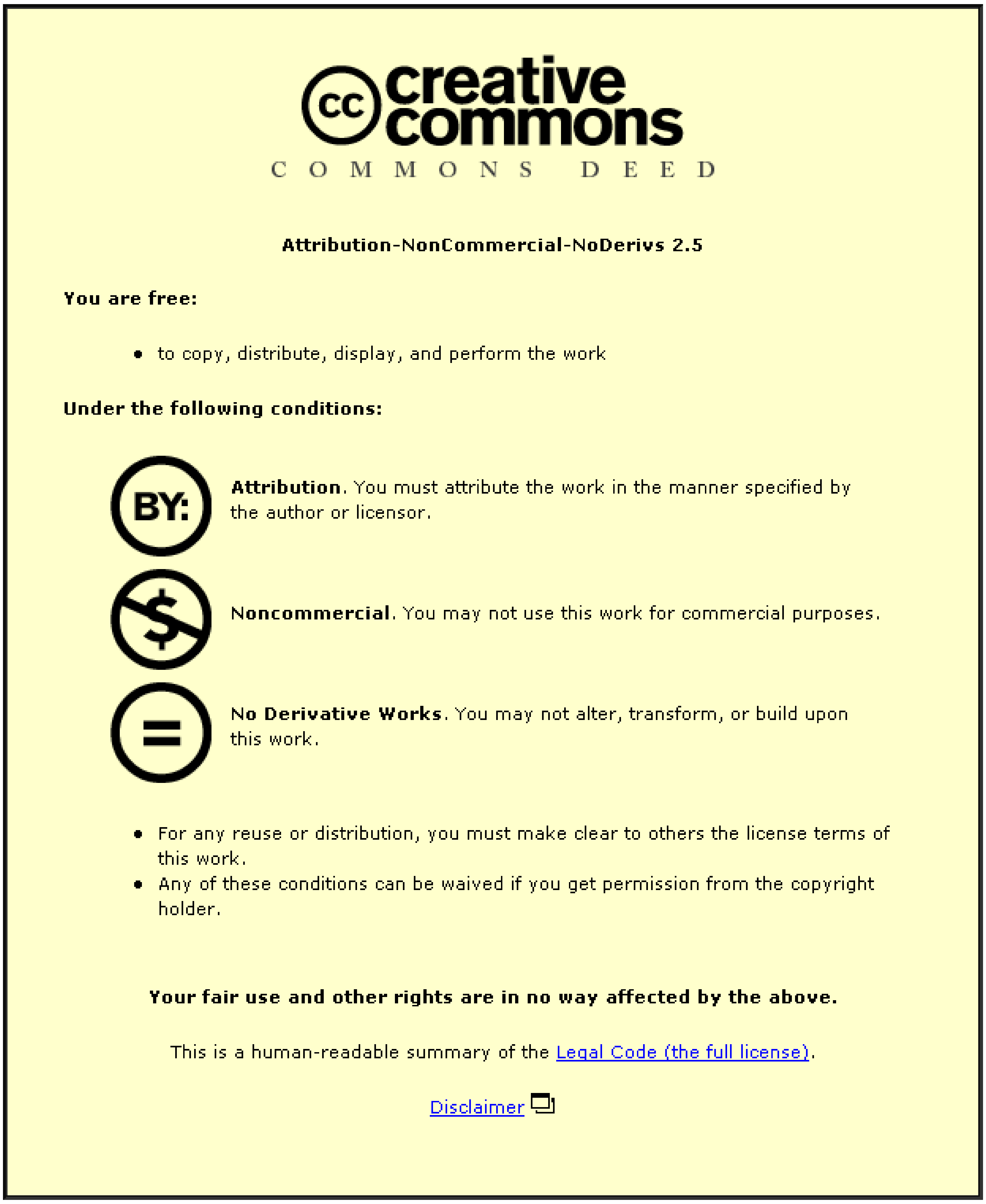

ADSORPTION OF TOXIC METALS FROM WATER USING COMMERCIAL AND MODIFIED GRANULAR AND FIBROUS ACTIVATED CARBONS

by

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ABSTRACT

Commercial granular and fibrous activated carbons have been studied for the removal of heavy metals from aqueous solutions. A wood based activated carbon (AUG WHK) and an activated carbon cloth (KoTHmex TC-66 C) based on polyacrylonitrile fibre as a precursor, were oxidised for different periods of time using nitric acid, ozone and electrochemical methods to introduce various acidic groups at the surface, thereby, enhancing metal binding capacity. Modified samples were subsequently studied for the specific removal of cadmium and mercury ions in solution and compared with the performance of a commercially available weak acid fibrous exchange material (Ecofil-Deco Ltd. K-4).

Carbonaceous adsorbents were physically characterised by scanning electron microscopy, surface area and porosimetry (using N_2 adsorption at 77K). There was a decrease in BET surface area between untreated and oxidised samples. Acid and electrochemically oxidised samples were completely stable although there was clear evidence of physical damage to ozone-oxidised carbons. Samples were also chemically characterised by pH titration, direct titration, X-ray photoelectron spectroscopy and elemental analysis. A significant increase in oxygen content was obtained after oxidation, which increased the total ion exchange capacity by a factor of approximately 3.3 compared to commercial as-received carbonaceous adsorbents. As the degree of oxidation increased, the point of zero charge was shifted to lower pH values, i.e. from 4.5 to 3.6.

Batch equilibrium tests indicated that oxidised materials have an approximately 16.5 and 10 times higher maximum sorption capacity (at pH 6) for cadmium and mercury, respectively, compared to conventional carbonaceous materials. Experimental equilibrium data were fitted by Langmuir and Freundlich isotherms. The Freundlich isotherm gave a best fit of the cadmium sorption isotherms whereas the Langmuir isotherm gave a better fit of mercury sorption isotherms. Equilibrium sorption isotherms were determined at pH 4, 5 and 6 and these showed that cadmium and mercury uptake increased with increasing pH.

Small-scale mini-column experiments (3 cm^3) were performed and indicated that mercury breakthrough occurred after about 70 bed volumes (BV) of feed solution (1 mM cadmium and mercury at pH 6) were passed through electrochemically oxidised WHK, whereas cadmium breakthrough occurred at 20 BV. This indicated that electrochemically oxidised carbon is more selective for cadmium. Desorption experiments showed that the cadmium adsorption is highly reversible whereas mercury is more tightly bound to the carbon surface. This suggests that mercury uptake is more complex and may due to chemical reaction as well as adsorption/ion exchange.

Kinetic studies indicated that the uptake of trace metals on carbon fibres was faster than for granular carbons, even after the samples were oxidised.

KEYWORDS
Carbonaceous materials, oxidation, surface groups, adsorption, breakthrough, kinetics.

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Chapter 1:

INTRODUCTION

1.1 Introduction

The importance of environmental issues has increased in the last few decades. Researchers working on wastewater treatment are primarily concerned with the presence of heavy metals, radionuclides and synthetic chemicals in aqueous solutions due to their high toxicity to human and aquatic life.

Wastewaters that contain high concentrations of metal ions mainly originate from industrial establishments and domestic residences. The Environmental Protection Agency (EPA) has highlighted eight of the most common heavy metals in residual waters: arsenic, cadmium, chromium, copper, lead, mercury, nickel, and zinc. Different techniques have been developed and used to remove or recover a wide range of micro-pollutants, including metal ions, from a variety of industrial effluents. Examples are: ion exchange, electrochemical processes, adsorption, chemical treatment, liquid-liquid extraction, electrochemical ion exchange and membrane processes.

Adsorption has been widely applied for the removal of trace contaminants from potable water, domestic water and industrial effluents. Different adsorbents have been applied, for example zeolites, activated carbon, clays, metal silicates and biosorbents. However, activated carbon has been the most widely used.

Activated carbon materials are versatile adsorbents that can be applied in both gas and liquid phase applications due to their excellent physical and chemical properties. These carbonaceous materials are extensively used in wastewater treatment for the removal of a wide range of contaminants. They offer extensive surface area for sorption of metal ions from aqueous solutions and have been investigated for treatment of solutions bearing inorganic species. By far the most extensively developed large-scale application of activated carbon is the recovery of gold from dilute cyanide leach solutions[1]. Sorption of heavy metals on activated carbon is not a simple process as it depends on several factors such as metal speciation, water chemistry and the chemistry of the carbon surface.

Commercial activated carbon exists in granular and powder forms, and more recently activated carbon fibre in the form of cloth (ACC) and felt (ACF) have been developed and have received some attention as potential adsorbents for water treatment applications. These new types of adsorbents are robust and compact and therefore offer opportunities for the design of novel intensified water treatment systems. These novel carbonaceous materials are highly microporous, possessing micropores that are directly accessible thereby increasing intraparticle diffusion so that the overall sorption rate is faster than in granular activated carbons that possess a combination of micro, meso and macropores.

The metal binding ability of conventional activated carbon is very limited. However, this can be significantly enhanced by chemical modification. These modifications can be carried out by addition of oxygen, nitrogen, sulphur, and phosphorus onto the surface of the original precursor. Oxidation is commonly used to increase the number of weakly acidic groups on the carbon surface, e.g. carboxylic, carbonic, phenolic and lactonic. Hence, metal ions can interact directly with these mainly oxygen-containing groups and are thereby removed from solution. The groups added during the oxidation affect the acidity and the adsorption performance of modified carbons[2].

Oxidation has been carried out mostly by using air at high temperature or nitric acid solutions[3]. Other oxidants such as ozone and hydrogen peroxide have also been used[4]. Electrochemical oxidation of carbon fibres has been carried out mainly to increase tensile strength as well as improving metal binding capacity[5]. However, only a limited amount of work has been carried out on electrochemical oxidation of granular activated carbons.

The aim of this research is to investigate the sorption performance of commercial and chemically modified (using ozone, nitric acid and electrochemical methods) granular and fibrous activated carbons, and also to analyse the effect of solution pH and adsorbate concentration on the sorption process. Cadmium and mercury were selected as adsorbates.

1.2 Water pollution by metal ions

A vast amount of pollutants have been discharged to the environment since the start of industrialisation. Initially, contaminants were released into open waters such as rivers and oceans. Nowadays, environmental laws exist that force industry to modify existing chemical processes, develop new technology and treat wastewater prior to discharge, in order to protect the environment.

As mentioned earlier, heavy metals such as arsenic, cadmium, chromium, copper, lead, mercury, nickel, and zinc are listed by the EPA as the most common in residual waters. Other metals of considerable importance are selenium, cobalt, molybdenum, manganese and aluminium. Metals can also exist in organic form, i.e. from dyeing and textile industrial waste, and microbial reactions with metal ions.

The European Community Directive 98/78/EC[2] has published a list of the most toxic organic and inorganic pollutants present in drinking water, and the maximum permissible concentration in water for human consumption has been established (see Table 1.1).

Table 1.1. Limits of concentration of the most toxic metals present in drinking water established by the European Community

Parameter	Parametric value	Unit
Arsenic	10	µg/l
Boron	1	mg/l
Cadmium	5	µg/l
Chromium	50	µg/l
Copper	2	mg/l
Lead	10	µg/l
Mercury	1	µg/l
Nickel	20	µg/l
Selenium	10	µg/l

The concentration of these pollutants in the environment is increasing rapidly due to their intensive use in industrial processes. This is of great concern because of the damage that these contaminants cause to living species. Most metal ions are highly toxic and must, therefore, be removed from drinking water to protect consumers.

1.3 Contamination by cadmium and mercury

Cadmium and mercury are two of the most toxic metals present in aqueous solutions, hence, the maximum permissible concentration in drinking water has been set at 5 and 1 $\mu g\ l^{-1}$ (ppb), respectively.

Cadmium originates in the general environment from nature and humans. Dispersions of cadmium to the environment can result from industrial processes, domestic activities, agricultural practices (i.e. use of fertilisers), the use of cadmium containing goods, and disposal of waste. For example, cadmium is used to produce a variety of pigments, in special alloys, coatings stabilisers and in rechargeable nickel-cadmium batteries.

Cadmium is present as an impurity in various metallic ores and also in some of the fuels used during smelting and refining. As a consequence, several of the heating processes involved in metal production are expected to lead to volatilisation of cadmium (during fuel combustion) and possible emission to air. Water and soil may also become contaminated as a result of the release of metal-containing wastes and effluents[3].

Cadmium can affect human health in different ways. It accumulates in the kidneys, and in high concentrations it can reach a critical threshold that can lead to serious kidney failure. Cadmium can enter the body by ingestion of food and water, and can also be inhaled when smoking, as it is present in cigarettes, and from suspended particles in air. It can then pass to the blood and be transported to diverse organs where it accumulates. Different diseases have been associated with cadmium, for instance cancer of the prostate and nasopharynx.

The contamination by heavy metals specially in rivers and estuaries close to industrial discharges creates a serious problem to aquatic life, especially the accumulation of metals, i.e. mercury, in fish flesh. It has been reported[4,5] that mercury can exist as elemental mercury(0), mercurous(+1) and mercuric(+2) state in natural water. The distribution of these species will depend on several conditions such as total mercury concentration, pH, redox potential and anion concentration that form complexes with mercury. The same authors have also reported that mercury is discharged into the aquatic environment mainly in the form of elemental mercury Hg(+2) and phenyl mercuric acetate $C_6H_5Hg(CH_3COO)$. Hg^{2+} is not an aggressive toxin, however, it tends to form methylated derivatives and compounds with elements such as chlorine and oxygen that are highly toxic.

Mercury enters the environment from burning coal and waste, mining ore deposits, natural deposits, volcanic activity, etc. It is used in the production of chlorine gas, batteries, dental fillings and in thermometers. Humans are exposed to mercury by breathing contaminated air, ingesting contaminated food and liquids, and having dental and other medical treatments. High levels of mercury in the human body may damage the brain, which results in memory problems, change in vision and hearing. Moreover, the EPA has determined that mercury chloride and methyl mercury are possible human carcinogens.

1.4 Separation processes applied to wastewater treatment

It is obvious that the presence of metals in aqueous solution even in very low concentrations can be extremely toxic to many life forms. As a consequence, equipment and processes are continuously being developed to remove and/or recover metals from wastewater streams. Different processes have been applied, such as: adsorption, ion exchange, chemical precipitation, electrochemical processes, membrane processes, biological, and liquid-liquid extraction. The selection of one or other of these separation processes will depend on the solution characteristics and concentration of contaminants. The application of some of the processes mentioned above will be discussed in this section.

1.4.1 Precipitation

This process is one of the most commonly used to remove metals from wastewater streams arising in the chemical and metallurgical industries. However, this process requires secondary treatment steps such as filtration and dewatering. Hydroxide, sulphide, phosphates and carbonate are the most commonly used precipitants[6]. Metals such as nickel, zinc and copper are easy to precipitate while others such as mercury and chromium are not. The optimum pH for streams containing different metals differ for each contaminant so that the solution needs to be treated in stages under different pH conditions.

Na_2S has been very effective for the precipitation of cadmium, zinc and copper from aqueous solutions. The high reactivity of sulphur (S^{2-} and HS^-) with metal ions and the low solubility of sulphur complexes formed with metals, over a wide range of pH, makes sulphur a more attractive reagent than hydroxide[7].

Carbonate precipitates normally at lower concentrations than hydroxide, and the precipitant separates from solution better. Sulphide precipitation occurs at lower pH than carbonate. The reaction time is also less but fine solids are formed and hence coagulation is needed at the separation stage. The main obstacles to sulphide precipitation are production of H_2S and the toxicity effect of sulphides, although the sludge produced is subject to less leaching.

Other chemical methods are also used to either assist separation following a precipitation step or as a stand alone method for treatment of wastewater streams. For instance, Whang[8] designed a plant to treat a wastewater stream from a plating shop. The design had to consider the removal of Cr(VI) and cyanide. The design of the plant included: cyanide oxidation, Cr(VI) reduction, neutralisation, sulphide addition, flocculation, clarification and filtration. Hydrogen peroxide was also used at the end of the process to oxidise any traces of sulphide.

Reed and Nonavinakere[9] have mentioned that precipitation is the most common method to remove metals present at high concentrations in wastewater, however, the success of the process strongly depends on the characteristics and chemical composition of the solution to be treated.

1.4.2 Electrochemical processes

These methods are based on the reduction and oxidation reactions occurring at an electrode and the transport of ions across the electrolytic cell due to the applied voltage. The reactions generate electrons to convert metal ions to their elemental state. Therefore, electrochemical techniques do not need additional reagents to conduct the process.

Electrochemical processes have been extensively utilised to remove and recover metals from wastewater, mainly in hydrometallurgy and the semi-conductor industries[6]. Wastewater streams containing more than 1% w/w trace metals can be successfully treated by applying an electrochemical process. However, it is necessary to modify the process in order to obtain high efficiency without excessive consumption of energy for dilute solutions.

Abda and Oren[10] studied the cathodic reduction of cadmium in the presence of other metals such as nickel and cyanide. The authors found that a local alkaline pH is generated in the interface between the solution and electrode. Under these conditions, $Cd(OH)_2$ is formed which can be removed by adsorption on the electrode as a charged colloidal particle. Many other investigators have studied the removal of heavy metals from aqueous solution by using an electrochemical process, i.e. copper, nickel, zinc, iron and silver[11,12,13].

1.4.3 Membrane processes

These processes have the advantage of selectivity compared to other techniques. Membrane processes involve the flow of a permeate through a porous media induced by a driving force and also promote retention of particle contaminates. A membrane technique is divided into three types based on the applied driving force: pressure, concentration and electrical. The pressure gradient process can be subdivided into ultrafiltration, microfiltration, nanofiltration and reverse osmosis.

Other membrane processes work according to the size of the suspended solids. Particles smaller than a certain size are allowed to pass through the membrane whilst the largest are retained. Technology has advanced in this field and new kinds of membranes have been developed, for instance chemically active membranes that enhance the separation process.

An electric current can also be applied when a membrane is used to separate certain species from wastewater streams. This enhances the process as the transport of ions across the porous or permeable membrane becomes faster. Either cations or anions are allowed to pass the membrane whilst the species of opposite charge is restricted. This technique has been widely applied in desalination plants.

Membrane processes can be used at the end of a series of separation processes to reduce the concentration of metal ions below statutory discharge limits[14]. This technique has been proved to be very efficient, however, it involves higher operational and capital costs.

1.4.4 Ion exchange

Ion exchange involves the counter exchange of ions of similar charge between a particulate solid phase, e.g. a polymeric resin, and an aqueous solution[15]. This process is reversible and has been used to remove metal ions from wastewater, e.g. cobalt, iron and zinc[6]. The saturated ion exchange resin can be regenerated with an acid or alkali solution, depending on the nature of the resin. The resulting eluant solution is highly concentrated and small in volume. This means that this process needs a second treatment in order to recover the metals. The more commonly used ion exchangers are polymeric resins, however, other materials have also been applied as ion exchangers, such as clays, activated carbon and zeolites[15].

Many researchers have studied the removal of heavy metals from aqueous solution by using a variety of natural and synthetic ion exchangers. For instance, Gopala Rao *et al*[16] and Suzuki *et al*[17] investigated the removal of cadmium using a chelating resin, Chelex100, and modified calcium carbonate, respectively. Mazidji *et al*[18] focused their studies in the removal of metal ions such as copper, mercury, silver, cadmium, lead and zinc using ion exchange resins, Dowex 50W-X8, and chelating resins, Chelex 50-100. The authors found that silver and mercury were not removed efficiently by these materials. They also pointed out that the optimum pH was between 5 and 8.

The removal of metal ions by ion exchangers is recommended for concentrations <1000 ppm, and in solutions with low quantities of competitive ions. The process can be selective, however, this requires a sophisticated design resulting in high cost. It is essential that the solution to be treated does not contain insoluble colloidal matter in order to obtain high efficiency in ion exchange and regeneration.

1.4.5 Adsorption

Adsorption differs from ion exchange, since it involves physical interaction of molecular species in solution with the surface of a porous adsorbent. The mechanism of interaction is by weak electrostatic forces, e.g. Van der Waals forces, London forces, hydrophobic interactions, hydrogen bonding, etc. For ionic species, e.g. trace metals, it is possible to obtain interaction by semi-sorption with specific functional groups at the surface of the adsorbent. In the case of activated carbon, adsorption involves an ion exchange mechanism and/or a specific chemical interaction between the ions and the surface functional groups.

Adsorption on solid materials, mainly activated carbon, has been widely applied in water treatment. Many organic and inorganic adsorbents have been used to remove metal ions from aqueous solutions. For instance: chitosan[19], aquatic plants[20], iron oxide[21], magnesium oxide[22], silica gel[23] and a variety of granular activated carbons. Activated carbon is most widely studied and used in the adsorption of organic and inorganic micropollutants from water.

The physico-chemical properties, uses and applications of carbonaceous adsorbents will be studied in detail in chapters 2 and 3.

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Chapter 2:

ACTIVATED CARBONS

2.1 Introduction

The term *activated carbon* defines a group of materials with a highly developed internal surface area and porosity and hence a large capacity for adsorbing chemicals from gases or liquids[1].

The basis for industrial production and utilisation of activated carbon was established in the late 18th century. Since those early days, industry has developed a wider range for both liquid and gas phase applications. Granular carbons found a number of applications after the First World War in the purification of gases and extraction of vapours from gas streams. This sorptive material was then used at industrial scale in the recovery of liquid petroleum from natural gas, the extraction of benzene from manufactured coal-gas and the recovery of volatile solvent vapours from various industrial processes. Activated carbons have also been extensively used to remove chemical species by adsorption from aqueous solutions, in order to accomplish water purification, metals recovery, etc.

Activated carbons have a wide area of application, a strong market position and low cost compared with possible competitive adsorbents. This has given rise to the production of new forms and shapes of activated carbons with special characteristics for specific applications. For instance, carbon fibres and microbeads have been developed in the last decade. These new types of carbonaceous materials have very high surface area, >1200 $m^2 g^{-1}$, excellent mechanical properties and fast kinetics. Moreover, carbon fibres are easier to handle than granular carbons. Applications continue to be developed in response to growing demands for environmental protection and for emerging technologies, such as natural gas storage and catalytic reduction of NO_x[1]. The most successful new carbon product to be commercialised in the modern age, is probably activated carbon fibre. This type of carbon was first commercialised by Union Carbide[2] in the 1960s and is now produced to satisfy the world-wide market of 6000 tons per year[3].

2.2 Precursors

Activated carbon can be produced from any material that is high in carbon content and low in inorganic substances. These adsorbents have been produced from different types of raw materials such as animal bones, fruit stones, nutshells, wood, coconut shell, coal, peat, lignin, pitch and wastes from the processing of petroleum and lubricants. Only five of all these precursors have been used on an industrial scale, and in the order of importance they are wood, coal, lignite, coconut shell and peat[4].

There are many potential raw materials for the production of activated carbon. However, not all of these produce an activated carbon of high quality. Hence, the following factors have to be taken into account[2,5].

- Presence of low amount of inorganics.
- Volume and cost.
- Potential for obtaining a high quality activated carbon.
- Workability of the raw materials.
- Storage of the raw material.

Activated carbon fibres have been produced from cellulosic materials which include cotton, linen, ramie, sisal, hemp and flax, pith, nonheterocyclic aromatic polymers, aromatic heterocyclic polymers, linear polymers, coal and polyacrylonitrile (PAN). The choice of precursor is largely dependent on its availability, cost, and purity, but the manufacturing process and intended application of the product is also vital. PAN is recognised as the most important precursor and has considerable potential for the manufacture of activated carbon fibre due to its high degree of molecular orientation, high melting point and large carbon fibre production[6]. Nowadays, PAN based carbon fibre dominates world consumption, and represents nearly 90% of world wide sales[7].

2.3 Carbonisation

The production of activated carbon starts with carbonisation. This stage involves thermal decomposition wherein the non-carbon species are eliminated, and a carbon mass with simple pore structure is produced. The carbonisation is usually conducted below 800 °C in an inert atmosphere, and some times at 1000 °C in the absence of gas. There are some factors that affect the final product of carbonisation, such as the rate of heating, the final temperature and the natural and physical properties of the raw material. The rate of heating is a very important factor that has to be controlled depending principally on the physical properties of the precursor. For instance, raw material of low density can produce carbon with excellent pore volume, but there is a problem with semi-hard and hard precursors where shrinkage can reduce the pore volume[8].

The manufacture of PAN based fibres consists of several stages. Stabilisation has to be done prior to carbonisation, with the aim of cross-linking PAN chains to prepare a structure that can withstand the rigours of high temperature processing[7]. Oxidative stabilisation is highly exothermic and is frequently conducted at temperatures between 200 and 300 °C for extended periods of time in the presence of oxygen[2]. Fibres must be kept under tension during oxidation to maintain alignment of the PAN polymer while it transforms to ladder polymer to limit relaxation of the polymer structure[9,10]. The PAN stabilisation process also includes cyclisation and dehydrogenation reactions, along with reactions leading to binding of oxygen.

Once stabilisation has finished, PAN fibres are carbonised between 1000 and 1500 °C in an inert atmosphere, usually nitrogen. During this process, the non-carbon species are eliminated as volatiles, e.g. H_2O, HCN, NH_3, CO, CO_2 and N_2, to produce approximately 50% carbon from the original raw material[11]. Between 400-500 °C, the hydroxyl groups present on PAN start to link up in lateral directions generating a graphite structure consisting of three hexagons in the lateral direction bounded by nitrogen atoms. The elimination of nitrogen is conducted between 700 and 1300 °C; some authors have reported values of 0.3% nitrogen in the final product[12]. The processes described above can be presented in schematic form (see Fig 2.1).

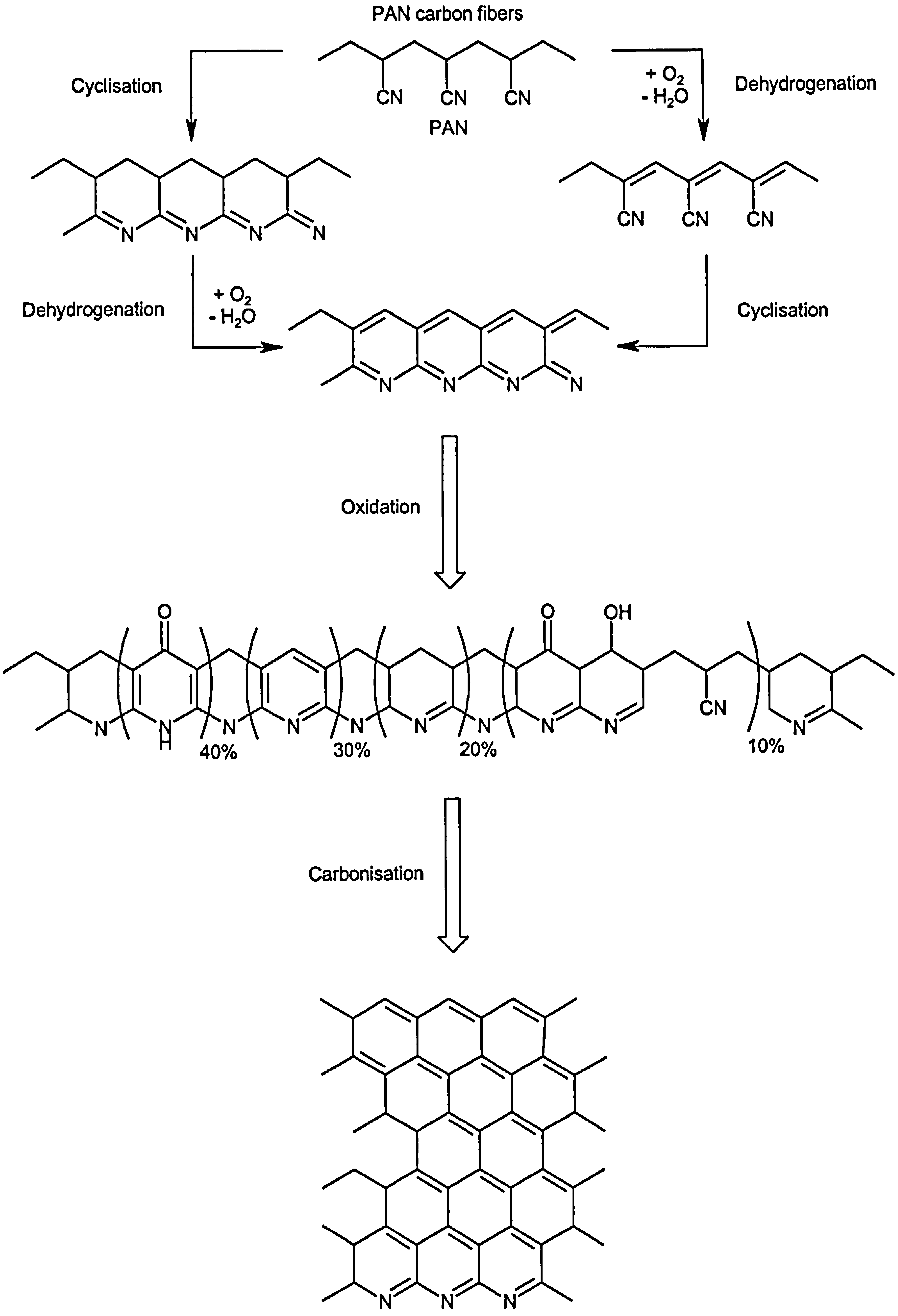

Fig 2.1. Stabilisation and carbonisation of PAN based carbon fibre

Both the stabilisation and carbonisation processes of PAN can be controlled by the introduction of various additives. These additives not only influence the kinetics and reaction mechanism during PAN stabilisation and carbonisation, but also lead to a certain combination of properties in the final element-carbon fibres. Additives improve mechanical and sorption properties. For instance, the inclusion of iron in the PAN fibres prevents the sticking of individual filaments, improving the mechanical properties of the final product. It is to be noted that the product obtained after stabilisation and carbonisation has a relatively low internal surface area.

2.4 Activation

The activation method involves increasing the volume and widening the diameter of the pores generated during carbonisation, and creating new porosity. This process can be conducted by two methods; chemical and physical activation.

Chemical activation is carried out by thermal decomposition (400 to 600 °C in the absence of air) of the precursor impregnated with a chemical agent such as phosphoric acid, sulphuric acid, potassium sulphide, zinc chloride, chloride of calcium, magnesium and ferric iron[13,14]. Chemical activation by using zinc chloride was originally preferred up to about 1970. However, the residual zinc in the carbons caused corrosion problems and low recovery efficiency contributed to its replacement by phosphoric acid[15]. The preferred precursors, when phosphoric acid is used as chemical agent, are lignocellulosic material such as olive stones and wood[4]. Activated carbons with extraordinary surface area, more than 3000 m^2 g^{-1}, have been produced by using potassium or sodium hydroxides as activating agents, but only at laboratory scale[16].

Physical activation is usually conducted between 800 and 1100 °C in the presence of an oxidising gas such as steam, carbon dioxide, air or mixtures of these. It is known that some elements or compounds catalyse the reaction of carbon with oxidising gases. The best results have been obtained by adding chlorine or halogen- containing compounds to the reaction gas or by treating the carbon surface with boron oxide or phosphorus compounds[17].

The activation mechanism consists of two stages; firstly the disorganised carbon on the surface is burned off, and in the second stage the carbon of the aromatic sheets starts burning, producing active sites, wider pores and thus new porosity. The quality of the activated carbon depends on the type of oven used during activation. Generally a decrease of mesopority is observed in the following order: fluidised bed, multiple hearth furnace, rotary kiln[18].

Physically processed carbons are generally microporous when activated with carbon dioxide, whereas steam produces a wide pore size distribution with greater development of meso and macropores. Air and oxygen are rarely used to activate carbons because the reaction between carbon and these reagents is highly exothermic, resulting in significant burning and therefore causing excessive weight loss[19].

2.5 Physical properties

Apart from high surface area and well-defined pore size, activated carbons are characterised by their high strength, good thermophysical and electronic properties[20].

Electrophysical properties of carbons such as electroconductivity and paramagnetism are attributed to their electronic structure. Conductivity is due to π-electrons moving along hexagonal aromatic planes in the system of conjugated bonds. Electronic properties have been studied extensively in the past and it has been concluded that the precursor, conditions of thermal treatment and the factors influencing the structural transformation of carbonaceous materials define the electrophysical characteristics of the final product[21].

2.5.1 Porous structure

Activated carbon and carbon fibre have a large surface area (usually between 800 and 2500 m^2/g) and large pore volume, favourable pore size for the adsorption process and excellent mechanical properties. According to IUPAC[22] the porosity in carbons is classified in three groups:

i). Micropores (width less than 2nm)

ii). Mesopores (width between 2 nm and 50 nm)
iii). Macropores (width greater than 50 nm)

Micropores have been also classified as ultra (<0.5 nm width) and super (1.0-2.0 nm width) micropores.

It is well known that granular carbons have a combination of micro, meso and macropores. Supermicropores occupy an intermediary position between micro and mesopores and their filling follows the micropore mechanism. Micropores contain high adsorption energy and surface area, greater than 95% of the total area, which make them the most important in adsorption processes. Mesoporous adsorbents are characterised by capillary condensation of organic compounds in their pores, whilst polymolecular sorption of organic compounds takes place in macroporous adsorbents.

The specific area of macropores is so small that it can be considered negligible, hence, macropores do not have an appreciable effect on adsorption value. They are, however, transport arteries providing passage of the adsorbate into the interior mesopore and the micropore surface where most of the adsorption takes place[23].

Alternatively, carbon fibres are highly microporous (often more than 90% by pore volume is microporous), with micropores of diameter 5 - 21 Å directly connected to the external surface. Thus, adsorbates reach active sites inside the pores quickly without additional diffusion resistance in the macropores[24,25]. The difference in porosity between granular carbon and carbon fibre is illustrated in Fig 2.2. Many authors have presented a number of structural models for carbon fibres however none of them is sufficiently comprehensive. For instances, Barnet and Norr[26] proposed one of the most complete models and this is presented in Fig 2.3.

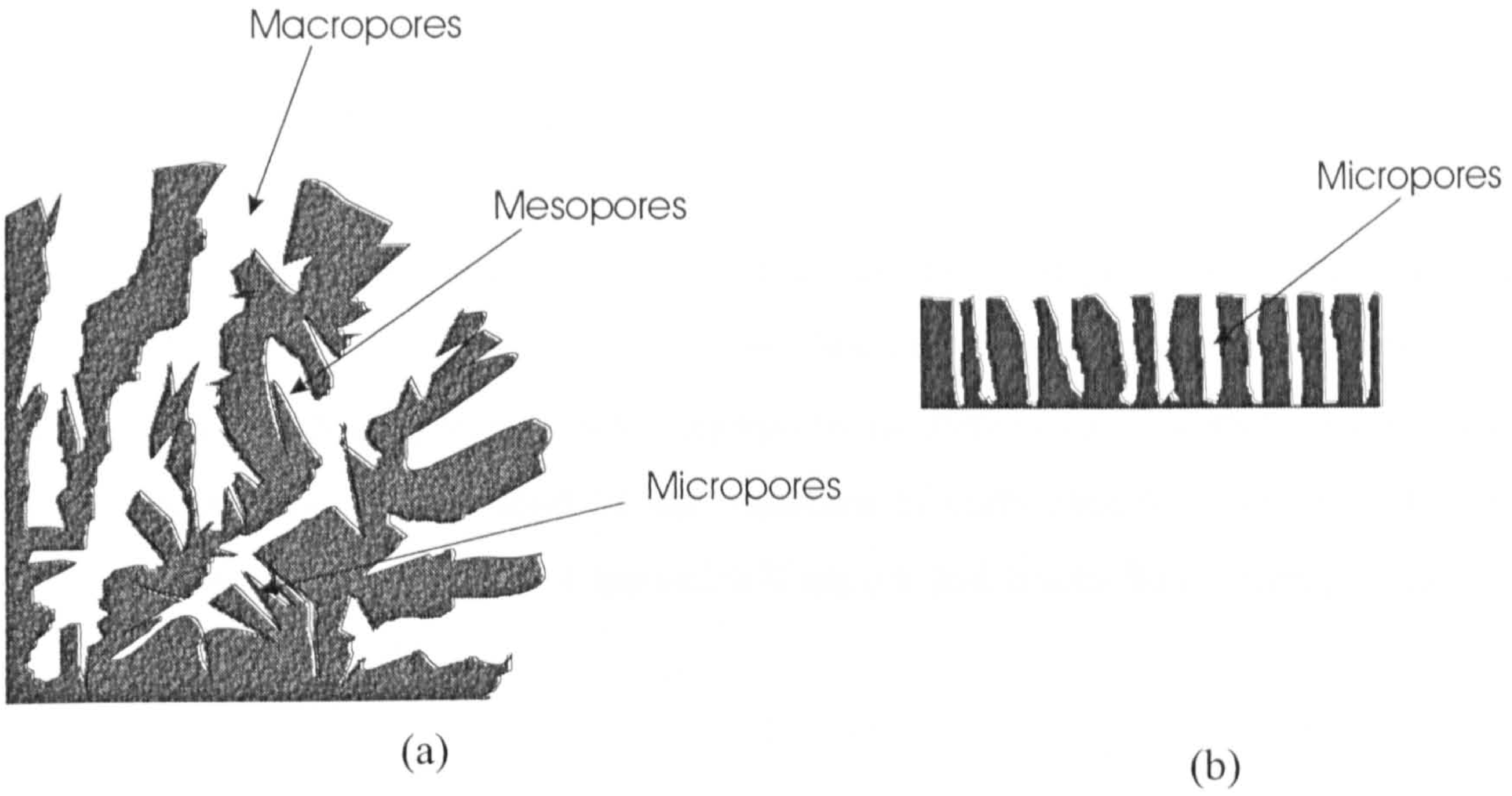

Fig 2.2. Porosity in granular (a) and fibrous (b) activated carbons.

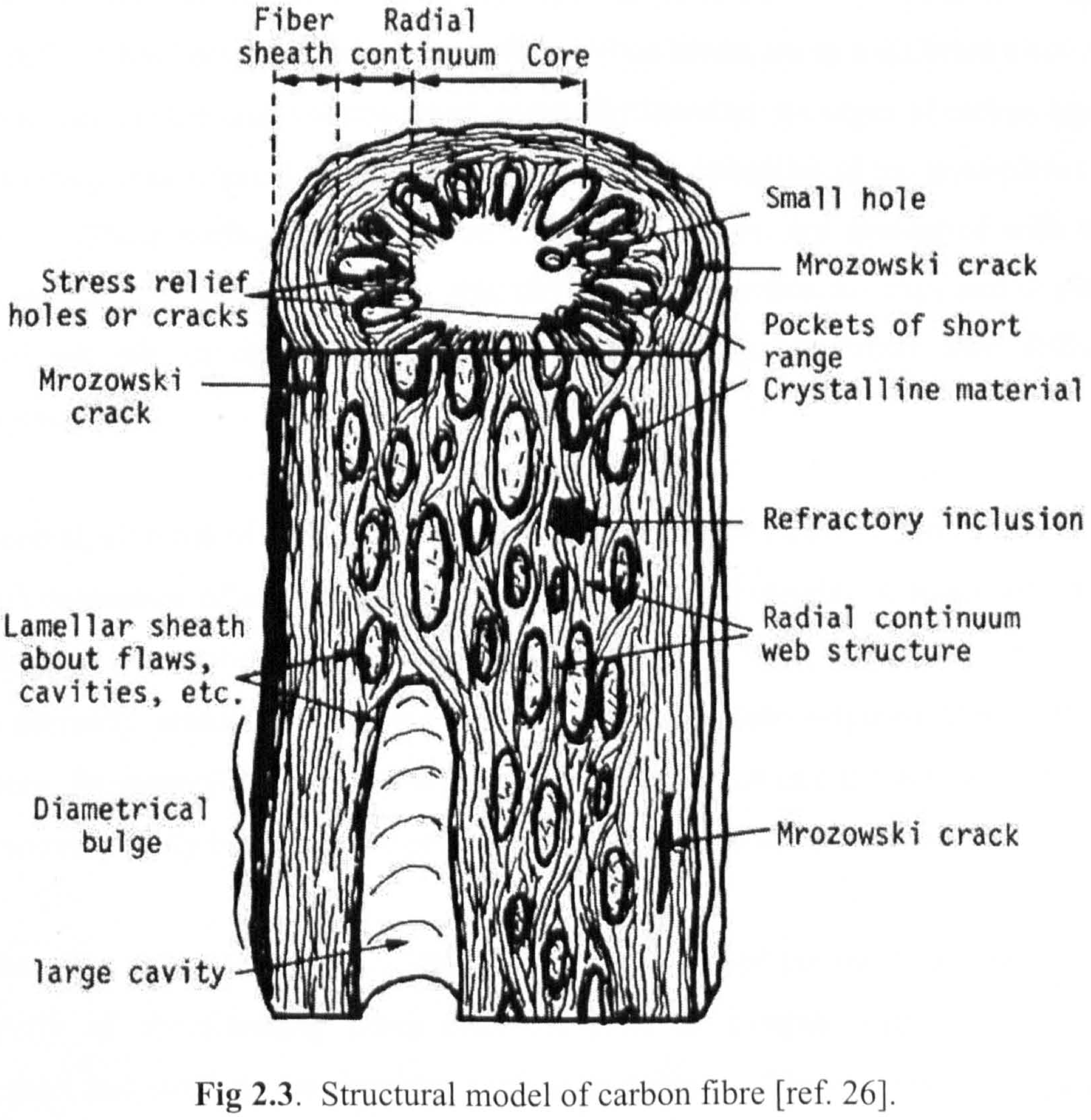

Fig 2.3. Structural model of carbon fibre [ref. 26].

The size, shape (e.g. ink-bottle shape, regular slits between two planes, and V-shape pores[27]), interconnectivity and pore size distribution depend on a great number of factors such as carbon precursor, carbonisation and activation method[28]. A number of techniques have been used to elucidate the structure within porous materials: for example Transmission Electron Microscopy, Scanning Tunnelling Microscopy, Small Angle X-ray scattering techniques, adsorption isotherms and mercury porosimetry. Many researchers have focused on the structure of carbonaceous materials and as a result a considerable number of specialised papers and books have been published[22-29].

2.6 Chemical properties

The chemical properties of activated carbon have been extensively studied and analysed in recent years. The structure of activated carbon has been described as a twister network of defective carbon layer planes cross-linked by aliphatic bridging groups[30]. It has been mentioned that surface carbon atoms are in a different electronic state to those in the bulk volume phase, especially those on the edges of carbon layers; *e.g.* in the places where defects, dislocations and discontinuities of the layer planes are present. These surface carbon atoms, called *active sites,* are associated with high concentrations of unpaired electron spin centres and, therefore, are expected to play a significant role in chemical and adsorptive interaction of carbon with different compounds[31].

