for longer reaction periods (Fig 1A). Very little change in mercury(II) sorption occurred with variation of the

Table 3. pH values of the carbon sorbents as a function of preparation conditions

Reaction time (min)^{a,b,c}	pH	Reaction temp (°C)^{a,b,d}	pH	Ratio of flax shive: H_2SO_4 (wt:vol)^{a,c,d}	pH	H_2SO_4 concn (mol dm^{-3})^{b,c,d}	pH
10	3.18	100	3.35	1:5	3.10	10	3.24
20	3.11	120	3.26	1:7	3.05	12	3.06
30	3.03	140	3.11	1:9	3.05	14	3.02
45	3.01	160	3.05	1:12	3.05	16	3.00
60	2.95	180	3.01			18.2	2.79
		200	2.85				

[a] sulfuric acid concentration 12 mol dm^{-3}; [b] flax shive: H_2SO_4 ratio 1:9; [c] reaction temperature 160 °C; [d] reaction time 25 min.

Table 4. Moisture content of carbon sorbents as a function of preparation conditions

Reaction time (min)^{a,b,c}	Moisture (%)	Reaction temp (°C)^{a,b,d}	Moisture (%)	Ratio of flax shive: H_2SO_4 (wt:vol)^{a,c,d}	Moisture (%)	H_2SO_4 concn (mol dm^{-3})^{b,c,d}	Moisture (%)
10	84.20	100	84.99	1:5	83.17	10	84.19
20	86.08	120	84.83	1:7	87.00	12	86.61
30	86.67	140	86.44	1:9	86.74	14	86.67
45	86.35	160	86.95	1:12	87.62	16	86.35
60	84.90	180	85.18			18.2	84.90
		200	85.34				

[a] sulfuric acid concentration 12 mol dm^{-3}; [b] flax shive: H_2SO_4 ratio 1:9; [c] reaction temperature 160 °C; [d] reaction time 25 min.

shive: sulfuric acid ratio (Fig 3A), but mercury(II) uptake does increase with reaction temperature up to 160 °C after which it is approximately constant. Here, unlike cadmium, the difference in mercury(II) uptake at 160 °C compared with that at 100 °C is less than two-fold (Fig 2A). Finally little variation in sorption behaviour was found with changing acid concentration (Fig 4A).

A comprehensive study of the mercury(II) sorption and mechanism of adsorption has been carried out and will be published later.

DISCUSSION

Effect of sulfuric acid on flax shive

Hemicelluloses are readily hydrolysed by dilute acids and bases, even water at high temperatures causes a conversion of hemicellulose into soluble products.[17] Cellulose, as a result of its high crystallinity and cohesive density, is insoluble in water[18] and more resistant to dilute acids,[17] however strong acids, strong alkalis, and concentrated salt solutions can swell and even dissolve cellulose.[19] Thus Vanzetti[6] obtained a black colloidal suspension by mixing concentrated sulfuric acid at room temperature with carbohydrates (cellulose and sugars). Also Nikitin noted that concentrated sulfuric acid rapidly dissolves cellulose in the cold, forming a clear solution which on standing blackens as a result of carbonisation of cellulose.[20]

Carbonisation also occurred when dilute sulfuric acid was used at higher temperatures. Hanzawa and Satonaka[9] prepared carbon from saw-dust by treatment with different concentrations of sulfuric acid at 120 or 150 °C for times up to 24 h. They found the best results were obtained using 70 or 98% acid concentration and although carbonisation occurred with 15 and 40% acid, a lower yield was obtained.

The work reported in this paper confirms these results showing that although carbonisation did take place using 4, 6, 8 mol dm^{-3} acid the yield of the carbon and the sorption capacity for both cadmium(II) and mercury(II) was improved by using 12 mol dm^{-3} acid. Lignin is the third major component of flax shive, and it has been shown on studies treating saw-dust with concentrated sulfuric acid that the polysaccharides are hydrolysed and can be removed whereas lignin is left as a non-hydrolysed dark-coloured residue.[20]

Optimising the preparation of carbon by dehydration of any woody material is a difficult task since it depends on the type of raw material, the method of treatment, and the intended use for the carbon. From this study it is also evident that the method of preparation influences the formation of active groups on the carbon which can affect the sorption behaviour of different metals. Pichugin *et al*[11] investigated the preparation of carbon from flax shive by dehydration using sulfuric acid, basing the optimisation on the sorption of mercury(II) and the yield of the sorbent. These studies recommended using 12 mol dm^{-3} sulfuric acid at 150–155 °C with a weight ratio of 1: 5–6 shive:acid and a reaction time for 15–20 min. In the current work three main factors were chosen to assess the preparation of a suitable sorbent:

- sorption capacity of metal ion from solution (Hg(II) and Cd(II))
- yield of the carbon
- consumption of acid and energy

Comparing the difference in yield of carbon (Figs 1(C), 2(C), 3(C), 4(C)) shows that reaction tempera-

Table 5. Elemental analysis and microprobe elemental analysis carbon sorbents C160 and C200

Adsorbent	Element (wt%) *C*	*H*	*N*	*O*	*S*
C160	59.87	3.20	-		1.13
	66.38_m		-	32.20_m	1.42_m
C200	59.58	2.60	-		0.84
	64.82_m		-	34.03_m	1.15_m

$_m$ refers to the microprobe elemental analysis which was performed in a standard-less mode and wt percentage was measured excluding the other components including hydrogen and other trace metals

ture and concentration of sulfuric acid have the greater effect. Both the reaction time (Fig 1), and weight-volume ratio (Fig 3) have little effect on the yield and other related properties. The difference between these results and those obtained by Komoto,[10] who found that change of sulfuric acid concentration had little effect and increasing reaction temperature decreases the sorbent yield, may be related to the different conditions of preparation and the different starting materials.

If flax shive is considered as a woody material then three processes can take place by the reaction of sulfuric acid: swelling and hydrolysis, carbonisation and partial oxidation. The extent of each reaction depends mainly on temperature and concentration of the acid and to some extent on the reaction time. Thus room temperature and low sulfuric acid concentration enhances hemicellulose hydrolysis and causes cellulose to swell. Increasing the reaction temperature at low concentrations of sulfuric acid starts the process of carbonisation that increases with increasing sulfuric acid concentration. Partial oxidation of the carbonised product also takes place at high temperature and high acid concentration. These processes can be used to explain the above experimental results.

With respect to reaction time (Fig 1), it is found that as this increases the yield and pH of the product decrease slightly while the sorption of cadmium(II) and the cation exchange capacity increase slightly. This is probably the result of the evaporation of water from the reaction mixture and the resulting increase in acid concentration leading to an increase in oxidation of the carbon. This in turn leads to partial fragmentation of the carbon skeleton and hence a slight decrease in the yield and an increase in the carbon–oxygen groups on the surface of the product which act as additional cation exchange groups.

Varying the reaction temperature using 12 mol dm^{-3} sulfuric acid (Fig 2), the yield increases to a maximum at 160 °C and then decreases. At the lower temperatures, eg 100 °C, hydrolysis of the hemicellulose, which acts as a binding agent between cellulose and lignin,[19] occurs. This leads to a loss of lignin from the reacting shive pieces, the filtrate becomes dark and a low yield of residual material is obtained. Oxidation at such low temperatures is not significant and the lower cation exchange capacity and cadmium(II) sorption reflect this. As the temperature increases, evaporation of water takes place, the acid becomes more concentrated, and carbonisation of the polysaccharides increases, until it reaches a maximum at 160 °C. Under these conditions lignin seems to be encased inside the carbon particles where it is retained and so the filtrate shows less blackening than at the lower temperatures. Oxidation again leads to an increase in the carbon–oxygen groups as shown by increases in CEC and cadmium(II) sorption. As the temperature increases further to 200 °C, the oxidation process continues to create more carbon–oxygen groups and also maybe fragmentation of the carbon particles begins giving a lower yield of sorbent with higher CEC and cadmium sorption.