In general, all types of carbon e.g. cokes, activated carbon, powders and fibres contain a high percentage of elemental carbon, i.e. about 90% by weight. A small percentage of different elements, such as nitrogen and sulphur and other organic impurities are also normally present in carbons. These contaminants can originate from different sources, for example from the precursor, the carbonisation and the activation process and should mostly be eliminated prior to any analysis or characterisation.

Carbon is a unique element for diverse reasons. One of the most important is the property of chemisorbing other elements such as oxygen, hydrogen, nitrogen, halogens and sulphur, that increase surface complexes. These surface groups alter properties such as acidity, porosity, cation exchange capacity and selectivity and thereby enhance the adsorptive properties[22]. Chemically modified sorbents of this type are normally called " impregnated carbons".

The surface properties of carbons are influenced to a large extent by foreign elements bonding on the surface. Oxygen is attached to carbon more easily than many other elements, and the oxygen-containing groups formed on the surface are by far the most important in influencing surface reactions, wettability, surface behaviour, electrical and catalytic properties. For instance, a clean carbon is hydrophobic, however, when oxygen is chemisorbed it becomes hydrophilic. This is because surface oxides have the property of adsorbing water and other polar compounds.

Chemisorption of oxygen on carbons can occur at different temperatures. It has been reported that carbons that have adsorbed oxygen at room temperature (conventional activated carbon or H-carbons) are different from those that adsorbed oxygen at high temperature (oxidised carbons or L-carbons)[32].

The identification and quantification of surface oxides on carbons has been achieved by using titration techniques and chemical identification methods developed by well known researchers, e.g. Boehm[33] and Donnet[34]. Spectroscopic methods have also been used recently to identify functional surface groups on carbons. The most commonly applied spectroscopic methods are Fourier Transform Infrared spectroscopy (FT-IR), X-ray Photoelectron Spectroscopy (XPS), Low-Energy Ion Scattering Spectroscopy (ISS) and Attenuated Total Reflection (ATR).

It has been mentioned above that chemisorption on carbons generates well-defined surface groups that are bound to the solid[34, 35]. These groups are classified as basic and acidic surface oxidised.

2.6.1 Acid surface groups

A carbon surface is mostly saturated with hydrogen. However, oxygen is the most important element. The higher the oxygen content, the more acid the surface properties, and these carbons have high cation exchange properties.

It has been reported that acidic groups are associated with the oxygen that has been chemisorbed on the carbon surface, at high temperature, during the contact with an oxidising media[23, 24]. The structures presented in Fig 2.4 are oxygen functional groups that might be found at the edges of graphene layers. Carboxyl groups (a) might give carboxylic anhydrides (b) if they are close together. Carbonyl groups might condense to lactone groups (c) when they are close enough to hydroxyl or carboxyl groups. Single hydroxyl groups (e) would be of phenolic type. Carbonyl groups could exist either isolated (f) or arranged in quinone-like fashion (g), and finally, oxygen could simple be substituted for carbon atoms forming ether-type oxygen groups (h)[36].

Evidence of the existence of oxygen-containing groups (a) to (e) have been found by chemical detection methods, such as esterification with hot ethanol. Boehm[36] has proposed a method, based on individual acidity constants, which allows identification and quantification of oxygen-containing surface groups. This technique uses different alkaline solutions of increasing strength to neutralise specific oxygenated surface groups. Carboxyl, lactone and phenolic groups are titrated by sodium hydrogen carbonate ($NaHCO_3$), sodium carbonate (Na_2CO_3) and sodium hydroxide ($NaOH$), respectively, whereas sodium ethoxide ($NaOC_2H_5$) neutralises groups of weaker acidic strength. Carbons usually contain more oxygen than can be explained by the detected oxygen-containing groups. Undetected oxygen by acid/base titrations is attributed to ether-type oxygen groups[37].

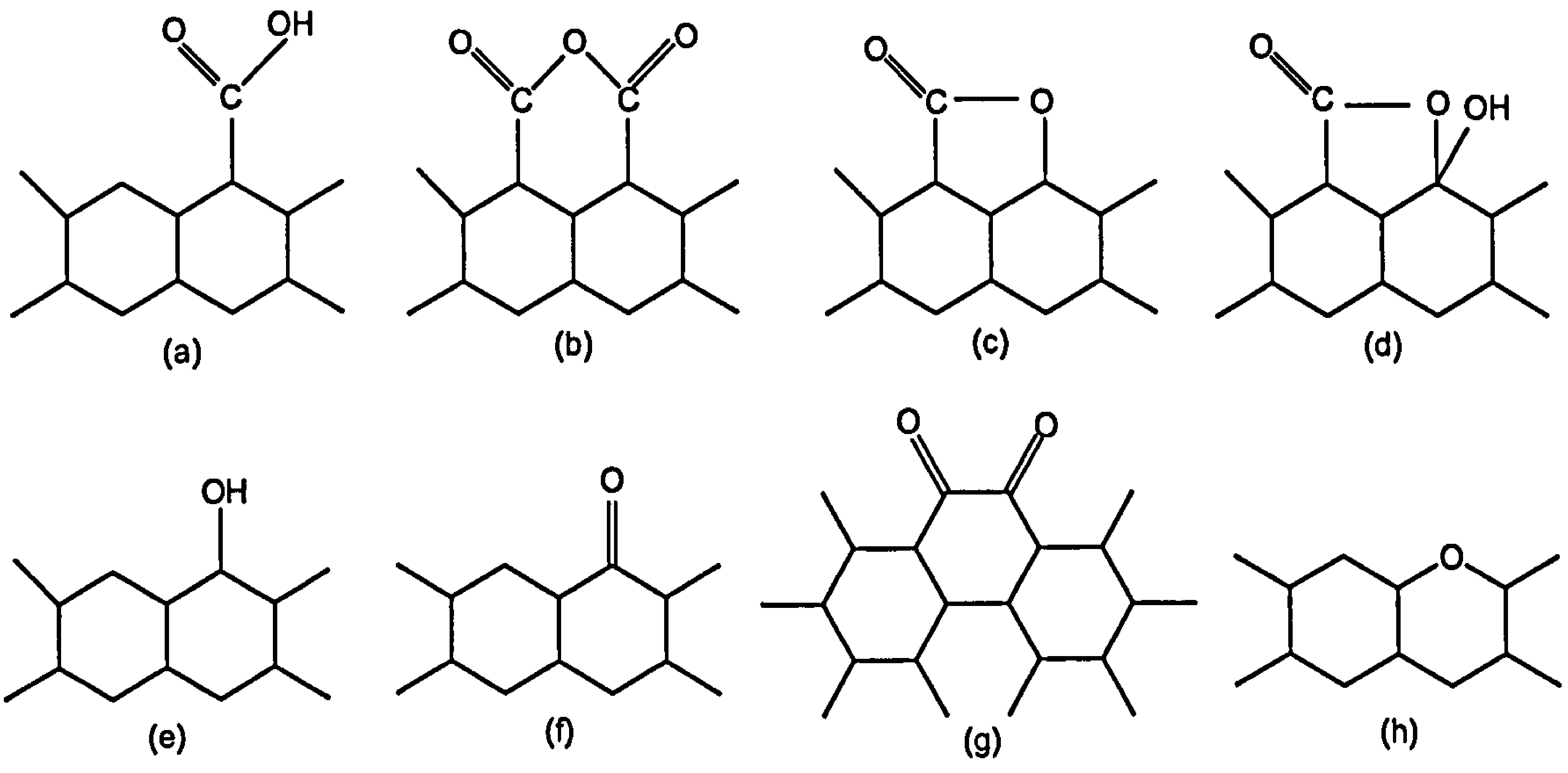

Fig 2.4. Possible structures of surface oxygen groups [ref. 36].

Carbon surfaces contain a variety of functional surface groups. It is possible that neighbouring groups react with each other giving rise to different oxygenated groups[36]. For example, lactol groups might form by a reaction between carboxyl and carbonyl groups (see Fig 2.5).

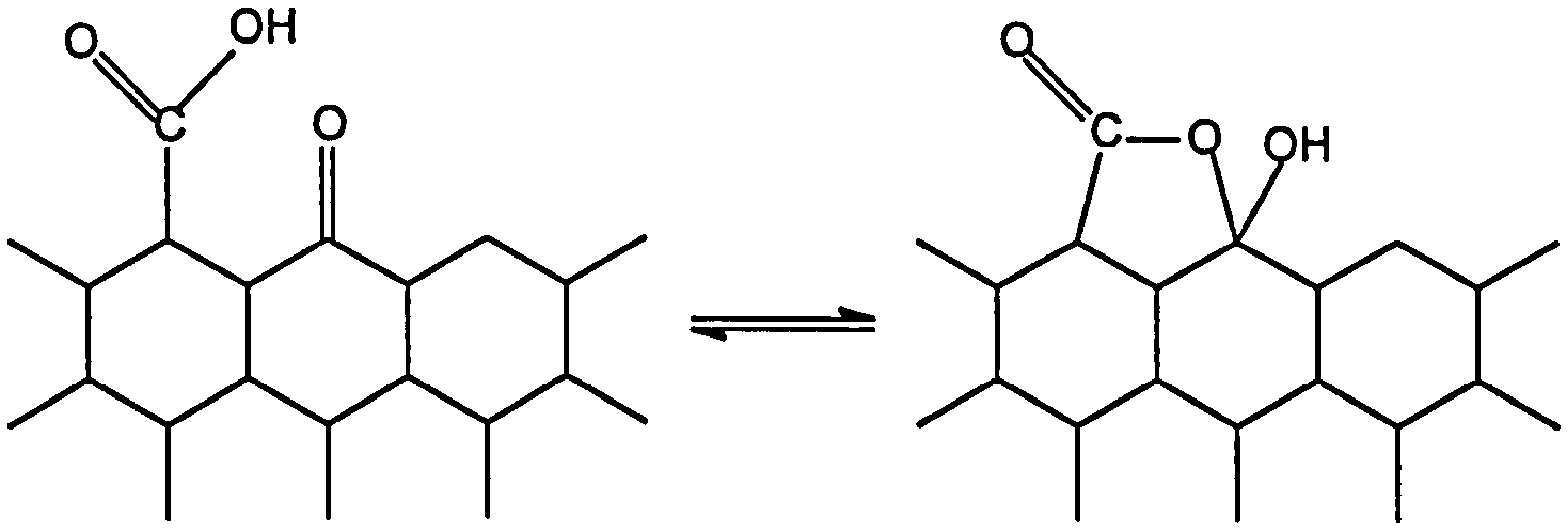

Fig 2.5. Similar structures of oxygen-containing groups.

The reactivity of a specific type of functional group differs due to the influence of neighbouring groups even with more distant groups. This is due to electronic interaction via surface carbon crystallites[38]. For this reason, the dissociation constant of a particular kind of oxygenated group differs by some orders of magnitude in different carbons.

2.6.2 Basic surface groups

Not much is known about these surface groups, even though they were discovered before acid groups. Carbons with low oxygen content show basic surface characteristics and have anion exchange properties. These surface groups are formed when carbon reacts with oxygen at low temperature; these reactions already occur at -40 °C. Basic sites are identified as Lewis basic sites associated with the carbon structure itself[23, 24], that exhibit the following properties: the oxides adsorb acid only in the presence of oxygen and a part of the acid adsorbed in this way may be desorbed by solvents such as toluene[34].

Garten and Weiss[32] proposed a chromene type structure for basic groups. However, earlier studies conducted by Voll and Boehm[39] suggested that basic groups are more likely to exist as γ-pyrone-like structures as shown in Fig 2.6.

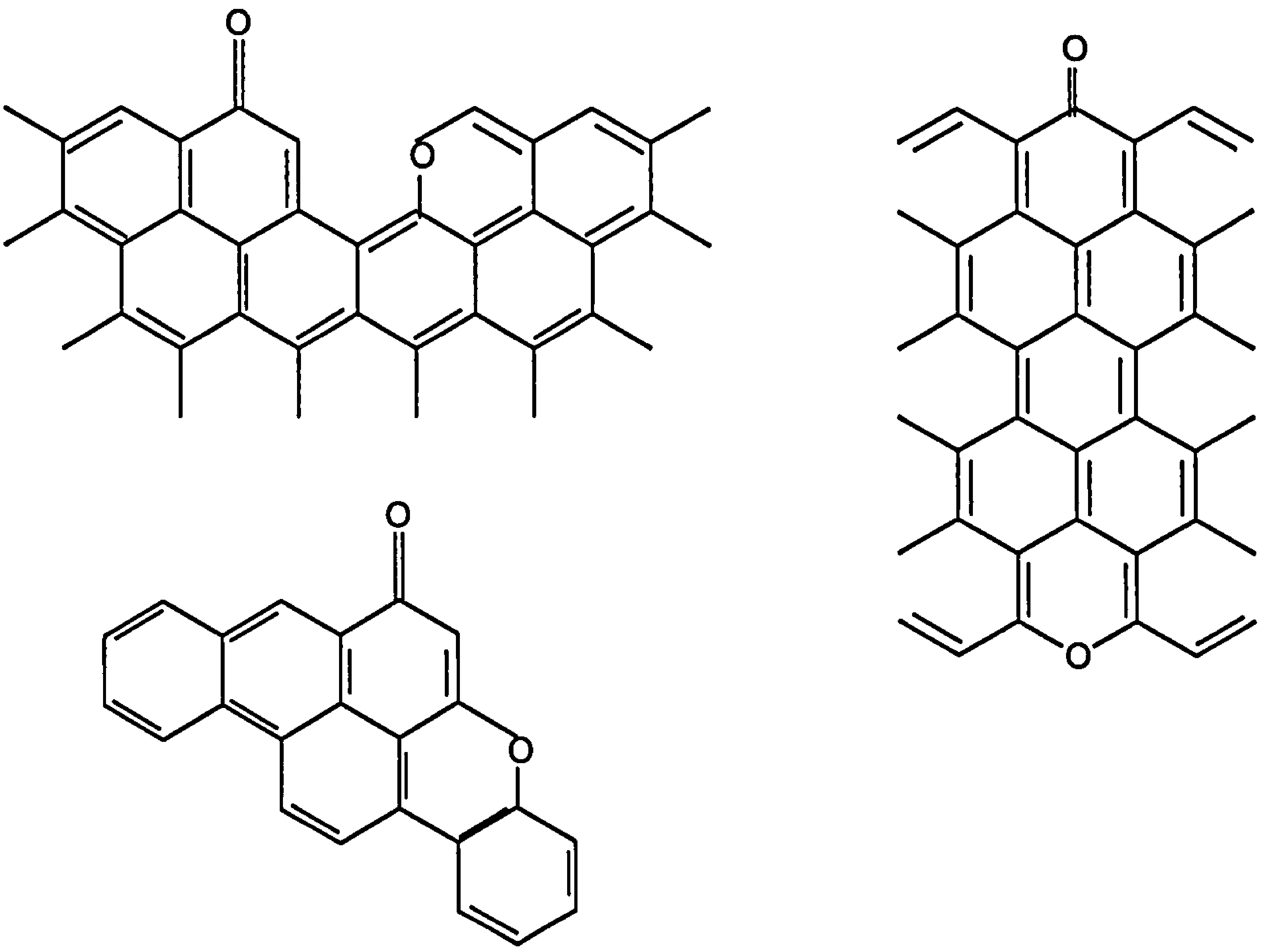

Fig 2.6. Possible structures of basic surface sites on a ghaphene layer.

Oxidised carbons contain basic sites in addition to the acidic groups, however, their quantity is normally much less even when acid oxides are partially removed at high temperature.

2.7 Chemical modification

It has been reported that activated carbons offer a great potential for the removal of organic and inorganic micropollutants. This can be significantly improved by surface modification. There are different techniques that modify the interfacial region of carbons, that multiply contact points or increase the reactivity of the region by developing functional groups, e.g. oxygen-containing groups, on the carbon surface. These techniques may be classified as follows:

i). *Wet chemical oxidation*; using different reagents such as nitric acid, acidic potassium dichromate, acidic potassium permanganate, sodium hypochlorite and hydrogen peroxide.

ii). *Dry oxidation*; by oxygen, air and ozone at different temperatures.

iii). *Anodic oxidation*; by an electrochemical process using different electrolytes, for instance, ammonium bicarbonate, potassium hydroxide, potassium chloride, potassium nitrate and nitric acid.

iv). *Thermal treatments*; e.g. applying the hot briquetting method[40].

v). *Pyrolytic carbon coating* and *polymer grafting*[6]

The most common methods to oxidise carbonaceous materials have been air at high temperature and nitric acid [41]. Other oxidants such as ozone and hydrogen peroxide have also been used to a lesser extent[42].

In this research, three methods of oxidation were selected to modified granular and fibrous activated carbons: nitric acid (aqueous phase), ozone (gas phase) and anodic oxidation (electrochemical process). The aim was to enhance the ion exchange capacity of the adsorbents by introducing a significantly higher amount of oxygen-containing surface groups.

2.7.1 Acid oxidation

In the last few years the modification of carbonaceous adsorbents, such as granular activated carbons and carbon fibres, has been carried out using different reagents and adopting different methodologies. Some relevant publications are reviewed and presented in this section.

Kuzin *et al* [41] have reported that activated carbon oxidised by nitric acid has a high selectivity for multivalent cations. As a consequence of oxidation, the amount of functional groups is altered and the acidic properties increase with increasing degree of oxidation. Moreno-Castilla *et al* [43] studied the effects of non-oxidant acid HCl and HF, and oxidant acid HNO_3 on a carbon obtained from olive stones. It was found that the activated carbon treated with HCl had slightly lower surface area and micropore volume than the original sample, which was attributed to chemisorption of chlorine. Treatment with HF did not affect surface area and pore volume, and the amount of CO type surface groups increased. Alexander *et al* [44] modified the surface of a gas-activated carbon and a chemically activated carbon with nitric acid, hypochlorite and ammonia. The results showed that the amount of surface groups formed during the oxidation was much higher using nitric acid. When activated carbon was oxidised with gaseous ammonia at low temperature (200 °C) the amount of basic groups increased. In general, chemically activated carbon was more sensitive to oxidation than gas activated carbon, which was attributed to the low content of conjugated ring structures. Barton *et al* [45] modified granular activated carbon, Calgon BPL, by acid oxidation using HNO_3 at different temperatures. The characterisation was conducted by titration and measuring the heat of neutralisation. It was found that the acid heat value increased rapidly with the concentration of surface oxides while the basic heat value decreased.

The effect of acid oxidation on carbon fibres has also been studied in the last few years. For instance, Zhihong *et al* [46] carried out an acid oxidation of carbon fibre THORNEL T-300 and investigated the effects of subsequent treatment in aqueous sodium hydroxide. They found that nitric acid oxidation created acidic functional groups on the carbon fibre and the acidic capacity increased with acid-oxidation time. The surface area of this adsorbent increased after oxidation, while tensile strength decreased and weight was lost. It was concluded that sodium hydroxide treatment removes partially oxidised graphitic fragments and also induces the formation of new acidic groups on the surface by opening lactone and anhydride rings generated during nitric acid oxidation. McKee and Mimeault[47] studied the effect of oxidation by nitric acid on many kinds of carbon fibres. The conditions under which the treatment occurred involved refluxing the fibres with 65% HNO_3, washing with water and drying at 150 °C for 48 h. Conventional and oxidised fibres were characterised by thermogravimetric analysis and the results showed that modified samples presented appreciable amount of oxygen-containing groups. Bahl *et al*[48] studied the optimum conditions for oxidising PAN-based fibres. The optimum conditions were reaction with 50% nitric acid for 50 minutes. More experiments were carried out under different conditions, but in general it was found that the oxidation resulted to removal of many organised portions most of which are very significant for the strength of the fibres. Thus, after prolonged periods of time and by using high concentrations of nitric acid the strength of the fibres decreased. Pittman *et. al*[49] characterised carbon fibres after oxidation by using 70% nitric acid at 115 °C for different periods of time, 0-90 minutes. It was found that carboxyl and phenolic surface groups were mainly introduced during oxidation. It was also mentioned that the fibre surface continuously increased due to crevasses, pits and expanded microvoids that were formed as oxidation proceeded since the detached graphite did not come off as a perfect concentric layer (see Fig 2.7).

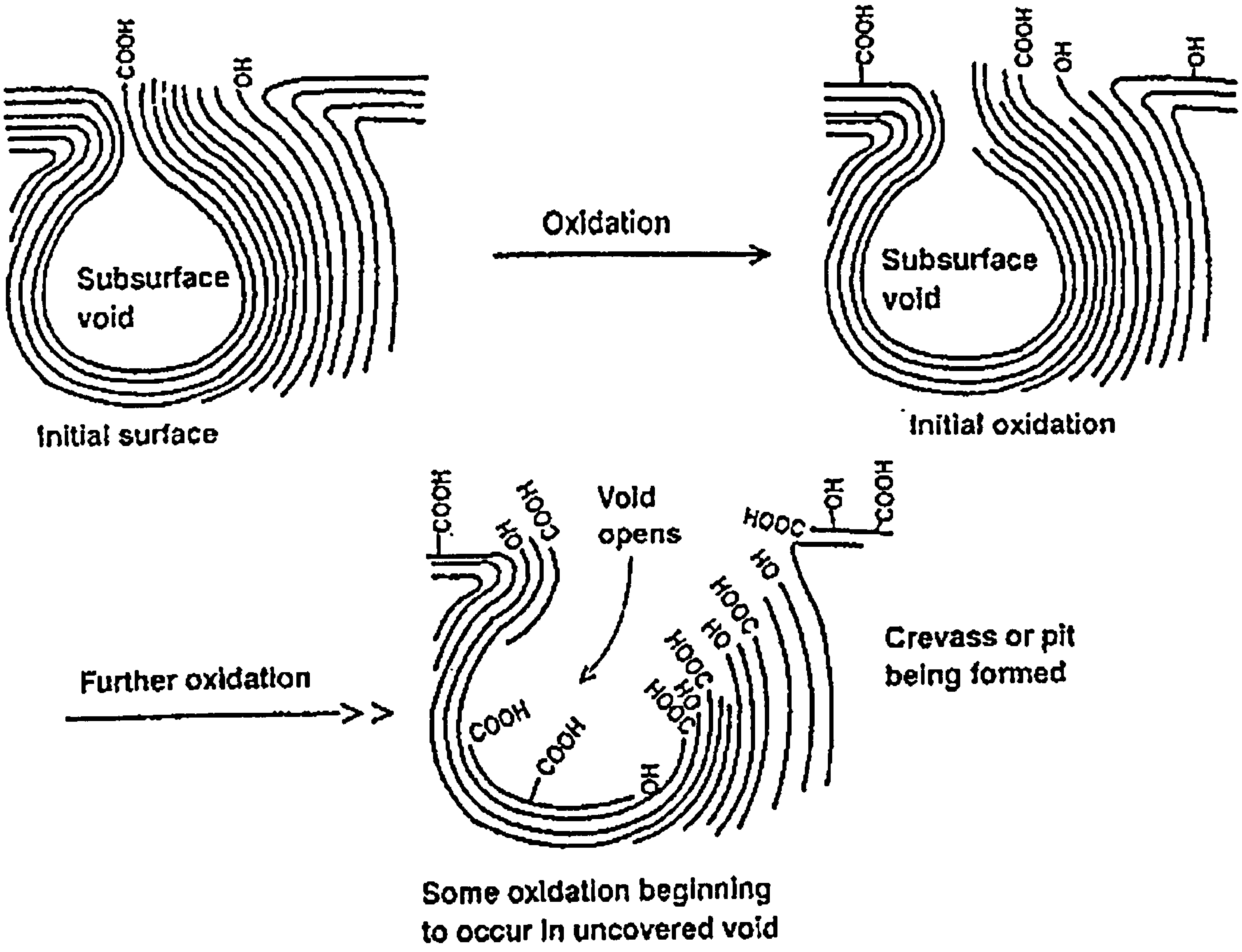

Fig 2.7. Introduction of acidic groups during nitric acid oxidation of carbon fibre [ref. 49].

Different models to represent the oxidation of carbons by nitric acid have been proposed. Vinke *et. al*[50] mentioned that nitric acid oxidation of carbons may be analogous to the oxidation of aromatic hydrocarbons. In this case, the aliphatic side chains of the molecules are susceptible to oxidation and in many cases the oxidised product is an arylcarboxylic acid (see Fig 2.8).

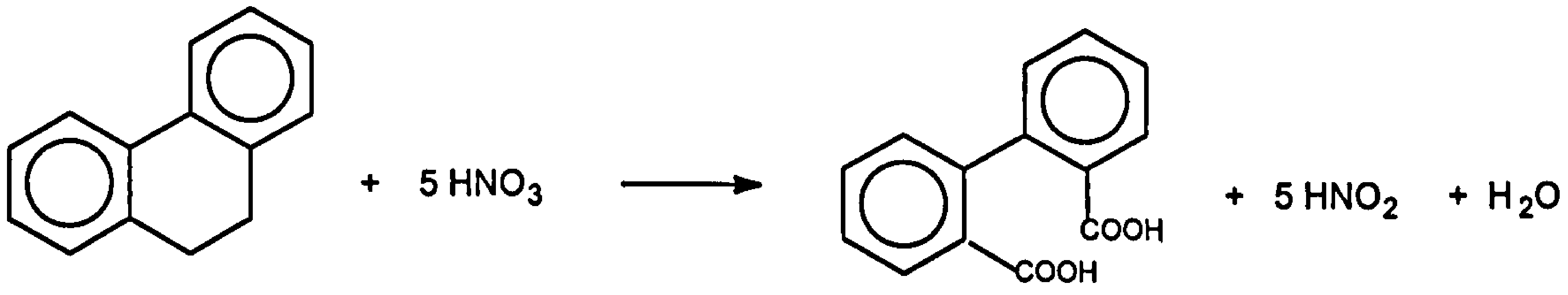

Fig 2.8. Nitric acid oxidation of a hydrocarbon.

2.7.2 *Ozone oxidation*

Some investigators have modified activated carbons using ozone at different concentrations and temperatures. Deitz *et al* [42] investigated the reaction of ozone with activated carbon at 26 °C. Carbon was contacted with O_3 for various times resulting in an immediate increase in weight which passed through a maximum and then slowly decreased. This behaviour was explained by a three-model reaction of ozone with carbon represented as follows,

$$C_xO_y\,(s) + O_3 \begin{array}{llll} \nearrow & C_xO_{y+1}(s) & + O_2 & \text{(I)} \\ \rightarrow & C_{x-1}O_{y+1}(s) & + CO_2 & \text{(II)} \\ \searrow & C_{x-2}O_y(s) & + CO_2 + CO & \text{(III)} \end{array}$$

Reaction (I) represents the chemisorption of oxygen atoms without loss in weight. This is followed by the carbon gasification resulting from reactions (II) and (III), when progressive etching takes place. Reaction (II) generates less carbon loss than reaction (III). However, the amount of oxygen groups continuously increases. The adsorption of nitrogen decreased when ozone oxidised carbon was used. This phenomena was attributed either to the progressive removal of the wall structure, which obstructs the micropores, or to the micropores plugging by chemisorbed oxygen.

Sutherland *et al*[51], studied the effect of ozone oxidation on carbon black surfaces. They found that the dominant functional groups introduced by the oxidation were carboxylic acid groups, which was corroborated by high-resolution X-ray photoelectron spectroscopy and Fourier transform-infrared spectroscopy (FT-IR). This oxidation method decreased the tensile strength of carbon.

From the relatively few publications on ozone oxidation, it can be concluded that ozone is one of the strongest gaseous oxidants, that seriously damages the physical structure of carbon. Therefore, properties such as surface area, conductivity and strength decrease considerably, which is undesirable for any potential adsorption process.

This oxidising reagent may be useful to generate oxidised carbons with high sorption capacity and good mechanical properties provided parameters such as temperature, contact time (oxidant-carbon) and ozone concentration are carefully controlled during the oxidation process.

2.7.3 Electrochemical oxidation

Electrochemical oxidation has been used in the last few years to modify carbonaceous materials. This technique has succeeded because of the good electric conductivity exhibited by activated carbon and carbon fibre. Moreover, this technique allows easier control of the oxidation level than acid and ozone oxidation[52,53].

Anodic oxidation has been applied more to modified carbon fibres than granular carbons since this kind of material is easier to handle and allows continuous processes, for instance, in a U-tube reator[57,54].

Alexander *et al* [44] electrochemically modified commercial carbon fibre (Hercules Inc, type AU) by using ammonium bicarbonate as an electrolyte. It was mentioned that surface acid groups are formed by reaction with oxygen that is generated at the fibre anode. Studies of XPS and Secondary Ion Mass Spectrometry (SIMS) indicated that nitrogen in the form of amide, aza, imide and protonated amine exists on the carbon fibre after the electrochemical oxidation. This was attributed to erosion of the fibre surface, that revealed remnants of the PAN precursor or alternatively to the adsorption of species from the electrolyte. Bradley *et al*[55], performed an anodic oxidation of two types of carbon fibre: low modulus (LM) materials that had been heat-treated in the temperature region 1473-1773 K and a high modulus (HM) material heated from 2273-3073 K. Ammonium bicarbonate was used as an electrolyte. The XPS results showed that fibre HM slightly increased the quantity of oxygen (in the form of C-O, C=O and COOH) and nitrogen. In contrast, carbon fibre (LM) markedly increased the amount of surface groups. This was attributed to the high level of exposed edge area and unpaired valence electrons. Jannakoudakis *et al* [56] carried out an electrochemical oxidation of carbon fibre (ceilon GY 70) in aqueous solution and analysed the surface oxides. It was found that surface groups (-COOH and $\equiv C-OH$) can be obtained electrochemically by choice of current and electrolyte.

Horita *et al* [57] conducted an anodic oxidation of carbon black using KOH as an electrolyte. The results obtained showed that the carbon black surface changed from hydrophobic to hydrophilic and the electric conductivity decreased with anodic oxidation time. More information about electrochemical oxidation of carbons is available in the literature, however, it is orientated towards voltametric studies where reaction kinetics is the main topic under discussion. Carbon has mainly been used in electrochemical cells as electrodes and sufficient information has been determined. However, only one publication was found concerning the production of electrochemically oxidised granular carbon.

The introduction of oxygen-containing groups on carbons by anodic oxidation is not as easy to explain as that for nitric acid and ozone oxidation. This process involves a series of complex reactions, for example the decomposition of water produces subproducts such as $OH^{\cdot}$ and $HO_2^{\cdot}$. These reaction products subsequently react with carbon (working as an anode) introducing oxide groups. Moreover, the electrolyte used and current applied during the process influence the reaction mechanism between species in solution and carbon, which may be give rise to the introduction of different types of functional groups [58,59,60].

2.8 Uses

Granular activated carbon was used in gas masks during World War I and more recently it has been extensively applied to remove odour and colour in solvent recovery, purification of water and air, and in food processing. It has been used in hydrometallurgy to recover gold and silver, and in the treatment of industrial wastewater and domestic effluents. [4,61,62].

Activated carbon fibres have been used mainly in metal cleaning, solvent recovery in the manufacture of semi-conductors, drinking water treatment, in home appliances, gas masks, cigarette filters, air filter paper, exhaust pipes of vehicles and protective clothing[6,63].

Nowadays carbons with special characteristics are tailored for use in special applications such as the treatment of ailments of the digestive system in humans, purification of electroplating solutions from organics and removal of toxins from blood. Development of new types of carbon, i.e. nanotubes, is in progress to satisfy new technologies, for instance, the storage of hydrogen and the catalytic reduction of NO_x.

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Chapter 3:

EARLIER STUDIES: REMOVAL OF METAL IONS FROM WATER BY CARBONACEOUS MATERIALS

3.1 Introduction

Activated carbon materials posses high sorption capacity, high selectivity for trace metal ions in solution and in certain cases are more effective than conventional ion exchange resins. More recently, activated carbon fibres in the form of cloth and felt have been developed and have received considerable attention as potential adsorbents for water treatment applications.

Several papers and books have been published about the removal of metal ions from aqueous solutions by granular carbons and to a lesser extent carbon fibres[1-35]. Selected manuscripts will be discussed in this chapter, with special emphasis on the removal of cadmium and mercury, as these two metals were used to evaluate the commercial and modified carbonaceous materials utilised in this project.

3.2 Use of conventional granular and fibrous activated carbons

Several researchers have studied the adsorption of heavy metals on activated carbon, in granular and powder form. The use of activated carbon fibres has not yet been fully explored since this material was only recently produced commercially, hence, only a limited amount of information is available in literature.

The ability of carbons to remove cations and anions from electrolyte solutions has been known since 1922[1]. However, it was not until 1970 that the use of activated carbon was exploited in the metallurgical industry for the removal of metal ions. Sigworth and Smith[2] published a review paper in the early 1970's on the use of activated carbons for the removal of heavy metals from water. These researchers emphasised the great potential for the removal of chromium, bismuth, arsenic, antimony, tin, silver, cobalt, mercury, lead, zinc, iron and titanium by carbon. It was concluded that adsorption is more successful when aqueous conditions render heavy metals less soluble. Following this publication, the interest in the sorption of heavy metals from aqueous solution by carbonaceous materials increased and a subsequent series of papers have been published[3-35].

One of the first research groups to study the adsorption of metal ions from aqueous solution on different types of activated carbons was Netzer *et al*[3] in 1982. The adsorption of lead, copper and cobalt was studied and important parameters such as solution pH, equilibrium time, carbon type and carbon dose were taken into account. The sorption of a single component and selectivity was investigated. The authors noted that solution pH is the most influential parameter in the sorption process. However, it was concluded that the complexity of the carbon surface and water chemistry caused no single carbon property to be dominant in determining its adsorptive characteristics. Corapcioglu and Huang[4] obtained similar results when the adsorption of copper, lead, zinc and nickel by fourteen brands of activated carbon was investigated at pH 2.5 to 10.5. The authors concluded that carbon type, solution pH and surface groups are the most important factors affecting the extent of metal removal.

Budinova *et al*[5] studied the sorption of cadmium, lead, copper and zinc by activated carbons prepared from coconut shells and apricot stones. The authors pointed out that all the carbons tested could remove metal ions, however, the sorption capacity increased in the following order: cadmium<zinc<copper<lead. It was also noted that the removal of these metals was negligible at low pH, however, between pH 3 to 4 a significant increase occurred. The sorption of an individual ion decreased in presence of other metals. This was attributed to factors such as chemical properties, hydrolysis and ionic radius. Taylor and Kuennen[6] investigated the removal of the same metal ions and found exactly the same trend in sorption capacity. These researchers carried out mini-column studies, instead of batch experiments, with a relatively high concentration of cadmium, zinc, copper and lead using granular activated carbon (coconut shell based) at pH 7. The results revealed that the adsorbent used had a relatively low capacity for cadmium and zinc, compared with copper and lead. Lead uptake was the greatest of the four metals studied.

The sorption of heavy metals by activated carbons has also been studied in the presence of complexing agents, e.g. ethylenediamintetraacetic acid (EDTA). Bhattacharya and Chen[7] investigated the removal of cadmium (II) and nickel (II) in the presence of chelating agents EDTA and triethylenetetramine (TRIEN) at a initial metal concentration of 0.8 mM and carbon dosage 20 g l^{-1}. More than 98 % of cadmium and nickel was successfully removed in the presence of EDTA and TRIEN at a solution pH of 5. Ferro-Garcia *et al*[8] have also studied the sorption of metal ions (zinc, cadmium and copper) in the presence of EDTA and various anions, Cl^-, CN^- and SCN^-. Three carbons, produced from olive stones, almond shells and peach stones, were utilised in these studies. The authors found that the removal of the metals mentioned above increased in the presence of Cl^-, CN^- and SCN^-, whereas EDTA restrained the sorption process. The authors suggested that the removal of zinc, cadmium and copper was enhanced by the presence of anions due to the formation of complex anions, which adsorb more easily on the carbon surface because of a positive carbon surface charge potential. Alternatively, EDTA-metal complexes were poorly adsorbed since the size of the metal complex was larger than the carbon pore size, hence a low surface area was available for adsorption.

Other investigators have focused on the removal of single ions such as cadmium and mercury. A series of studies on the adsorption of cadmium from wastewaters by activated carbon have been carried out in the last twenty years. These studies have proved that cadmium is adsorbed by carbon and that the uptake depends on factors such as solution pH and temperature. Many activated carbons have been tested: commercial powder activated carbons Nuchar SA, Nuchar SN, Darco HDB, Darco KB and Nuchar C190-N (Huang and Ostivic[9], Huang and Wirth[10], Reed and Nonavinakere[11], Reed and Matsumoto[12]); commercial granular activated carbons Darco HD300, Filtrasorb 400, Darco HD 4000, and Nuchar 722 (Huang and Ostovic[9], Huang and Wirth[10], Reed and Nonavinakere[11], Reed and Aruchalam[13], Marzal *et al*[14], and Leyva-Ramos *et al*[15]); bituminous granular activated carbon (Bhattacharya and Venkobachar[16]) and activated carbon produced from olive stones, almond shells and peach stones (Ferro-Garcia *et al*[8]).

Most of these studies have focused on the determination of adsorption isotherms and the effect of solution pH and temperature on the sorption process. The main findings are: adsorption of cadmium increases with pH[12] and it precipitates out as $Cd(OH)_2$ at pH values above 9[15]; cadmium is not adsorbed by carbon at pH values lower than 3[15,16]; the sorption capacity increases with temperature[14]; powder activated carbons have higher sorption capacity than granular carbons[10]; and the adsorption of cadmium at pH values below the point of zero charge is due to chemical interaction with functional groups rather than electrostatic attraction[9, 16]. It is concluded that it is possible to have a high degree of heavy metal removal by activated carbon, and with the proper selection of the adsorbent and operational conditions, carbon is as effective as other adsorbents such as iron and aluminium hydroxide.

Langmuir and Freundlich isotherm models have been widely applied to fit experimental data[12, 16]. Marzal *et al*[14] represented the adsorption of cadmium on activated carbon by the triple layer model, which considers adsorption as a reaction forming surface complexes. This model includes corrections for the electrostatic interaction between ions in solution and surface complexes. Huang and Ostovic[9] applied the surface complexation model, which is based on the interaction of hydroxo surface groups with metallic ions. Different models have been applied to represent the adsorption of metal ions by activated carbons, however, none of them have given adequate results. This is due to the fact that the carbon surface composition is highly heterogeneous and a series of different reactions can occur with metal ions in solution; temperature, pH and solution chemistry are influencing factors that have not yet been included into a single model.

Carbon fibres have mainly been used to remove organic molecules such as phenolic compounds[17,18]. In an extensive literature review of the removal of heavy metals by carbonaceous material, only one publication has reported the adsorption of metal ions by carbon fibres. Pimenov and Lieberman[19] studied the adsorption of methylene blue and cadmium by polyamphoteric activated carbon fibre (Aqualen) produced from rayon fibre, and the results were compared with granular activated carbon (F-400) and ion exchange resin [Dowex-50W(H^+)]. The survey showed that Aqualen adsorbed two orders of magnitude faster than activated carbon F-400. They assumed that the enhanced adsorption properties of Aqualen are due in part to the small fibre diameter, high porosity and open pore structure. Moreover, Aqualen showed an order of magnitude faster adsorption than Dowex-50W resin, although the total cation-exchange capacity of Aqualen was much smaller.

The sorption of mercury from aqueous solutions has been studied in the last year by different researchers. Knocke and Hemphill[20] used vulcanised tyre rubber, which contains butadiene, styrene, sulphur and carbon black, to remove inorganic mercury from solutions. The effect of temperature, particle size, pH and hydrogen ion concentration was studied. The authors found that solution pH is the most critical parameter in the sorption process; the optimum pH was found to be in the range of 5-7 with a maximum sorption capacity of 0.67 mg g^{-1}.

Namasivayan and Kadirvelu[21] studied mercury removal by using an activated carbon produced from an unwanted agricultural solid by-product, coirpith. The metal ion concentration, sorbent dose and solution pH were investigated. The mercury sorption capacity increased from pH 2-5 and subsequently remained constant up to pH 11. The maximum mercury removed was 154 mg g^{-1} at pH 5 for the particle size 250-500 μm. These researchers also investigated the desorption of Hg(II) using 0.5 M hydrochloric acid and 2.0% potassium iodide solutions. It was found that the maximum percent recovery of mercury was 63 and 84 % using HCl and KI, respectively. Anirudhan and Sreedhar[22] have performed out similar work using a coconut husk based carbon. They observed maximum mercury sorption of 120 mg g^{-1} at pH 5 for an initial concentration of 250 mg l^{-1}. In this research 1 M HCl was used to regenerate the activated carbon saturated with mercury. The maximum mercury desorbed was 95%.

Huang and Blankenship[23] removed mercury(II) using 11 commercial activated carbons. It was found that 99-100% of the total mercury present in solution was removed in the pH range of 4-5. It was also concluded that two mechanisms, adsorption and reduction/volatilisation are responsible for Hg removal. The first mechanism dominates in the mid-pH range, approximately between 5 and 8, and the second one at pH approximately <4 and 9-10. Lopez-Gonzales[24] has reported that mercury chloride can be removed by adsorption of $HgCl_2$ and also by reduction to Hg(I) by phenolic and hydroquinonic surface groups, according to the following reaction,

$$2(-OH) + 2HgCl_2(aq) \rightarrow 2(=O) + Hg_2Cl_2(s) + 2HCl$$

Adams[25] focused his studies on the sorption mechanism of $HgCl_2$ on activated carbons. He proposed that the removal of Hg(II) by activated carbon is possible by the reduction of Hg^{2+} to Hg_2^{2+} since this reaction has a much higher potential, +0.905 V, than that of activated carbon, +0.24 V. Therefore, mercury is removed by forming a precipitate, Hg_2Cl_2, through the following reactions,

$$2Hg^{2+} + 2e^- \leftrightarrow Hg_2^{2+}$$

$$Hg_2^{2+} + 2Cl \leftrightarrow Hg_2Cl_2(s)$$

It has been mentioned that the application of carbon fibres to remove metal ions from aqueous solutions has not yet been exploited since this adsorbent material has only recently been commercialised. Jayson and Sangster[26] have studied the removal of mercury (II) acetate [$Hg(OOCCH_3)_2$] by activated charcoal cloth (ACC). It was found that more than 90% of the adsorbate was removed when 300 cm^3 of mercury (II) acetate ($1x10^{-6}$ mol dm^{-3} initial concentration) was passed through six discs of ACC, to which a negative potential was applied. It was noted that the adsorption in batch experiments was higher than in continuous flow, which was attributed to a decreasing concentration gradient and limitations of film diffusion.

3.3 Application of chemically modified granular and fibrous carbons

It has been mentioned in previous chapters that oxidised carbons have large quantities of oxygen surface groups and a great affinity for polar molecules, which enhance ion exchange properties.