Similar results were found when the concentration of the sulfuric acid was changed (Fig 4). Using 10 mol dm^{-3} sulfuric acid, significant hydrolysis occurs accompanied by lignin fragmentation which releases it from the carbon particles. As a result, a darker filtrate is found and a lower yield of sorbent obtained. At 12 mol dm^{-3} acid the yield reaches a maximum, then with higher concentrations of acid, the carbonised product is oxidised which produces a higher concentration of the carbon–oxygen groups on the surface and fragmentation to lower molecular weight compounds giving lower yields. The CEC, sorbent pH, and cadmium sorption results reflect the greater increase in the functional groups as acid concentration increases.

Two carbons were selected for further studies, both using the same sulfuric acid concentration (12 mol dm^{-3}) and ratio of flax:acid (w/v 1:9) but varying in their reaction temperature. Thus C160 was treated at 160 °C and C200 at 200 °C, both for 25–30 min. The sample C160 was best suited for the sorption of reducible metals such as mercury(II), whereas C200 performed best for metals such as cadmium(II) which follows the CEC value.

Elemental analysis

The chosen sorbents were subjected to elemental analysis both by conventional micro-analysis CHNS and also using electron microprobe attachment to the scanning electron microscope. The results (Table 5) show little variation in CHS between the samples. Nitrogen, which was found in the composition of flax shive as a minor component, does not appear in the product, probably as a result of oxidation during the

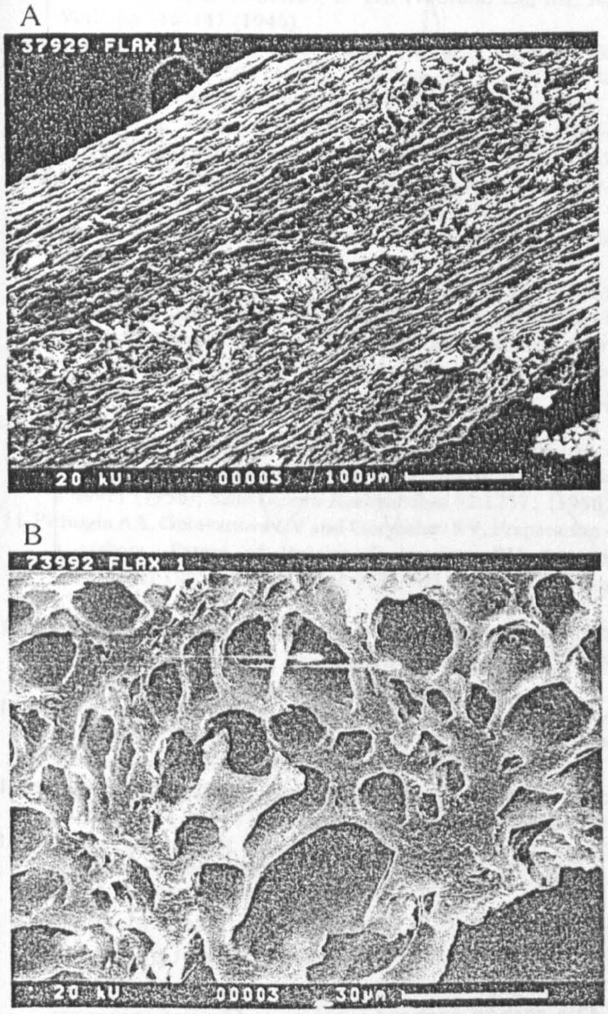

Figure 5. Scanning electron micrograph of the carbon C160: (A) exterior surface. (B) cross-section.

preparation. The total percentage of C, H and S in C160, 64.20%, is a little higher than in C200, 63.02%. This suggests that there may be more oxygen in C200 than C160, which is also indicated by the higher CEC in the former sample arising from an increase in C—O functional groups. Electron microprobe elemental analysis, even though it was performed in a standardless mode, showed a similar pattern for carbon and sulfur (Table 5). The oxygen results support the observation of a higher concentration of C—O groups in the C200 sorbent.

Surface area

The surface area of both of carbon C160 and C200, respective apparent density 0.243 and 0.278 mg cm^{-3}, was measured by nitrogen adsorption. The sample particles ranging from 1 mm to 212 μm were activated at 120 °C for 3 h under high vacuum to ensure the desorption of any sorbed gases or vapours. The higher temperatures that are used for activated carbons (200–350 °C) were avoided to minimise any possible chemical changes that might take place at the carbon surface.

The surface area was calculated from the BET equation.[21] The surface area of the carbons C160 (19 m^2 g^{-1}) and C200 (22 m^2 g^{-1}) are not much different to that of peat (about 27 m^2 g^{-1}) and lower than that of lignite (around 100 m^2 g^{-1}).[22] The untreated peat and lignite contain many complex organic waxes and esters and these result in the peat and lignite having a closer non-porous structure with little or no micropores.

The carbons produced by dehydration, C160 and C200, keep their fibrous woody structure and their pore structure seems to be derived from the tubular pores of the dehydrated woody material (Fig 5). On drying, the carbon becomes compacted so the opportunity of micropores occurring in the structure is either very low or non-existent. This type of carbon thus has a very high organic content with compounds such as lignin, esters, humic substances and waxes probably present. X-ray powder diffraction spectra were obtained for both samples using CuK$_\alpha$ radiation and as no peaks could be identified both carbons seem to be amorphous.

Ash content

The ash content of C160 (0.51%) seems to be less than C200 (0.87%). This may be related to the lower yield of the carbon at 200 °C, with the result that the percentage of ash seems to be relatively higher than in C160.

FTIR studies

Even though the carbonised materials, C160 and C200, are rather complex, FTIR still can give some information about the probable functional groups on the surface. FTIR spectra for C160 and C200 are shown in Fig 6. The intense and broad bands at 3388 cm^{-1} (C160) and 3387 cm^{-1} (C200) are connected with (O—H) stretching vibrations. As the frequency of free OH groups is sharp and are located above 3500 cm^{-1},[23] these vibrations are associated with hydrogen bonds and thus the surface OH groups probably interact with water molecules adsorbed by the carbon samples, as suggested by Zawadzki.[24] The shoulders at 2924 cm^{-1} and 1849 cm^{-1} in both spectra denote the presence of stretching C—H vibrations in CH$_2$ groups.[25] The intense broad band at 1702 cm^{-1} (C160) and 1707 cm^{-1} (C200) suggests the presence of stretching C=O vibrations arising from groups such as lactone, quinone,[23] and carboxylic acids.[25] The intense band around 1600 cm^{-1} for both carbons, C160 at 1610 cm^{-1} and C200 at 1604 cm^{-1}, may be due to the asymmetric and symmetric stretching COO$^-$ vibrations or to skeletal C=C aromatic vibrations.[23,26] Bands also appearing in the range 1600 cm^{-1} in spectra of carbonaceous films were attributed to vibrations in iono-radical structures[24,27] (see Fig 7) and in the spectra of coal to hydroxyl groups combined with conjugated C=C.[28]

The various bands and shoulders from 1300 to 900 cm^{-1} are variously ascribable to stretching C—O vibrations in hydroxyl groups and ether type struc-

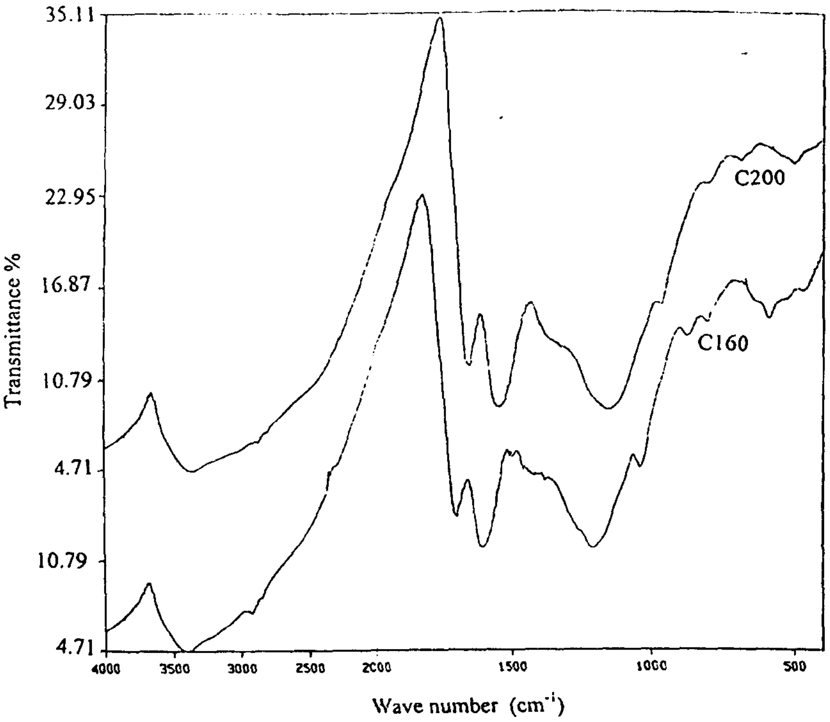

Figure 6. FTIR spectra of carbon sorbents C160 and C200.

tures;[23] aromatic ether or epoxy groups (C160: 1209 cm^{-1}, C200: 1222 cm^{-1});[23] =C—O symmetric stretching 1038 cm^{-1},[23] and phenolic OH or aliphatic OH which could also occur in this range.[23,26]

Comparison of the spectra shows that the bands at ~3390 cm^{-1}, ~1700 cm^{-1}, 1600 cm^{-1}, and ~1210 cm^{-1} are more intense and are slightly broader, which could indicate a greater concentration of C=O and COO$^-$ in the sorbent C200 as a result of greater oxidation of the carbon surface at 200 °C.

CONCLUSIONS

1. (1) Carbon sorbents prepared from flax shive by sulfuric acid treatment were optimised upon: metal sorption (mercury(II) and cadmium(II)), yield, and energy and sulfuric acid consumption. The optimised conditions for preparation were: 12 mol dm^{-3} sulfuric acid; ratio shive:acid 1:9 w/v; reaction time 25–30 min, with varying reaction temperatures.
2. (2) Cation exchange capacity is favoured by high reaction temperatures, eg 200 °C, and such materials are most suitable for the sorption of metals such as cadmium, which follow an ion exchange mechanism.
3. (3) The carbon prepared at 160 °C, C160, is suitable for the removal of mercury(II) from aqueous solution which has a different mechanism from that for cadmium(II) (ie not purely ion exchange).
4. (4) The carbon sorbent retains its fibrous structure and as the sorbent appears to be amorphous, no significant presence of carbon crystallites is likely.
5. (5) The carbon sorbents possess low nitrogen surface areas, probably due to the presence of a large residual organic content in the carbon structure.
6. (6) This material is an efficient alternative sorbent to activated carbon for removing heavy metals from aqueous solution.

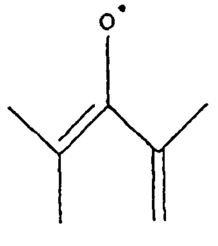

Figure 7. The iono-radical structure.

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Removal of mercury(II) from aqueous solution on a carbonaceous sorbent prepared from flax shive

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Abstract: Treatment of flax shive with sulfuric acid produced a carbonaceous material which has been used to remove mercury(II) from aqueous solution. The kinetics of sorption follows a first order reaction equation with the rate of sorption being higher for the wet material than for that which had been previously dried. Sorption of mercury depends on the pH of the aqueous solution with maximum uptake occurring in the pH range 6–7. Sorption capacity also increases with the increase of temperature. The presence of other metal ions such as K^+, Na^+, Mg^2+ and Ca^2+ decreases Hg(II) uptake capacity. A high capacity which exceeds the cation exchange capacity was observed, cumulative Hg(II) sorption exceeding $1\,g\,g^{-1}$. This arises from the reduction of mercury(II) to mercury(I) chloride and elemental mercury from chloride media and to elemental mercury from nitrate media. This was confirmed from the identification of deposits on the carbon surface by scanning electron microscopy and X-ray diffraction. The reduction of mercury was accompanied by the oxidation of the carbon which was confirmed by the evolution of carbon dioxide. This observation was also supported by changes in the infra-red spectrum of the carbon after reaction. The sorption mechanism is discussed.
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Keywords: mercury; sorption; carbon; dehydration; reduction; flax

INTRODUCTION

The presence of mercury in the aquatic environment is known to cause severe health problems in both animals and humans.[1,2] Even though the flux of mercury into the aquatic system has declined in recent years, there is still a lack of an effective, cheap means for the treatment of mercury-containing wastewater.

Among the many methods available for the removal of trace metals from water, namely chemical precipitation, ion exchange, coagulation, solvent extraction and membrane processes, adsorption has been shown to be an economically feasible alternative.[3–6] Activated carbon is one of the most popular adsorbents for the removal of mercury from aqueous solution[7–9] although other materials have been used including onion skins,[10,11] bark[12] and waste rubber.[13]

Waste agricultural materials have been used for many years as a source of carbon. Normally the feed material is heated to high temperatures (700–1200 °C) to remove the volatile matter and the resulting carbon is then activated either physically or chemically.[14] Carbonization of agricultural materials can also be performed by dehydration with sulfuric acid and phosphoric acid.[15,16] Thus treating sawdust with sulfuric acid produces a carbon,[17] which has the capability of decolorizing dyes, and possesses ion exchange properties related to the presence of surface functional groups on the carbon. Pichugin *et al*,[18] prepared a carbon from flax shive using sulfuric acid and showed that the sorbent had a good sorption affinity for the removal of heavy metals from water. This paper describes the use of a similar material prepared from flax shive by dehydration with sulfuric acid for the removal of mercury from chloride and nitrate media.

EXPERIMENTAL

Carbon was prepared from flax shive by dehydration with sulfuric acid, details of the preparation and characterization of the material is the subject of an earlier publication.[19] In this study the carbon was prepared as follows: sulfuric acid ($12\,mol\,dm^{-3}$) was added to flax shive in a ratio of flax: acid (w/v 1:9) at a temperature of 160 °C for 25–30 min. The black product was washed carefully with distilled water until free of acid. For experiments with the 'wet' material the carbonized product was stored under distilled water which was replaced periodically (twice a week) to avoid possible bacterial growth. Before use, the wet carbon was washed with a stream of distilled water between two sieves of mesh size 1 mm and 212 μm to

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remove fine particulates and to select a size range for the sorption experiments. The sample was then filtered and left under suction for 30 min. The moisture content of the material was determined by drying samples to constant weight at 120°C. For experiments with 'dried' material the carbonized product was placed in an oven at 120°C overnight, transferred to a desiccator to cool and finally stored in dry, clean and well-sealed polyethylene containers. The carbon product was ground and the portion retained between 1 mm and 212 µm sieves used in subsequent experiments.