Strelko[27] has reviewed many papers on the use of oxidised carbons for metal removal from aqueous solution that were published in the USSR between the 1950's and 1970's. A common conclusion by researchers such as Strazhesko and Tarkovskaya, and Kuzin *et al* (see ref. 27) was that oxidised carbons are polyfunctional cation exchangers with high concentrations of weakly acidic oxygen-containing groups. The ion exchange capacity of these materials is mainly attributed to carboxylic and phenolic surface groups.

In 1968 Tarkovskaya *et al*[28] studied the adsorption of a series of cations on an air-oxidised carbon, FOU. The authors noted a marked difference in adsorption for each cation in a wide range of pH. From these findings, a selective series of cations adsorbed by oxidised adsorbent was established as follows; $Na^+ < Sr^{2+} < Cd^{2+} < Mn^{2+} < Ca^{2+} < Zn^{2+}$; $Co^{2+} < Ni^{2+} < Cr^{3+} < La^{3+}$; $Sc^{3+} < Cu^{2+} < Fe^{3+}$.

There have been recent general publications on the production and application of chemically modified carbons. For example, Tai and Streat[29] studied the adsorption of zinc on modified and conventional activated carbons. Commercial activated carbon F-400 (coal based) was acid-oxidised using nitric acid. The authors found an improvement in zinc adsorption of ten times compared to the unoxidised material, and a 12 % reduction in surface area after 9 hours of oxidation. The same authors investigated the adsorption of copper, nickel and zinc on acid and air oxidised activated carbon BGP (wood based)[30]. The acid oxidation was carried out for 9 h using 8 M nitric acid at 90 °C, whereas the air oxidation was conducted for 24 hours at 420 °C. The results showed an increase in copper adsorption of 10 and 50 times on air and acid oxidised activated carbon, respectively. The air-oxidised adsorbent had higher surface area, however, the acid oxidised sample had higher adsorption capacity.

Activated carbons have been chemically modified in different ways and using various reagents. For instance, Strelko and Streat[31] investigated the kinetics of lead sorption on three types of modified activated carbons: KAU-1.8 (apricot stones based), F-400 and CKC (styrene/DVB copolymer based), and on a phosphorus-containing carbon, PGP-P (phenol-formaldehyde polycondensation resin based). The activated carbons F-400 and CKC were oxidised using nitric acid and KAU-1.8 was modified by air. CKC showed the fastest kinetics, which was attributed to a well-developed mesoporous structure. On the other hand, phosphorus-containing carbon had the slowest kinetics, this was attributed to the high proportion of micropores.

Dobrovolski *et al*[32] studied the equilibrium exchange kinetics of cadmium on a commercial activated carbon (Merck), activated carbon oxidised by hydrogen peroxide and on another one heat treated in argon at 1400 K using an isotope exchange technique. The experimental data showed fast adsorption in the initial stage at high pH values, that was attributed to the exchange of cadmium at easily accessible surface sites and micropores. The slow adsorption stage, at low pH values, was attributed to cadmium physisorption into deep micropores and ion exchange with surface functional groups. The authors found higher cadmium uptake by modified carbons. This was attributed to a higher concentration of functional surface groups. Activated carbon modified by hydrogen peroxide showed a higher sorption capacity that the heat-treated one.

Karthikeyan and Chaudhuri[33] chemically pre-treated bituminous coal with nitric acid and hydrogen peroxide. Moreover, sulfurisation and manganese oxide impregnation was also conducted. The results showed that chemical pre-treatments applied to carbon tended to enhance mercury sorption. The highest sorption capacity was found for coal treated with nitric acid, i. e. approximately 10 mg g^{-1} at initial pH 6.8 and 32-34 °C. The mercury sorption capacity was almost the same between pH 5-10, except for Filtrasorb 400 where a decrease in sorption at high pH was noticed.

It is to be noted that in the extensive literature review carried out on the removal of metal ions from aqueous solution by modified carbonaceous materials no information was found on the use of chemically modified carbon fibres. However, we have already published two conference papers[34,35] and a full paper has been accepted in an international journal (Water Research) with the results obtained from our work on the modification and use of activated carbon cloth[36].

The objective of this project is to investigate the effects of ozone and electrochemical oxidation on granular carbon and carbon fibre for improving the physico-chemical properties and metal sorption performance of these materials. These studies have not been reported in detail in the published literature. The methods that will be developed in this study will be compared with acid oxidation (using HNO_3) that has historically been a common process for modifying carbonaceous materials.

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Chapter 4:

EXPERIMENTAL PROCEDURE

4.1 Chemicals

Cadmium and mercury solutions were prepared using laboratory grade $CdCl_2 \cdot H_2O$ (May & Baker Ltd., Dagenham, England) and $HgCl_2$ (Fisher, UK), respectively. Aldrich Chemicals, USA, supplied volumetric standard solutions of sodium hydroxide, sodium carbonate and HPLC grade ethanol, and the analytical reagents sodium hydrogen carbonate and sodium ethoxide. Nitric acid, hydrochloric acid, potassium chloride, Rhodamine 6G and sodium thiosulfate were supplied by Fisher, UK. Potassium iodide and gelatine were purchased from Fisons and potassium hydrogen phthalate from Analar UK.

4.2 Adsorbents

Three types of granular activated carbons: 207EA (coal based, Sutcliffe Speakman Carbon Limited), 207C (coconut shell based, Sutcliffe Speakman Carbon Limited) and WHK (wood based, AUG), and two kinds of activated carbon fibres in form of cloth (TC-66 C) and felt (TC-66 F), supplied by KoTHmex, were used in this study. Granular activated carbons were sieved to obtain a particle size between 170 and 210 μm. These were washed several times with distilled water and dried in an oven at 378 K for 24 h.

Table 4.1. Specifications of activated carbon fibres (provided by KoTHmex)

Specification	TC-66 C	TC-66 F
Surface area (m^2/g)	1000~1100	1000~1200
Total pore volume (ml/g)	0.5~0.6	0.45~0.55
Average pore dia. (Å)	19~20	19~20
Fibre weight (g/m^2)	95~105	256±20
Fibre thickness (mm)	0.40~0.50	About 2.5 mm
Fibre width (cm)	100±2	100±2 cm
Texture	Plain	-
Decomposition temp. (°C)	>500	>500

All adsorbents were converted to acid form before use by contacting them with 0.1 M hydrochloric acid for 24 hours. Then the samples were washed with distilled water to remove excess acid and dried in an oven at 378 K for 24 h. Table 4.1 lists specifications of activated carbon fibres used in this study.

In order to remove humic substances produced during oxidation, modified carbon fibres were contacted with 1M NaOH in a conical flask, sealed with Parafilm and agitated at 100 min^{-1} for 1.5 h. The excess of sodium hydroxide was extracted with distilled water in a Soxhlet apparatus for 48 h. Alternatively, modified granular carbons were washed in a column with 0.1 M sodium hydroxide solution until the outlet solution was colourless. Finally, the modified samples were converted to hydrogen form by contacting them with 0.1M HCl and then rinsed with deionised water. All samples were dried in an oven at 378.15 K for 24 h until no change in the weight was observed.

A weak acid cation fibrous exchanger K-4, supplied by Ecofil-Deco Ltd, containing predominantly carboxylic acid groups was also used in this investigation in order to compare the sorption performance with carbonaceous materials.

4.3 Sample analysis

A Varian SpectrAA 200 Atomic Absorption Spectrophotometer (AAS) in flame emission mode was used to determine the cadmium concentration. The spectrophotometer conditions were: acetylene-air flame under oxidising conditions at a wavelength of 228.8 nm for cadmium concentrations from 0.02 to 3.0 mg/L, and 326.1 nm for cadmium concentrations from 20 to 1000 mg/L. Samples of 3 mg/L and 200 mg/L were analysed ten times and the standard deviation $\left(\sqrt{\sum_{i=1}^{n}(x_i-\bar{x})^2 / n}\right)$ was calculated. The calculation gave 2.87 and 0.03 for low and high concentration, respectively. Mercury was analysed at 575 nm against a blank reagent using a UV/VIS spectrophotometer (Perkin Elmer lambda 12) with 10 mm quartz cells. A sample was analysed three times at the beginning of a set of analysis and the readings were always consistent. Rhodamine 6G was used in order to achieve these analyses[1]. pH was measured using a Mettler Toledo 340 pH meter.

4.4 Adsorbents modification

The metal binding ability of conventional carbonaceous materials is limited. However, this can be significantly enhanced by chemical modification. These modifications can be carried out by addition of oxygen, nitrogen, sulphur, and phosphorus onto the surface of the original precursor. Oxidation is commonly used to increase the number of weakly acidic groups on the carbon surface. Oxidation has been carried out mostly by using air at high temperature or nitric acid solutions[2]. Other oxidants such as ozone and hydrogen peroxide have also been used[3].

Granular carbons and carbon fibre were modified by nitric acid, ozone and applying an electrochemical process to enhance cation sorption capacity.

4.4.1 Acid oxidation

Activated carbons were oxidised using 8M nitric acid. The oxidation was carried out using the equipment shown in Fig 4.1. A round-bottomed flask with three openings was placed into a constant temperature water bath. A predetermined mass of granular (ratio 1:3 by volume) or fibrous (2 g /80 ml of acid) activated carbon was placed into the flask and 8M nitric acid was added. The temperature was monitored by a thermometer placed in one of the flask openings. A condenser was fitted to the reactor to prevent liquid loss by evaporation, and nitrogen was injected through a glass tube to stir the sorbent/acid mixture. The experiment was carried out for 1, 2 and 3 h at 360 ± 1 K. Fresh nitric acid was used in each experiment. The reactor containing the sorbent/acid mixture was cooled immediately after chemical oxidation had finished. The modified sample was removed from the acidic solution and rinsed with distilled water. Modified samples were then converted to H^+ form by following the procedure described in section 4.2.

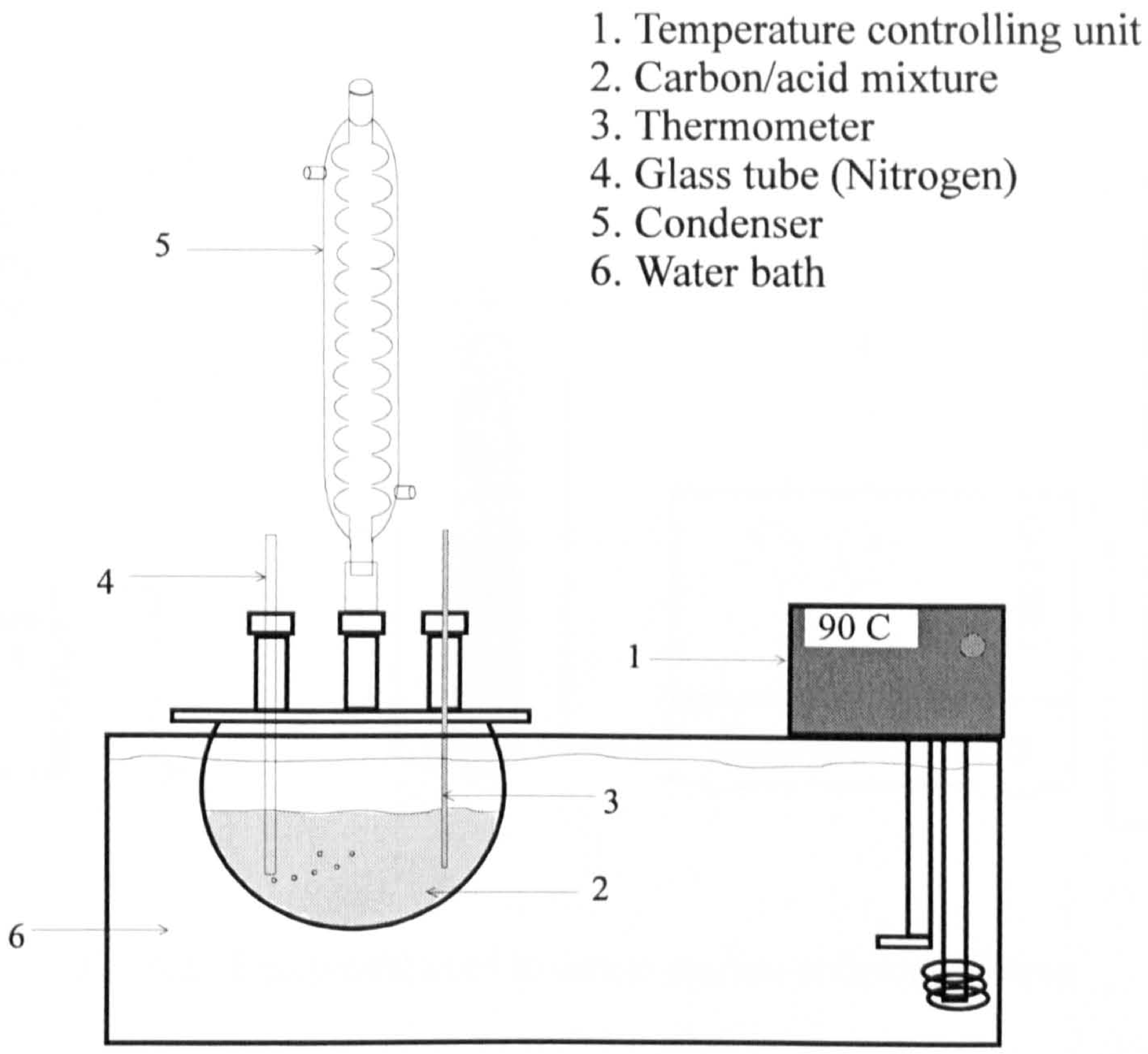


Fig 4.1. Equipment used to oxidise granular and fibrous activated carbons by nitric acid

4.4.2 *Ozone oxidation*

1000 cm^3 min^{-1} of air, measured by rotameter, was passed through a column of silica gel to remove moisture. The dry air was then passed through an ozone generator with the voltage set at 9 volts. The outlet of the ozone generator was connected either to a horizontal glass reactor (see Fig 4.3) containing 1 g of carbon fibre or to a glass column containing 3 g of granular activated carbon. The equipment used in these experiments is shown in Fig 4.2. Teflon tubing was used to direct the air/ozone mixture from the ozonator to the reactor. Ozone oxidation was carried out for 1, 2 and 3 hours at room temperature, approximately 293 ±1 K, for carbon fibre and at 393 K, monitored by a thermocouple, for granular carbon.

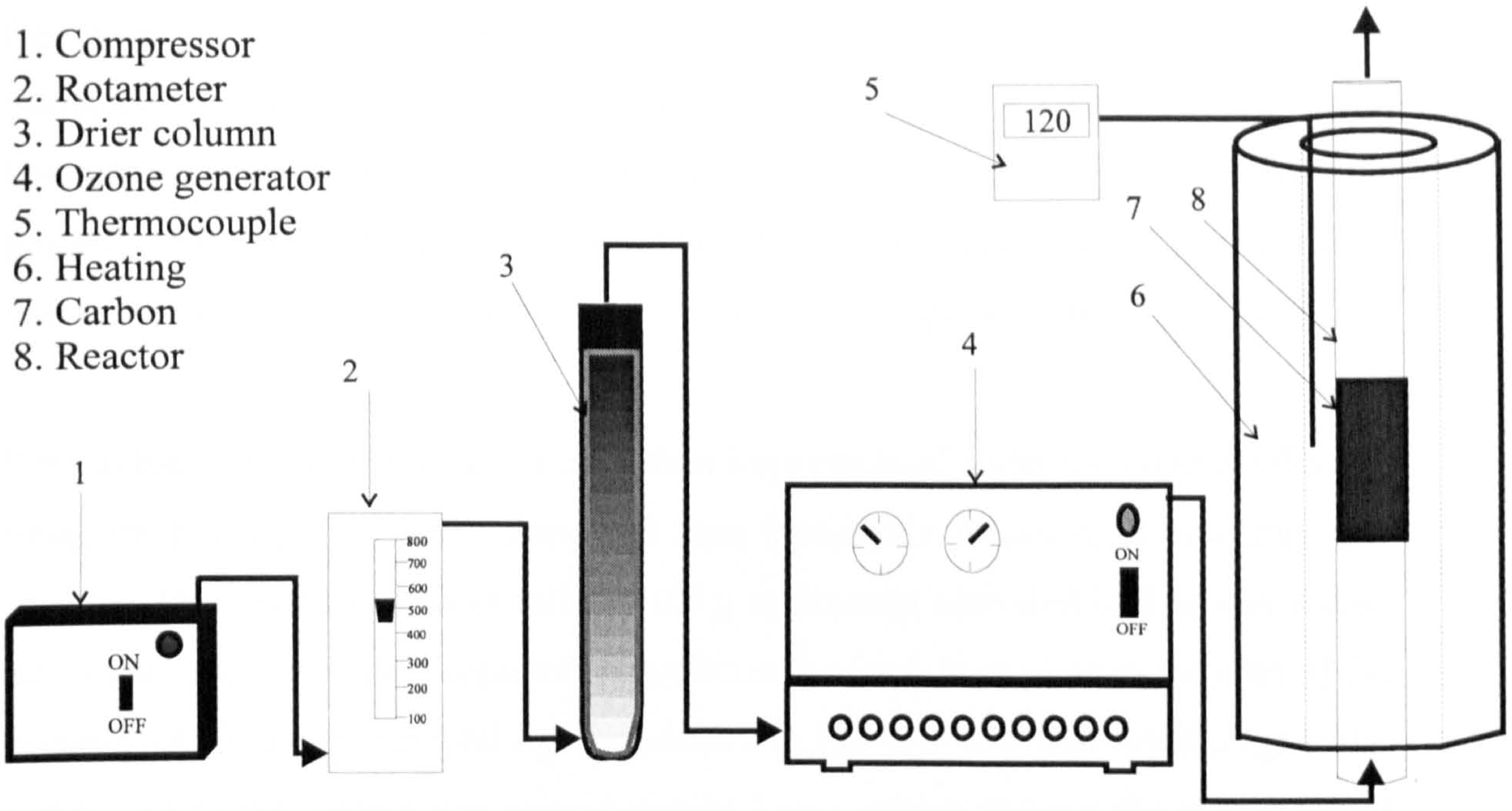


Fig 4.2. Equipment used to ozone oxidise activated carbon

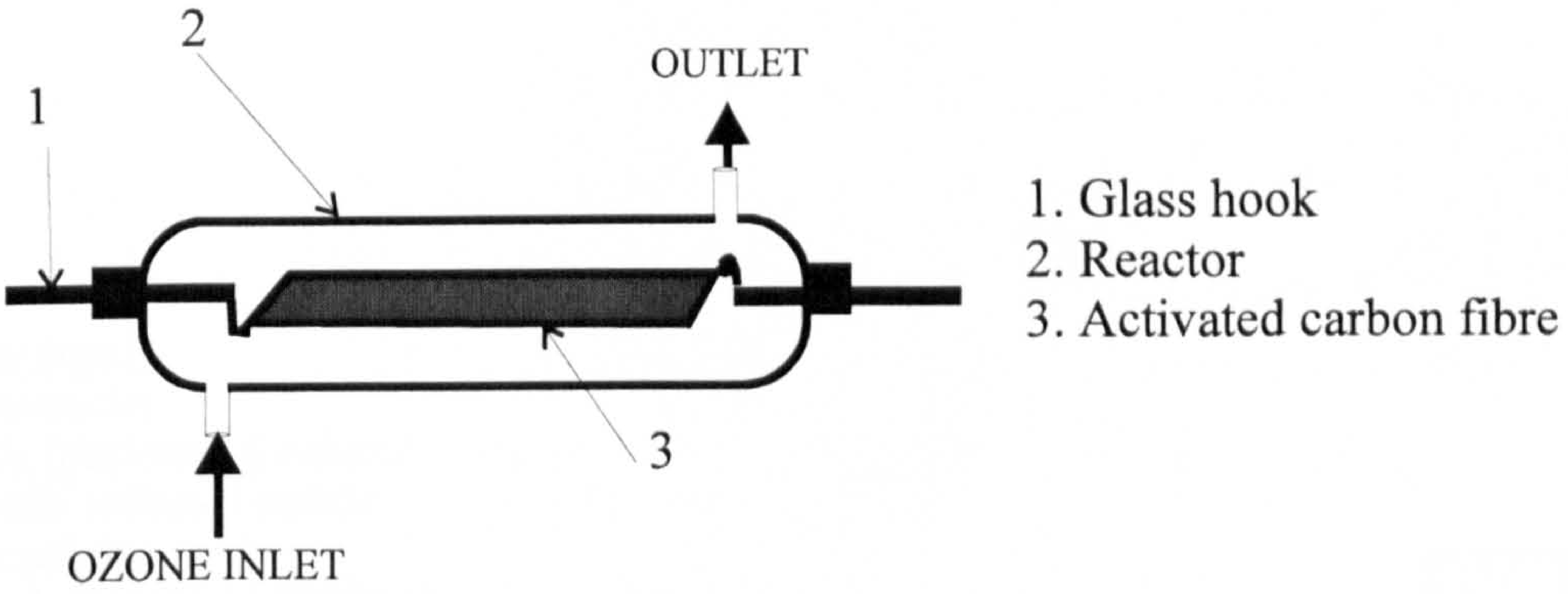


Fig 4.3. Reactor used to ozone oxidise activated carbon fibre

4.4.3 Electrochemical oxidation

The electrochemical oxidation of granular and fibrous activated carbons was carried out by applying a current of 3 mA/m^2 for 1, 2 and 3 h in the presence of different electrolytes such as KCl, KNO_3, NH_4HCO_3 and HNO_3. The current applied during the oxidation and the duration of the process were chosen on the basis of the studies conducted by several researchers in recent years [4,5,6]. Current is normally applied in the range 0.01-3 mA/m^2 for different periods of time depending on sample characteristics, such as surface area and conductivity. The current density used throughout the experiments was high in order to introduce as many oxygen-containing groups as possible in the minimum period of time. In this study, the BET surface area was taken into account in determining the total current applied during the oxidation.

Several batches of granular activated carbon were oxidised under the same conditions, using fresh electrolyte every time, and then thoroughly mixed to obtain only one sample. The procedure was as follows: 0.3 g of granular activated carbon was placed into a plastic column and contacted with electrolyte for 1 hour prior to the start of the experiment. The experimental rig can be seen in Fig 4.4. The bed depth of granular carbon inside the column was approximately 2 mm, which reduces the possibility of inhomogeneous oxidation. Alternatively, a 20 cm^2 sample of as-received activated carbon fibre was attached to the anode and immersed in electrolyte for one hour prior to the start of the experiment. The current applied and the oxidation period was the same as that for granular carbon.

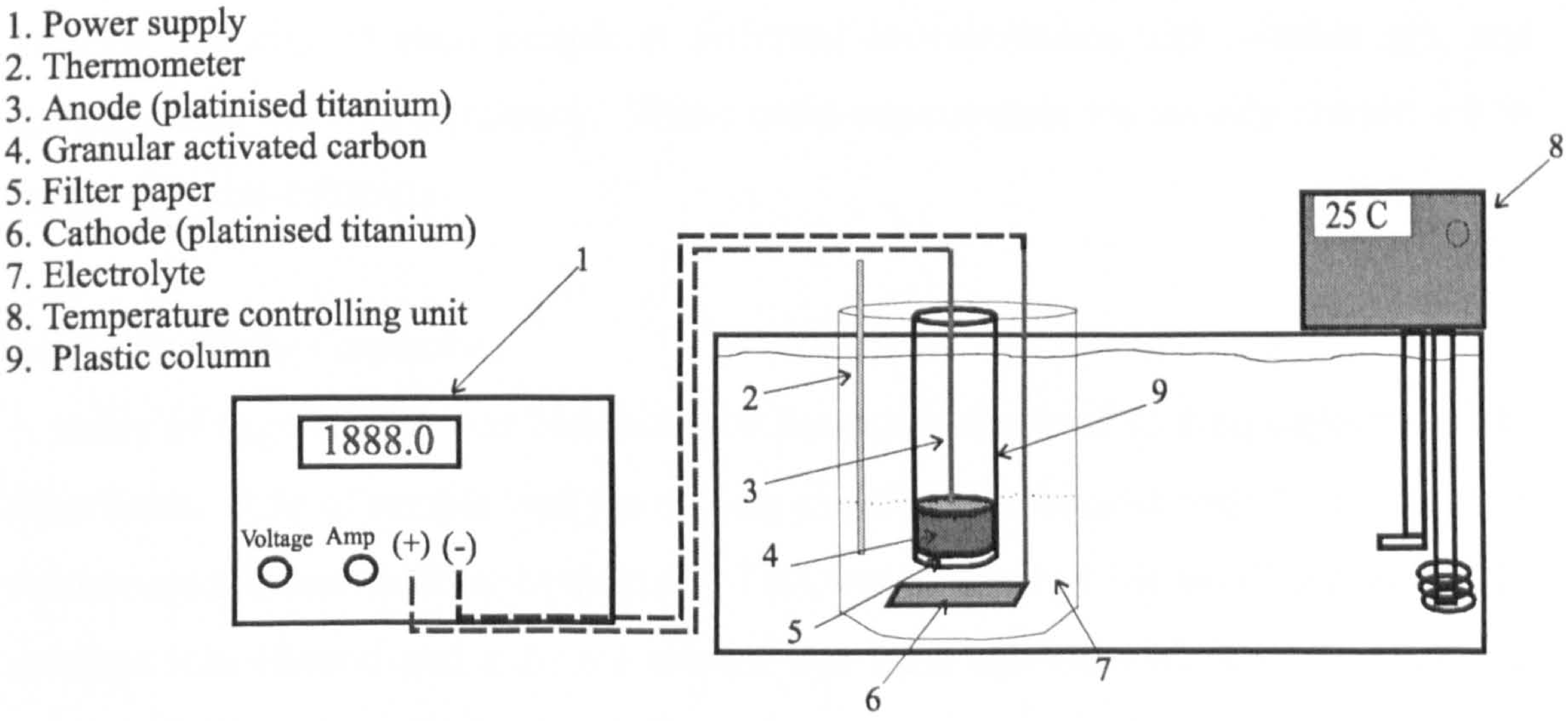
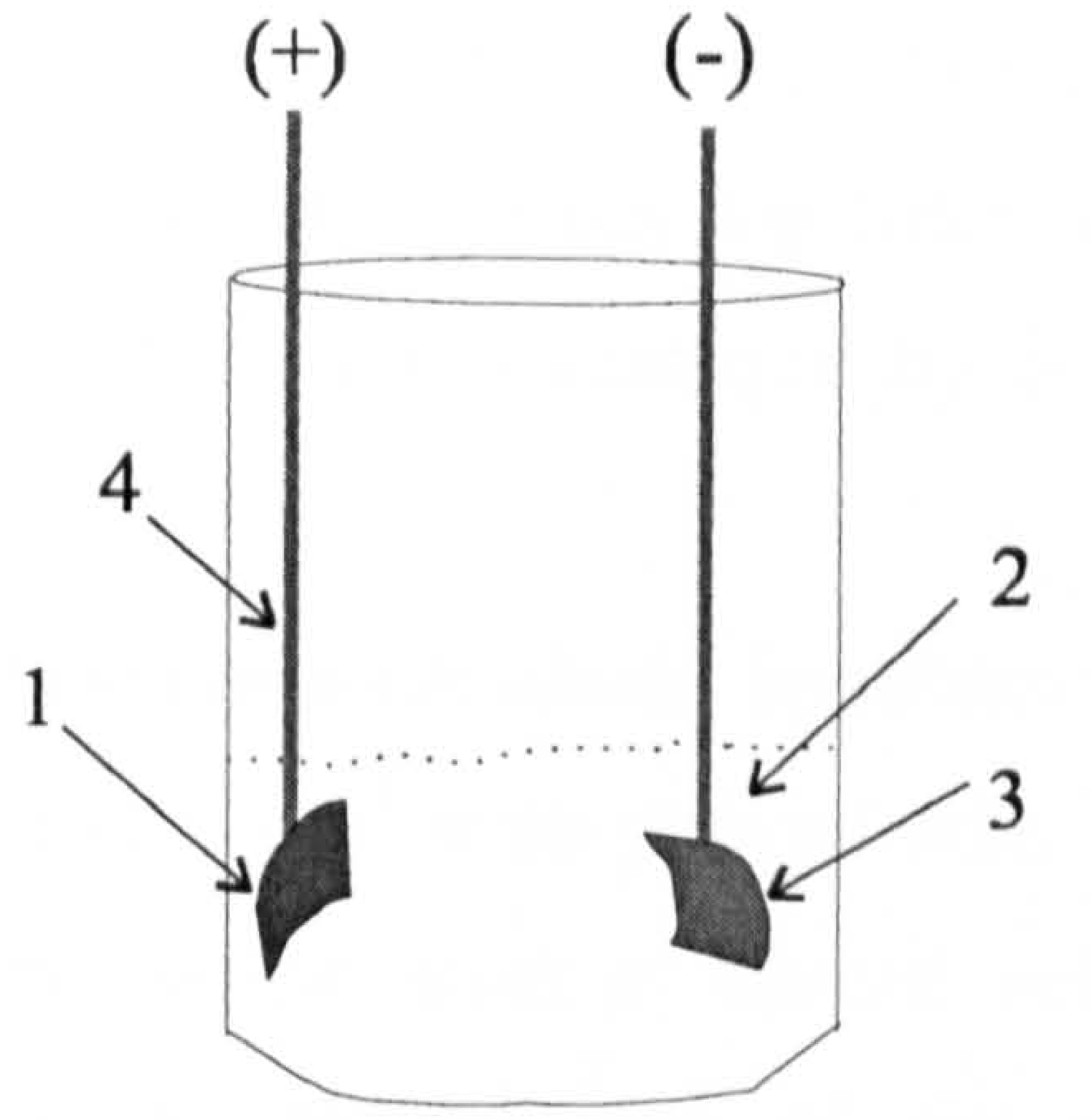

1. Power supply
2. Thermometer
3. Anode (platinised titanium)
4. Granular activated carbon
5. Filter paper
6. Cathode (platinised titanium)
7. Electrolyte
8. Temperature controlling unit
9. Plastic column

Fig 4.4. Equipment used to electrochemically oxidise granular activated carbon



1. Activated carbon fibre
2. Electrolyte
3. Cathode (platinised titanium)
4. Anode (platinised titanium)

Fig 4.5. Equipment used to electro-oxidise activated carbon fibre

4.5 Sorption studies

As-received and chemically modified granular and fibrous activated carbons and an ion exchange fibre were tested to remove metal ions such as cadmium and mercury from aqueous solutions. These experiments were performed so as to measure the sorption capacity of each sample at different concentrations and solution pH, and compare their relative efficiency. These basic experiments are usually carried out in batch and mini-columns.

4.5.1 Exchange capacity

A series of experiments was conducted to determine the total sodium capacity of the adsorbents. 0.5g of sample was placed into a conical flask containing 25 ml of 0.1 M volumetric standard sodium hydroxide. This was agitated at 300 min^{-1} for 48 h. The solution was filtered and a 10 ml aliquot was back titrated with 0.1 M volumetric standard HCl using methyl red as indicator.

4.5.2 Batch sorption experiments

50 ml of cadmium solution of known initial concentration and pH was agitated in a 100 ml conical flask with a predetermined mass of as-received or modified adsorbent using an orbital shaker at 300 min^{-1}. pH was adjusted daily by addition of 0.1 M NaOH or 0.1 M HNO_3 until a constant pH was reached. The equilibrated samples were filtered using 0.2μm PTFE syringe top filters to remove the adsorbent particles and the adsorbate concentration was subsequently determined.

4.5.3 Mini-scale column trials to obtain breakthrough characteristics

Small plastic columns of 3 cm^3 were packed with 0.5 g of unoxidised or modified granular (170-210 μm particle size) or fibrous activated carbons. In the case of carbon fibre, it was cut to the size of the mini-column internal diameter. Approximately 1 mM feed adsorbate solution at pH 6 was passed through the columns, at 10 bed volume (BV) h^{-1}, to obtain the breakthrough curves. The samples were collected automatically by a fraction-collector (each test tube collected solution for 50 minutes). Samples were analysed for cadmium and/or mercury concentration and pH. The equipment used to conduct breakthrough experiments is shown in Fig 4.6.

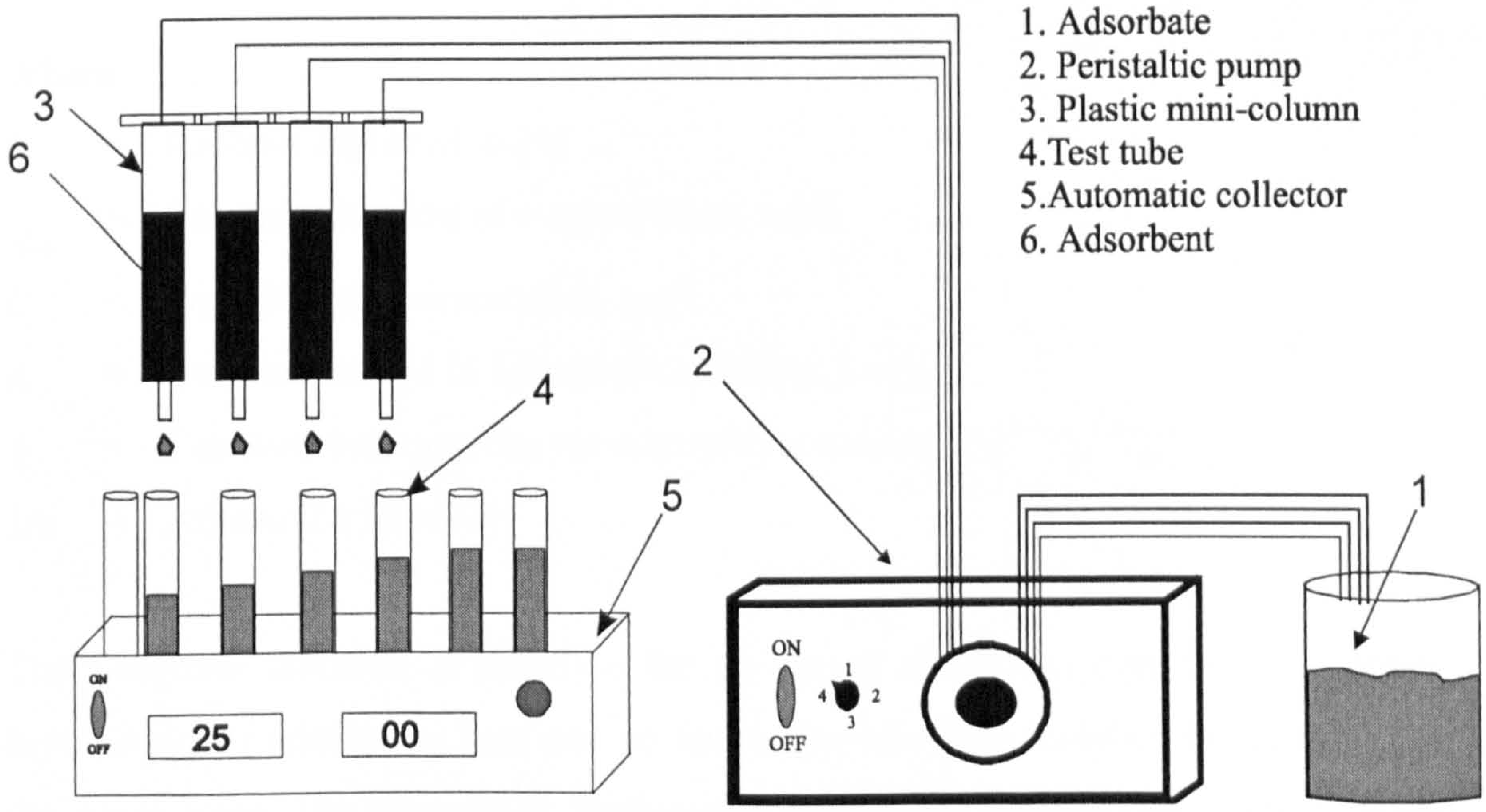


Fig 4.6. Equipment used in breakthrough experiments

4.6 Elution experiments

Regeneration was conducted after breakthrough curves were completed. Once the adsorbent was saturated with either mercury and/or cadmium, 2 bed volumes of distilled water were passed through the column to removed the excess of adsorbate. Solutions of HCl or NaCl, 0.2 to 0.5 M, at 10 BV h^{-1} were used to elute the adsorbed metal. Samples were collected automatically, 10 min/tube, and analysed for mercury and/or cadmium. The equipment utilised to perform these experiments was the same as that for breakthrough analysis (Fig 4.6).

4.7 Theoretical fit to adsorption isotherm data

There are various mathematical models that represent the relationship between the amount of adsorbate uptake and sorbent used once equilibrium has been reached at constant temperature. In this study, the adsorption isotherms were fitted by either the Langmuir or Freundlich isotherm models which are represented by Eq 4.1 and Eq 4.2, respectively:

$$q = \frac{q_m KC}{1+KC} \qquad \textbf{Eq 4.1}$$

$$q = kC^{1/n} \qquad \textbf{Eq 4.2}$$

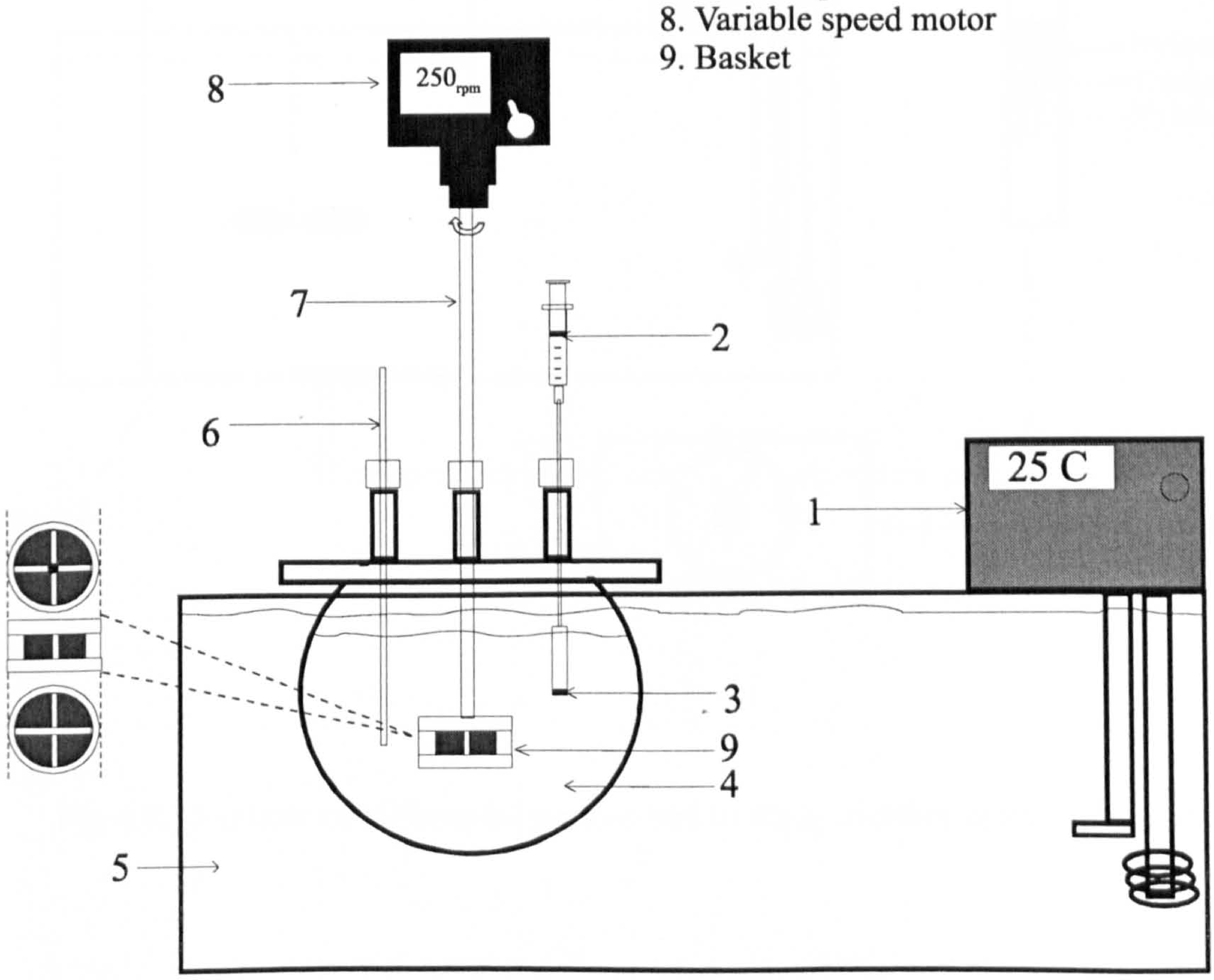
Where:

q = Amount adsorbed, mg/g
q_m = Amount adsorbed of a mono-layer, mg/g
C = Equilibrium concentration, mg/L
K = Constant related to adsorption enthalpy, L/mg
k = Constant that specifies the adsorption capacity, $mg^{1-1/n}L^{1/n}/g$
$1/n$ = Adsorption intensity

The Langmuir isotherm is based on the maximum adsorption capacity of a mono-layer, constant adsorption heat and no interaction between adsorbed molecules. On the other hand, the Freundlich isotherm is based on energetically heterogeneous surfaces[7]. The isotherm parameters were calculated using the method of least squares that employs the Rosenbrock and quasi-Newton optimisation algorithm.

4.8 Kinetic experiments

Kinetic experiments were conducted in the rig shown in Fig 4.7. 1990 ml of distilled water was added to a round-bottomed flask, and 1 g of adsorbent was placed into a rotating basket made of Perspex and plastic mesh (50 µm opening). The basket containing activated carbon was placed in the reactor and connected to a stirrer. The adsorbent was contacted with distilled water for 1 hour prior to the start of the experiment. 10 ml of cadmium solution, of known initial concentration, was added to the reactor and the timer and the stirrer motor (set between 150-250 min^{-1}) started immediately. This was noted as the zero-time of the experiment. Samples were collected at certain time intervals and analysed for cadmium concentration. The experiments were conducted for 2 h and the temperature was kept at 298 K by a temperature control unit.



1. Temperature controlling unit
2. Plastic syringe
3. Filter
4. Cadmium solution/adsorbent
5. Water bath
6. Thermometer
7. Glass impeller
8. Variable speed motor
9. Basket

Fig 4.7. Equipment used to conduct kinetic experiments

Alternatively, 0.5g of commercial activated carbon fibre TC-66 C was placed in a 3 ml mini plastic column. In order to avoid channelling in the column, plastic mesh was used before the sorbent bed (see Fig 4.8). Distilled water was pumped through the column for half an hour prior to the start of the experiment and then the line was drained. 10 ml of cadmium solution, of known initial concentration, was added to the reactor containing a known volume of distilled water and the timer and the stirrer motor started immediately. This was noted as the zero-time of the experiment. Samples of 3 ml were collected at certain time intervals for 2 h and analysed for cadmium concentration. The initial and final pH was measured. The temperature was kept at 298 K by a temperature control unit.