All sorption experiments were carried out in clean, dry polyethylene containers and constantly agitated in a thermostat. Mercury concentrations in the supernatant solution were measured using a Perkin-Elmer Plasma 40 Emission Spectrometer (ICP-AES) at wavelength of 253.652 nm.

For the kinetics of sorption, a sample of dry sorbent (~0.13 g) or the equivalent amount of the wet material was added to mercury(II) chloride solution (200 cm^3 of ~95 ppm) at an initial pH about 5. Samples of the aqueous solution were taken at defined time intervals and the mercury content analysed. The experiment was followed for up to 170 h.

For the experiments including the effect of pH, light metal ions and temperature, a sample range of the dry carbon (0.064–0.070 g), or the equivalent weight of the wet sorbent, was added to mercury(II) solution (50 cm^3) of different concentrations. To study the effect of pH on the sorption of mercury the initial pH of the mercury(II) solutions was adjusted using small amounts of dilute sodium hydroxide or hydrochloric acid solutions. The concentration of mercury was measured before and after the sorption process and the pH measured at the end of the experiment.

To measure the sorption capacity and effect of temperature, the mercury(II) solution at an initial pH of 6.5, which was the value at which maximum uptake of mercury occurred, was mixed with a weighed sample of the sorbent and shaken until equilibrium was reached. The process was carried out at 25, 35 and 45 °C.

To study the effect of light metal ions on the sorption of mercury, solutions of mercury(II) chloride (300 ppm) were mixed with different concentrations of some light metal ions prior to the addition of the carbon sorbent. Metal ions added were Na^+, K^+, Mg^{2+} and Ca^{2+} in their chloride form and in concentration ranges of 100–300 ppm.

Carbon dioxide determination

Carbon dioxide evolved from the sorption reaction of mercury(II) onto the carbon surface was flushed out by a stream of a nitrogen gas through a series of four Dreschel bottles containing barium hydroxide solution. The precipitated barium carbonate was left for 24 h to age and then quantitatively recovered on a preweighed glass microfibre filter dried at 105 °C, cooled in a desiccator and reweighed.

The cumulative metal sorption capacity

The cumulative metal sorption capacity of the sorbent was determined using a semi-continuous batch system as follows. A 50 cm solution of 500 ppm of Hg(II), chloride media, at pH of 4.5 was mixed with ~0.105 g of the dry material, or its equivalent in the wet form, for the appropriate equilibrium time (80 h for wet, 120 h for dry). The sorbent was separated by filtration, and mixed with a fresh sample (50 cm^3) of the same initial mercury solution. A sample of the filtrate after sorption was analysed by ICP. The process was continued for 12 cycles with both sorbents.

Sorption on a fixed bed column

A wet sample of the sorbent (equivalent to ~1 g on a dry basis) was loaded into a column of radius 0.67 cm and length 11.02 cm. Mercury(II) chloride solution (200 ppm at pH 4.5) was pumped through the column at a flow rate of 1.11 cm^3/min^{-1}, remaining in contact with the sorbent for 14 min. The process was carried out in both a continuous and intermittent regime. In the intermittent regime, mercury solution flowed for 4 h continuously and then the system was stopped for 8 h, and the process repeated for a number of bed volumes equal to the continuous regime.

Scanning electron microscope studies (SEM)

The carbon sorbent before and after contact with the mercury solution was examined using a Camscan CS44 Scanning Electron Microscope to obtain textural and surface information before adsorption. The equipment was fitted with a Camscan Editor Energy Despersive Analysis system which was used in the standard-less mode using the manufacture's calibrations.

X-ray analysis

X-ray powder diffraction was carried out using a Philips PW 1730 generator with a Philips 1050/25 powder goniometer, and Philips PW 1390 measuring electronics. Copper K_α was used as the incident radiation.

Infra-red spectroscopy

Infra-red spectroscopy was used to determine the surface functional groups on the surface of the carbon sorbents. Carbon samples, before and after sorption, were dried overnight to remove any water retained which could interfere with observation of hydroxyl groups on the surface. This was followed by encapsulation into dry potassium bromide (KBr) discs. The discs were scanned in transmission mode using a Perkin-Elmer Paragon 1000 FT-IR spectrometer through wavelength range from 800 to 4000 cm^{-1} with background subtraction using a summation of 16 scans.

Data analysis

Sorption experiments were repeated at least three times and mean values are reported. Standard devia-

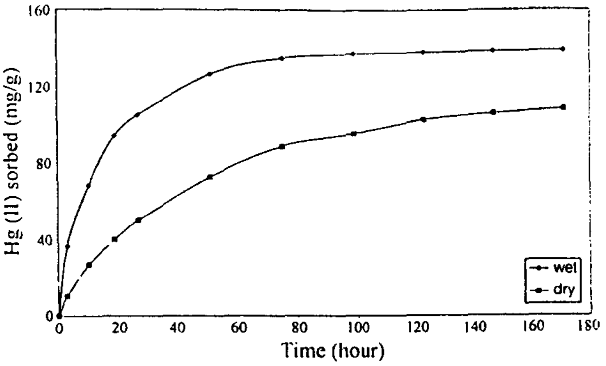

Figure 1. Kinetics of Hg(II) sorption onto wet and dry carbon at 25°C.

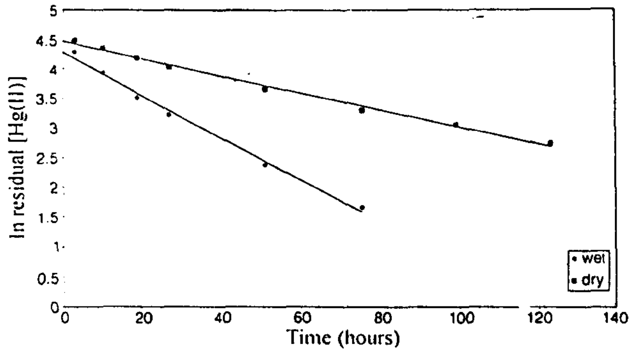

Figure 3. Plot of ln residual [Hg(II)] in solution against time for Hg(II) sorption on wet and dry carbon.

tions and analytical errors were calculated and the maximum analytical error was found to be ±5%.

RESULTS AND DISCUSSION

Kinetics of sorption

The kinetics of mercury(II) sorption is shown in Fig 1, with the wet sample reaching equilibrium in 80h compared with about 120h for the dried material. Since the moisture content of the wet form is relatively high (>80%) this reduction in rate for the dried sample is probably related to shrinking and compaction of the carbon on drying giving narrower pores for the diffusion of the mercury(II) ions. It was also observed that little swelling of the dry material occurred when placed in aqueous solutions.

The uptake of mercury(II) was found to vary almost linearly with the half power of time, $t^{0.5}$, in the initial stages of sorption, as shown in Fig 2 such behaviour is predicted when a large initial fraction of the reaction is controlled by intra-particle diffusion.[20]

It was found that the removal of mercury(II) from solution also followed a first-order reaction equation which can be expressed as:

$$\ln[\mathrm{Hg}^{2+}] = \ln[\mathrm{Hg}^{2+}]_o - k.t \qquad (1)$$

where $[\mathrm{Hg}^{2+}]$ is the concentration of mercury(II) at time t, $[\mathrm{Hg}^{2+}]_o$ is the initial concentration of mercury(II) and k is the rate constant of the reaction at 25°C. The results of the kinetic experiment, Fig 3, show a linear decrease of the log $[\mathrm{Hg}^{2+}]$ as a function of time for both sets of experiments. The rate constants for mercury(II) sorption on the wet and dry carbon were 0.0359 and 0.0144h^{-1} respectively.