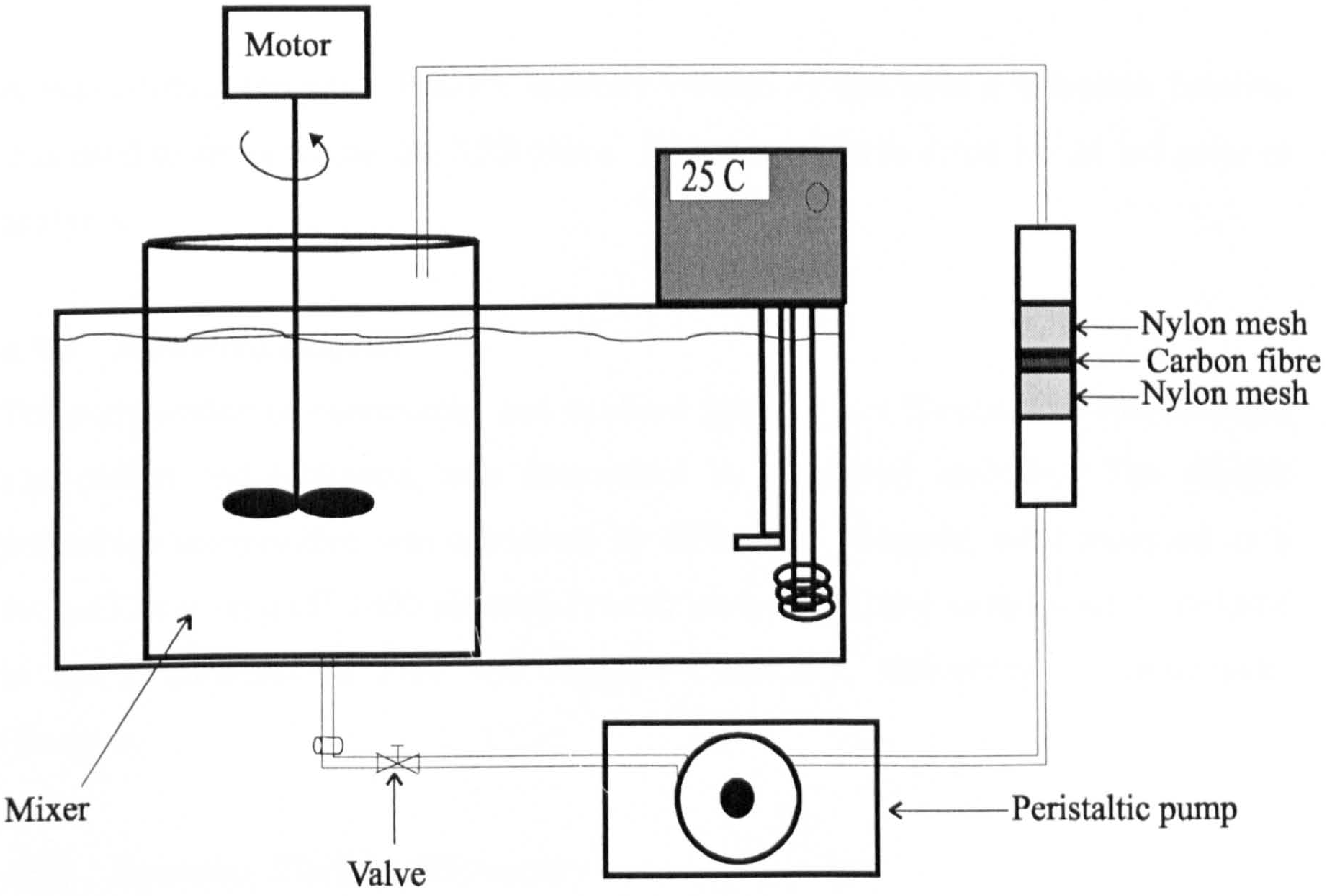


Fig 4.8. Shallow or differential packed bed to study kinetics using carbon fibre

4.9 Sorbents characterisation

Carbonaceous sorbents were chemically and physically characterised by using different techniques. It is extremely important to know the physico-chemical composition of these sorptive materials since these properties will define their most efficient working conditions.

4.9.1 X-ray Photoelectron Spectroscopy

Conventional and modified activated carbon cloth was analysed by XPS. Sample composition, e.g. oxygen, nitrogen and carbon, was calculated. This technique was carried out on a VG ESCALAB MK I spectrometer under a vacuum of 10^{-7} torr. The study scan spectra was recorded using a pass energy of 100 eV. Detailed information about this technique have been reported by Briggs and Seah[8]

A curve-fitting program (PeakFit software version 4) that uses a Gaussian function was used to deconvolute the XPS peaks. The samples were dried for 24 hrs prior to analysis.

4.9.2 Elemental analysis

The composition of commercial and oxidised granular and fibrous activated carbons, e.g. carbon and hydrogen, was determined by elemental analysis. The oxygen percentage composition was calculated by difference. Samples were analysed on a Perkin Elmer series II 2400 elemental micro analyser. These samples were analysed in the Department of Pure and Applied Chemistry, University of Strathclyde, Glasgow.

4.9.3 Scanning Electron Microscopy

A Cambridge Instrument 360 scanning electron microscope was used at an accelerating voltage of 10kV to visualise the surface morphology and structure of commercial and modified carbonaceous materials. Samples were dried for 24 h at 378 K prior to analysis. The samples where then glued to aluminium platforms and sputter-coated with gold. The magnification electron micrographs were obtained at the Institute of Polymer Technology and Materials Engineering (IPTME), Loughborough University.

4.9.4 Electrophoretic mobility measurements

A special procedure was followed to prepare the samples. Granular carbon was ground using an agate mortar and pestle. This material was sieved to obtain a particle size fraction less than 45 μm. Sieved particles were analysed by a Malvern Mastersizer 1000/3000 instrument given a particle mean diameter of 25.7 μm. 20 ml of sodium chloride were used, in a 25 ml conical flask, in each experiment as a supporting electrolyte. A determined volume of 0.1 M NaOH or HCl (0.1-5 ml) was added to the electrolyte in order to adjust the solution pH and generate a series of experiments over a wide range of pH. Then, 100 mg of sample were added to each flask. The flasks were sealed with Parafilm and agitated by an orbital shaker at 300 min^{-1} for 48 h at room temperature, approximately 294 K. After this period of time, the pH of the sorbent suspension was measured and recorded for each experiment.

A 5 ml aliquot of sorbent suspension was taken by using a plastic Luer syringe and injected directly into the electrophoretic cell. The zetapotential was measured immediately by a Mavern Zetamaster 3000HS_A analyser. After each measurement the electrophoretic cell was flushed several times with ultra pure distilled water.

4.9.5 pH-titration

This technique allows determination of acidic and basic properties of ion exchangers and the nature of their functional surface groups[9].

100 mg samples of adsorbent were weighed using a Sartorius BP210D balance, (accuracy ± 0.0005 g), and placed into 25 ml conical flasks. 20 ml of 0.1M NaCl was used in each experiment. A determined volume of 0.1M sodium hydroxide or hydrochloric acid (between 0.1 and 5 ml) was used to obtain the shape of the curve over the entire pH range. The flasks were sealed with Parafilm and agitated by an orbital shaker at 300 min^{-1} for 48 h. Finally, the equilibrium pH of the solution was measured. Blank experiments without adsorbent were also performed.

4.9.6 Boehm's titration

It is very important to quantify and qualify oxygen-containing groups in sorptive materials since these contribute to the removal of metal ions. Another important factor is the functional surface groups ability to dissociate in aqueous solutions. This can be achieved by acid/base titrations applying the method developed by Boehm[10,11]. This method consists of using alkaline solution of increasing strength: $NaHCO_3$, Na_2CO_3, NaOH and $NaOC_2H_5$, which titrate carboxylic, lactone, phenolic and groups of weaker acidic strength, respectively.

Samples of conventional and oxidised carbon cloth TC-66 C were contacted with 0.1 M solutions of NaOH, $NaCO_3$, $NaHCO_3$ and $NaOC_2H_5$ (dissolved in HPLC grade ethanol). Approximately 0.1 g of adsorbent was placed in a 50 ml conical flask and then contacted with 20 ml of each alkali solution. The flask was sealed and stirred using an orbital shaker at 300 min^{-1} for seven days. The solution was filtered using an 0.2 μm PTFE syringe top filter to remove adsorbent particles. Finally, a 5 ml aliquot was titrated with 0.1 M volumetric standard solution of HCl, by using a glass burette (tolerance ± 0.02ml), with methyl red as indicator. A simple mass balance was used to determine the ion exchange capacity of each oxygen-containing group.

4.9.7 Surface area and porosimetry

The surface area of as-received and chemically modified granular and fibrous activated carbons was determined by using a Micromeritics ASAP 2010 surface analyser. The adsorbents were outgassed at 378.15 K under a vacuum of <10 μmHg for a minimum period of 24 h. The degassed sample mass was determined by subtracting the weight of the empty tube from the nitrogen back-filled adsorbent sample tube. Adsorption isotherms were generated by dosing nitrogen (99.99% purity) at 77K and data were recorded using "high resolution nitrogen adsorption/desorption" mode.

Porosity distribution was calculated using Density Functional Theory (DFT)[12].

4.10 References

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Chapter 5:

RESULTS AND DISCUSSION

5.1 Chemical characterisation

This section discusses techniques utilised to chemically characterise carbonaceous sorbents used through this research. Typical techniques such as acid/base titration, ion exchange capacity, pH titration, elemental analysis and X-ray Photoelectron Spectroscopy where applied to identify and quantify functional surface groups responsible for metal removal.

5.1.1 Ion exchange capacity

The total ion exchange capacity is determined in alkaline solutions and the common salt used for this purpose is sodium hydroxide. Oxygen containing groups present on carbonaceous materials for instance; carbonyl, carboxyl, phenolic and lactonic, dissociate at increasing pH values[1]. Therefore, these surface groups are completely dissociated at high pH and are available for ion exchange. Under these conditions the total ion exchange capacity can be determined.

The sodium capacity was determined for three different activated carbons from different precursors (207EA, 207C and WHK), for carbon fibre in the form of cloth and felt (TC-66 C and TC-66 F) and for ion exchange fibre containing carboxylic groups (K-4). Ion exchange capacity is also reported for chemically modified carbonaceous materials.

Table 5.1 shows the sodium capacity for commercial sorbents. The sorption capacity increases in the following order for granular carbons WHK>207C>207EA. On the other hand, carbon fibre in the form of cloth has 1.6 times higher sodium capacity than that in the form of felt. The difference in ion exchange capacity is due to the quantity of oxygen-containing groups present on the adsorbents, which is generally related to surface area. Granular activated carbon WHK and carbon fibre TC-66 C have very similar sorption capacities and the highest of all carbonaceous material studied in this research. Ion exchange fibre K-4 has 35.5% higher sorption capacity than WHK and TC-66 C. Generally, ion exchange resins and fibres posses higher sorption capacity than carbonaceous adsorbents, however the production cost has to be taken into consideration.

Table 5.1. Sodium adsorption on different types of commercial adsorbents

Adsorbent	Sodium capacity [mmol/g]
207EA	0.25
207C	0.50
WHK	1.57
TC-66 F	0.93
TC-66 C	1.47
K-4	4.28

Further experiments were conducted using the adsorbents that possess the highest sorption capacity. Granular carbon WHK and carbon fibre cloth TC-66 C were chemically modified to enhance their ion exchange capacity. Three methods were used for this purpose: acid, ozone and electrochemical oxidation. The modification was carried out for 1, 2 and 3 h. The total sorption capacity was determined for each modified adsorbent and the results are plotted in Figs 5.1 and 5.2.

The total sodium capacities for modified TC-66 C and WHK are shown in Figs 5.1 and 5.2, respectively. It is observed that the sodium capacity increases with increased duration of oxidation for all samples. However, electrochemical oxidation is the most effective and yields the highest ion exchange capacity. The sodium capacity for TC-66 C does not increase much beyond two hours of oxidation for the acid modified sample whereas extended ozone and electrochemical oxidation further increases sodium capacity. In contrast, acid and ozone oxidation hardly increases the sodium capacity of WHK after two hours of oxidation. The chemical modification of these carbonaceous adsorbents can be conducted for a longer period of time, however there is the possibility of physical damage.

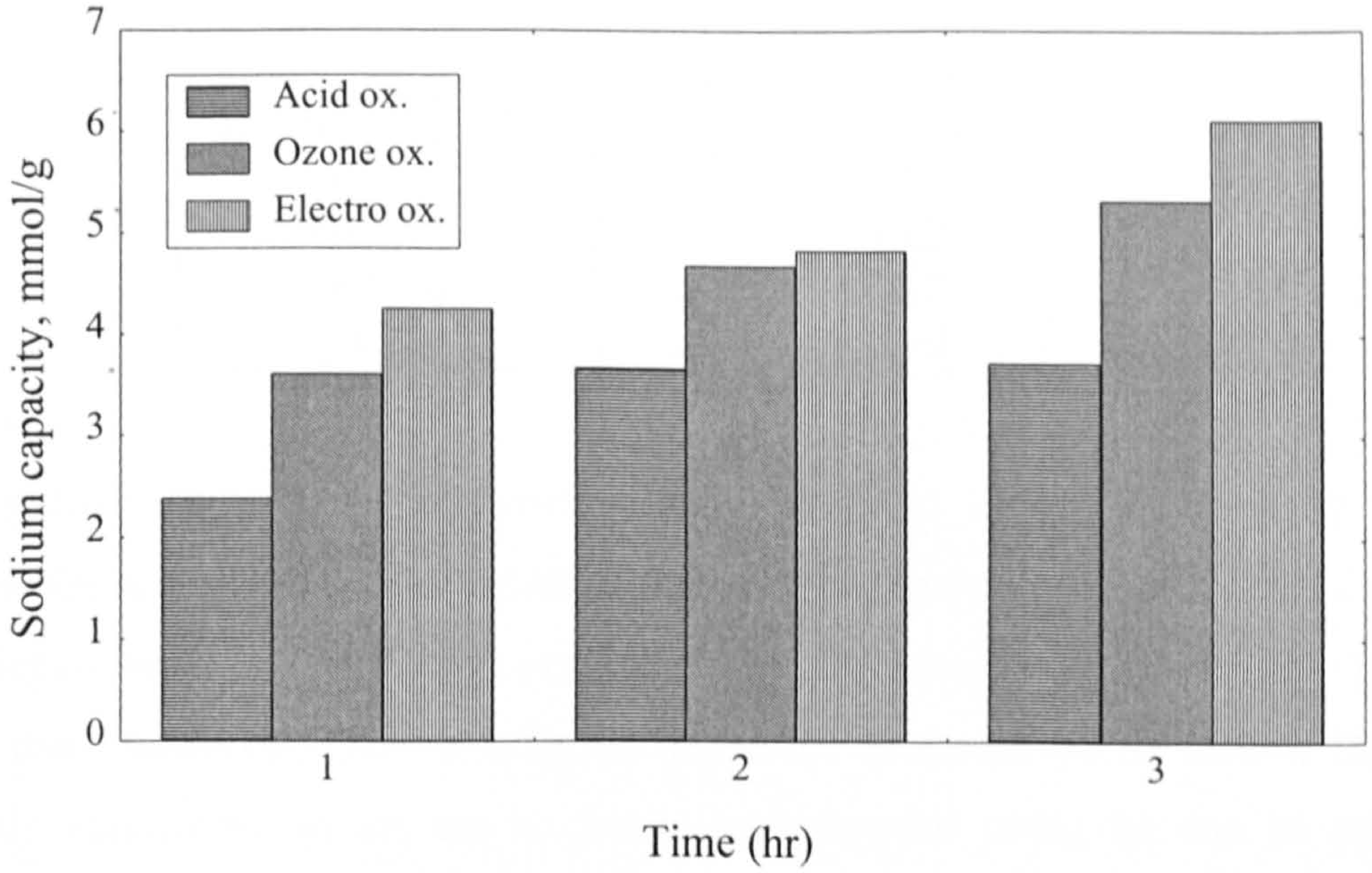


Fig 5.1. Sodium capacity using modified activated carbon fibre TC-66 C

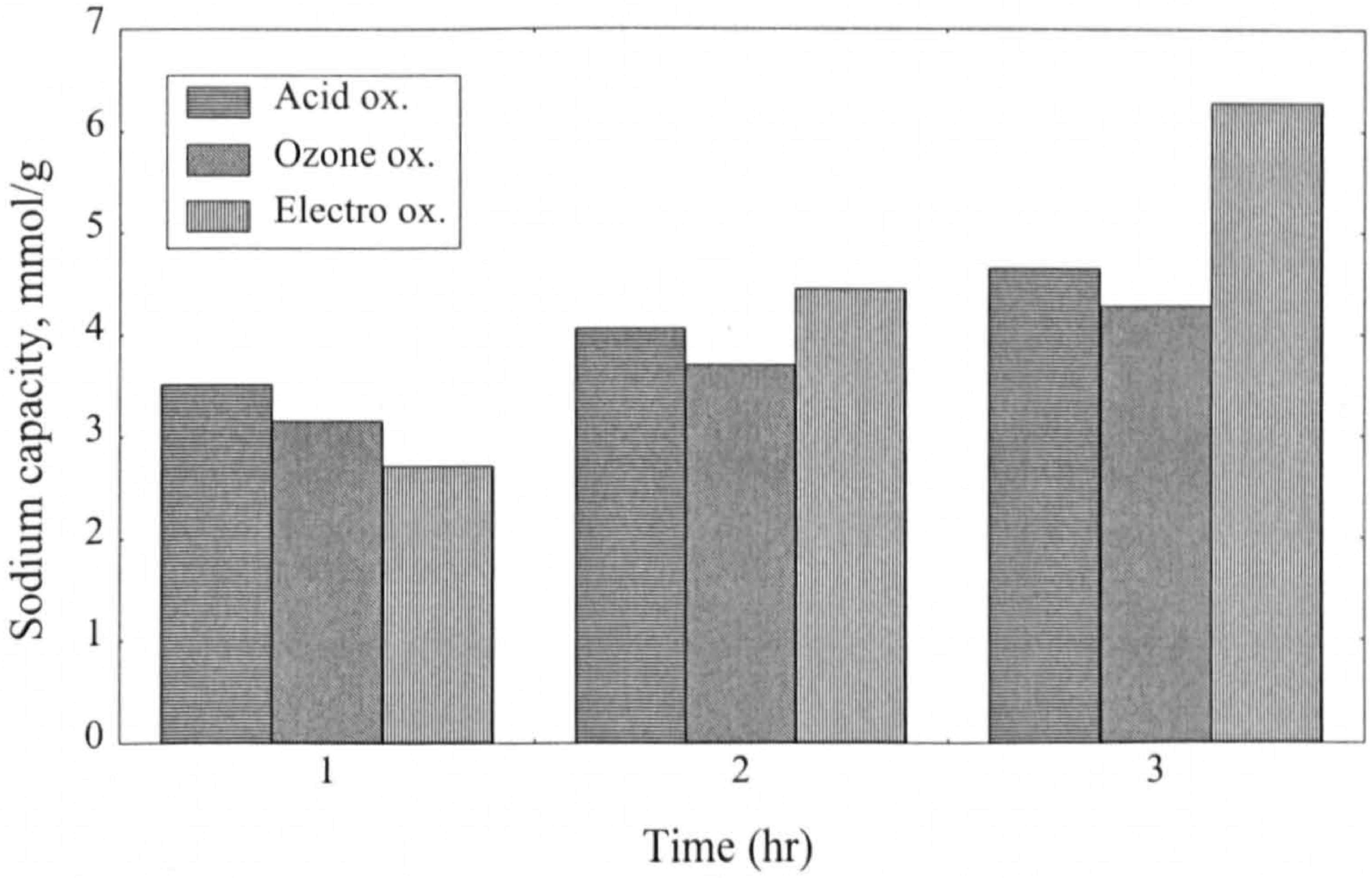


Fig 5.2. Sodium capacity using modified granular activated carbon WHK

It is to be noted that the results reported above for electrochemically oxidised samples were obtained using KCl as electrolyte. TC-66 C was also electrochemically modified, for 30 minutes, using different electrolytes and the sodium capacity is reported in Table 5.2.

Table 5.2. Sodium adsorption on electrochemically oxidised TC-66 C

Electrolyte [0.5M]	Sodium capacity [mmol/g]
KNO_3	1.60
NH_4HCO_3	1.62
HNO_3	1.92
KCl	2.80

The sodium capacity of electrochemically modified carbon cloth using KNO_3, NH_4HCO_3 and HNO_3 as electrolyte is very similar, however when KCl was used in the electrochemical cell the ion exchange capacity increased approximately 61.2 %. With this electrolyte, there is a higher degree of oxidation of the carbon fibre that directly contributes to the ion exchange capacity and could be due to enhanced mobility and conductivity of ions in solution[2]. Moreover, the chemical composition of the electrolyte may be a very important factor in the oxidation process. For instance, the Cl^{-1} ion and especially HOCl (hypochlorous acid), that forms when chlorine is present in water, are well known to be very strong oxidants[3]. These reasons may help to explain why the sorption capacity is higher using potassium chloride. The same trend in the level of oxidation was found when a voltammetric technique was used. These results are presented in section 5.1.2.

The data presented in this section show a marked increase in sodium capacity when the adsorbents are oxidised. This will significantly increase the sorption capacity of heavy metals from aqueous solutions.

5.1.2 Voltammetric studies

Electrochemistry studies the electron transfer reactions between electrodes and reactant molecules usually in the aqueous phase. Techniques such as linear-sweep voltammetry and cyclic voltammetry provide important information such as quantitative surface coverage of adsorbed species and kinetics of electrode reactions[4].

It has been reported by different researchers that at a sufficient anodic potential carbonaceous materials are oxidised, introducing weakly acidic groups[5]. It has also been mentioned that, by carefully choosing the current profile and electrolyte, it is possible to control the dominance of oxygen-containing groups introduced during the electrochemical oxidation[6]. Important factors have to be taken into consideration during the electrochemical process e.g. ionic strength, electrolyte pH, ionic conductivity and temperature. One of the most important parameters is pH. It was found by Kukushkina et. al.[7] that oxygen reduction is accelerated with increasing H^+ concentration.

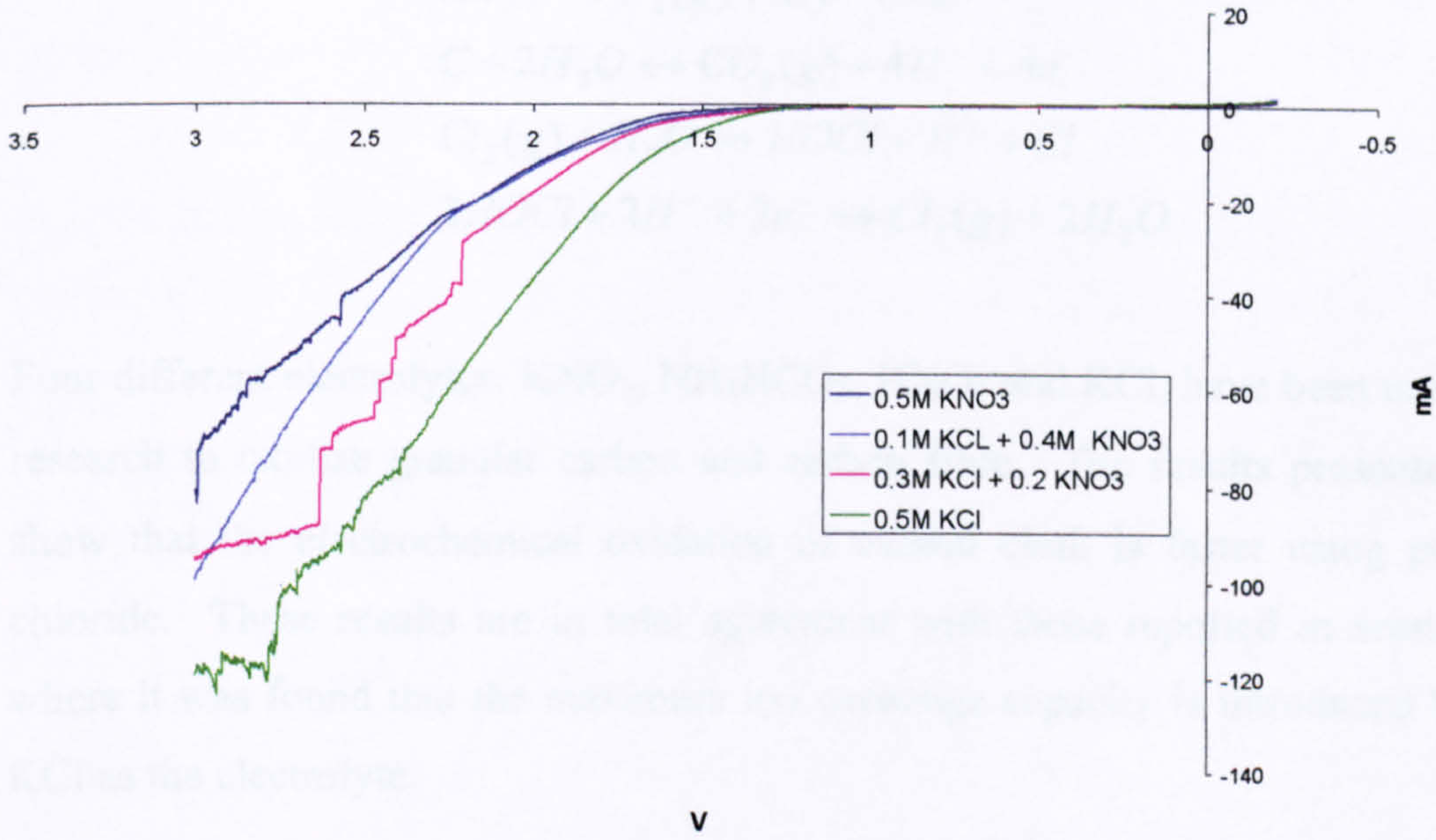


Fig 5.3. Linear sweep voltammogram for activated carbon cloth using different electrolytes

In order to compare the rate of oxidation between different electrolytes, KNO_3 and KCl, linear-sweep voltammetry was applied in the direction of oxygen reduction. Activated carbon cloth TC-66 C was used as the anode. The electrolytes used in this study have the same initial pH, similar conductivity[8] and the ionic strength was kept constant in all the experiments (these studies were carried out in the Department of Chemistry, Loughborough University). The increase of current with voltage applied (see Fig 5.3) is interpreted as the flux of material reacting at the electrode surface, in this case the electrochemical oxygen reduction on carbon, which can be represented as follows[9]:

$$O_2 + 2H_2O + 4e \rightarrow 4OH^-$$
$$O_2 + H_2O + 2e \rightarrow HO_2^- + OH^-$$
$$HO_2^- \rightarrow OH^- + 1/2\,O_2$$

The reaction products reported above react with carbon, generating oxygen-containing groups. The data presented in Fig 5.3 shows different characteristics for each electrolyte. The slope increases as the concentration of potassium chloride decreases. It is suggested that carbon oxidation is promoted in the presence of Cl^{-1} ion since the following further reactions can occur during the electrochemical process;

$$\begin{aligned}
&2H_2O + 2e^- \rightarrow H_2(g) + 2OH^- \\
&Cl_2(g) + 2e^- \leftrightarrow 2Cl^- \\
&2H_2O \rightarrow O_2(g) + 4H^+ + 4e^- \\
&C + 2H_2O \leftrightarrow CO_2(g) + 4H^+ + 4e^- \\
&Cl_2(g) + H_2O \leftrightarrow HOCl + H^+ + Cl^- \\
&2HOCl + 2H^+ + 2e^- \leftrightarrow Cl_2(g) + 2H_2O
\end{aligned}$$

Four different electrolytes: KNO_3, NH_4HCO_3, HNO_3 and KCl, have been used in this research to oxidise granular carbon and carbon fibre. The results presented above show that the electrochemical oxidation of carbon cloth is faster using potassium chloride. These results are in total agreement with those reported in section 5.1.1 where it was found that the maximum ion exchange capacity is introduced by using KCl as the electrolyte.

5.1.3 Direct acid/base titration

Carbon atoms situated at the active sites have a high concentration of unpaired electrons, hence these atoms tend to chemisorb other atoms such as hydrogen, oxygen, nitrogen, sulphur, etc. Of these atoms, oxygen is the easiest to chemisorb, and the oxygen-containing surface groups are the most important since they change surface behaviour and participate in surface reactions[10].

Carbon-oxygen complexes have been mainly classified as carboxyl, lactone, phenolic and carbonyl[11]. These surface groups have been identified and quantified by using different techniques (chapter 2, section 2.5.3). Boehm's method is one of the most commonly used; it is based on acid/base titration. This technique is able to identify weakly acidic groups: carboxyl, lactone and phenol, due to the fact that their acidity constants differ by several orders of magnitude[12].

Bases of different strength: $NaHCO_3$, Na_2CO_3, NaOH and C_2H_5ONa, have been used to neutralise oxygen-containing groups. $NaHCO_3$ neutralises carboxyl groups ($COOH$). The difference between the surface groups titrated with Na_2CO_3 and $NaHCO_3$ corresponds to lactone groups (COO), whereas NaOH neutralises phenolic groups (COH). Carbonyl groups ($C=O$) are quantifed by C_2H_5ONa in ethanol. The accuracy of this technique was proven by further research conducted by the same author, Boehm[13].

A significant increase in oxygen-containing functional groups occurred after oxidation. The results of this analysis are reported in Tables 5.3 and 5.4. The same data are presented in the form of a graph (Figs 5.4 and 5.5) for the purpose of visualising the distribution of surface groups. It is to be noted that the results shown in this section are for samples oxidised for three hours.

Table 5.3. Oxygen containing groups on as-received and modified carbon fibre TC-66 C

TC-66 C	Carboxyl	Lactonic	Phenolic	Carbonyl	Total capacity Meq g^{-1}
Unoxidised	0.36	0.44	0.24	1.43	2.48
Acid-ox	0.82	1.61	0.54	3.48	6.46
Ozone-ox	1.53	2.48	1.32	3.14	8.47
Electro-ox	2.37	2.19	1.56	2.54	8.66

The maximum ion exchange capacity for carbon fibre TC-66 C shows the following trend: electrochemical> ozone> acid oxidation, whereas for granular activated carbon WHK it is: electrochemical> acid > ozone. The electrochemical-oxidised samples present the highest ion exchange capacity, which was also found by sodium capacity analysis (section 5.1.1).

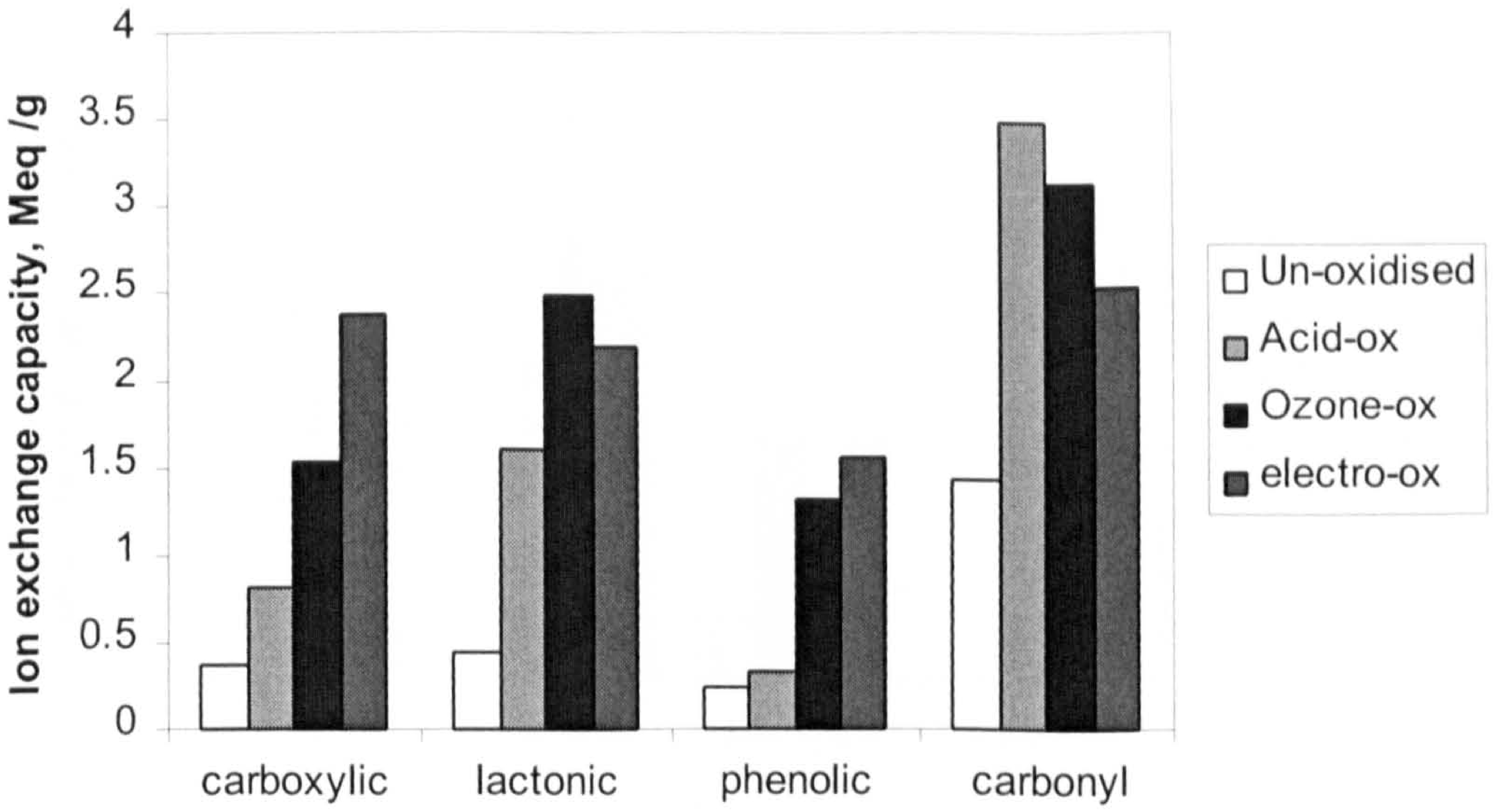


Fig 5.4. Oxygen containing groups on conventional and modified carbon fibre TC-66 C

Figs 5.4 and 5.5 indicate that phenolic groups are generally introduced to the least extent during the chemical modification without taking carbonyl groups into account. This was followed by carboxyl and lactone groups. It is known that carboxyl groups are the most important in the treatment of drinking water, since these groups dissociate between pH 3 and 6. Lactonic groups are not as important since they dissociate above pH 6[14].

Table 5.4. Oxygen containing groups on conventional and modified granular carbon WHK

WHK	Carboxyl	Lactonic	Phenolic	Carbonyl	Total capacity Meq g^{-1}
Unoxidised	0.24	0.49	0.26	1.17	2.16
Acid-ox	2.27	1.43	1.09	2.29	7.08
Ozone-ox	1.02	2.69	0.17	2.13	6.01
Electro-ox	1.39	2.45	1.11	2.34	7.29

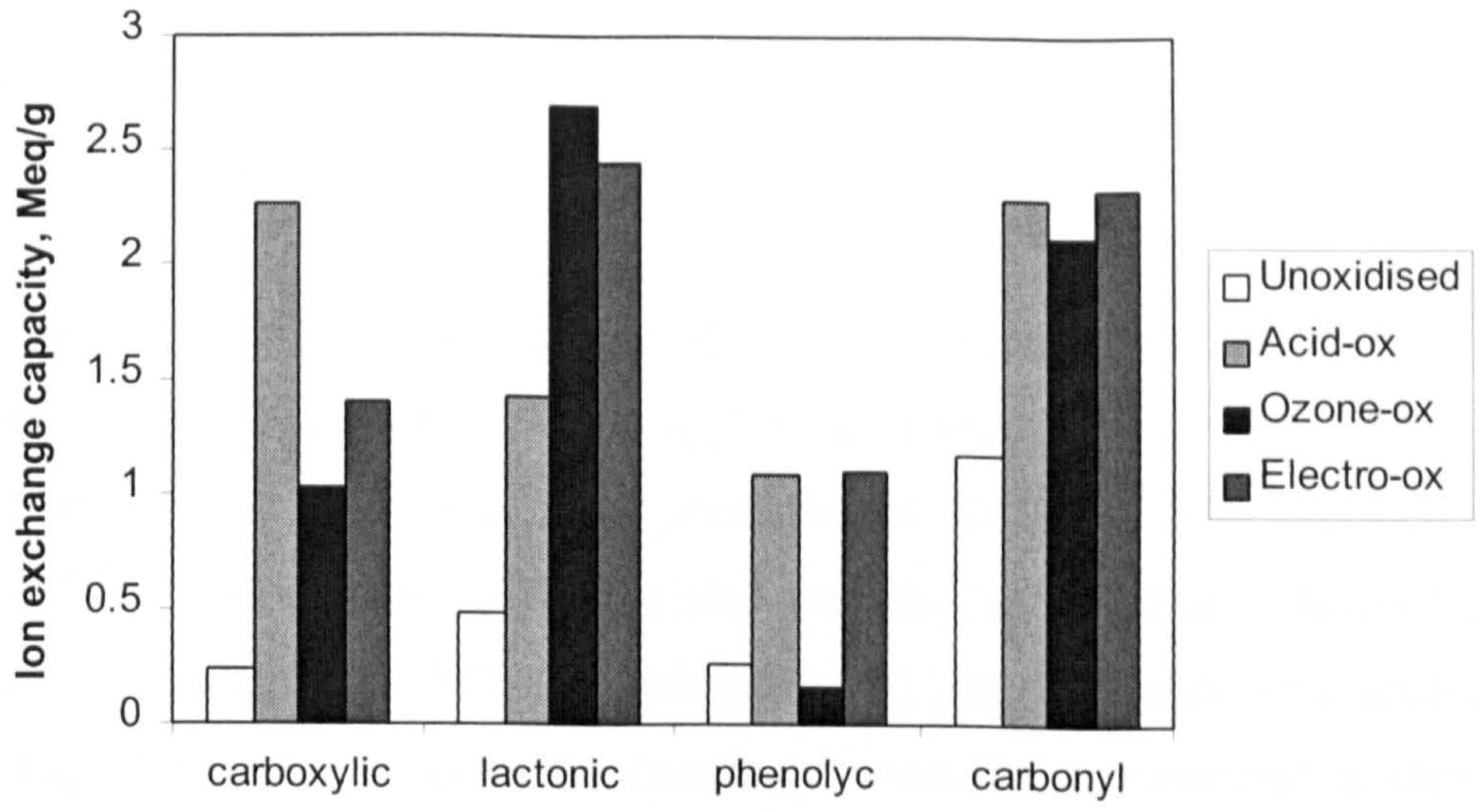


Fig 5.5. Oxygen containing groups on conventional and modified granular carbon WHK

Electrochemical oxidation introduces the highest amount of carboxyl groups on activated carbon cloth TC-66 C. On the contrary, acid oxidation seems the most effective way to increase the amount of carboxylic groups on granular carbon WHK.

It is difficult to make a direct comparison of the amount of oxygen-containing surface groups introduced by using different processes between granular carbon and carbon fibre, since their physical and chemical properties are different. Additionally, the electrochemical and ozone oxidation procedures were carried out differently because granular carbon and carbon fibre cannot been handled in the same way.

The enhancement of oxygen-containing functional groups in modified adsorbents will significantly increase the sorption of heavy metals from water and wastewater at near-neutral pH.

5.1.4 X-ray Photoelectron Spectroscopy

The surface chemical composition can also be studied using different surface spectroscopy techniques. The most commonly used are X-ray Photoelectron Spectroscopy (XPS or ESCA), Auger Electron Spectroscopy (AES), Secondary-Ion Mass Spectroscopy (SIMS) and Low-Energy Ion Scattering Spectroscopy (ISS).

Spectroscopy techniques such as Raman spectroscopy and Fourier Transform Infrared spectroscopy (FT-IR) have considerable utility in basic surface analysis but not an extensive application in surface analysis[15].

XPS is applied to gases, liquids and solids. This technique does not normally cause radiation damage, therefore it can be applied to a wide range of materials. More detailed information about the basic principles of XPS has been reported in the literature[16,17]. Conventional and chemically modified, oxidised three hours samples, granular activated carbon WHK and carbon fibre TC-66 C samples were analysed by XPS. Figs 5.6 and 5.7 show the broad spectrum for commercial adsorbent as received. The peaks presented in each diagram correspond to an element, which can be identified with its corresponding binding energy.