Effect of the pH on the sorption of mercury(II)

The effect of pH is an important factor in the sorption of metal cations onto different sorbents. At low pH values (pH 1.2–2), the sorption is extremely low and as the pH of the solution increases mercury(II) uptake increases with a consequent decrease of the final pH value of the solutions. The highest uptake occurred in the pH range 6–7, as shown in Fig 4 for the wet carbon. Increasing the initial concentrations of mercury(II) gave increased uptake but the trend was the same with highest uptake about pH 7. Above pH 7 precipitation takes place and so pH 6.5 was chosen for the sorption capacity and effect of temperature for mercuric chloride. However for experiments from nitrate, media pH value was 3.0. Similar behaviour was found for the dry carbon but with a lower mercury(II) uptake.

The sorption of mercury onto the carbon releases protons by an ion exchange mechanism resulting in a decrease in the solution pH at equilibrium

$$2\mathrm{C{-}H} + \mathrm{Hg}^{2+} = (\mathrm{C{-}})_2\mathrm{Hg} + 2\mathrm{H}^+ \qquad (2)$$

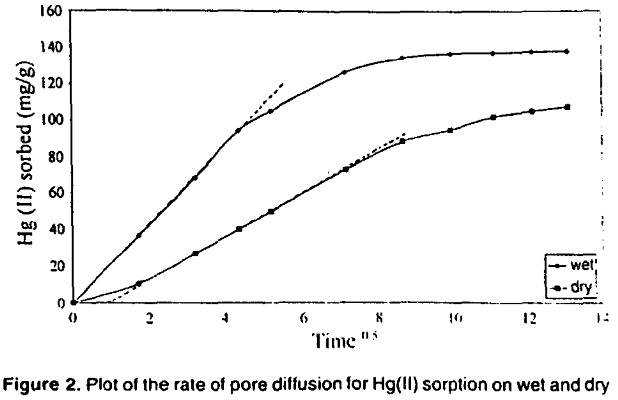

Figure 2. Plot of the rate of pore diffusion for Hg(II) sorption on wet and dry carbon.

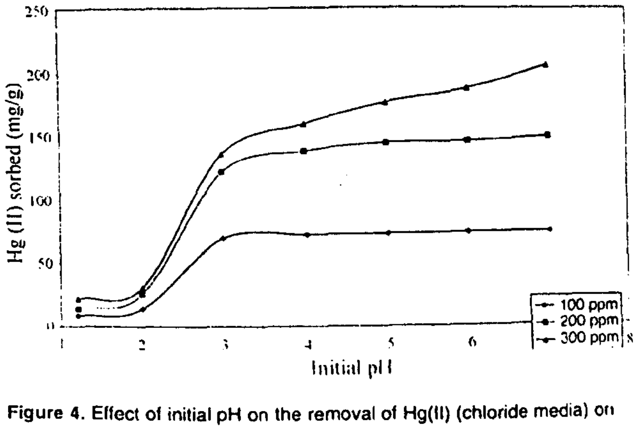

Figure 4. Effect of initial pH on the removal of Hg(II) (chloride media) on wet carbon with different initial concentrations of mercury.

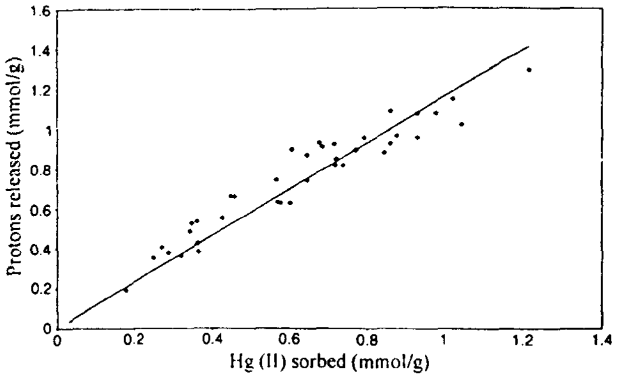

Figure 5. Relation between protons produced in solution and Hg(II) sorbed.

So from eqn (2) plotting the amount of hydrogen ion released against mercury uptake should give a straight line of slope 2. However although the results obtained, Fig 5, do give an approximate straight line, the slope is between 1 and 1.4, giving a value of 1.17 with a correlation value 0.8458, indicating that ion exchange is not the only process involved in mercury uptake.

Sorption capacity and temperature effect

Sorption of mercury(II) onto both forms of carbon follows an 'L- type' adsorption isotherm, with increasing capacity with temperature, Figs 6 and 7. Again the wet sample gave a better performance than that which had been dried. Mercury(II) from nitrate shows no significant difference from that from chloride solution at 25 °C. The data were found to obey the Langmuir isotherm over the complete range of concentrations, Fig 8. The Langmuir equation (eqn (3)) is given as:

$$X = (X_m bC_e)\ (1 + bC_e) \qquad (3)$$

where $X = x/m$, the amount of solute adsorbed, x, per unit weight of sorbent, m;C_e = equilibrium concentration of the solute; X_m = the amount of solute adsorbed of unit weight of adsorbent required for monolayer coverage of the surface, or monolayer capacity; and b is a constant.

Thus from Fig 8, it appears that the Langmuir equation gives a good representation of the experimental isotherm data. The derived Langmuir constants, Table 1, show that the monolayer capacity X_m (mg g^{-1}) is higher in the case of wet carbon than for the dry sample.

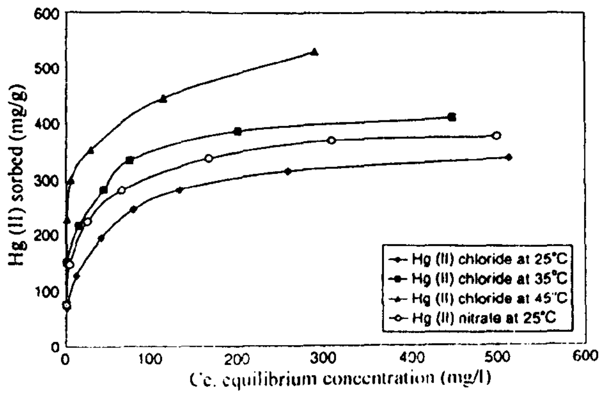

Figure 6. Sorption isotherms of Hg(II) onto wet carbon at 25, 35 and 45 °C.

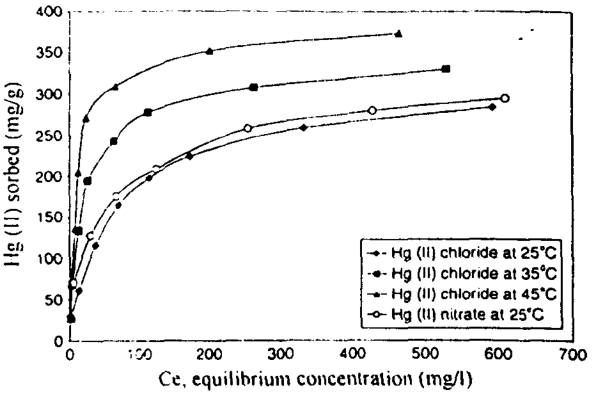

Figure 7. Sorption isotherms of Hg(II) onto dry carbon at 25, 35 and 45 °C.