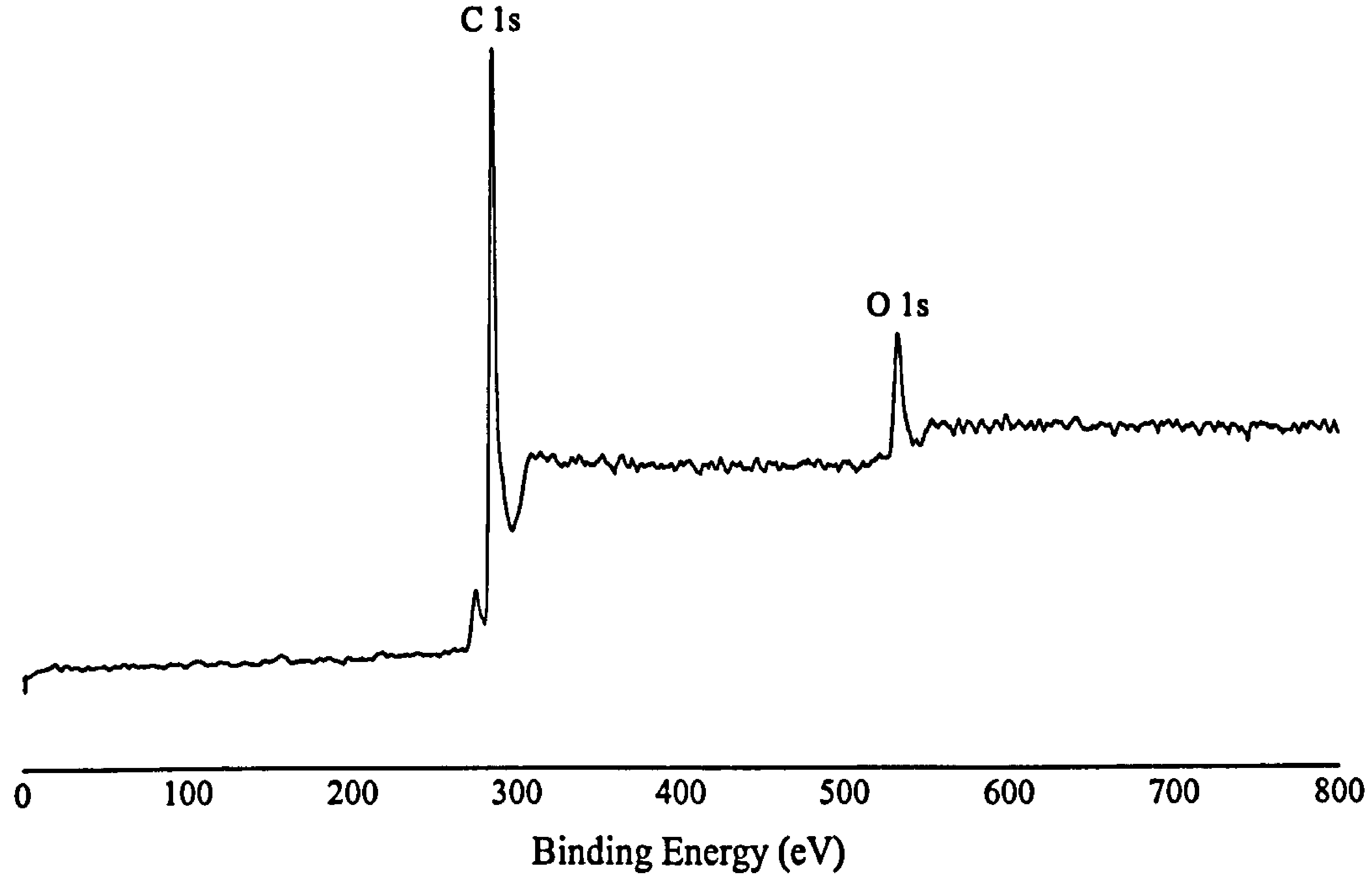


Fig 5.6. X-ray photoelectron spectrum of granular activated carbon WHK

The wide spectrum for conventional granular activated carbon WHK, illustrated in Fig 5.6, clearly shows the presence of carbon and oxygen at the binding energy of 285 and 533 eV, respectively. On the other hand, activated carbon fibre TC-66 C shows a different photoelectron spectrum (see Fig 5.7). Clear evidence of carbon, oxygen, nitrogen and traces of silicon were found. The existence of nitrogen on carbon fibre could be attributed to incomplete carbonisation of the precursor, polyacrylonitrile. The presence of silicon may be attribute to contamination during packing and storage.

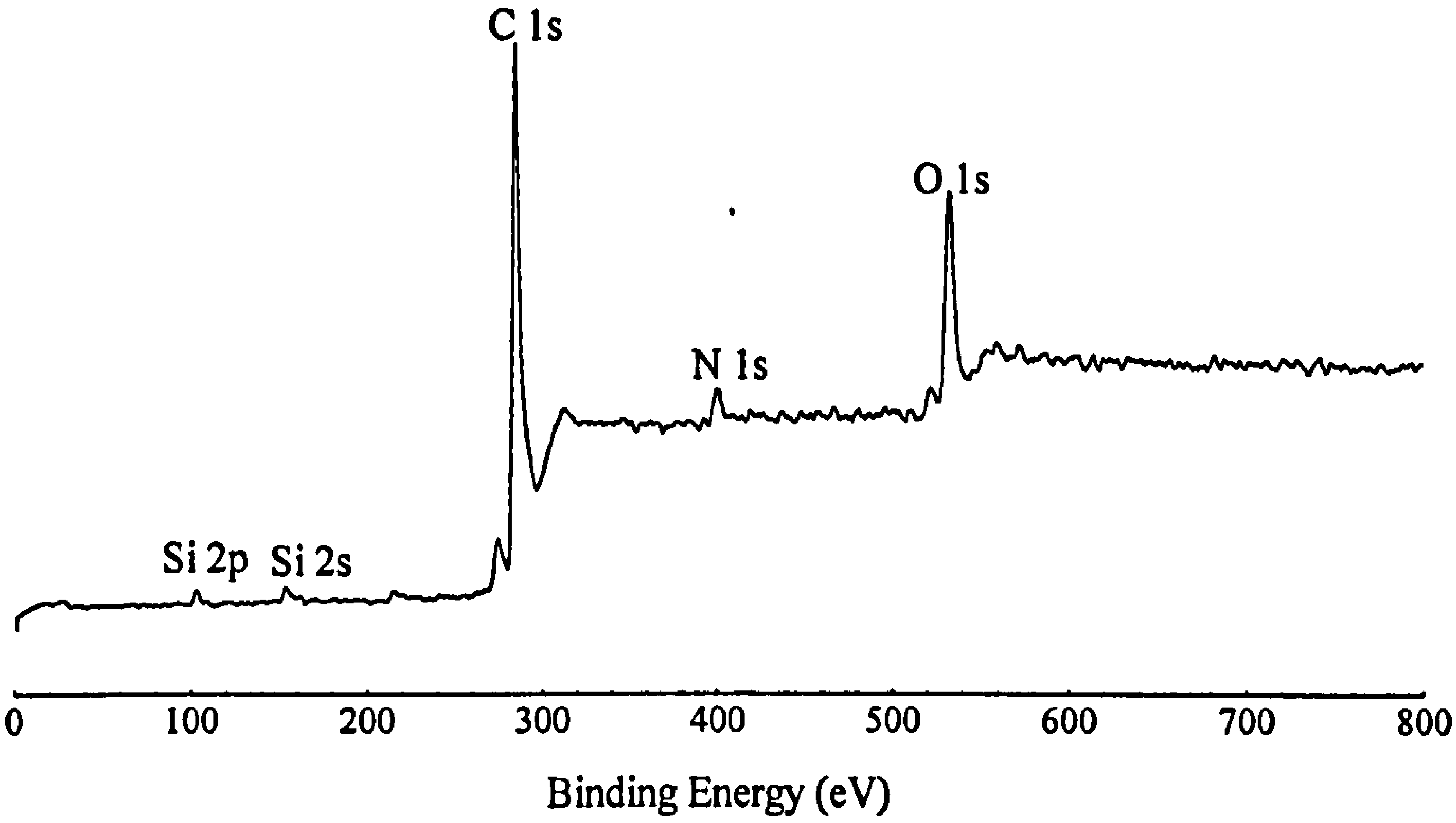


Fig 5.7. X-ray photoelectron spectrum of commercial activated carbon fibre TC-66 C

The surface composition of TC-66 C and WHK obtained by this technique is reported in Tables 5.5 and 5.6, respectively. The oxygen composition notably increased after chemical modification, but not in the same proportion in all the processes. The results obtained for carbon fibre show that the oxygen percentage increases in the following order; acid, ozone and electrochemical oxidation, whereas nitrogen composition increases in the opposite direction. The silicon traces found in commercial samples disappear after oxidation. On the other hand, the oxidation level in granular carbon was as follows; electrochemical> acid >ozone. Only a small amount of nitrogen was found in acid oxidised samples, that is attributed to residual nitric acid used as the oxidant.

Table 5.5. Surface composition of carbon fibre TC-66 C determined by XPS

TC-66 C	%			
	C	Si	N	O
Un-oxidised	82.8	1.7	3.4	12.1
Acid-ox	81.5	0.0	2.8	15.7
Ozone-ox	78.2	0.0	2.5	19.3
Electro-ox	79.1	0.0	0.5	20.4

Table 5.6. Surface composition of activated carbon WHK determined by XPS

WHK	%		
	C	N	O
Un-oxidised	91.5	0.0	8.1
Acid-ox	79.9	3.0	17.1
Ozone-ox	83.6	0.0	16.4
Electro-ox	79.4	0.0	17.2

Figs 5.8 and 5.9 show the high-energy resolution studies of commercial and modified carbon fibre and granular carbon, respectively. It is difficult to notice the difference between these spectra and as a consequence it is not easy to identify the chemical shift of possible oxygen-containing groups. However, by applying a curve fitting program, such as PeakFit software version 4, to deconvolute the XPS peaks it is possible to identify the chemical shift of surface groups containing oxygen related to saturated hydrocarbon (C 1s= 285 eV). The spectra of commercial and acid oxidised carbon fibre and granular carbon were deconvoluted and are presented in Figs 5.10 to 5.13. It is clear that modified adsorbents present more pronounced shoulders than conventional adsorbents, and in this case it is possible to identify the presence of oxygen-containing groups, that are recognised by their chemical shift.

The photoelectron spectrum of carbon fibre shows a major peak at an approximate binding energy of 284.6 eV, that can be attributed to a carbon ring structure (C-C) and CH_n. Other peaks detected at a shift of 2.9 eV, and 4.18-4.33 eV from the main peak can be attributed to C=O (carbonyl), and COOH (carboxylic), respectively[18,19].

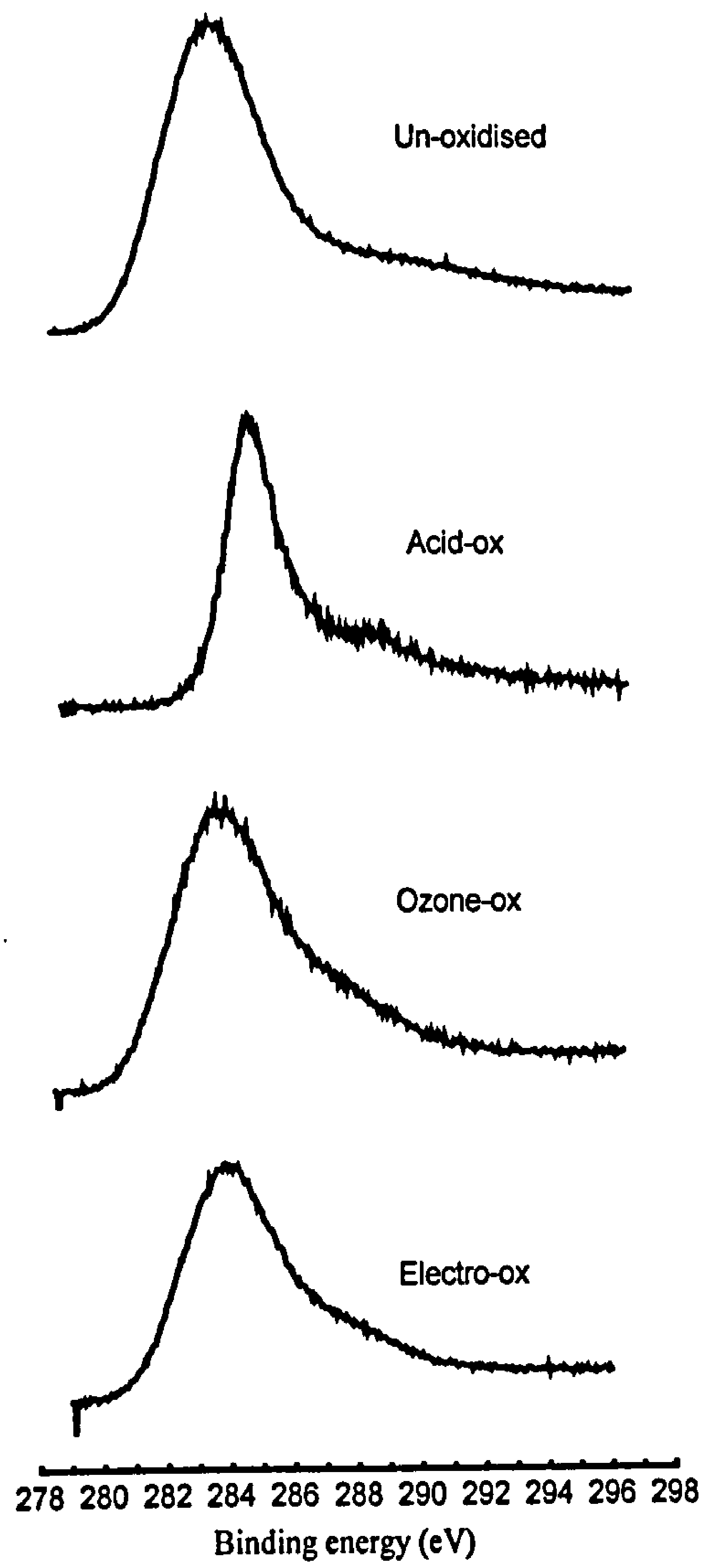


Fig 5.8. XPS of carbon fibre TC-66 C

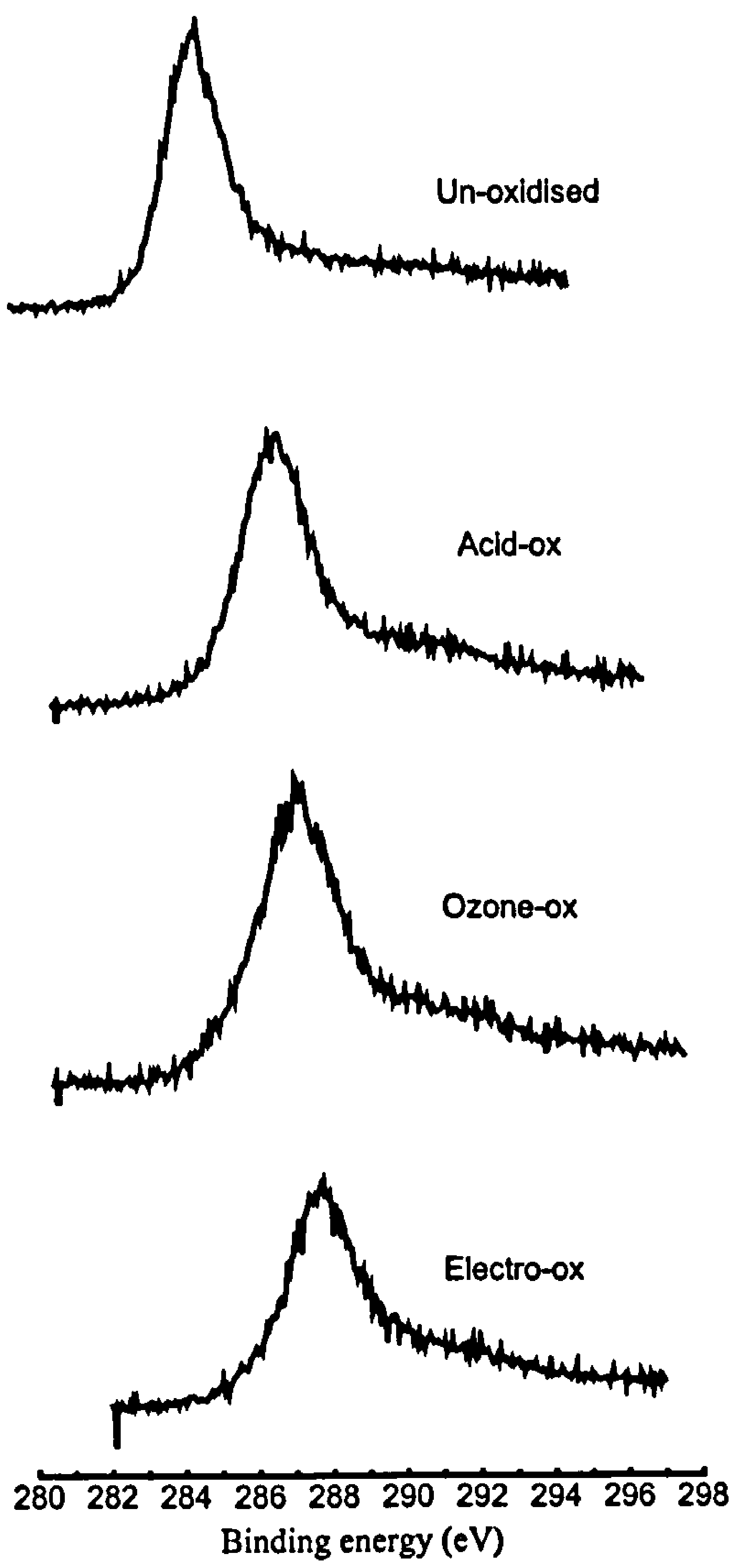


Fig 5.9. XPS of granular carbon WHK

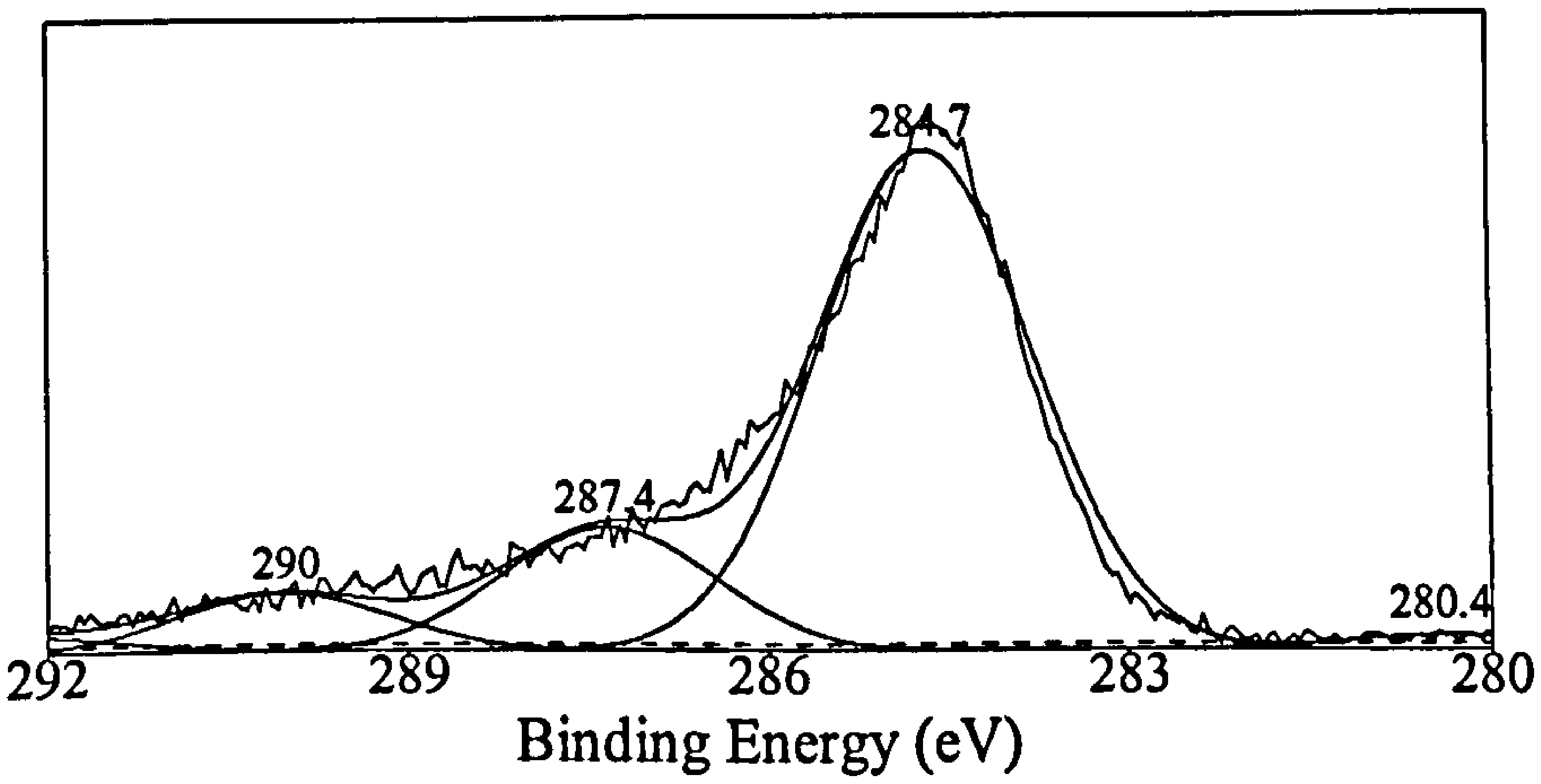


Fig 5.10. XPS spectrum of commercial TC-66 C

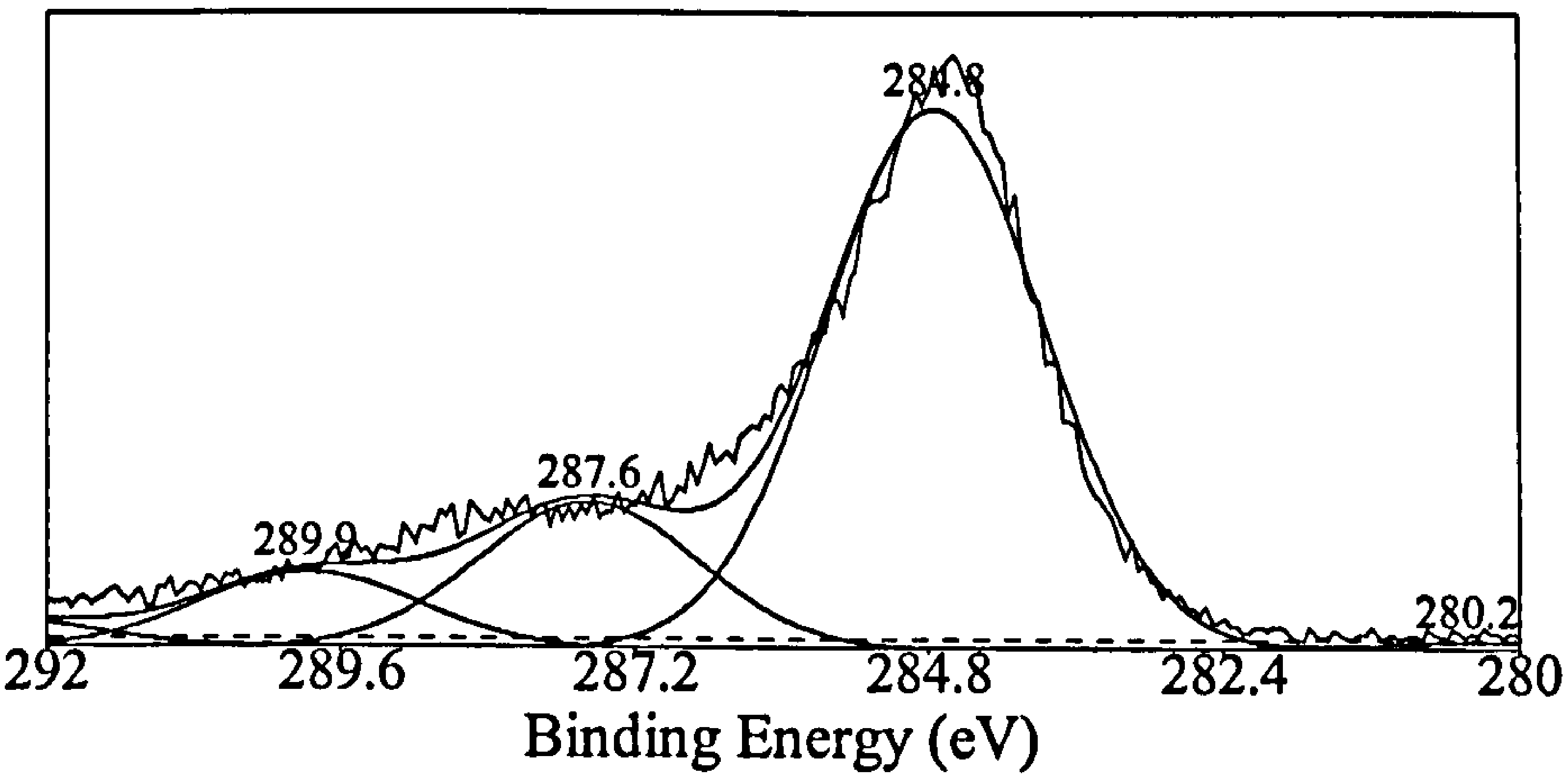


Fig 5.11. XPS spectrum of acid oxidised TC-66 C

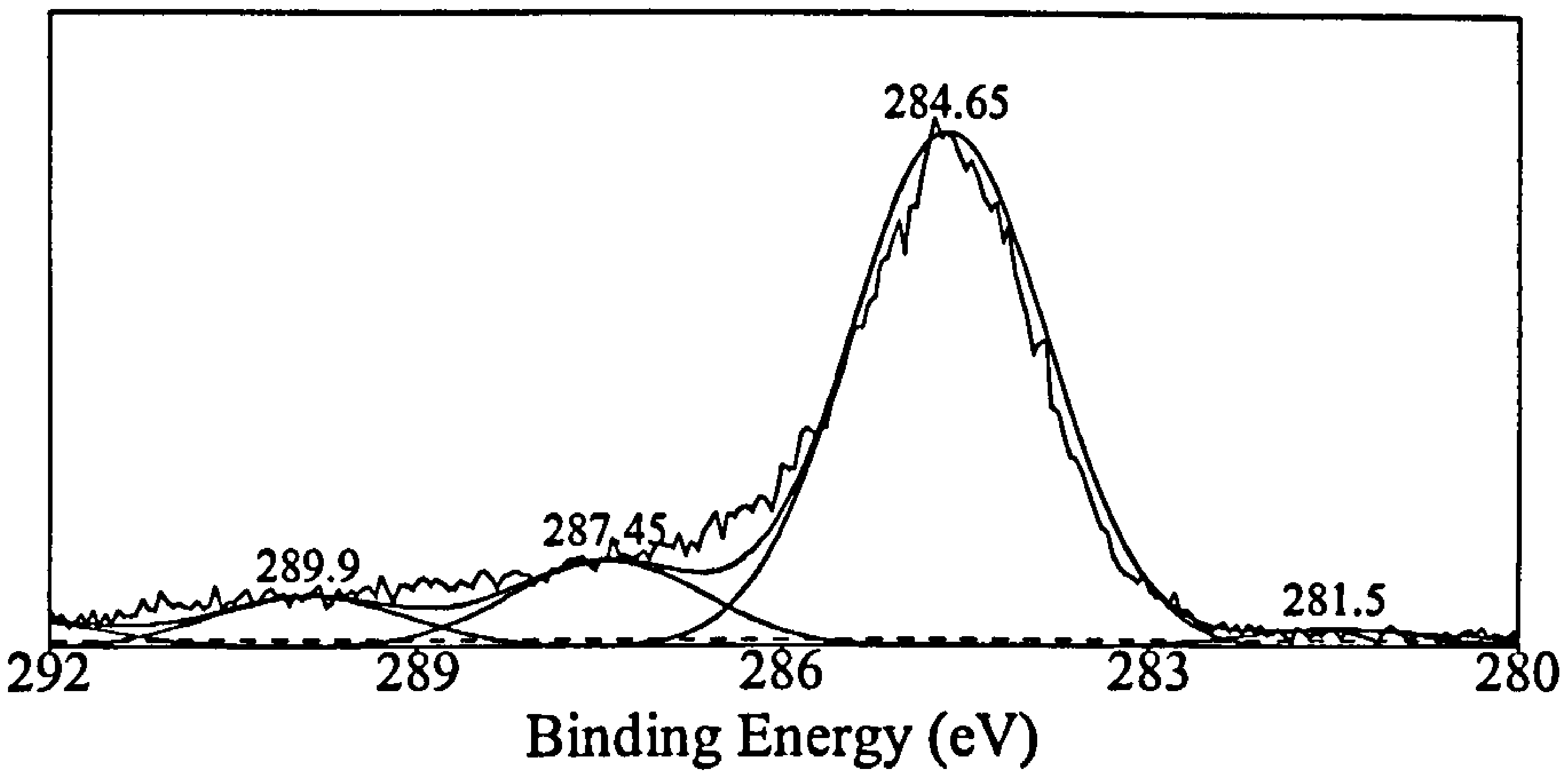


Fig 5.12. XPS spectrum of commercial WHK

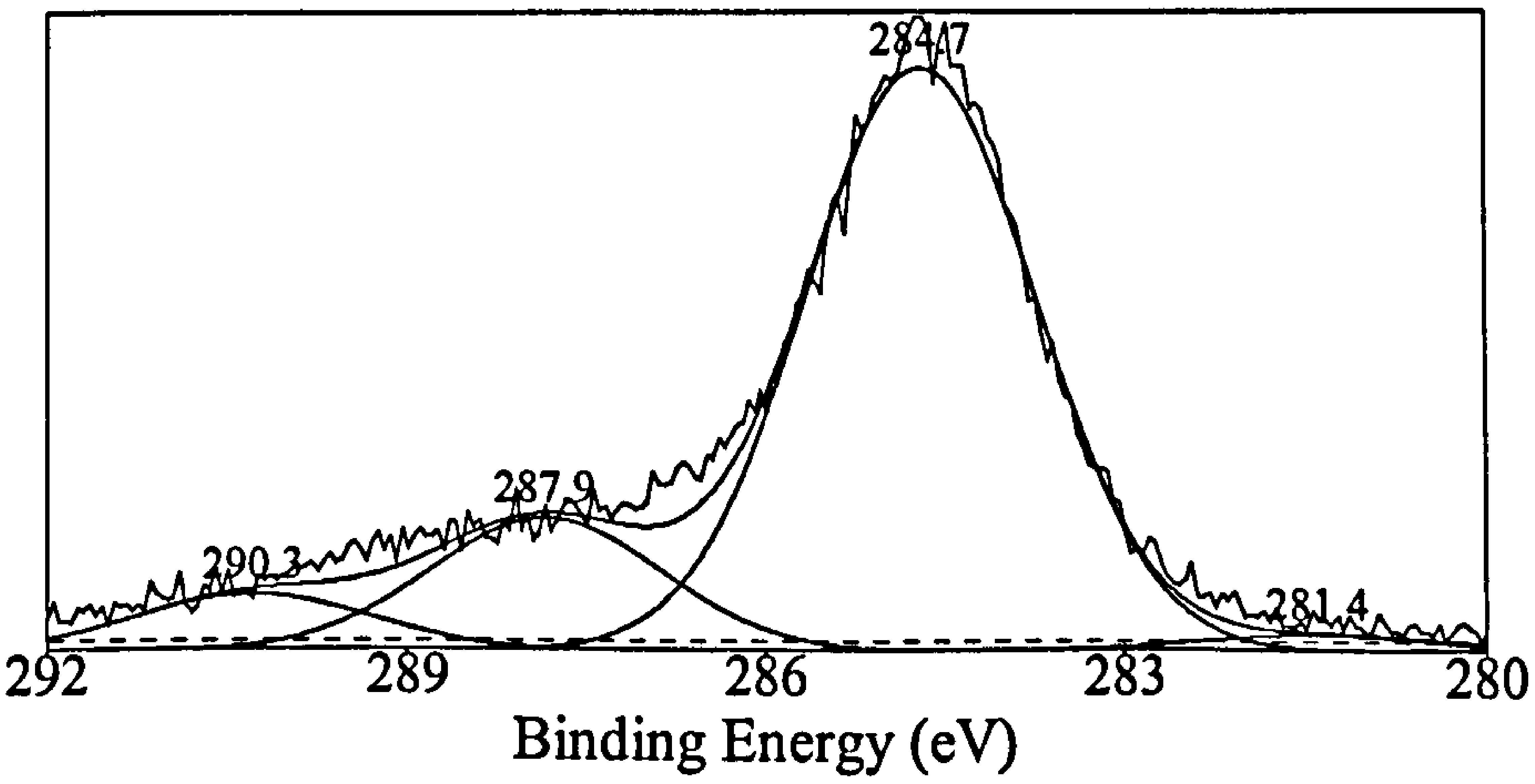


Fig 5.13. XPS spectrum of acid oxidised WHK

An increase in oxygen content is directly related to the amount of oxygen-containing groups on the carbon surface. Hence, this can be directly related to the total ion exchange capacity. The results presented in this section follow exactly the same trend as those obtained by sodium capacity (section 5.1.1) and Boehm titration (section 5.1.3).

5.1.5 Elemental analysis

Elemental analysis is an analytic technique that determines the composition of solid materials such as carbonaceous adsorbents. Conventional and oxidised granular carbon WHK and carbon fibre TC-66 C were characterised by this technique. The samples were analysed at Strathclyde University, Scotland. The oxygen content can not be determined directly by this technique, so it was calculated from the difference between one hundred percent and the percentage sum of carbon, hydrogen and nitrogen.

The results of these analyses for commercial and oxidised carbon fibre and granular carbon are shown in Tables 5.7 and 5.8, respectively. The results show a significant increase in oxygen content between the commercial and modified adsorbents. This is directly related to the increase in oxygen-containing groups. The percentage of oxygen found by XPS (section 5.14) is lower that that found by elemental analysis. It may be due to the fact that XPS analyses only a few atomic layers, a depth from 5 to 10 nm, and in this case the density of functional groups inside the pores probably will not be taken into account. It is to be noted that even though the oxygen percentage found by elemental analysis is different than that obtained by XPS the trend for the different pretreatments is exactly the same. Different researchers have also reported high oxygen content in chemically modified granular carbons[20,21].

Table 5.7. Composition of carbon fibre TC-66 C determined by elemental analysis

TC-66 C	%			
	C	H	N	O
Unoxidised	64.21	2.84	3.63	29.32
Acid-ox	60.97	2.81	3.9	32.32
Ozone-ox	58.71	1.73	3.02	36.54
Electro-ox	56.34	2.07	2.29	39.3

Table 5.8. Composition of granular carbon WHK determined by elemental analysis

WHK	%			
	C	H	N	O
Unoxidised	77.23	1.15	0.0	21.62
Acid-ox	66.87	1.54	2.51	29.08
Ozone-ox	70.61	1.68	0.0	27.71
Electro-ox	64.88	2.28	0.0	32.84

The results shown above also confirm that the oxygen content in TC-66 C increases as follows 10.23, 24.62 and 34.04 % for acid, ozone and electrochemical oxidised samples, whereas for WHK it increases in the following proportions 28.17, 34.50 and 51.90 % for ozone, acid and electrochemically modified samples. The difference in oxygen concentration on the adsorbents analysed by this technique may be related to the difference in surface area. Boehm titration, sodium exchange capacity and XPS analysis have found the same trend in oxygen content.

5.1.6 pH titration

It is well known that adsorption strongly depends on the nature of the surface, porosity and surface area [22,23]. Potentiometric titration or pH titration is a technique that has been used to evaluate the acid/base properties of ion exchangers[24]. The capacity and type of surface groups can be determined from the pH titration curves. These curves are usually plotted as equilibrium solution pH *versus* acid/alkali added, or amount of ions released *versus* equilibrium solution pH. The shape of these curves shows the nature of the surface groups present on the ion exchanger e.g. weak-acid, strong-acid or polyfunctional. Moreover, information such as pK values of functional groups and the optimum working range of the adsorbent or ion exchanger can be deduced from the same pH titration curves.

It is well known that carbonaceous materials are amphoteric, which means that they have both basic and acidic surface properties. Carbons with low oxygen content have a high concentration of basic groups and adsorb anions, whereas adsorbents with high oxygen content present acidic surface characteristics and show cation exchange properties. Therefore, carbonaceous materials have to be titrated with acid and base in order to determine their surface nature.

The pH titrations were conducted using commercial and chemically modified activated carbon fibre in the form of cloth TC-66 C, activated granular carbon WHK and carboxylic ion exchange fibre, K-4. Fig 5.14 shows typical pH titration curves using conventional granular carbon WHK.

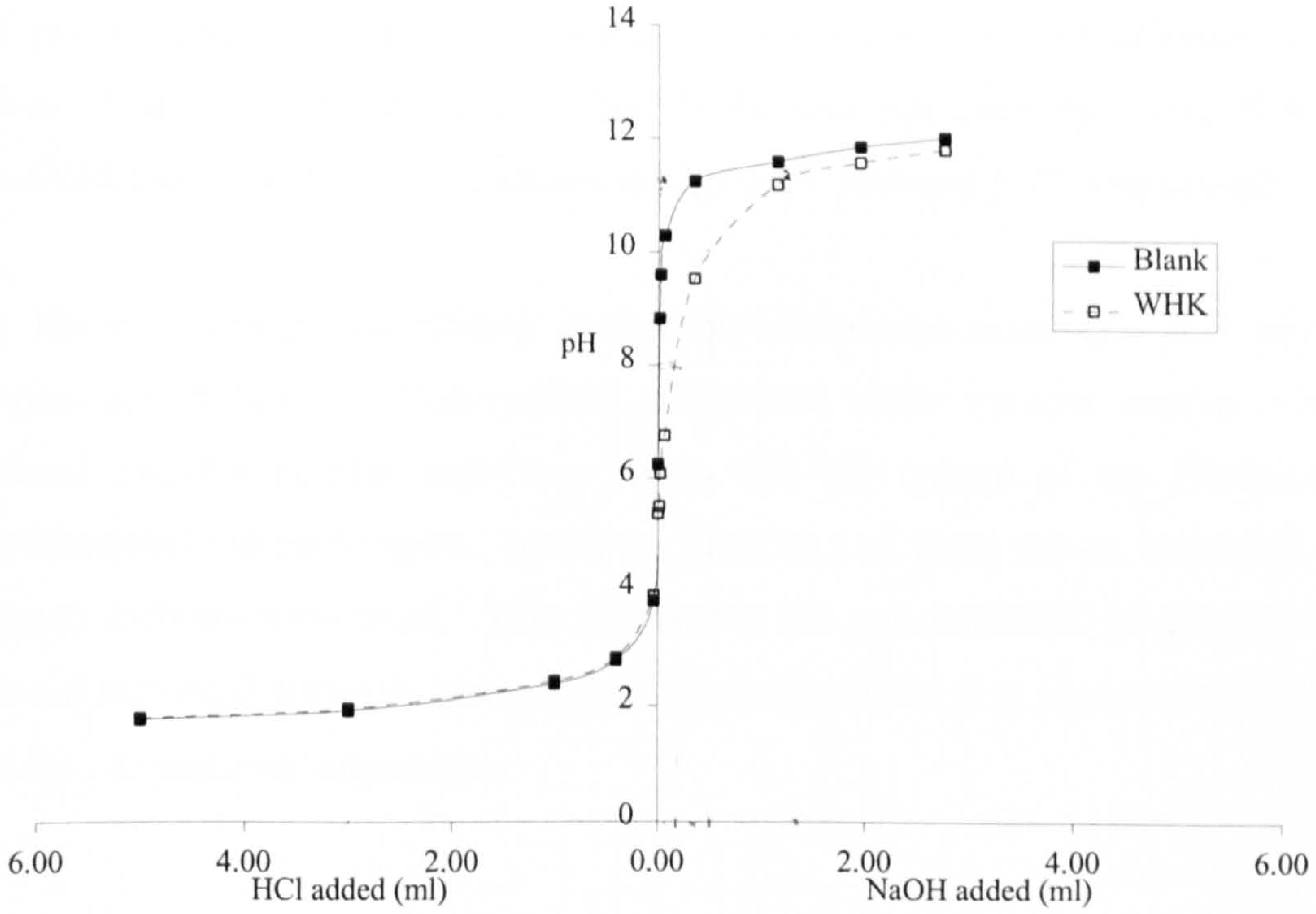


Fig 5.14. pH titration curves for granular carbon WHK and blank experiments

The data plotted in Fig 5.14 shows a decrease in pH when the adsorbent was contacted with alkali solution. This is attributed to the release of H^+ ions during the ion exchange with Na^+. It is possible to determine the total hydrogen ions released from the ion exchanger at a certain pH value. This can be calculated from the difference between the volume of NaOH or HCl added on the experimental curve and the value of the blank curve, at the same pH, which can be expressed by the following equation:

$$IR = \frac{C(V_b - V_{ie})}{W} \qquad \textbf{Eq. 5.1}$$

where,

C = Titrant concentration, M

IR = Ions released, mol/g

V_b = Volume of titrated alkali solution without ion exchanger at a given pH, ml
V_{ie} = Volume of titrated alkali solution in the presence of ion exchanger at a given pH, ml
W = Mass of ion exchanger, g

The proton-binding curves, concentration of ion release against solution pH, for carbon cloth TC-66 C, granular carbon WHK and ion exchange fibre K-4 were calculated using Eq. 5.1 and are shown in Figs 5.15, 5.16 and 5.17, respectively.

The shape of the proton-binding curves of commercial adsorbents and modified samples are different. Conventional adsorbents show smooth curves, whereas oxidised samples present inflection points that are typical of the behaviour of polyfunctional ion exchangers. Moreover, the slope of these curves increased when oxidised carbons were used. This means that the concentration of hydrogen ions released increased with pH, hence the ion exchange capacity is expected to be higher than for conventional adsorbents.

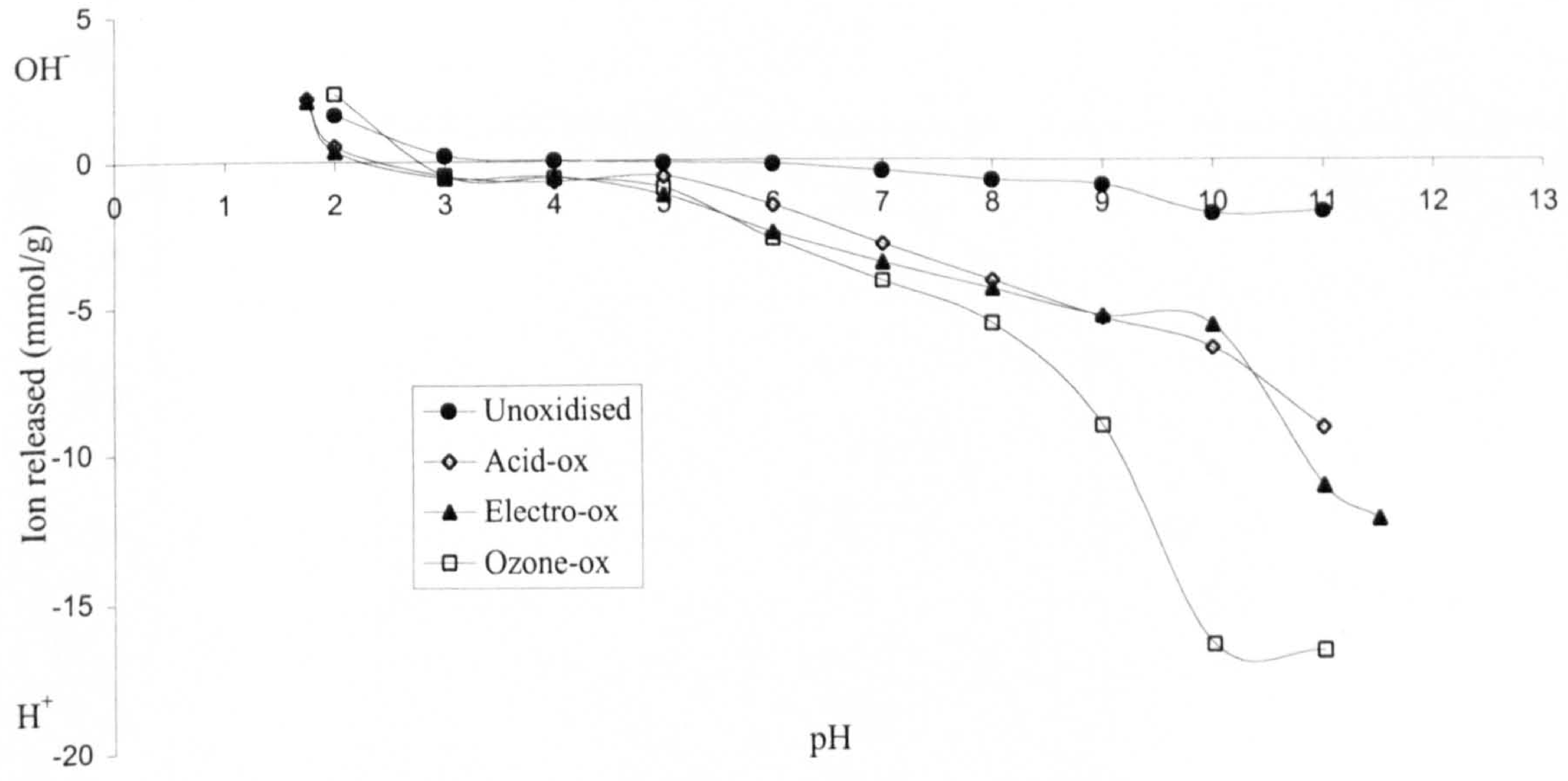


Fig 5.15. Proton-binding curves for conventional and modified carbon cloth TC-66 C

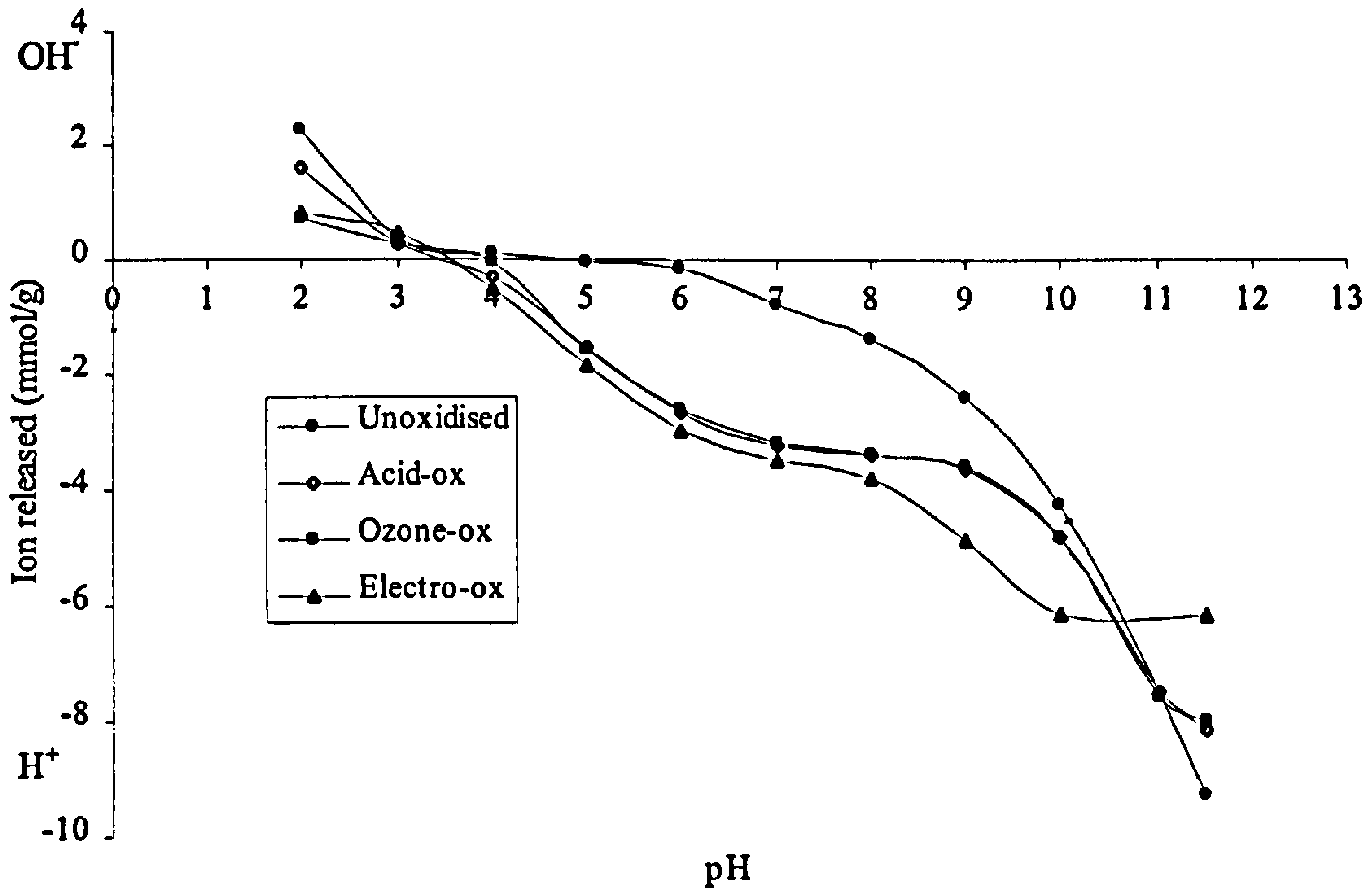


Fig 5.16. Proton-binding curves for conventional and modified activated carbon WHK

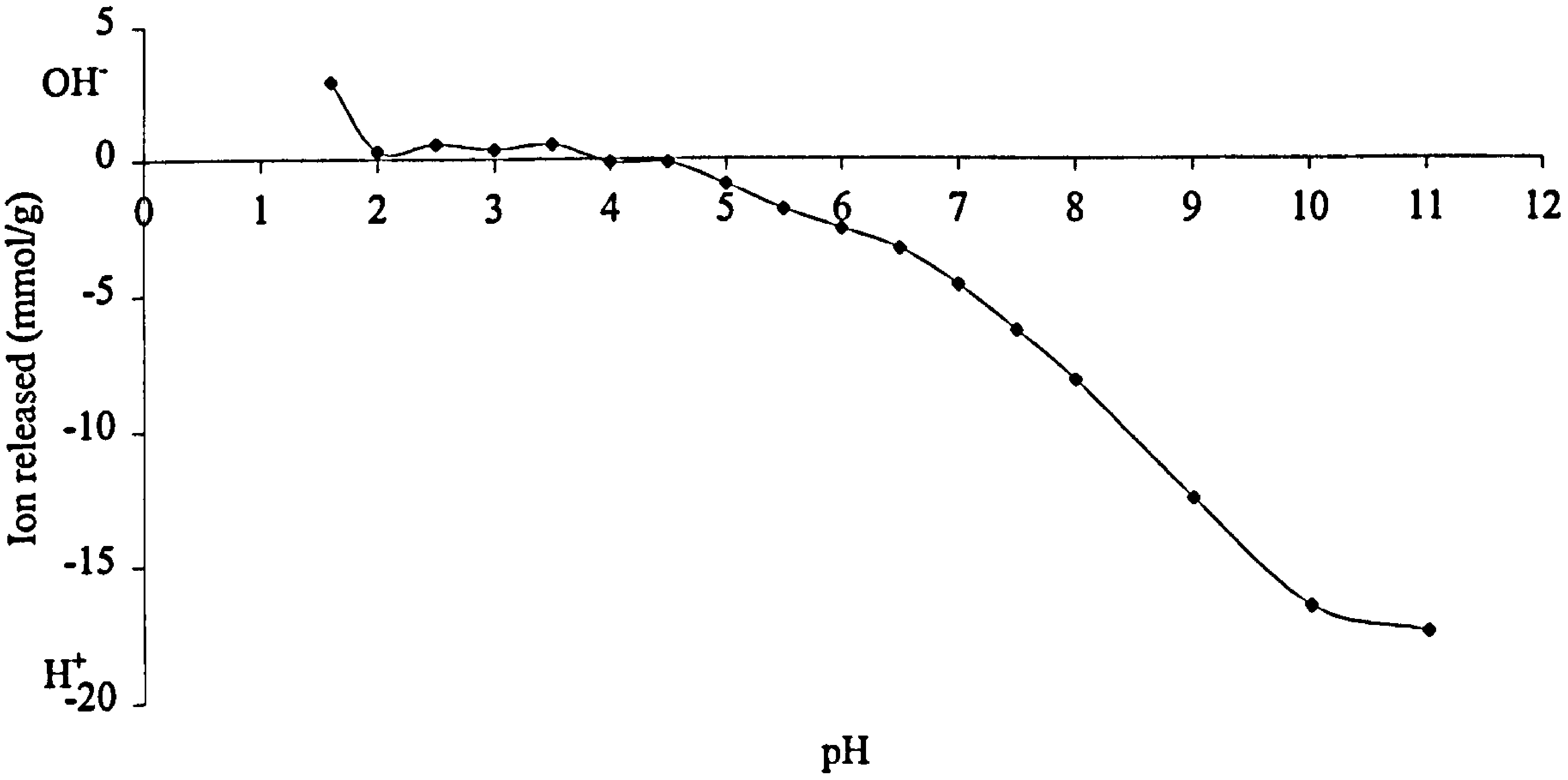


Fig 5.17. Proton-binding curve for ion exchanger K-4

The data plotted in Fig 5.17 represents the pH titration curve for carboxylic ion exchange fibre K-4. It is clear that the shape of this curve is smooth and different to that presented by modified granular carbon and carbon fibre. This is due to the dissociation of the only functional groups present on this ion exchanger, i.e. carboxyl groups. Ion exchange starts at approximately pH 4 and the concentration of hydrogen ions released increases rapidly with pH, confirming a high ion exchange capacity. On the other hand, the ions released on granular carbon and carbon fibre start about pH 2 and increase with pH, but in this case the pH titration curves show inflection points due to the dissociation of different surface groups as the pH increased.

It is very important to understand surface phenomena occurring during adsorption and ion exchange. The point where the pH titration curves crosses the pH axis has crucial significance. It is called the point of zero charge (PZC). This has been defined as the pH value at which surface charge is zero at a particular ambient temperature, applied pressure, and aqueous solution composition[25]. The PZC will change depending on the type and amount of functional groups present on the ion exchanger. It is shifted to lower pH values as the degree of oxidation increases due to the introduction of acidic groups such as carboxyl, phenolic, carbonyl and lactonic[26]. For instance, the PZC of unoxidised TC-66 C is at pH 4.2 whereas it is at pH 2.8 for ozone oxidised, at 2.4 for acid oxidised and at 2.25 for electrochemical oxidation. On the other hand, the PZC for granular carbon WHK is at pH 4.5 for untreated adsorbent and at pH 3.5, 3.6 and 3.9 for acid, electrochemical and ozone oxidised, respectively. It is well known that the sorption of metal ions strongly depends on the chemistry of the carbon surface[27]. The surface is positively charged at pH values below the PZC, since the oxygen-containing groups are undissociated and the adsorbent will remove anionic species from solution under these conditions. In contrast, at solution pH values greater than the PZC, the carbon surface becomes more negative due to dissociation of weakly acidic oxygen-containing groups. Thus, the adsorbent surface is able to attract and exchange cations in solution. This renders both TC-66 C and WHK capable of adsorbing trace metal ions from aqueous solution at pH values in excess of about 3.

5.1.7 Electrophoretic mobility measurements

When an electric field is applied to charged particles it results in electrokinetic effects. One of these is called electrophoresis, which is the movement of a charged particle suspended in an electrolyte under the influence of an applied electric field.

Zeta potential (ZP) is related to electrophoretic mobility and is an index of the magnitude of interaction between colloidal particles. Colloidal suspensions, dispersion of fine particles in liquid phase, possess an electric charge which depends on the nature of the solids and the surrounding medium[28]. The dissociation of acid or basic surface groups and the solution pH alter the surface density charge. The dissociation of oxygen-containing groups leaves a negatively charged surface (see Fig 5.18), whereas the ionisation of basic groups leaves the surface positively charged (see Fig 5.19). Hence the net surface charge can be adjusted to positive, zero or negative by changing the pH of the solution.

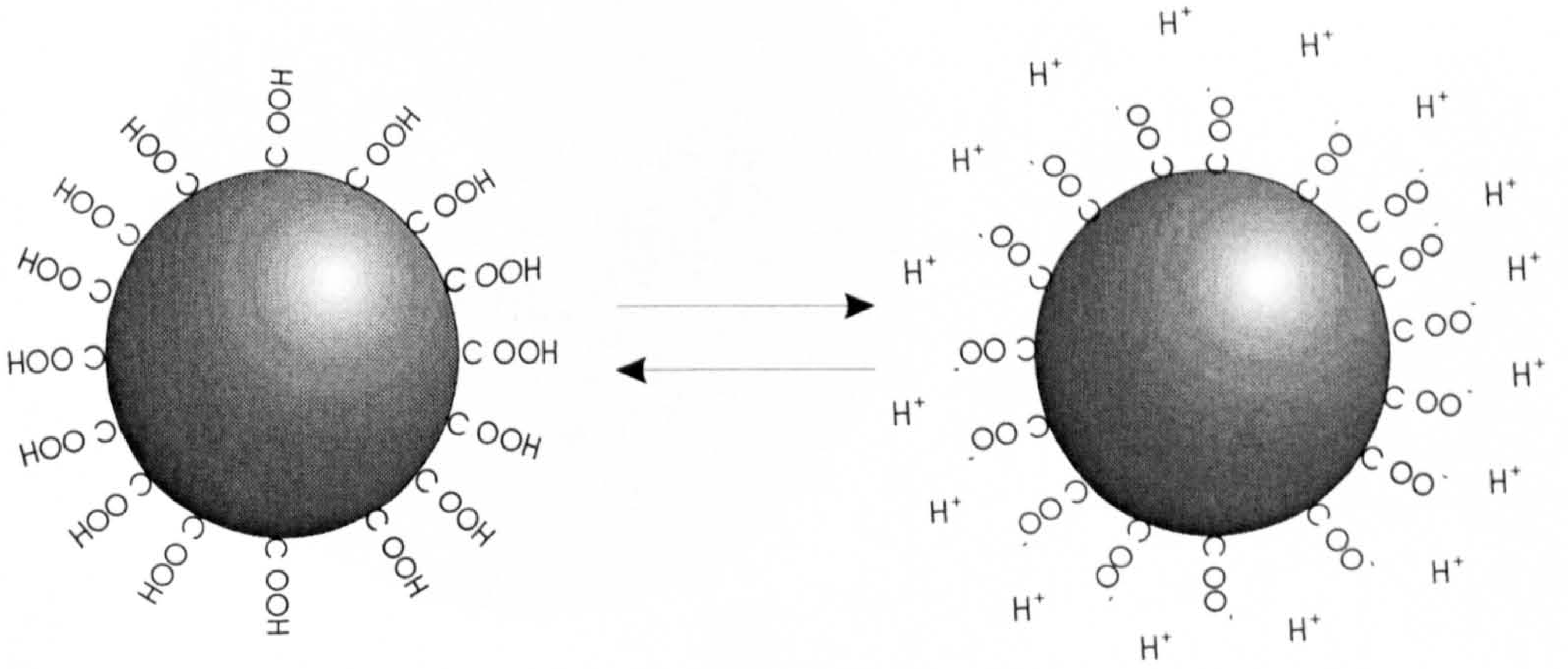


Fig 5.18. Ionisation of acidic groups

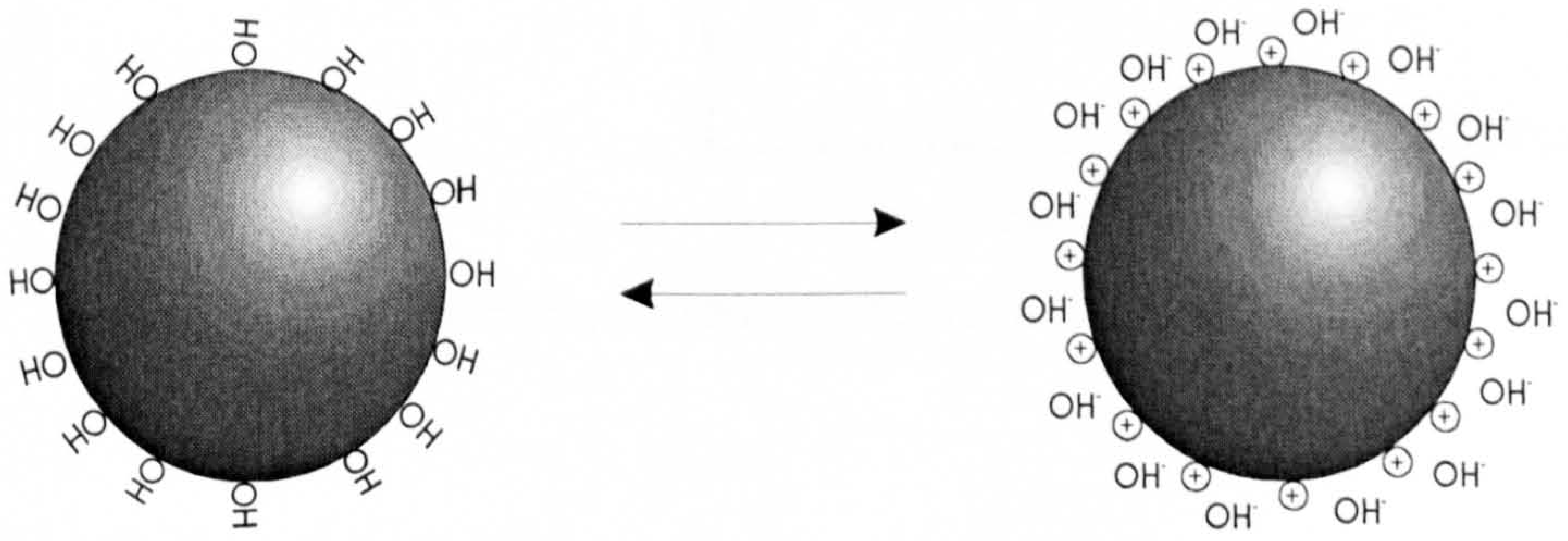


Fig 5.19. Ionisation of basic groups

A positively or negatively charged particle will have two surrounding liquid layers. The closest is an inner region called the Stern layer in which the ions are strongly bound to the particle. Adjacent to this region is a film layer called the diffuse layer where the ions are less associated with the particle. The potential at this last boundary is called the zeta potential. The diagram shown in Fig 5.20 shows the different layers and charge distributions on a negatively charged particle.

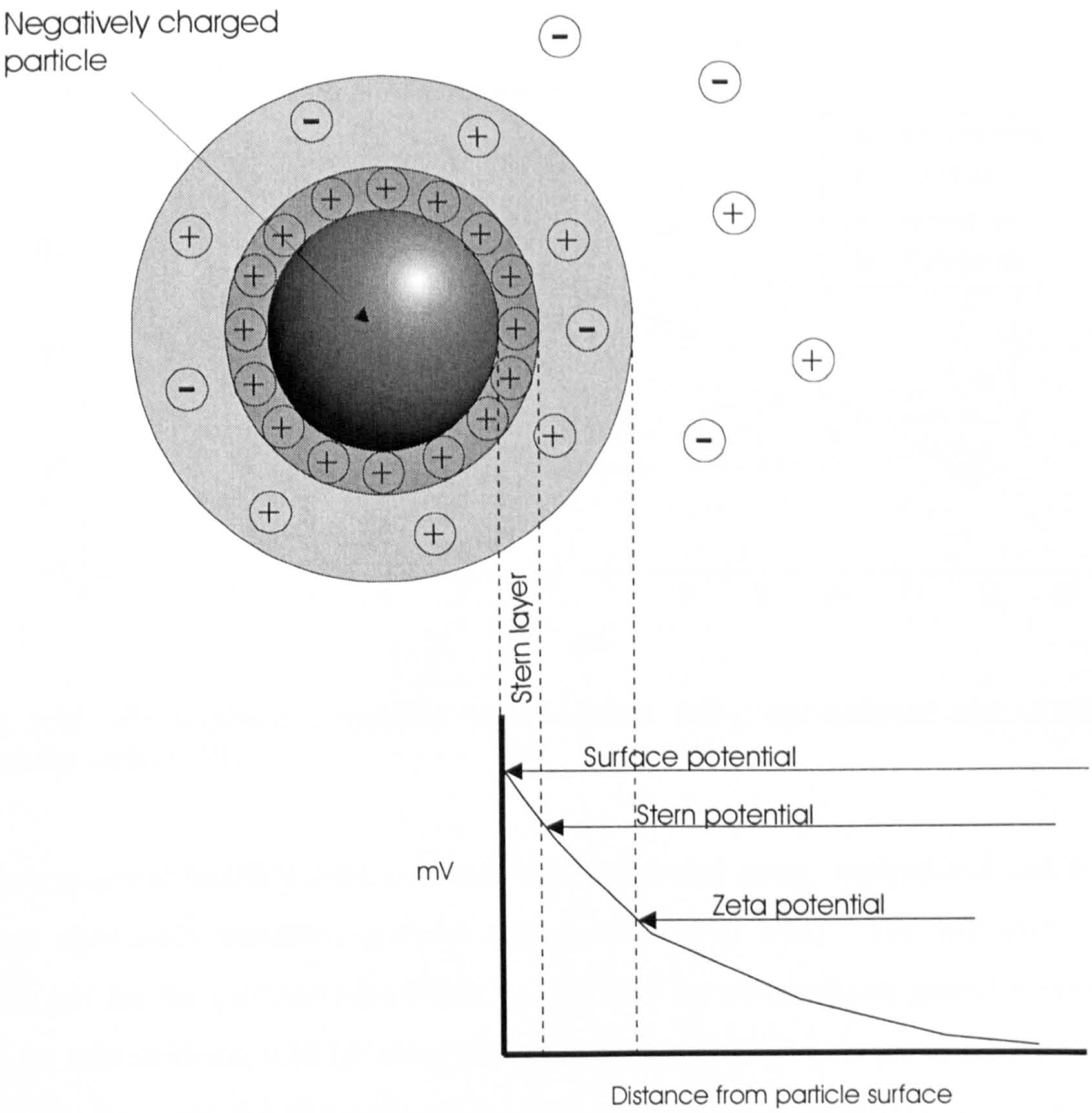


Fig 5.20. Schematic representation of zeta potential

Zeta potential is usually plotted against pH. This plot normally crosses over zero zeta potential. This point is called the isoelectric point (IEP) and its meaning is very important for practical studies. The surface charge is mainly positive at pH values lower than the IEP whereas the surface is negatively charged at pH values higher than the IEP. The same explanation applies to the point of zero charge (section 5.1.6). It is to be noted that IEP values are only representative of the external surface charge, whereas the PZC (section 5.1.6) varies in response to the net total, internal and external, surface charge of the particles.

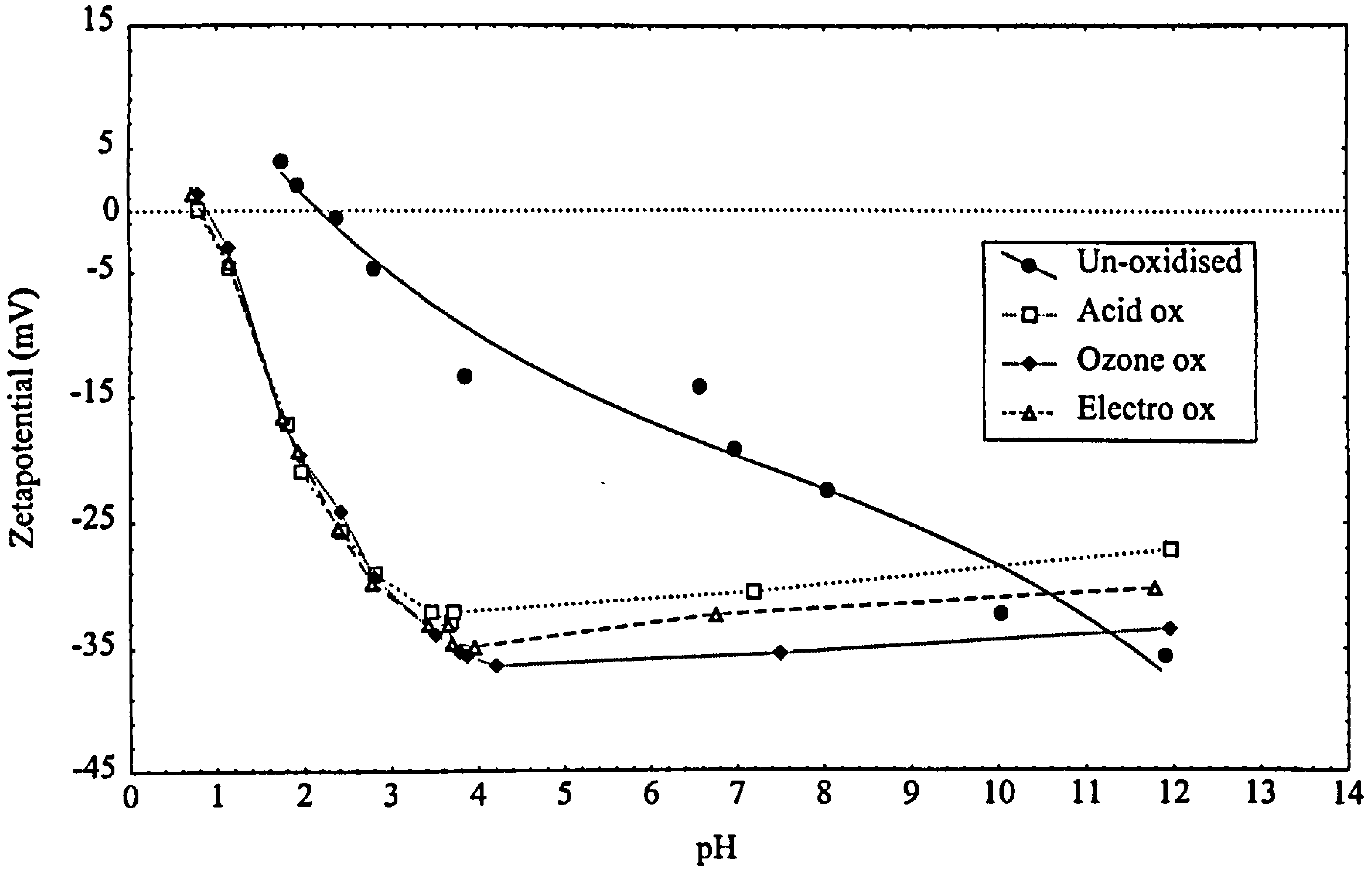


Fig 5.21. Electrophoretic mobility measurements using conventional and oxidised granular carbon WHK

Electrophoretic mobility measurements were conducted using conventional and three hours chemically modified granular carbon WHK (Fig 5.21). The IEP shifted to lower pH for the oxidised adsorbents, i.e. pH 2.19 for conventional granular carbon, 0.8 for acid oxidised, 0.83 for electrochemically oxidised and 0.91 for ozone oxidised. It is obvious that the IEP value decreases after chemical modification due to the increase in oxygen-containing groups. The rapid increase in voltage with pH, for oxidised samples, is attributed to an increase in surface charge density that can also be attributed to the introduction of oxygen-containing surface groups.

It has been reported in the literature that the (PZC-IEP) difference can be interpreted as a measure of the surface charge distribution of porous materials. Values of (PZC-

IEP) greater than zero indicate a more negative charge on the external surface than internal, whereas values closer to zero indicate a homogeneous surface charge distribution[29]. Table 5.9 reports PZC and IEP for conventional and chemically modified WHK.

Table 5.9. Point of zero charge and isoelectric point for conventional and modified granular carbon WHK

Description	PZC	IEP	(PZC-IEP)
Conventional	4.5	2.19	2.31
Acid oxidised	3.5	0.8	2.7
Ozone oxidised	3.9	0.91	2.99
Electrochemically ox.	3.6	0.83	2.77

The data presented in Table 5.9 shows that commercial granular carbon has a more homogeneous surface charge distribution than oxidised materials. The chemical modification introduces a greater amount of acidic oxygen-containing groups on the external surface of the adsorbents. In other words, oxidation takes place mainly on the surface of the particles. This is proven by an increase in the difference (PZC-IEP). It must be mentioned that the difference (PZC-IEP) increases with oxidation under the experimental conditions used in these studies. It has been reported that homogenous oxidation is obtained using dilute nitric acid, although external oxidation is predominant when concentrated oxidant is used[30].

It can be concluded that it is possible to determine the oxidation level and the surface charge distribution on carbonaceous material using the relation between PZC and IEP. This is extremely useful in adsorption and ion exchange studies.

5.2 Physical characterisation

Physical characterisation of sorptive materials used in this study was carried out using scanning electron microscopy and nitrogen sorption porosimetry. These techniques help to visualise the surface morphology and structure of adsorbents before and after any treatment or modification.

5.2.1 Surface area and porosimetry

Physical characteristics of porous materials, such as surface area and structure, are extremely important when applied in catalytic and sorption processes. Surface area is the reactive zone where chemisorption and/or physisorption occur. Alternatively, pore size and shape will define the process performance since kinetics are directly related to adsorbate intra-particle diffusion. Surface area and porosity can be determined by using several techniques, such as physical adsorption of gases, immersion calorimetry, flow microcalorimetry and mercury porosimetry. By far the most commonly used method is physical adsorption of gases[31]. Nitrogen, argon, krypton, n-butane and benzene are recommended as adsorptives[32]. However, nitrogen gas at its boiling point of 77K is the most widely used.

Gas adsorption isotherms are classified from I to V according to Brunauer, Deming, Deming and Teller (BDDT)[33]. The isotherms obtained using commercial and modified carbonaceous materials are presented in Figs 5.22 and 5.23. These isotherms corresponds to type I. They signify microporous solids having a small external area and are characterised by an almost horizontal plateau. The sharply rising area at very low relative pressure, <0.1 p/p$_o$, is due to the filling of narrow pores. The adsorption process is complete at ~0.5 p/p$_o$.

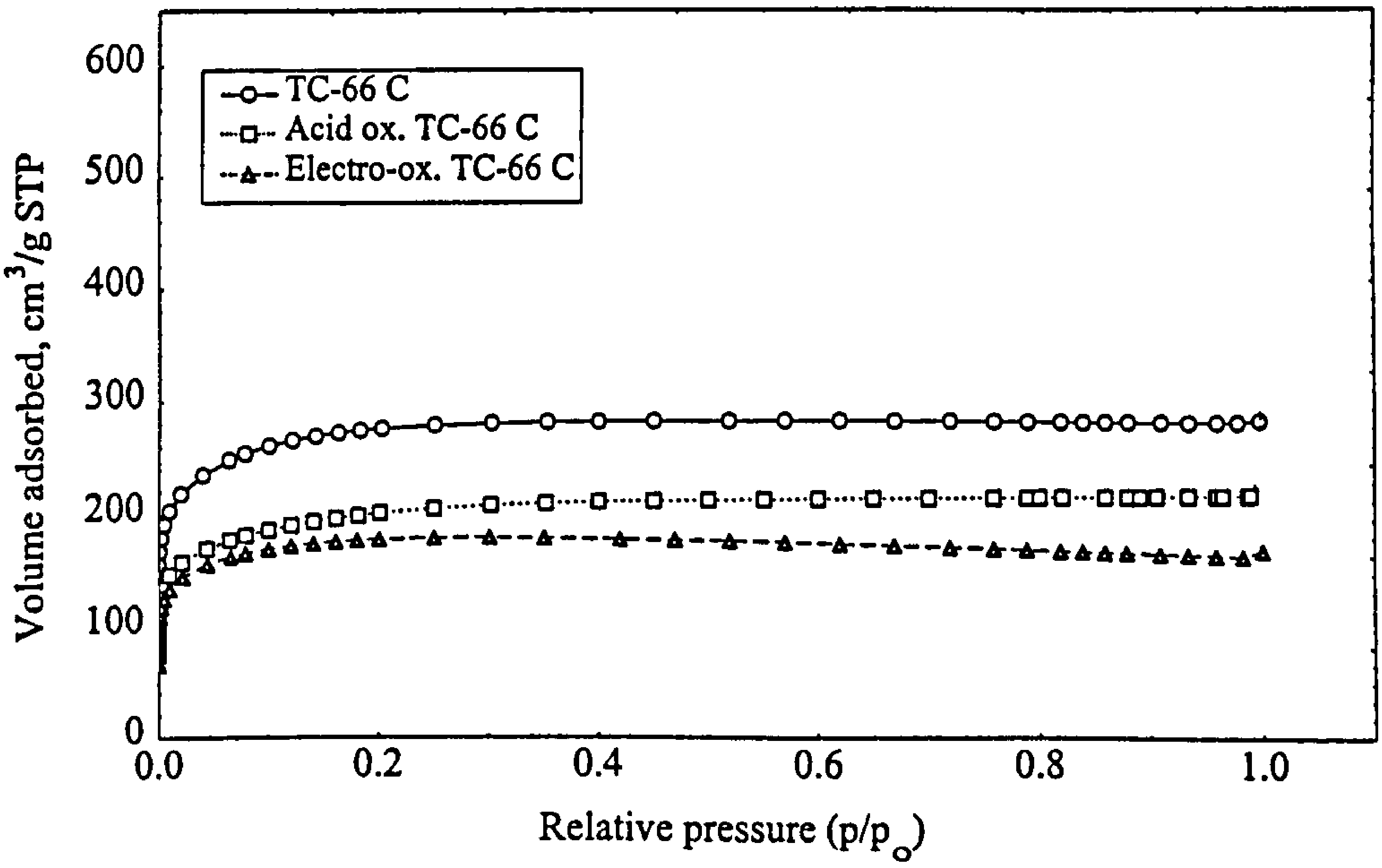


Fig 5.22. Nitrogen adsorption for commercial and oxidised carbon fibre TC-66 C at 77K

The isotherm obtained for unoxidised granular carbon WHK (Fig 5.23) does not show complete saturation at low relative pressure as compared to carbon fibres. This may be attributed to the presence of meso and macropores. Granular carbon WHK has a high nitrogen adsorption capacity, approximately 3.3 times higher than carbon fibre TC-66 C, which should be reflected in terms of surface area. On the other hand, oxidised samples show lower nitrogen sorption capacity.

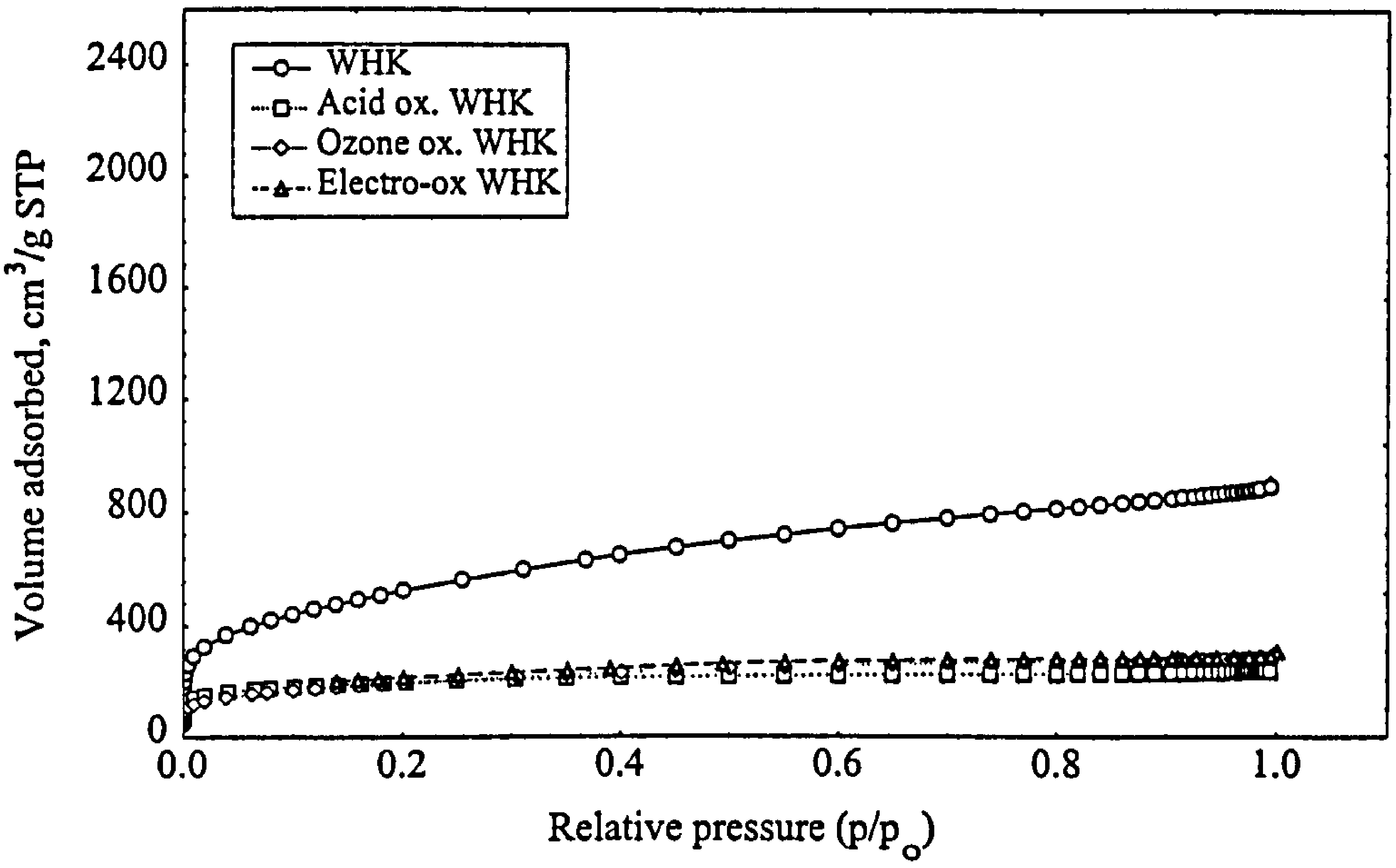


Fig 5.23. Nitrogen adsorption for commercial and oxidised granular carbon WHK at 77K

The adsorption-desorption isotherms of nitrogen on granular and fibrous carbons are different. The adsorption-desorption isotherms obtained for commercial carbon fibre TC-66 C (Fig 5.24) are virtually identical. However, the adsorption-desorption of nitrogen on granular carbon WHK (Fig 5.25) show a hysteresis effect, classified as type H 4 according to IUPAC[34]. Hysteresis loops are associated with capillary condensation in mesopores, due to a different adsorption-desorption mechanism, at quite high relative pressure, 0.4 to 1.