Effect of light metal ions

Light metal ions such as sodium, potassium, magnesium and calcium in solution compete with mercury (II) ions for the sorption sites on the carbon. Thus the mercury sorption decreases as the concentration of the light metal ions increases, Fig 9, with the greatest effect observed with the wet form of the carbon. This decrease in mercury uptake in the presence of other metal ions is due to competition of these ions for the cation exchange sites on the carbon. Similar behaviour was found for mercury(II) sorption in the presence of such metal ions onto modified bark[12] and Ma *et al*[9] also found that the presence of magnesium and calcium over 50 ppm decreased the uptake of mercury (II) onto granular activated carbon. However these concentrations of light metal ions are significantly higher than will be met in most natural waters. Thus when mercury was adsorbed from a local hard water the amount of mercury removed from solution was not appreciably reduced. Indeed because the pH of the

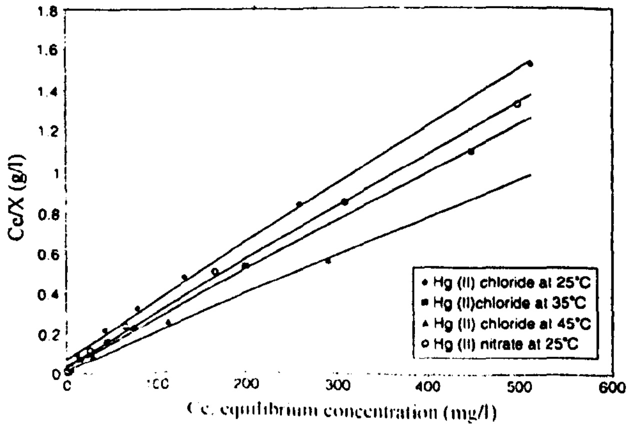

Figure 8. Langmuir isotherms for Hg(II) sorption on wet carbon at 25, 35 and 45 C.

Table 1. Langmuir constants for mercury(II) sorption onto wet and dry carbon at 25, 35 and 45 °C

Carbon (C160)	Sorption Temp (°C)	Langmuir constants X_m (mg g^{-1})	Langmuir constants b (dm^3 mg^{-1})	correlation coefficient
Wet	25 °C	345	0.0409	0.996
	25 °C^a	385	0.069	0.998
	35 °C	416	0.0805	0.998
	45 °C	526	0.1338	0.995
Dry	25 °C	303	0.0202	0.995
	25 °C^a	313	0.0223	0.997
	35 °C	344	0.0468	0.999
	45 °C	385	0.0790	0.999

[a] Data for mercury(II) nitrate and the rest for mercury(II) chloride.

water was higher than when deionized water was used a larger amount of mercury was actually removed, Table 2.

Carbon dioxide measurement

Previous studies by Fu *et al*[21] showed that reduction of mercury(II) was accompanied by evolution of carbon dioxide from the carbon sorbent. This experiment was repeated in the present study with a wet sample of the carbon and an aqueous solution with a high initial concentration of mercury(II) ions (6000 ppm). The pH was maintained in the range 5–6 and the temperature was kept at 60 °C by a thermostat. The experiment was carried out as described above and under such conditions the sorption capacity was 895 mg g^{-1} (4.46 mmol g^{-1}). The amount of barium carbonate precipitated, which is equivalent to the carbon dioxide evolved from the sorption reaction, was 0.091 mmol g^{-1}. It is clear from these results that more mercury(II) is sorbed that the amount of carbon dioxide evolved. So these results indicate that although oxidation of the carbon to produce carbon dioxide does occur this is not the only process involved in the mercury uptake.

Cumulative mercury(II) sorption capacity

Successive sorption of Hg(II) on both forms of the sorbent (wet and dry) showed an increase of more than five times compared with the first cycle of sorption, Fig 10. The precipitation of mercury(II) to mercurous chloride and metallic mercury, frees the ion exchange groups and also creates more sites by surface oxidation. In addition, the ability for reduction does not seem to be diminished by earlier sorption batch experiments. In addition, maintaining the pH of the sorption experiment, pH 5–6, and heating the system up to 60 °C, leads to a higher uptake of 895 mg g^{-1} as discussed earlier. This suggests that the equilibrium time was not really related to the availability of sorption sites on the surface, but is mainly related to the decrease in solution pH thus preventing the loading of more mercury. So changing the solution

Table 2. Sorption of mercury(II) on wet carbon cumulatively from tap water (initial concentrations: Hg(II): 430, K: 5.35, Na: 27.0, Ca: 11.3 and Mg: 6.6 ppm, initial pH 6.6)

Cycles	Hg (II) sorbed (mg g^{-1})	Hg (II) sorbed cumulatively (mg g^{-1})
1	185.3	185.3
2	182.1	367.4
3	180.0	547.7
4	178.0	725.7
5	177.7	903.4
6	173.5	1076.9
7	165.6	1242.5

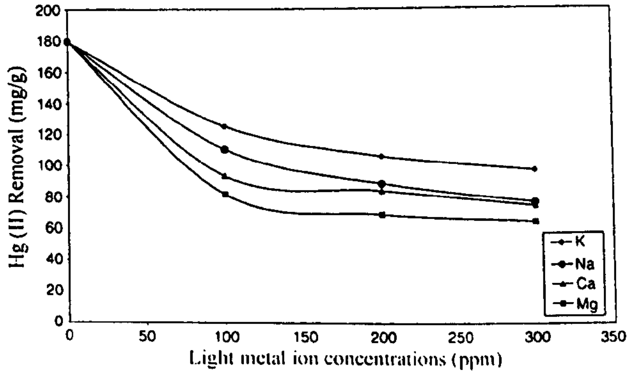

Figure 9. Effect of added metal ions on Hg(II) sorption on wet carbon.

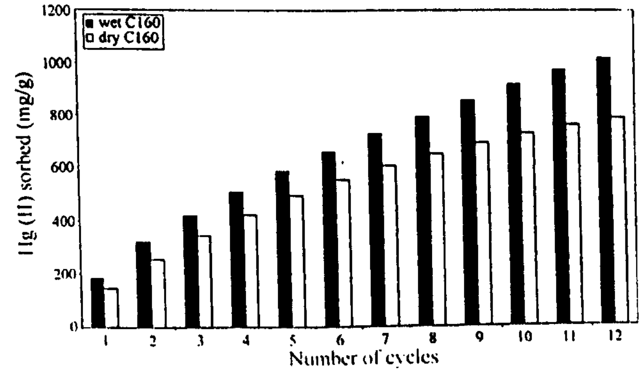

Figure 10. Cumulative sorption of Hg(II) on wet and dry carbon.

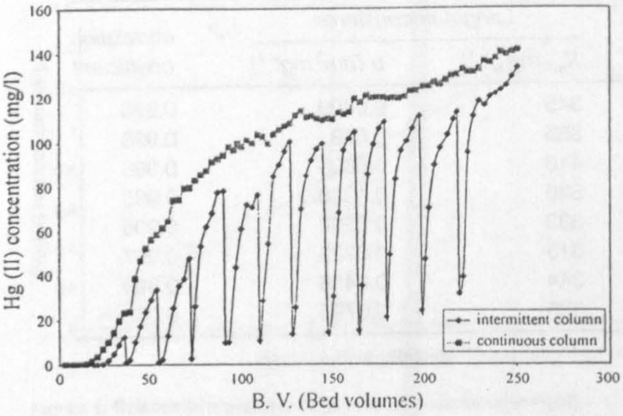

Figure 11. Column studies for Hg(II) on wet carbon.

for a fresh one at the same initial pH, or readjusting the pH to the optimum pH 5–6, leads to further removal of mercury.

Column studies

Sorption of Hg(II) in the continuous column work, showed a breakthrough after around 4h (~17 bed volume), as shown in Fig 11. Thus 4h was chosen as the breakthrough for the intermittent column.