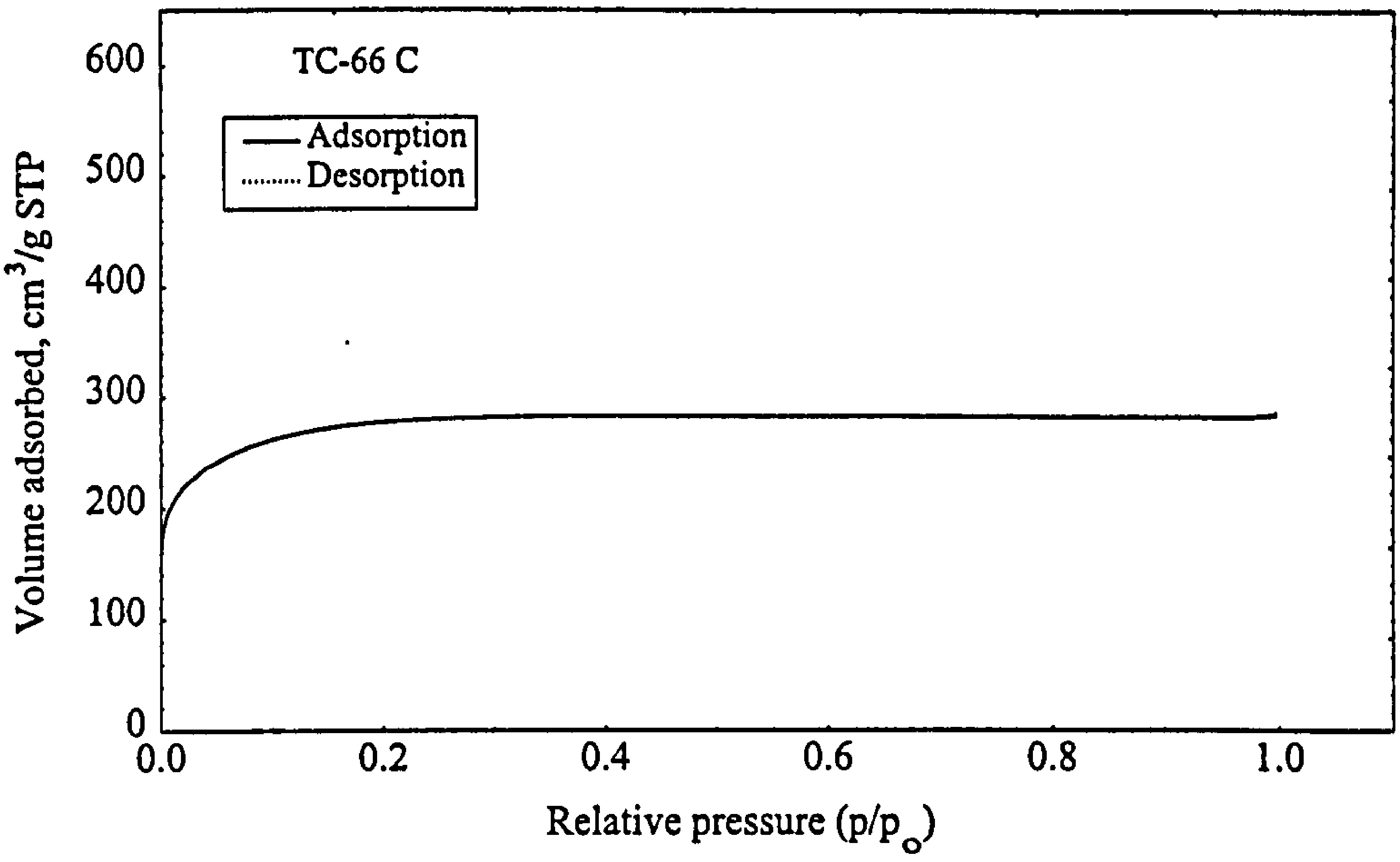


Fig 5.24. Nitrogen adsorption-desorption for commercial and oxidised carbon fibre TC-66 C at 77K

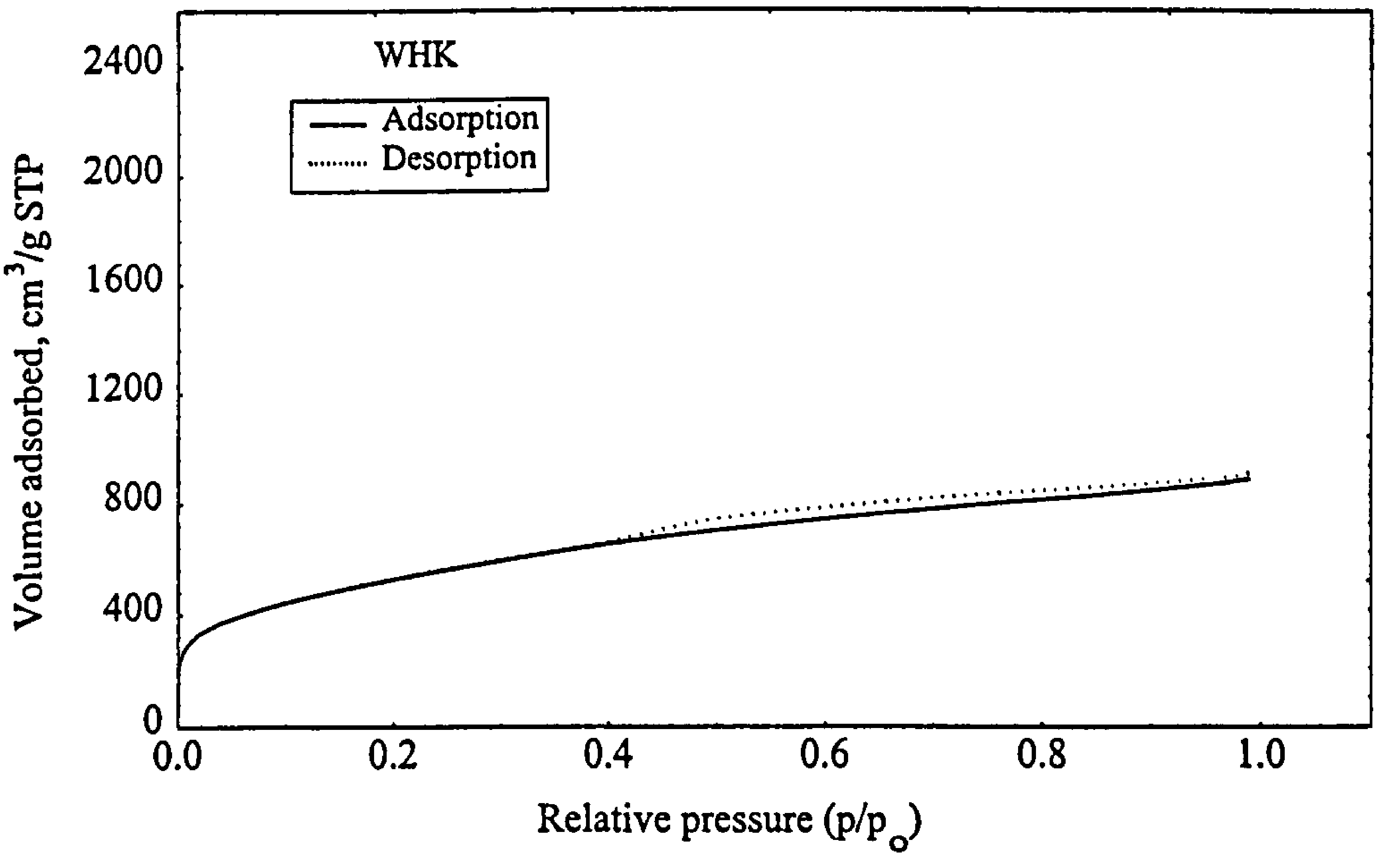


Fig 5.25. Nitrogen adsorption-desorption for commercial and oxidised granular carbon WHK at 77K

Using the isotherm and the adsorbent/adsorbate properties it is possible to determine the monolayer capacity, which can be used to calculate the solid specific surface area. Many theories have been used to interpret the isotherm in quantitative terms, but the most reliable is that of Brunauer, Emmett and Teller (BET). This method extends the Langmuir model to multilayer adsorption. It assumes that adsorption is conducted on sites of uniform energy, molecules adsorbed in the first layer act as sites for the next layers and the evaporation/condesantion properties of the layers above the first one are similar to the adsorbate. This model is mathematically represented as:

$$\frac{p}{n(p^\circ - p)} = \frac{1}{n_m C} + \frac{C-1}{n_m C}\frac{p}{p^\circ} \qquad \textbf{Eq. 5.2}$$

where n_m is the monolayer capacity and C is a constant related to the heat of first layer adsorption. The BET plot $1/n(p^\circ - p)$ *versus* p/p° should be linear. The linearity of this model is limited to only a part of the isotherm. Generally BET plots are set between p/p_o 0.05 and 0.3, although for graphitised and microporous carbons this may be related to a relative pressure <0.1. Fig 5.26 shows the BET plots for commercial carbon fibre (TC-66 C) and granular carbon (WHK).

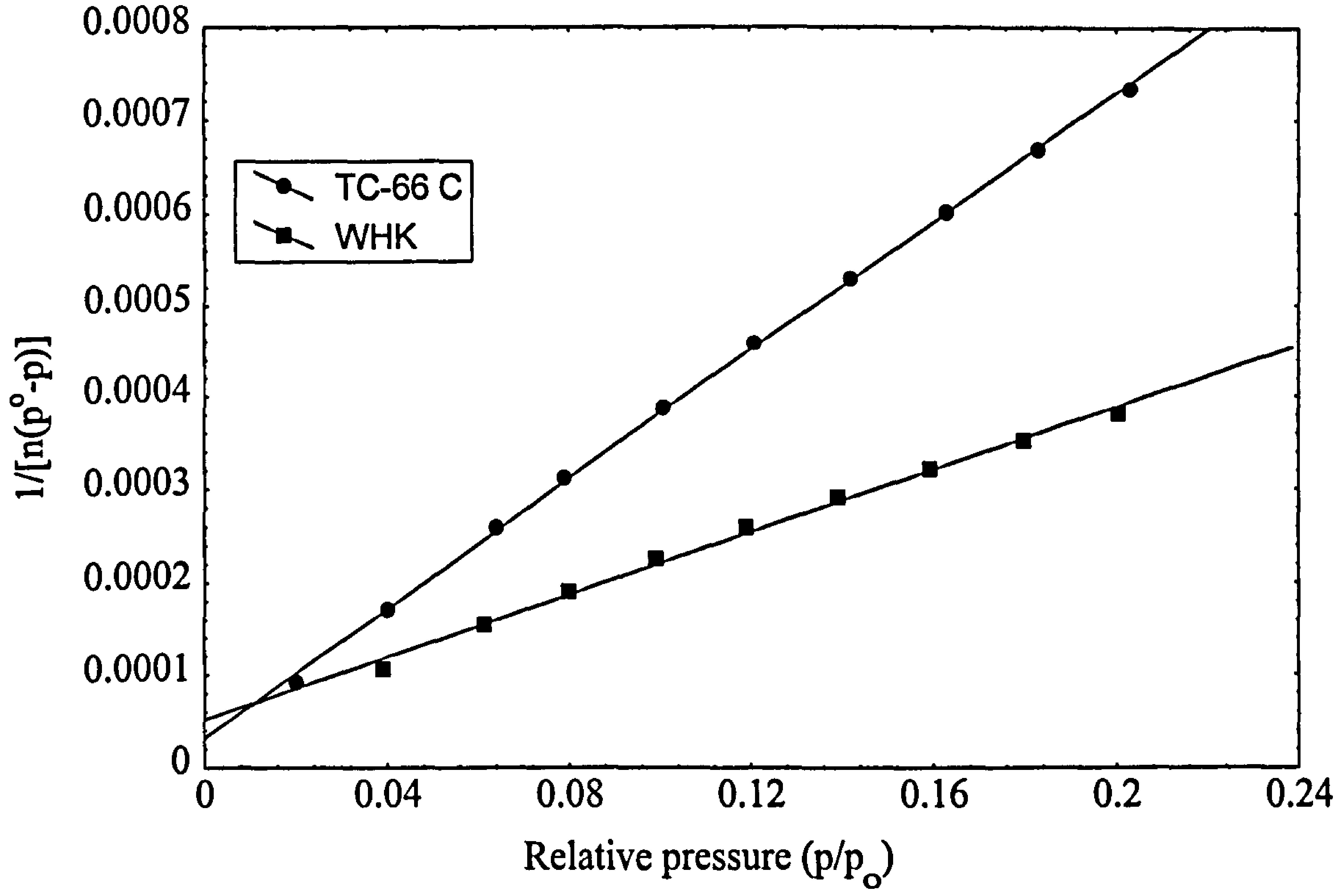


Fig 5.26. BET surface area plots for commercial granular carbon WHK and carbon fibre TC-66 C

BET is commonly used to determine surface area of highly porous materials. However, it has limitations when applied to activated carbons[35]. For instance, adsorption on microporous carbons is not conducted by successive building-up of molecular layers, as set in the BET model. Moreover, the carbon structure consists of a twisted network of defective carbon layer planes and an interconnected network of slit-shaped micropores formed by the spaces between the carbon layer planes and the gaps between stacks of layer planes. This controls the access to a part of the pore void. In addition, highly microporous carbons can present molecular sieve behaviour, e.g. selective adsorption of small molecules in narrow micropores. Hence, BET surface area should only be taken as an approximation. Tables 5.10, 5.11 and 5.12 show BET surface area for commercial and three hours modified granular activated carbons and activated carbon fibres using nitrogen gas as adsorbate. Note that CO_2 adsorption was used for ozone oxidised TC-66 C (Table 5.12).

Table 5.10. BET surface area for carbonaceous material

Adsorbent	BET surface area (m^2/g)	C (BET constant)
207 EA	960.79	598.72
207 C	1256.87	1020.77
WHK	1912.40	91.15
TC-66 F	1033.39	-108.96
TC-66 C	972.73	-408.56

Table 5.11. BET surface area for conventional and modified granular carbon WHK

WHK	BET surface area (m^2/g)	C (BET constant)
Commercial	1912.40	91.15
Acid ox.	714.34	-1998.24
Ozone ox.	713.28	131.05
Electro-ox	747.89	327.56

Table 5.12. BET surface area for conventional and modified carbon fibre TC-66 C

TC-66 C	BET surface area (m^2/g)	C (BET constant)
Commercial	972.73	-408.56
Acid ox.	730.19	1001.55
Ozone ox.	206.33*	427.67
Electro-ox	627.23	-307.03

* BET surface area determined by CO_2 adsorption

The ozone oxidised TC-66 C could not be analysed by nitrogen adsorption since the volume adsorbed below 0.2 p/p_o was insignificant and there were not enough points to generate the BET surface area plot. The low nitrogen adsorption may be due to a weak adsorbent-adsorbate interaction. Hence, it was decided to use carbon dioxide as adsorbate since the adsorption process is conducted at a higher temperature, 273 K, and so diffusion problems are minimised. In other words, the adsorbate may have sufficient kinetic energy to penetrate more easily into the micropores. It has been reported that adequate characterisation of carbon fibres containing a high concentration of ultramicropores, < 1nm, can be achieved by CO_2 (minimum size 0.3 nm) adsorption at 273K[36].

The carbonaceous adsorbents analysed in this study have an extensive BET surface area that is ideal in the treatment of drinking and waste-waters. Granular carbon WHK and carbon fibre TC-66 C were modified to increase the ion exchange capacity, which was achieved by different methods (section 5.1.1). However, there was a loss in surface area attributed to chemical reaction. Granular carbon lost approximately 63 % of its original BET surface area after been chemically oxidised, although a surface area of about 700 $m^2\ g^{-1}$ is entirely adequate for most water treatment applications. A marked difference in loss of surface area was observed when carbon fibre was oxidised by different methods. A loss of 25, 36 and 79 % in surface area was found for acid, electrochemical and ozone oxidation, respectively. This difference may be due to the fact that acid and electrochemical oxidation is conducted in aqueous medium and because the reactive solution could not easily penetrate the micropores, therefore oxidation took place mainly on the external surface. Alternatively, ozone oxidation is carried out in the gas phase, hence diffusion problems are minimised and the internal surface of micropores could be more easily penetrated. This probably means that the micropore surface area is heavily oxidised causing the pores to shrink and/or get blocked by by-products produced during chemical reaction. This results in a drastic loss of surface area. The reduction in surface area of carbonaceous materials and by-products generated after oxidation have been discussed by other researchers[37,38,39].

Carbonaceous adsorbents are porous materials that contain a mixture of macropores, mesopores and micropores. This makes them suitable as adsorbents, catalysts and catalysts supports. The total porosity can be classified, according to IUPAC, into three groups. Macropore-width greater than 50 nm, mesopore-width from 2 to 50 nm and micropore-width less than 2 nm. Micropores can be subdivided into ultramicropores, < 0.7 nm, and supermicropores, from 0.7 to 2 nm[40]. It is extremely important to take pore size distribution (PSD) into account when considering the adsorption of pollutants from aqueous solutions. Adsorbates must be able to diffuse into the pores to occupy the total surface area. For instance, large molecules such as biological molecules are mainly adsorbed in mesopores, whereas metal ions can penetrate and adsorb in micropores. Due to these factors, pore size distribution (PSD) is an extremely useful parameter for a better understanding of sorption processes.

The PSD has been calculated using methods that use the Kelvin-base theory, for example the method of Barrett, Joyner and Halenda (BJH)[41]. However, these methods are only strictly valid to obtain mesopore distribution. In the last few years, the density functional theory (DFT) has been applied to describe the adsorption process at the fluid-solid interface. This has mainly been applied to model physical adsorption in a pore space of slit-like or cylindrical geometry, which has been very useful for extracting surface area and pore size distribution information from experimental adsorption isotherms[42,43].

Pore size distribution was extracted from as-received and modified granular carbons and carbon fibres using the DFT method. Carbon fibres in the form of cloth (TC-66 C) and felt (TC-66 F) are predominantly microporous (see Fig 5.27), average pore diameter at about 18 Å, but also possess a small fraction of mesopores below 30 Å. The data plotted in Fig 5.28 shows that granular carbons 207EA have a combination of micro, meso and macropores. WHK is mainly mesoporous containing a low percentage of micro and macropores. Granular activated carbon 207C is highly microporous with a small amount of mesopores, <30 Å.

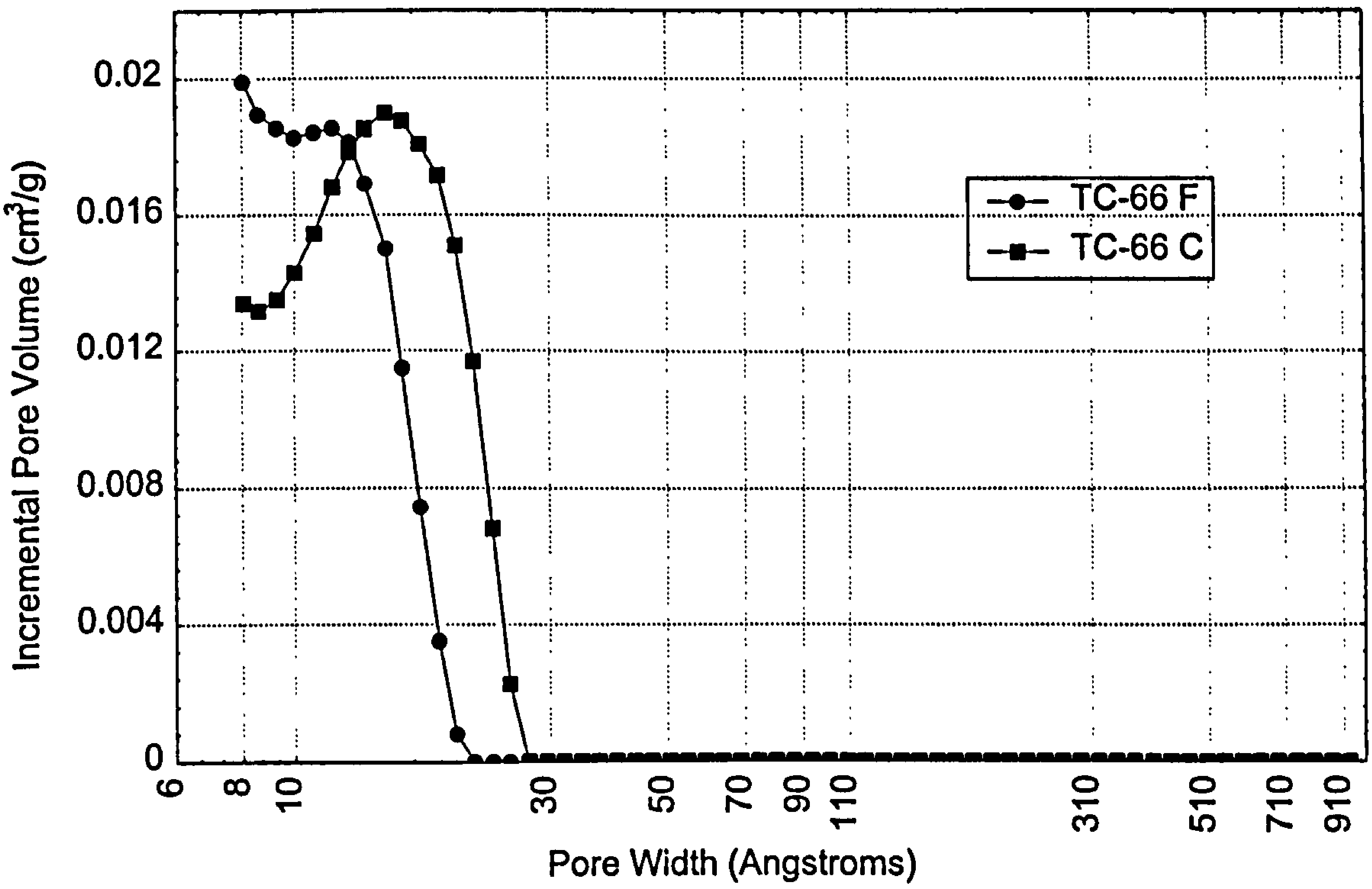


Fig 5.27. Pore size distribution of commercial carbon fibre TC-66 C and TC-66 F

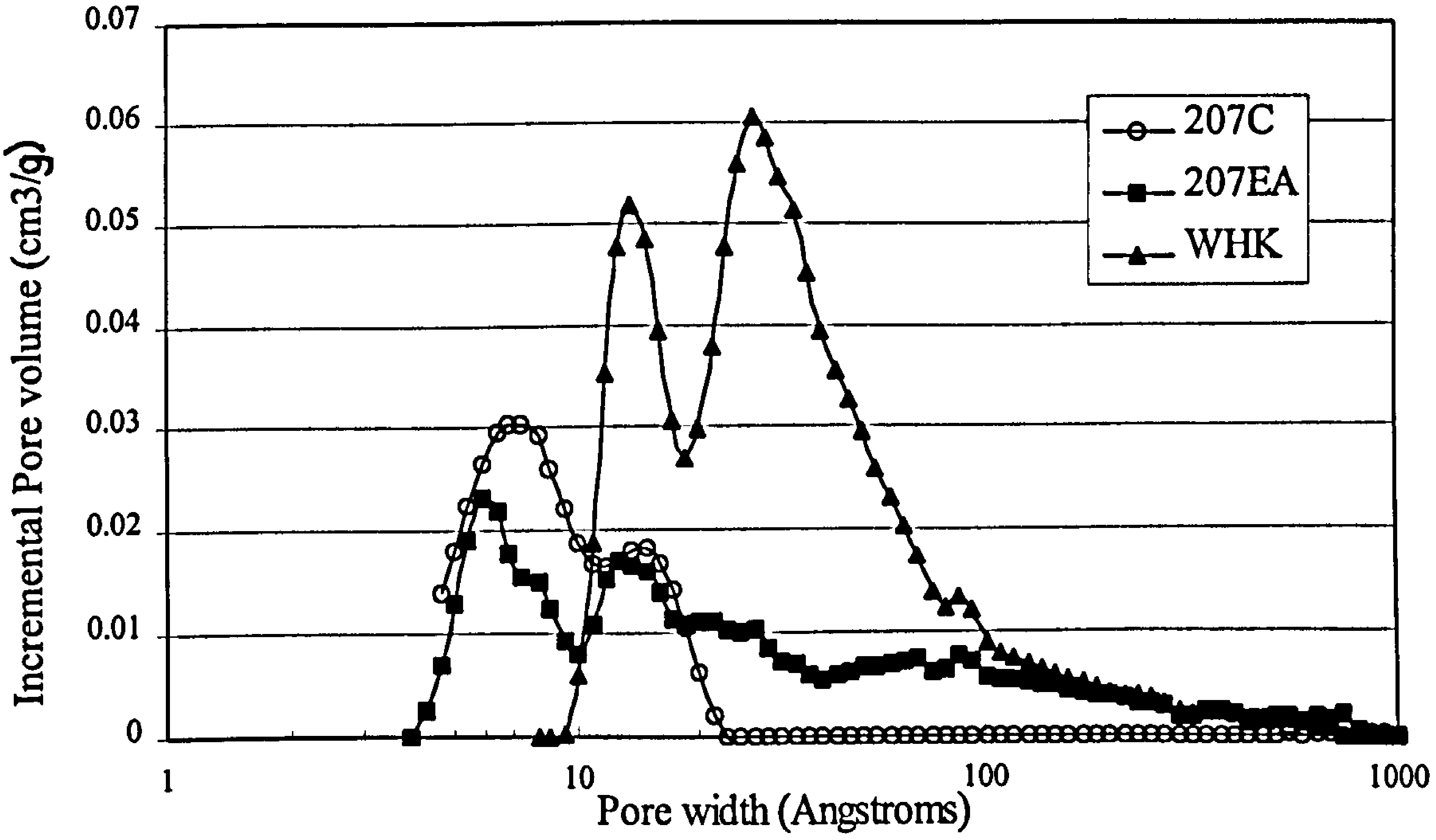


Fig 5.28. Pore size distribution of commercial granular activated carbons

It is important to compare the pore size distribution between carbon fibre TC-66 C and granular activated carbon WHK since these adsorbents were chemically modified and used to remove heavy metals from aqueous solutions. It can be seen in Fig 5.29

that the carbon fibre is highly microporous compared to granular carbon, which possesses a higher concentration of mesopores than micro and macropores.

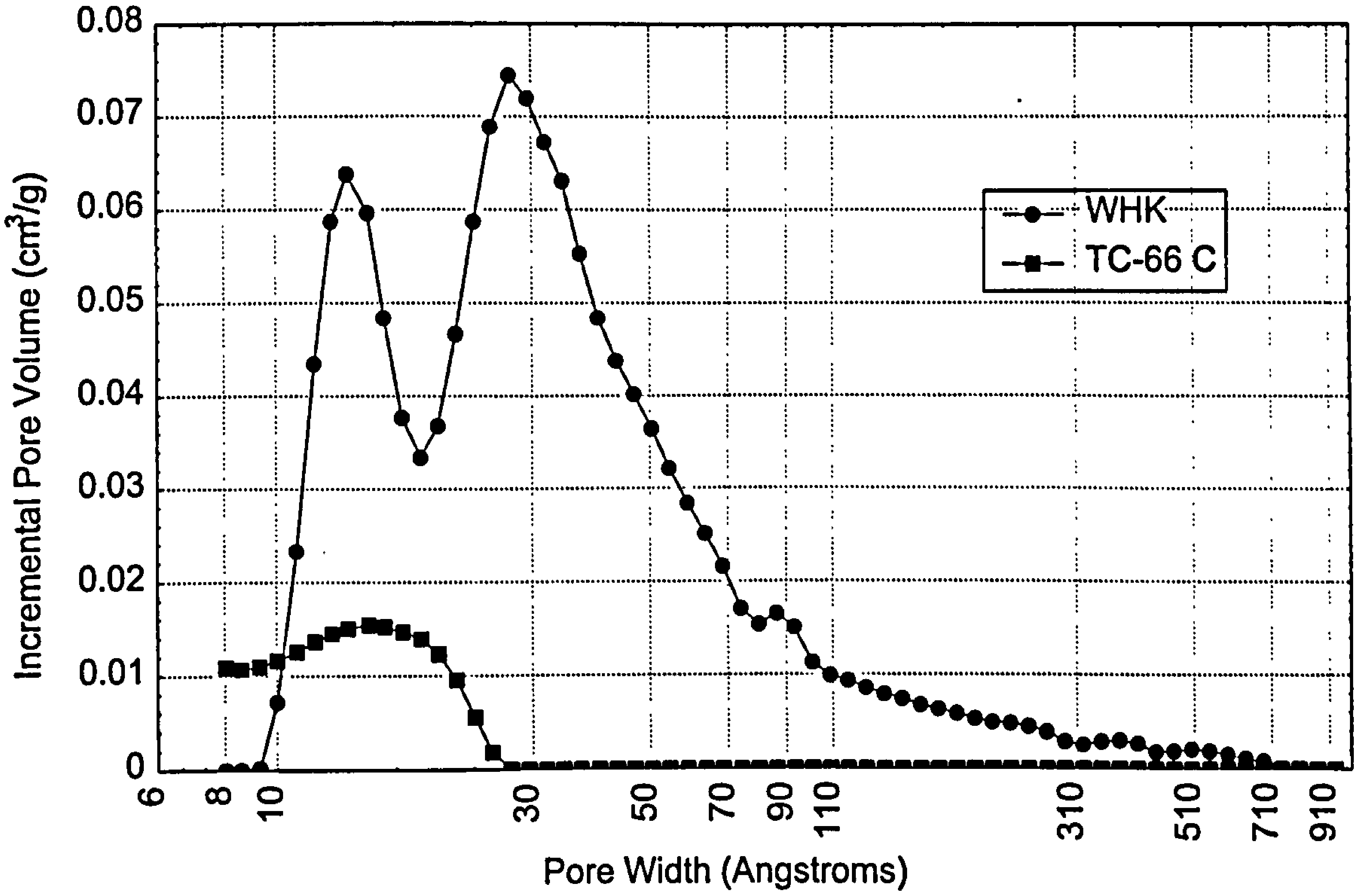


Fig 5.29. Pore size distribution of unoxidised WHK and TC-66 C

Chemically modified carbonaceous adsorbents, WHK and TC-66 C, were also characterised for pore size distribution by DFT. The PSD of electrochemical oxidised TC-66 C slightly reduced the pore width from approximately 27 to 23 Å, whereas acid oxidation generates mesopores which increased the pore width to about 43 Å. Carbon fibre TC-66 C is still highly microporous after chemical oxidation (see Fig 5.30). Alternatively, ozone, acid and electrochemical oxidation of WHK reduced the pore width of macropores from approximately 510 to 110 Å. It is clear that the reduction of pore volume and pore width generates loss of surface area. This may be attributed to blockage of the pores by solids by-products produced during chemical reaction or by surface functional groups.

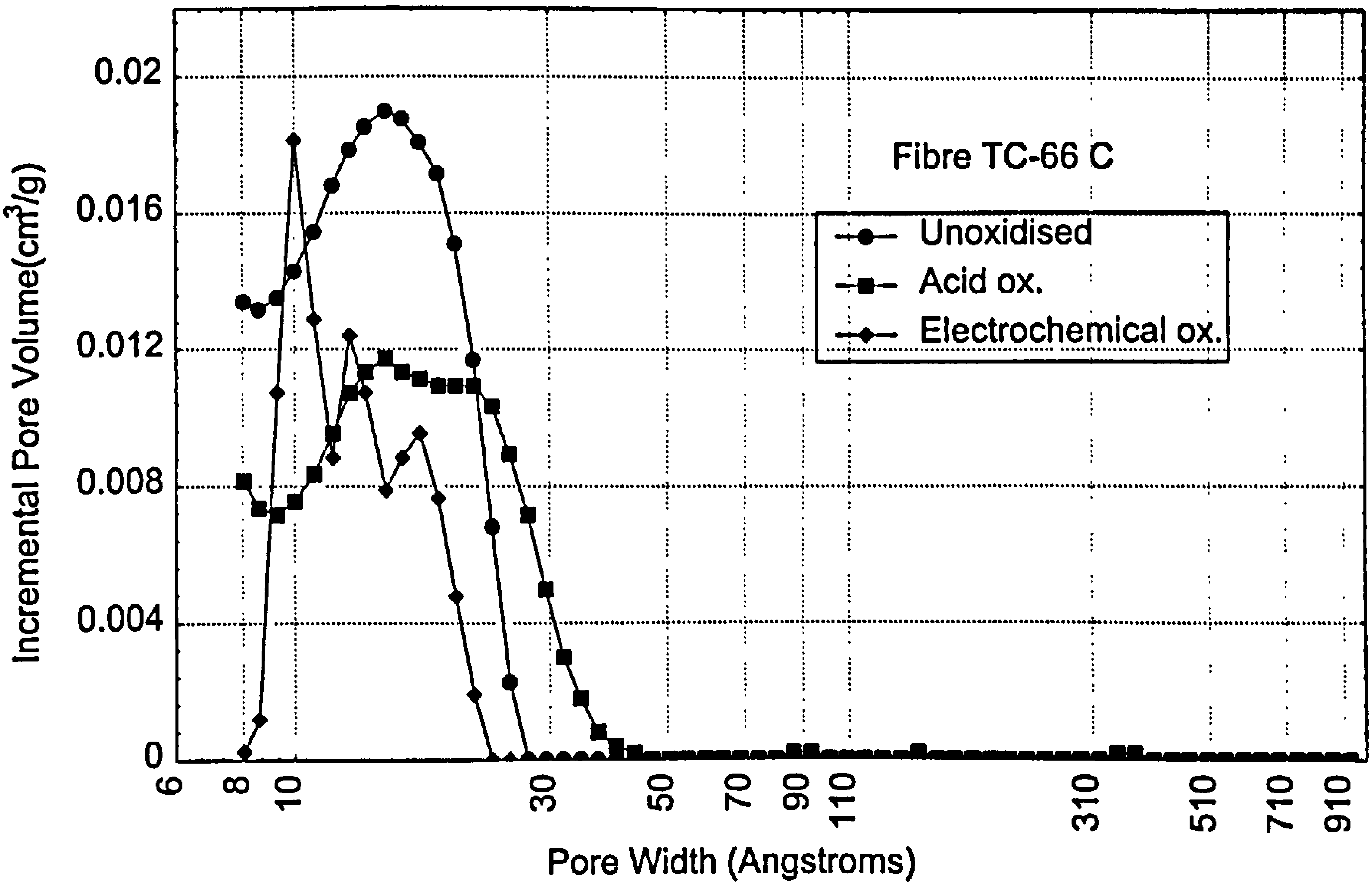


Fig 5.30. Pore size distribution of unoxidised and oxidised activated carbon fibre TC-66 C

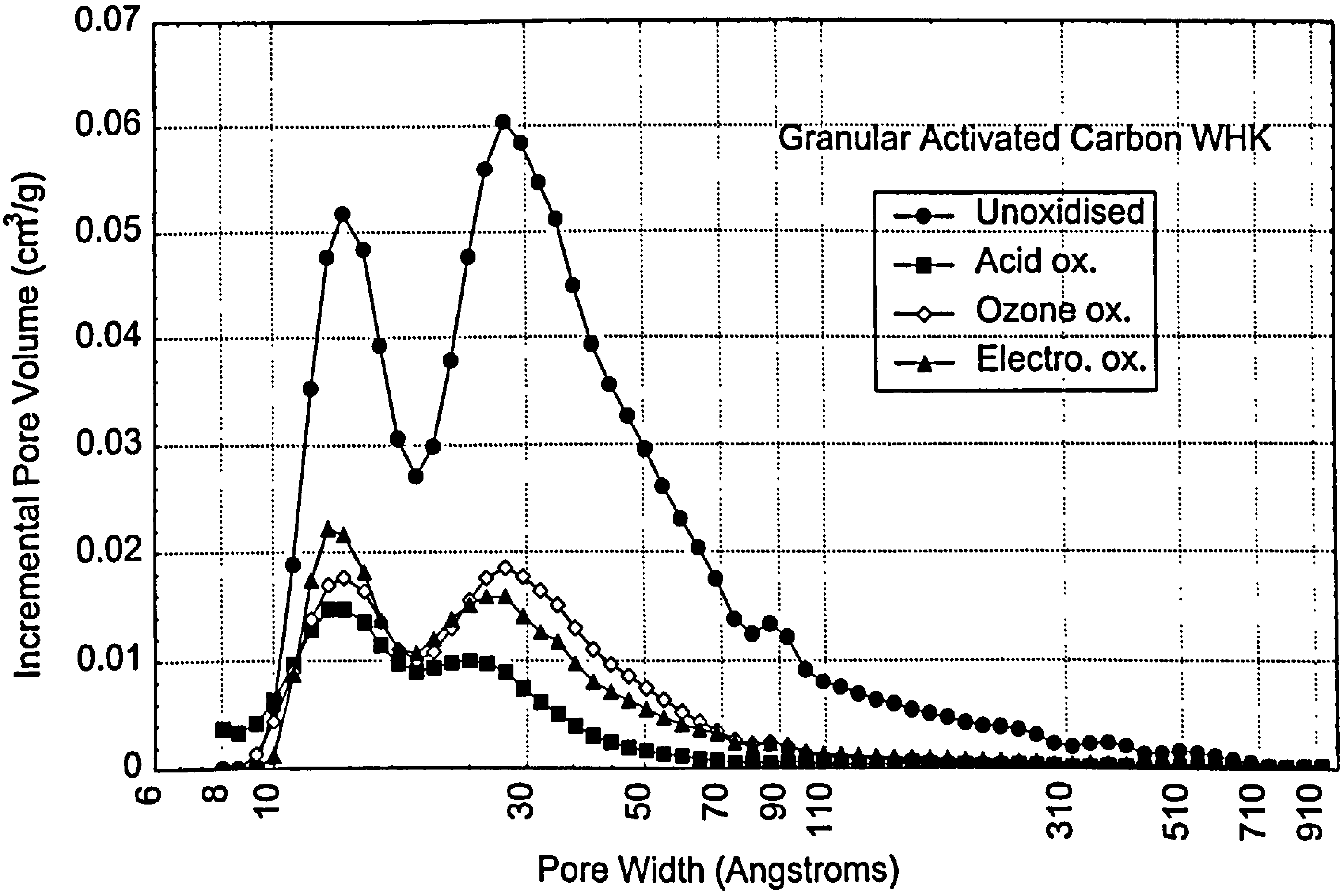


Fig 5.31. Pore size distribution of unoxidised and oxidised granular activated carbon WHK

5.2.2 Scanning Electron Microscopy

Scanning Electron Microscopy (SEM) reveals that there is no physical damage or change in morphology on the acid and electrochemically oxidised carbon cloth TC-66 C, over periods up to 3 hours, compared to the commercial sample (Figs 5.32 to 5.34). However, clear evidence of damage to the ozone oxidised fibre is observed when compared to the other three samples. A single fibre was visualised at high resolution (see Fig 5.36) and a smooth surface with many ribs along the fibre was observed, but with no sign of porosity. Pittman et.al.[44] found that SEM was unable to discern any difference in the surface between commercial and acid oxidised carbon fibre 3k-HTA-7C-NS01, PAN based, at magnifications up to 7500X. In contrast, Le Cloirec et.al[45] reported SEMs of a rayon base carbon fibre RS 1301 where the porosity is clearly visualised (see Fig 5.37) even though this material is highly microporous with pore width less than 10 Å.