The experiment was under the same conditions for the same number of bed volumes (250 bv, which is equivalent to 48 working hours) in an intermittent manner, namely 4h flow followed by 8h rest. After the initial period following breakthrough the flow is stopped and the liquid in the column allowed to equilibrate for 8h. This allowed the slow reduction reaction to occur reducing the mercury(II) to insoluble mercury(I) chloride and metallic mercury, thereby releasing the ion exchange sites. Thus on restarting the flow the initial samples of eluate have very low mercury concentrations. The eluate concentration increases with time until the next period when again reduction is completed and the mercury concentration in the eluate again falls. This saw-tooth pattern is repeated but with a general slow increase in the initial eluate concentration and higher mercury concentration at the end of the flow regime indicating a general reduction in the number of ion exchange sites available. During the rest periods small gas bubbles were observed on the carbon surface, presumably carbon dioxide resulting from the surface oxidation described above.

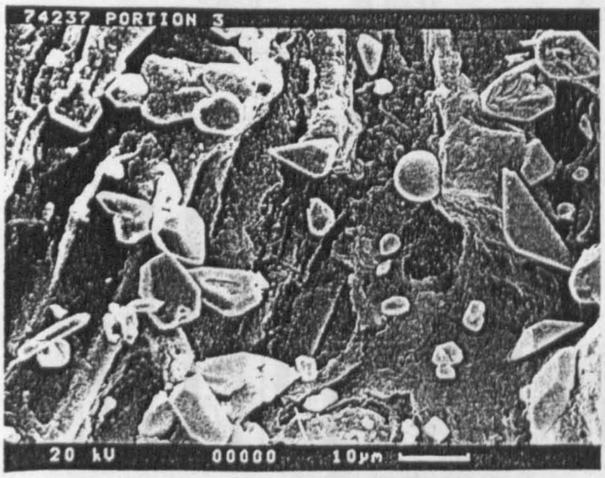

Figure 12. Scanning electron micrograph of carbon after mercury(II) chloride loading.

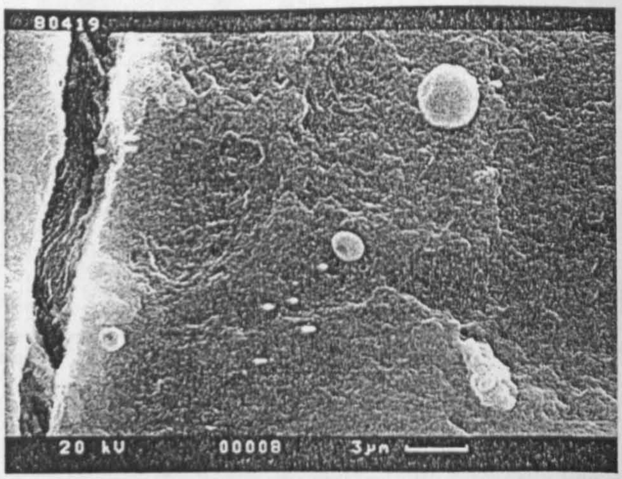

Figure 13. Scanning electron micrograph of carbon after mercury(II) nitrate loading.

Scanning electron microscope studies

During the loading experiments white crystals were observed on the surface of the carbon particles. Samples of these carbon particles were examined by scanning electron micrographs which clearly identified needle-like crystals and, in addition, some round micro-droplets were also found on the surface and within the pores, Figs 12 and 13.

These crystals and droplets were examined by electron microprobe elemental analysis and even

Table 3. X-ray powder diffraction after mercury(II) chloride loading confirming that the crystals available are of mercury(I) chloride

Observed		*Literature*	
d (Å)	*Intensity (I)*	*d* (Å)[a]	*Intensity (I)*[a]
4.168	75	4.15	75
3.184	100	3.17	100
2.838	12	2.824	12
2.736	40	2.727	30
2.247	14	2.240	14
2.072	36	2.067	40
1.967	30	1.97	16
1.757	3.4	1.756	4
1.735	8.8	1.732	12
1.588	5.4	1.5841	6
1.477	8.8	1.4755	10
1.42	2.9	1.4164	3
1.37	3.9	1.3696	6

[a] Data from JCPDS-ICDD copyright © 1994 PDF-2 Sets 1–44 database (26-312).

though the analysis was carried out in the standard-less mode an estimate of the elemental composition could be formed. Only mercury could be identified in the round microdroplets confirming them as elemental mercury. The white crystals showed a mercury: chlorine ratio of about 1:1 which, with X-ray powder diffraction, confirmed the identification of mercury(I) chloride with the interplanar spacing (*d*) and relative line intensities (*I*) agreeing with those recorded (Table 3). In the case of removal of mercury from a nitrate solution as expected only microdroplets of mercury could be identified, Fig 13.

FTIR studies

Another parameter which can provide information on changes to the carbon sorbent following mercury uptake is infra-red analysis, and in this work the infra-red spectra of the carbon after mercury(II) sorption showed a change in the surface functional groups, when compared with the initial material, Fig 14. These spectra were recorded on KBr discs of the dried sorbent and therefore any deduction must be considered tentative as accurate quantitative measurements could not be made. However with these limitations some useful collaborative evidence can be obtained. Thus comparing these spectra shows that the bands at around 3400cm^{-1}, which are connected with the O—H stretching vibrations, become relatively more intense and broader after sorption, indicating the formation of more OH groups by mercury(II) reduction. On the other hand bands at around 1700 cm^{-1} related to C=O stretching vibrations showed an obvious decrease after the mercury sorption, which probably reflects the process of decarboxylation accompanying the oxidation process with evolution of CO_2. The band around 1600 cm^{-1} became more intense after the mercury (II) sorption onto the carbon. This band is connected to skeletal C=C aromatic vibrations[22] and thus probably reflects a dehydrogenation process[23] accompanying the redox processes. An observed increase in the intensity of the bands and shoulders in the range between 1300 and 900 cm^{-1} which may be ascribed to the C—O vibrations associated with hydroxyl groups and ether type structures reflects the increase of carbon-oxygen groups on the surface after mercury sorption as a result of oxidation.

Mechanism of the sorption process of mercury(II)

Previous workers[24,25] have found that mercury(II) chloride can be reduced to mercury(I) on an activated carbon surface and on carbon fibres.[21,26] This has led to the suggestion that the adsorption process involves a sequence of ion exchange, complex formation, redox reactions and precipitation.[27] Experimental results obtained during this investigation, eg infra-red spectra, suggest that the carbon sorbent possesses abundant functional groups on the surface. As the carbon material includes some lignin, an important component in the structure of most humic materials,[28] humic compounds may also be available within the structure of the carbon. Such materials are known to adsorb metal ions and also can act as a reducing agent for some metal ions.[29]

Therefore it is suggested that the sorption of mercury consists of at least two processes: ion exchange and reduction. Initially the mercury(II) ions are sorbed onto the carbon by an ion exchange mechanism as indicated by the various adsorption experiments, and confirmed by the competition of these sites by other ions. Concerning the possible redox reactions, the potentials of the various mercury couples are very similar (eqns ((5)–(7)) so that, depending on the precise experimental conditions, either the mercury(I) ion or metallic mercury can be produced.

$$2Hg^{2+} + 2e^- = Hg_2^{2+} \qquad (E^\circ = +0.905\,V) \quad (5)$$

$$Hg^{2+} + 2e^- = Hg^\circ \qquad (E^\circ = +0.851\,V) \quad (6)$$

$$Hg_2^{2+} + 2e^- = 2Hg^\circ \qquad (E^\circ = +0.796\,V) \quad (7)$$

Thus in the system under investigation the mercury(I) ions from the reduction, eqn (6), can either gain more electrons to be reduced to metallic mercury or interact with the chloride ions available in the solution to give mercury(I) chloride which is sparingly soluble in water. Then the mercury(I) chloride crystallites precipitate onto the carbon surface and also within the pores, migrating from the reduction site towards earlier deposited crystallites for crystal growth, so in time crystals develop, as shown in Fig 12. The process of mercury(II) reduction has to be accompanied by an oxidation process of the carbon surface, eqns (8)–(12). Evolution of carbon dioxide was confirmed by the precipitation of barium carbonate during the absorption process. However the evolved carbon dioxide was found to be less than the amount of mercury(II) sorbed onto the surface which suggests either flaws in the experimental procedure or the presence of other surface oxidation processes. The latter possibility is indicated by the infrared spectra of the sorbent before and after reduction had occurred, Fig 14.

Possible reactions at the carbon surface which may be involved are:

- oxidation of carbon in the presence of water and mercury ions:

$$C + 2H_2O + 4\,Hg^{2+} = CO_2 + 2\,Hg_2^{2+} + 4H^+ \quad (8)$$

$$C + 2H_2O + 2\,Hg^{2+} = CO_2 + 2\,Hg^\circ + 4H^+ \quad (9)$$

- surface oxidation reaction: in addition to the above reaction which removes carbon from the surface, partial oxidation can also occur to carbon compounds giving rise to the formation of hydroxyl (or phenolic) groups, carbonyl groups or carboxylic

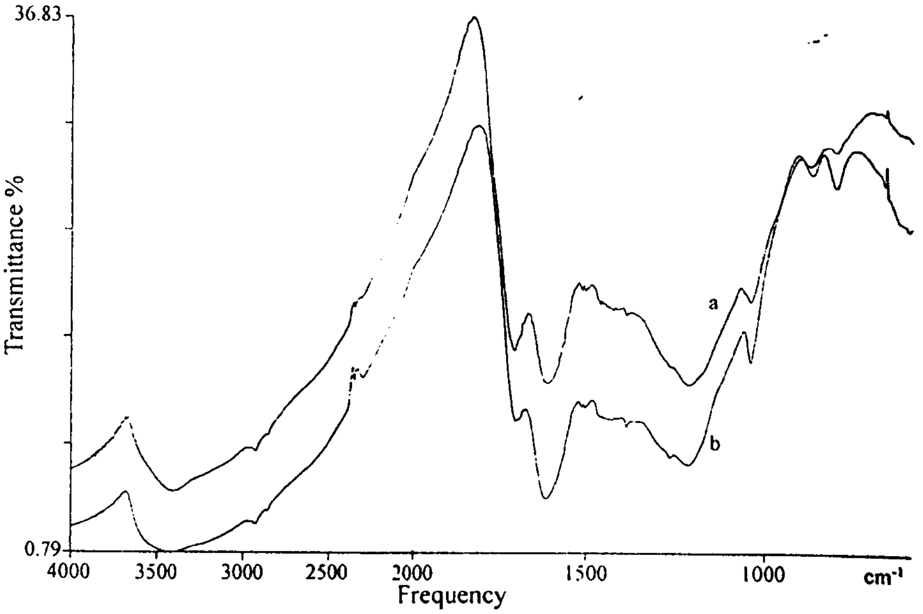

Figure 14. FTIR spectra of the carbon (a) before Hg(II) sorption (b) after Hg(II) sorption.

acids.

$$>\mathrm{C{-}H} + \mathrm{Hg(oxidized)} + \mathrm{H_2O} = >\mathrm{C{-}OH} + \mathrm{Hg\ (reduced)} + \mathrm{H^+} \tag{10}$$

$$>\mathrm{C{-}H}\ >\mathrm{C{-}OH} + \mathrm{Hg\ (oxidized)} + \mathrm{H_2O} = >\mathrm{C{=}O} + \mathrm{Hg\ (reduced)} + \mathrm{H^+} \tag{11}$$

$$>\mathrm{C{-}H}\ >\mathrm{C{-}OH} + \mathrm{Hg\ (oxidized)} + \mathrm{H_2O} = >\mathrm{COOH} + \mathrm{Hg\ (reduced)} + \mathrm{H^+} \tag{12}$$

From the infra-red spectra it was found that the band associated with the carbonyl group decreases after adsorption at high temperature (60 °C) which suggests that the concentration of carbonyl groups decreases as a result of decarboxylation to CO_2.

The infra-red band at $1600\,\mathrm{cm^{-1}}$ may be assigned to —COO⁻ or aromatic —C=C— vibrational modes.[22] As already indicated, the intensity of the —C=O vibrations has decreased, suggesting that the increase in $1600\,\mathrm{cm^{-1}}$ band is associated with the formation of —C=C— bands. This can be explained by a dehydrogenation reaction such has been postulated for the reduction of gold(III) onto lignite.[23] Thus in this process the reaction could be:

$$>\mathrm{CH{-}CH}< +\mathrm{Hg\ (oxidized)} = >\mathrm{C{=}C} < +2\mathrm{H^+} + \mathrm{Hg\ (reduced)} \tag{13}$$

CONCLUSIONS

(1) The sorption of mercury(II) onto the carbon sorbent is faster and has higher uptake when samples which have been maintained in a wet condition are used. The kinetics of mercury(II) sorption was found to follow a first order reaction process, which depends mainly on the diffusion of the mercury ions through the carbon pores.

(2) The sorption of mercury(II) is dependent on the pH of the initial solution with pH 6–7 the most suitable for high mercury(II) uptake. The ratio of protons evolved to the mercury(II) sorbed was found to lie between 1 and 1.4 which indicates that the process is not only ion exchange but also involves other reactions such as reduction.

(3) The higher mercury capacity for the wet sorbent is probably related to changes in the pore structure with the pores becoming narrower on drying with a resulting decrease in surface area. Swelling of the dried material by immersion in water is limited indicating the process is not completely reversible.

(4) The presence of high concentrations of light metal ions such as Na^+, K^+, Mg^{2+} and Ca^{2+} showed a large decrease in mercury(II) uptake, indicating competition for the ion exchange sites available on the carbon surface. However the uptake of mercury is not significantly affected by the presence of such metal ions at the concentration found in natural waters.

(5) The sorption process is dependent on temperature with the mercury(II) uptake increasing with increase in temperature. Such changes in temperature may cause an increase in swelling of the adsorbent allowing more active sites to become available.

(6) The overall sorption process is complex and includes both ion exchange and reduction steps. Precipitation of mercury(I) chloride on the surface and within the pores has been observed together with the formation of micro-droplets of elemental mercury. These results have been confirmed by X-ray powder diffraction and scanning electron microscopy.

(7) The reduction properties of the carbon sorbent is related to the functional groups present on the

surface and probably also to the matrix of the carbon which contains lignin, and probably humic acids.

(8) With the mercury sorption mechanism including both reduction and ion exchange, the following conceptual picture of the overall process is proposed:

- Mercury(II) cations first approach the sorbent as a result of electrostatic interaction with the ion exchange centers on the carbon surface replacing the protons on these functional groups:
- The sorbed mercury ions either migrate from these ion exchange groups to be reduced at another site on the surface leaving the ion exchange centre active or are reduced at the same functional group, eg —COO^- by decarboxylation to carbon dioxide:
- Reduction can occur either directly to elemental mercury or to mercury(I) cations which combine with chloride ions to form mercury(I) chloride crystallites:
- Subsequent mercury(II) cations behave in a similar way to form a new crystallite of mercury(I) chloride which migrates to aggregate with previous formed crystallite to build up a crystal form.
- In the case of mercury removal from nitrate solution as expected only droplets of elemental mercury are observed.

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