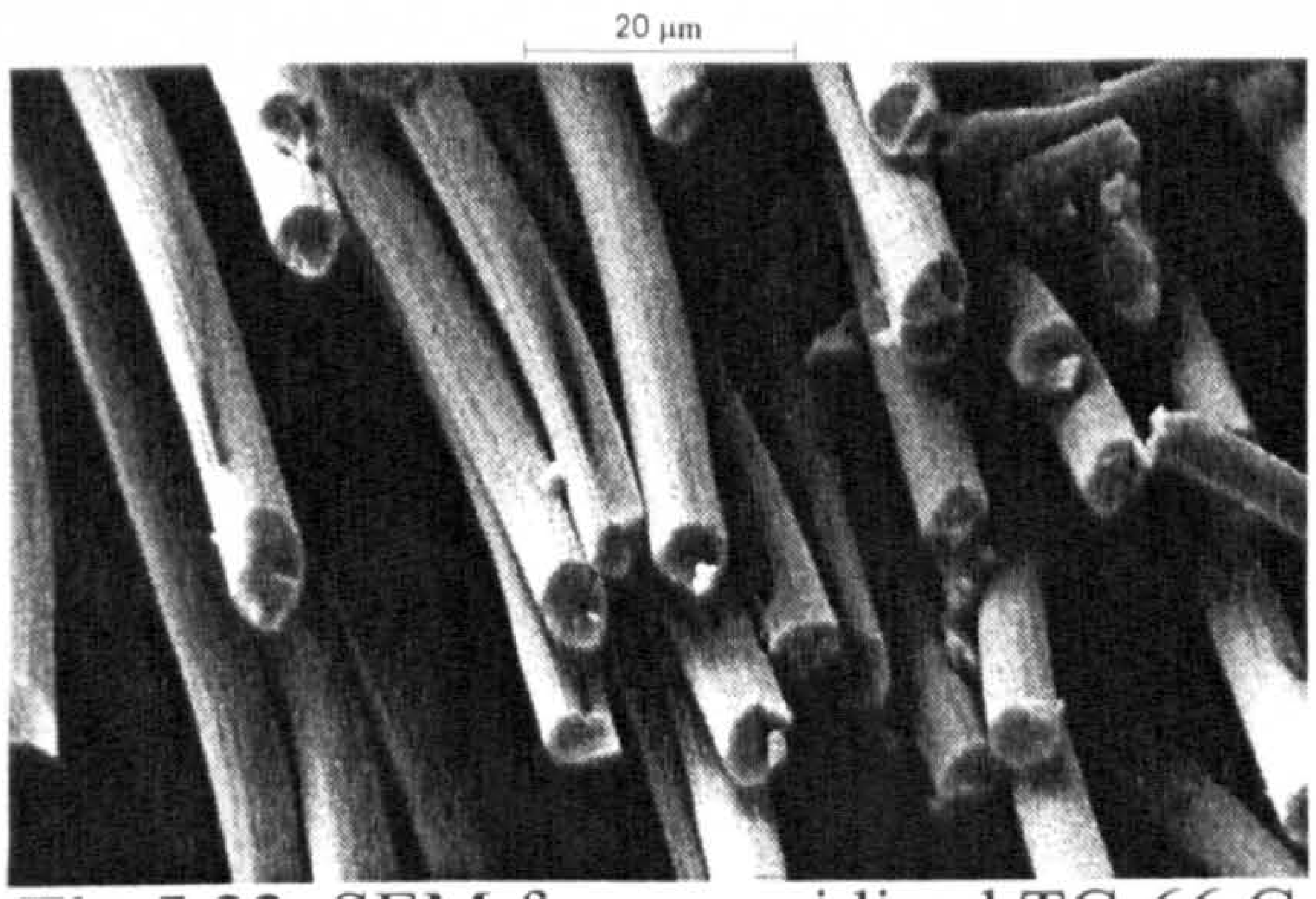


Fig 5.32. SEM for un-oxidised TC-66 C

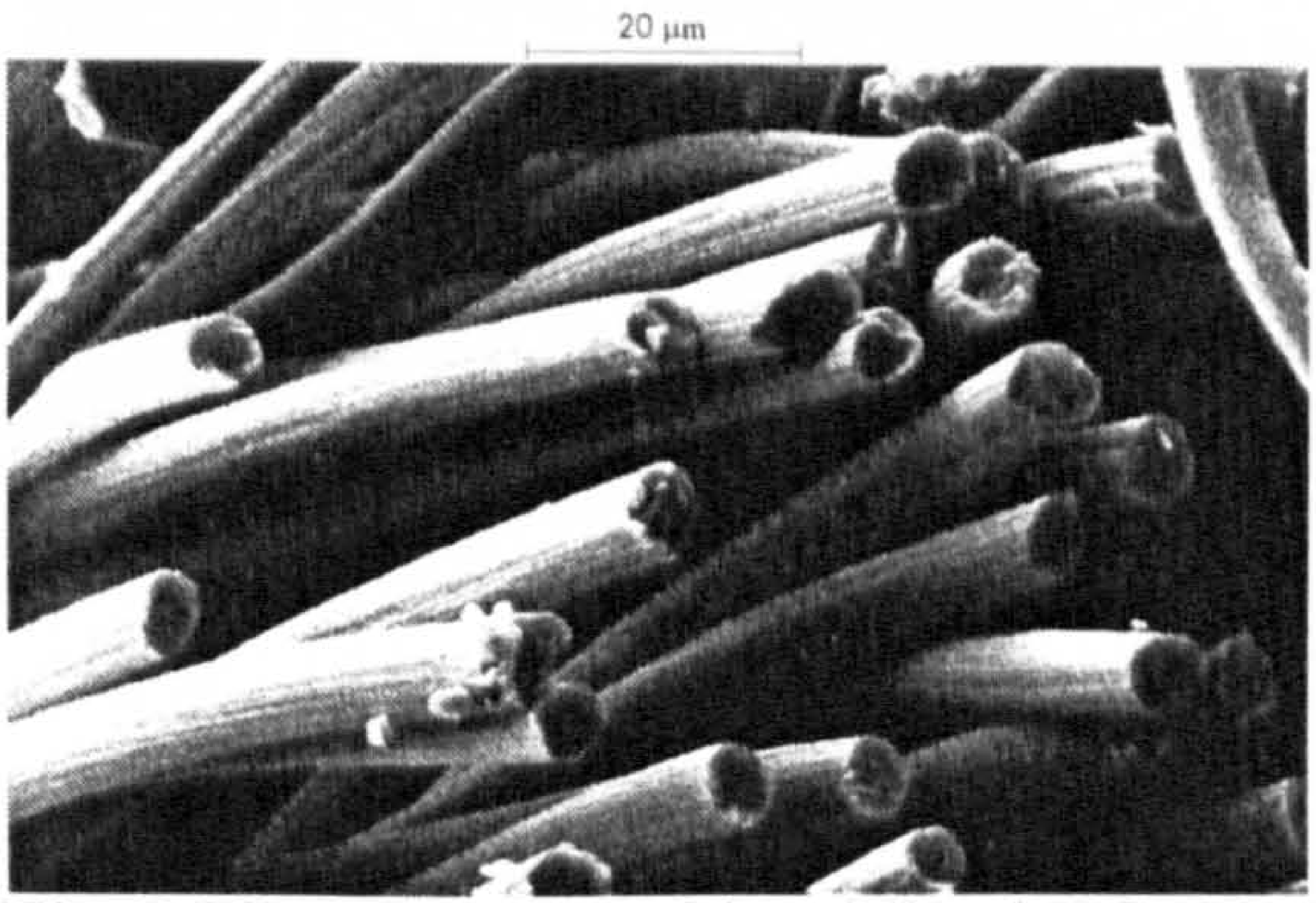


Fig 5.33. SEM for acid oxidised TC-66 C

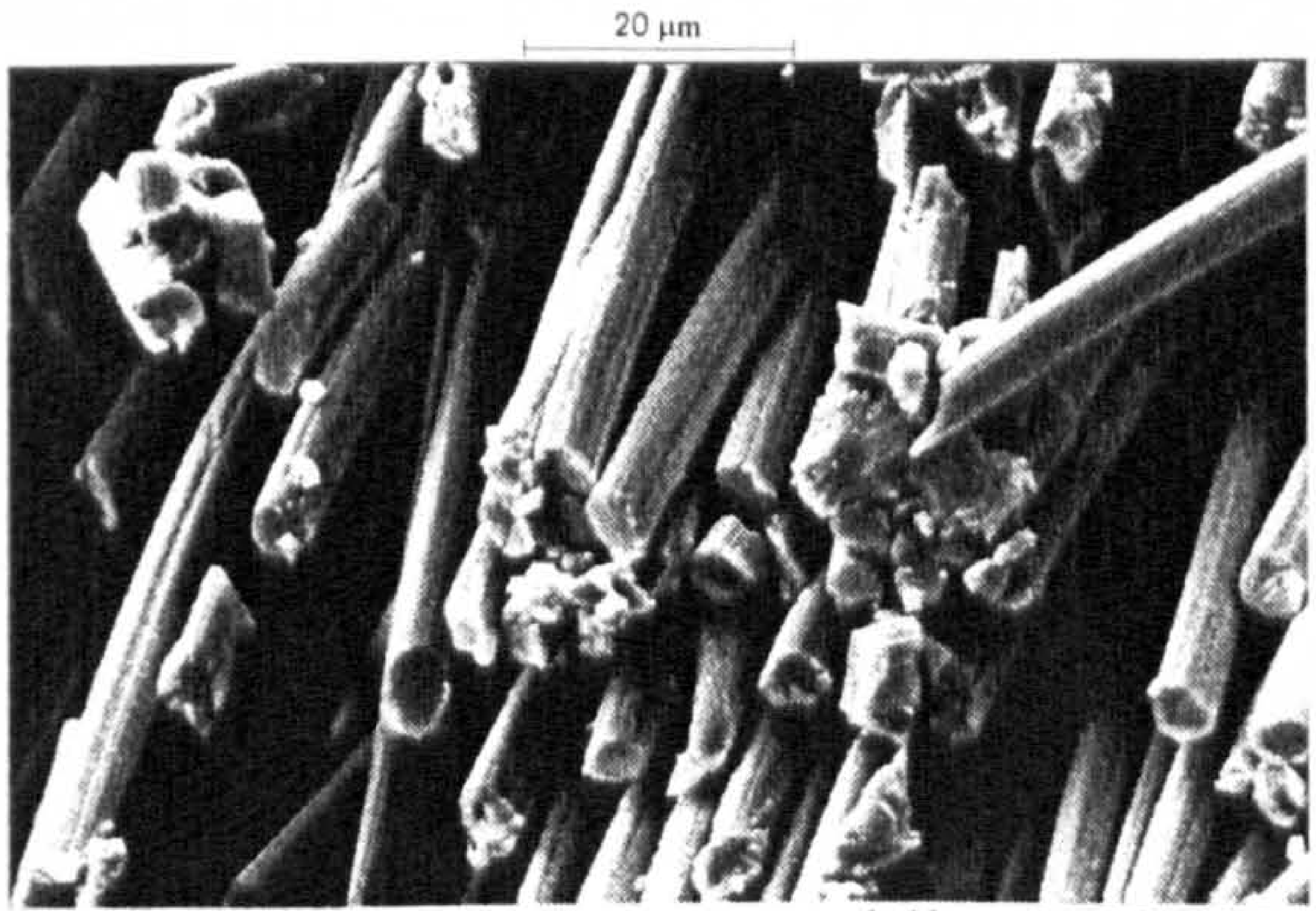


Fig 5.34. SEM for ozone oxidised TC-66 C

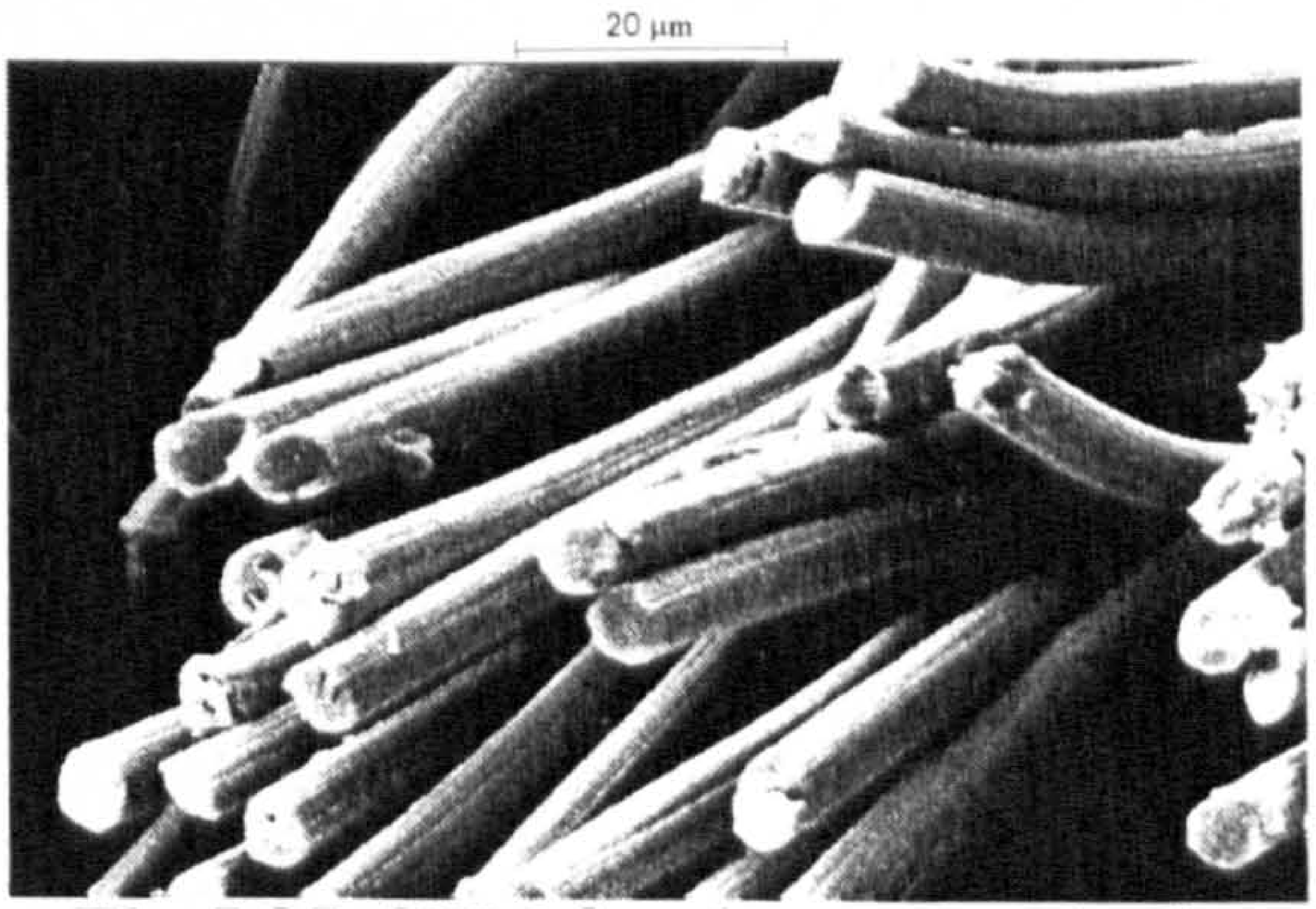


Fig 5.35. SEM for electrochemically oxidised TC-66 C

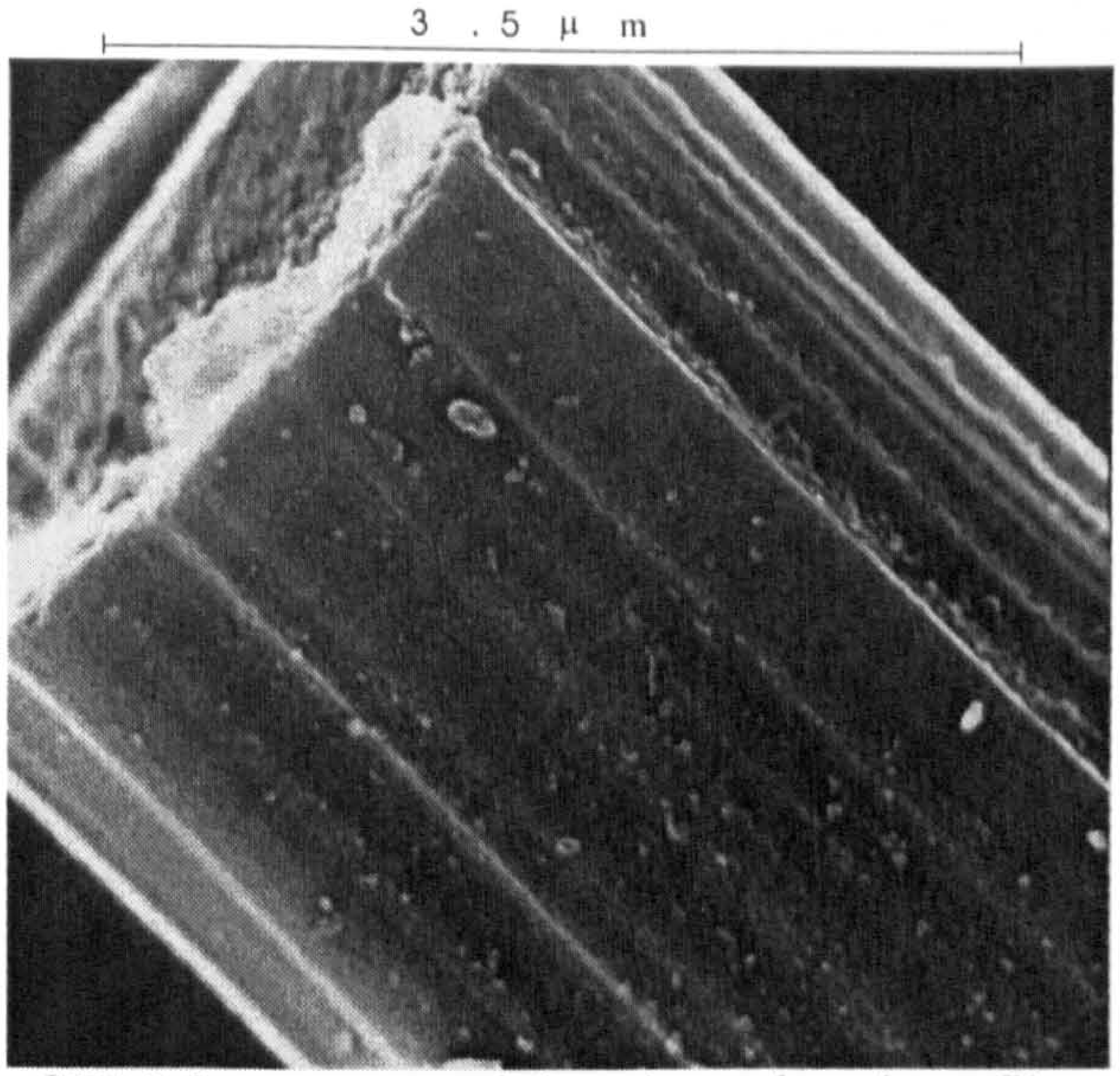


Fig 5.36. SEM for commercial activated carbon fibre TC-66 C

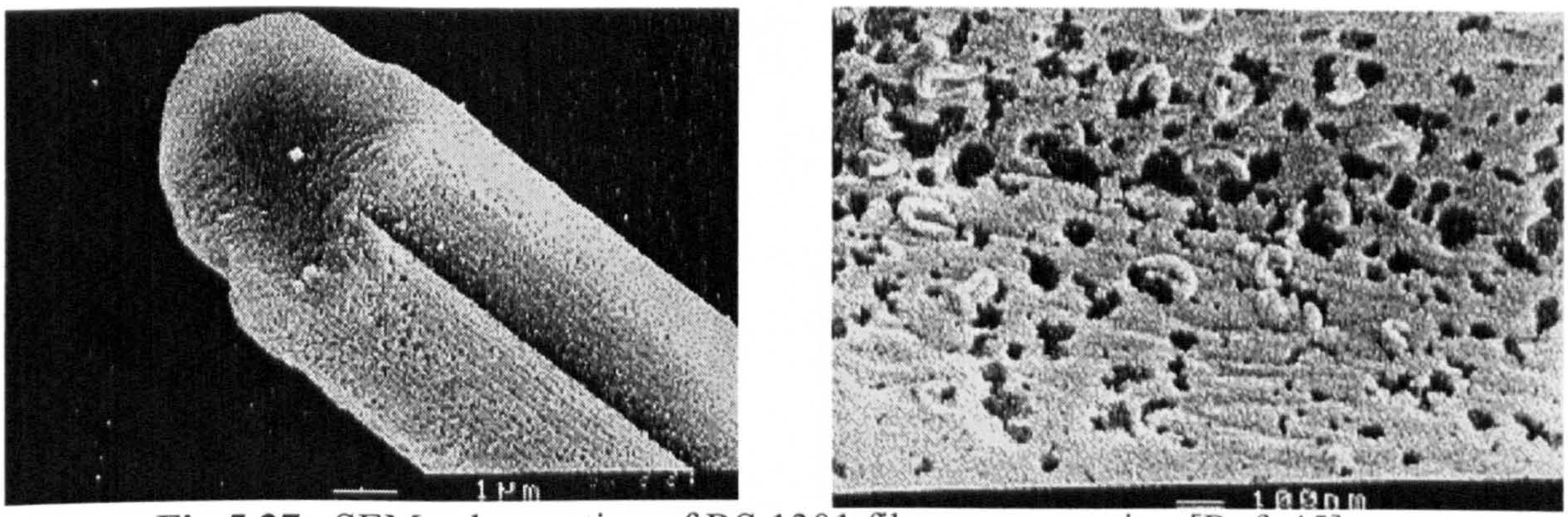


Fig 5.37. SEMs observation of RS 1301 fibre cross section [Ref. 45]

Figs 5.38 to 5.41 correspond to the SEMs for as-received and modified granular carbon WHK. In this case, the surface morphology is clearly visualised in each sample and the presence of pores can be easily observed. It can be seen that the surface morphology of the acid and electrochemically oxidised samples do not change much compared to the as-received one. In contrast, the morphology of the ozone oxidised sample completely changed and only irregular openings and roughness are observed instead of regular pores. It is obvious that changes in morphology are due to erosion caused by oxidation. However, the erosion caused by each oxidation method used in this research is different. It has been seen on SEMs that ozone is the strongest oxidant and generates drastic changes in morphology.

Carbon WHK is in the form of irregular porous granules, whereas carbon fibre is composed of long and regular cylindrical fibres with a diameter of about 5 μm. The physical structure of these carbonaceous materials could contribute to fast or slow kinetics, which is extremely important in water treatment.

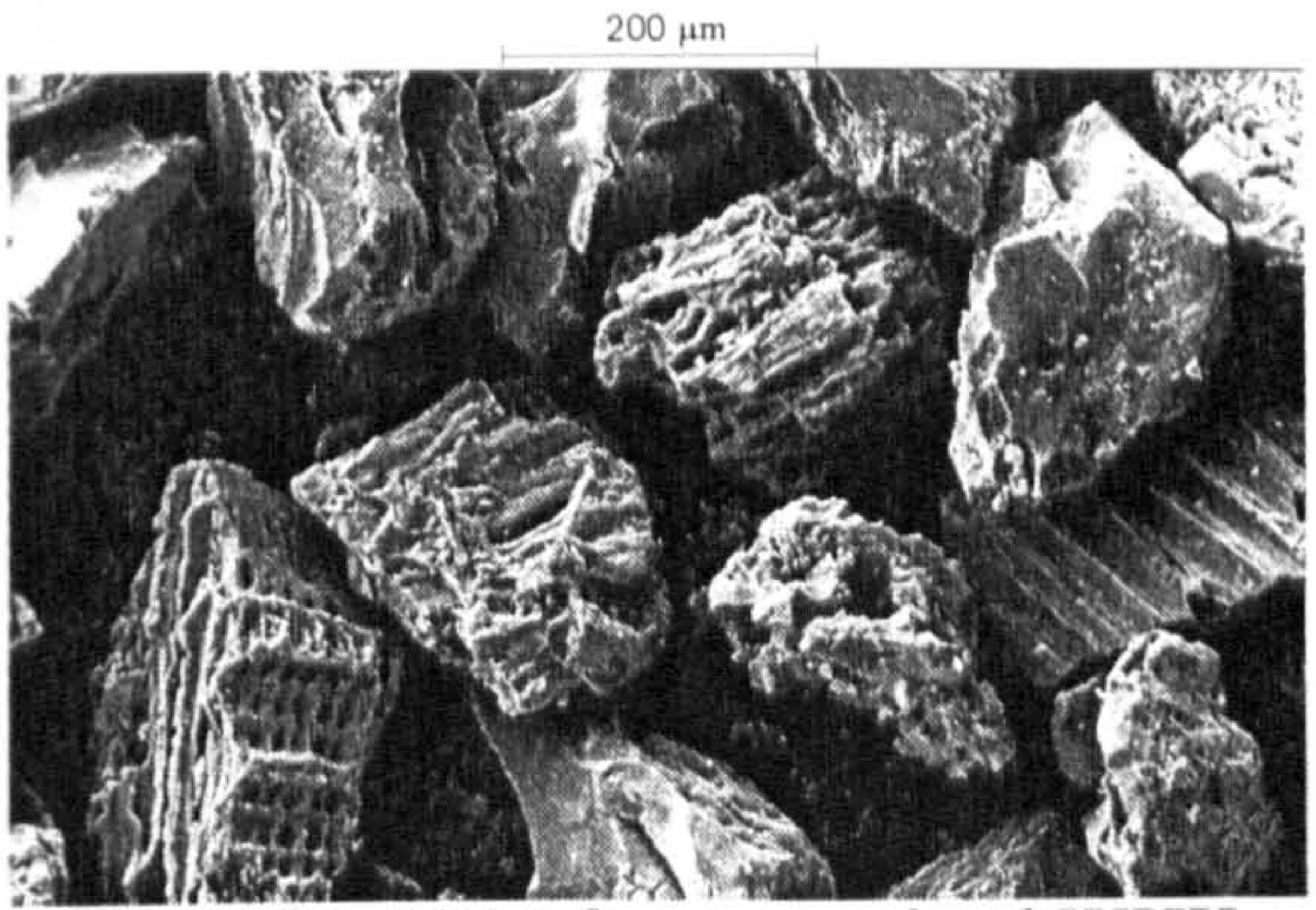


Fig 5.38. SEM for as-received WHK

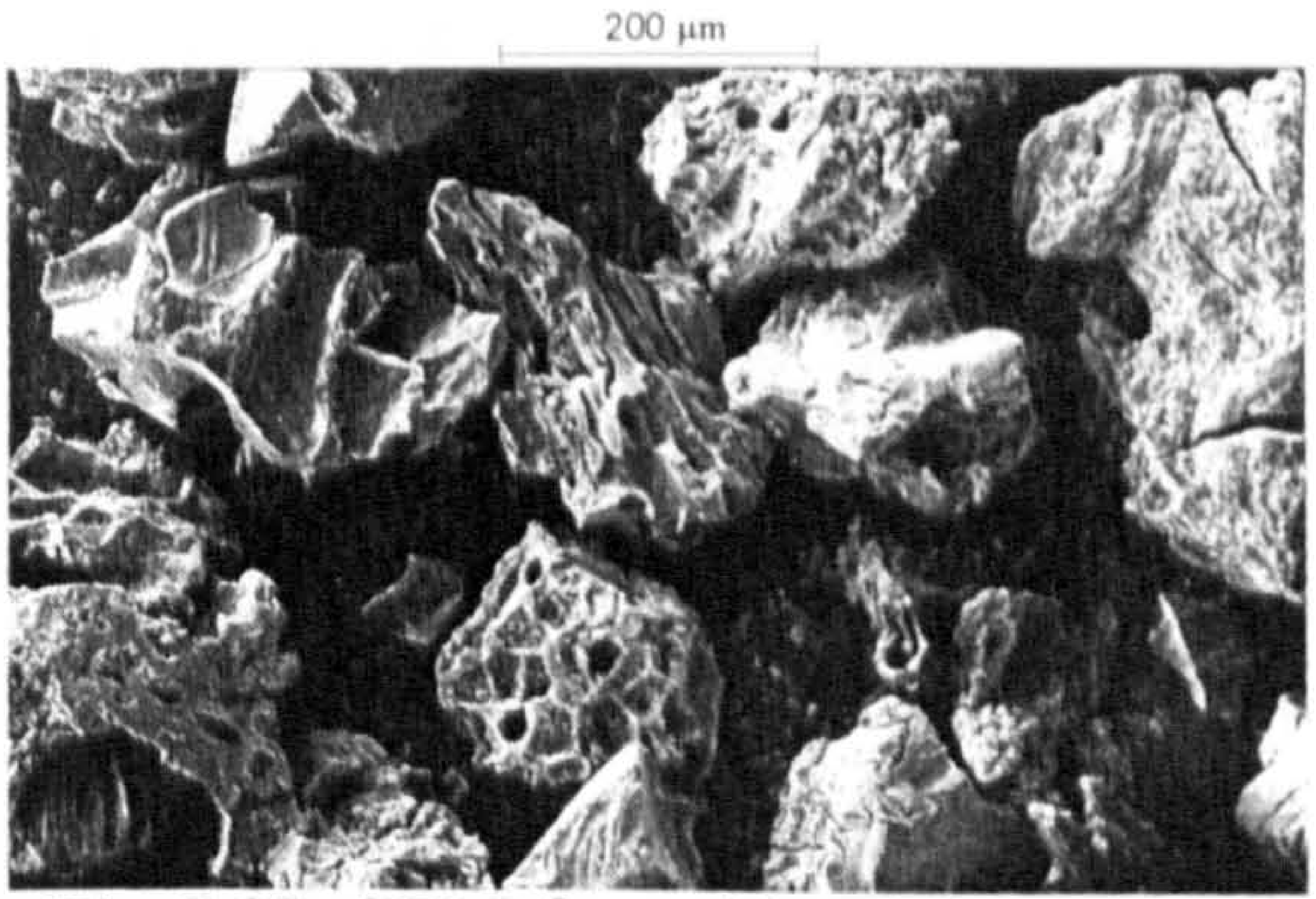


Fig 5.39. SEM for acid oxidised WHK

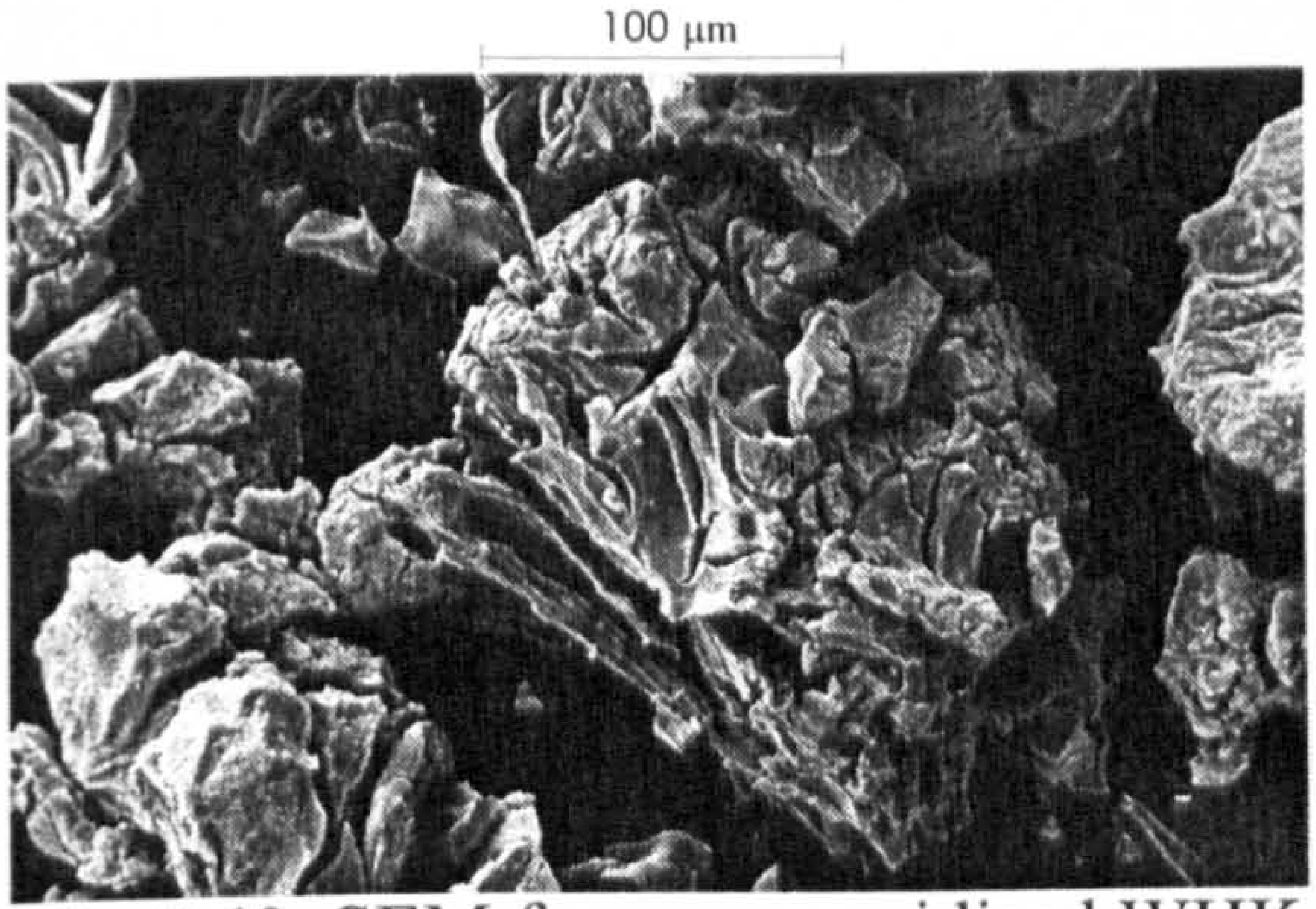


Fig 5.40. SEM for ozone oxidised WHK

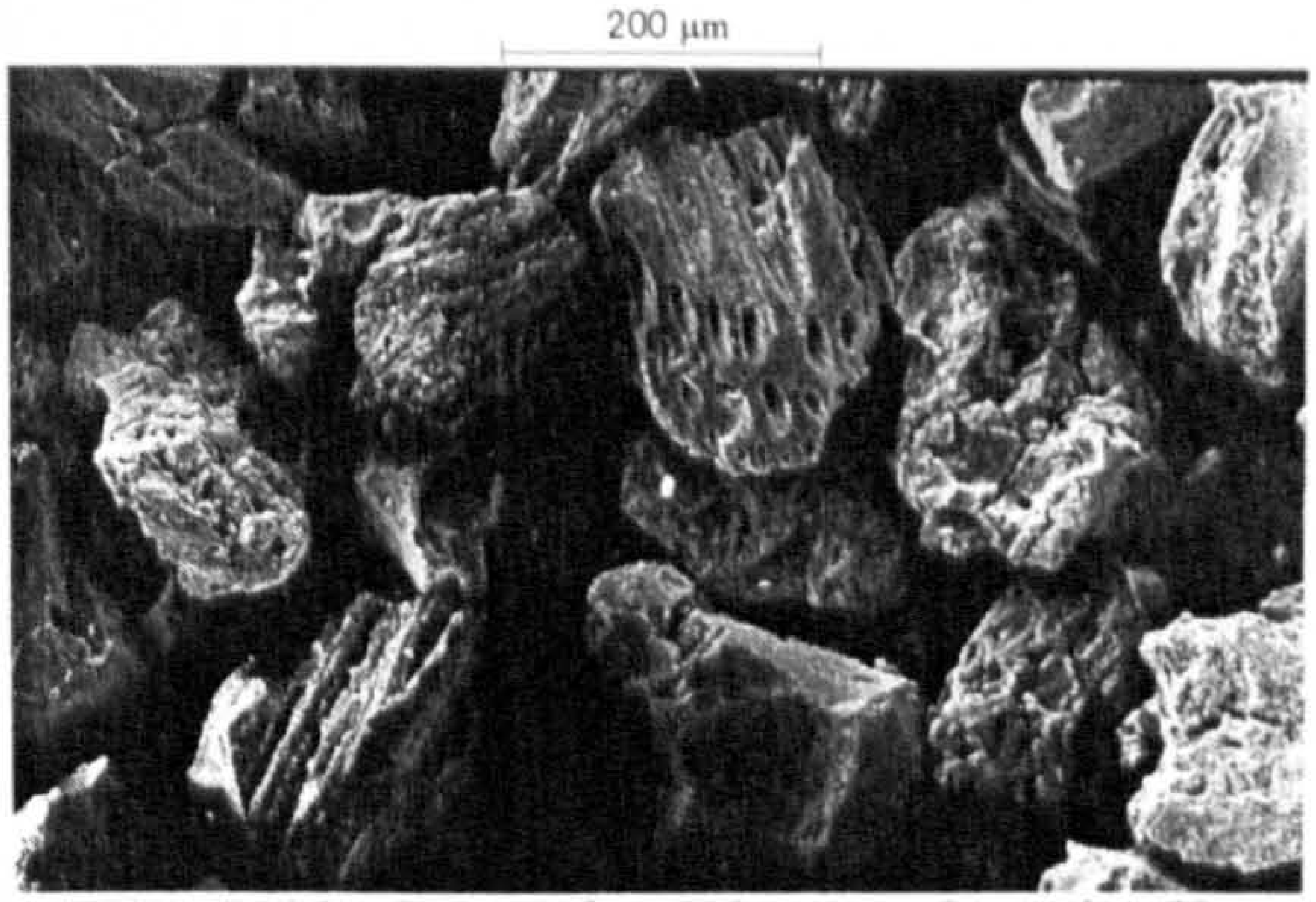


Fig 5.41. SEM for Electrochemically oxidised WHK

5.3 Sorption studies

The adsorption and ion exchange capacity of carbonaceous material depend on several factors such as surface area, pore size and quantity of functional surface groups used at specific conditions. Additionally, the chemistry or speciation of micro-pollutants in solution is also extremely important for a better understanding of the sorption process. The sorption of cadmium and mercury from aqueous solution is discussed in this section.

5.3.1 Sorption of Cadmium

The removal of cadmium from aqueous solutions using as-received granular and fibrous activated carbons and an ion exchanger fibre is reported in this section. The data plotted in Fig 5.42 shows equilibrium isotherms generated by using different types of conventional carbonaceous adsorbents. As-received granular activated carbons show the following trends; 207EA has the lowest capacity followed by 207C and WHK at about 0.01, 0.02 and 0.075 mmol/g, respectively. Carbon fibre in the form of felt (TC-66 F) possesses the lowest cadmium uptake, approximately 0.05 mmol/g, compared to carbon cloth (TC-66 C) that has a similar uptake to granular carbon WHK (about 0.075 mmol/g).

The results mentioned above were calculated at an equilibrium concentration of 1 mM, pH 6 and room temperature. These results follow exactly the same trend as the sodium capacity (Table 5.1-see page 63) corresponding to the total ion exchange capacity. Moreover, the sorption capacity of the granular activated carbons used in this study increased with surface area (Table 5.10-see page 90). In contrast, carbon fibre TC-66 F shows lower cadmium capacity than carbon cloth TC-66 C even though the surface area is slightly higher.

Granular activated carbon WHK and carbon fibre TC-66 C were chemically modified by ozone, acid and electrochemical oxidation, and then tested for removal of heavy metals. The equilibrium isotherms reported in Fig 5.43 correspond to the cadmium uptake of oxidised carbon fibre TC-66 C. The highest sorption capacity, approximately 1.5 mmol/g, was obtained with electrochemically oxidised fibre though the cadmium uptake by ozone and acid modified samples was also significantly enhanced. This is directly attributed to the enhancement of acidic surface groups introduced on the carbons surface by oxidation. This has already been discussed and reported in Table 5.3.

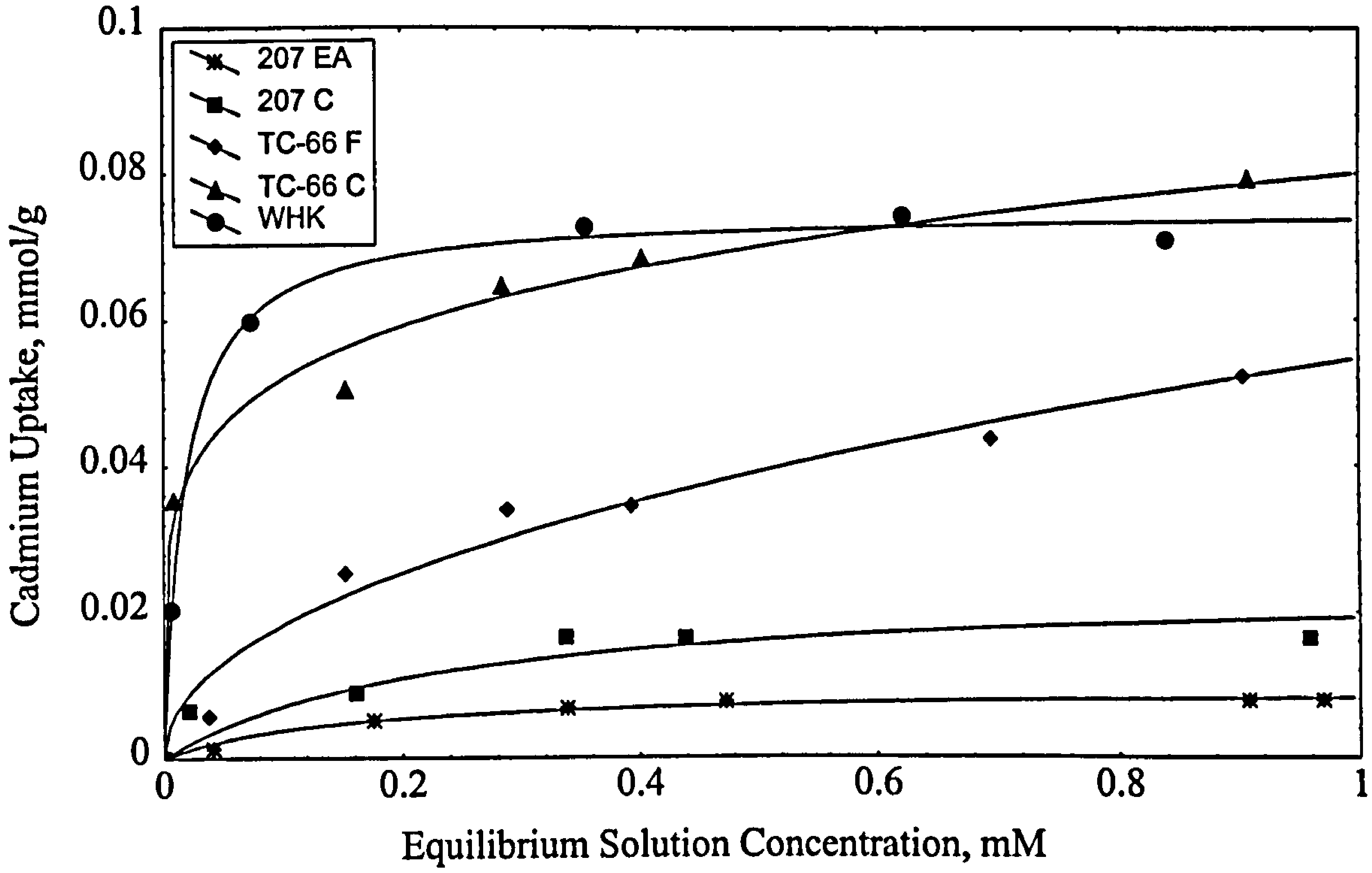


Fig 5.42. Adsorption of cadmium on different types of conventional granular and fibrous activated carbons at pH= 6 and room temperature

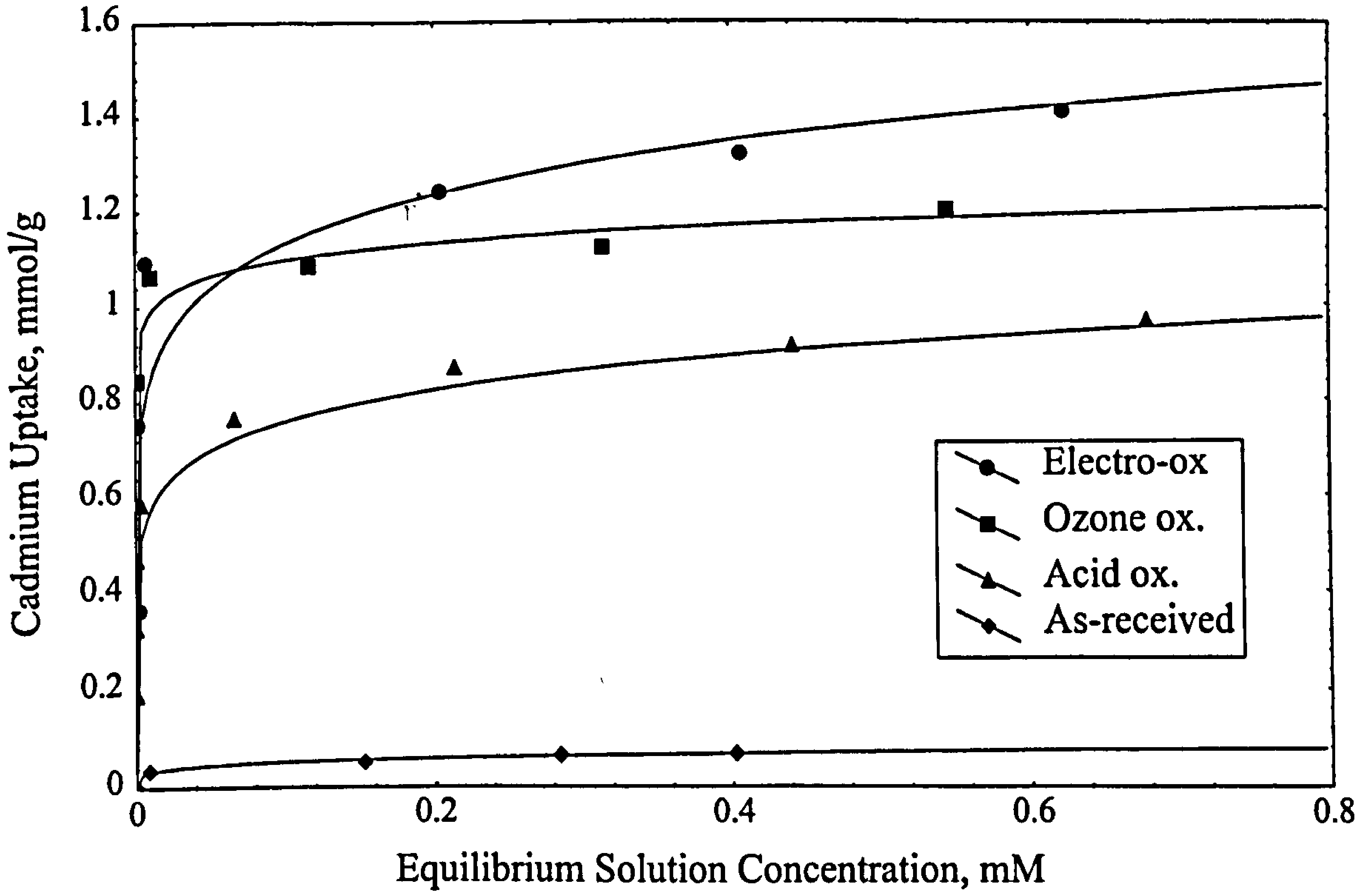


Fig 5.43. Equilibrium isotherms for cadmium using oxidised TC-66 C (ACF), at pH 6 and room temperature

Table 5.13. Langmuir and Freundlich adsorption isotherm parameters for oxidised TC-66 C (ACF)

Method of oxidation	q_mK [L/g]	K [L/mmol]	$R_{Langmuir}$	k $\left[L^{1/n}/\mathrm{mmol}^{1-1/n}\,g^{-1}\right]$	n	$R_{Freundlich}$
Electro.	541.82	403.45	*0.86*	1.51	8	*0.90*
Acid	1599.19	1843.55	*0.96*	0.99	8.36	*0.95*
Ozone	3354.32	2967.88	*0.93*	1.22	22.22	*0.94*

Langmuir and Freundlich isotherms models that are represented by Eq. 5.3 and Eq.5.4, respectively, were used to fit the adsorption isotherms.

$$q = \frac{q_m KC}{1 + KC} \qquad \textbf{Eq. 5.3}$$

$$q = kC^{1/n} \qquad \textbf{Eq.5.4}$$

The corresponding parameters for each model were calculated using a method of least squares based on Rosenbrock's optimisation method, solved by Microsoft Statistica, which uses the objective function:

$$R = \sum \left(q_{exp} - q_{cal}\right)^2 = \text{minimum} \qquad \textbf{Eq. 5.5}$$

The lines in Figs 5.43 and 5.44 represent the Freundlich isotherm calculated using parameter values from Tables 5.13 and 5.14. The correlation coefficient (R) was higher for the Freundlich isotherms than for those fitted by the Langmuir model in all the cases, therefore the experimental data were fitted using the Freundlich isotherm.

Modified granular activated carbon WHK also showed considerable improvement in cadmium capacity, increasing by a factor of 18.5, 17 and 15 for electrochemical, ozone and acid oxidised samples, respectively. The maximum adsorption capacity, 1.4 mmol g^{-1}, was shown by electrochemically oxidised carbon at a solution concentration of about 0.8 mM, whereas negligible cadmium uptake was observed for conventional as-received WHK (0.075 mmol g^{-1}). It has already been mentioned that the large increase in adsorption capacity is directly related to the increase of oxygen-containing groups, as detected by direct acid/base titration (section 5.1.3) and confirmed by XPS (section 5.1.4) and elemental analysis (section 5.1.5).

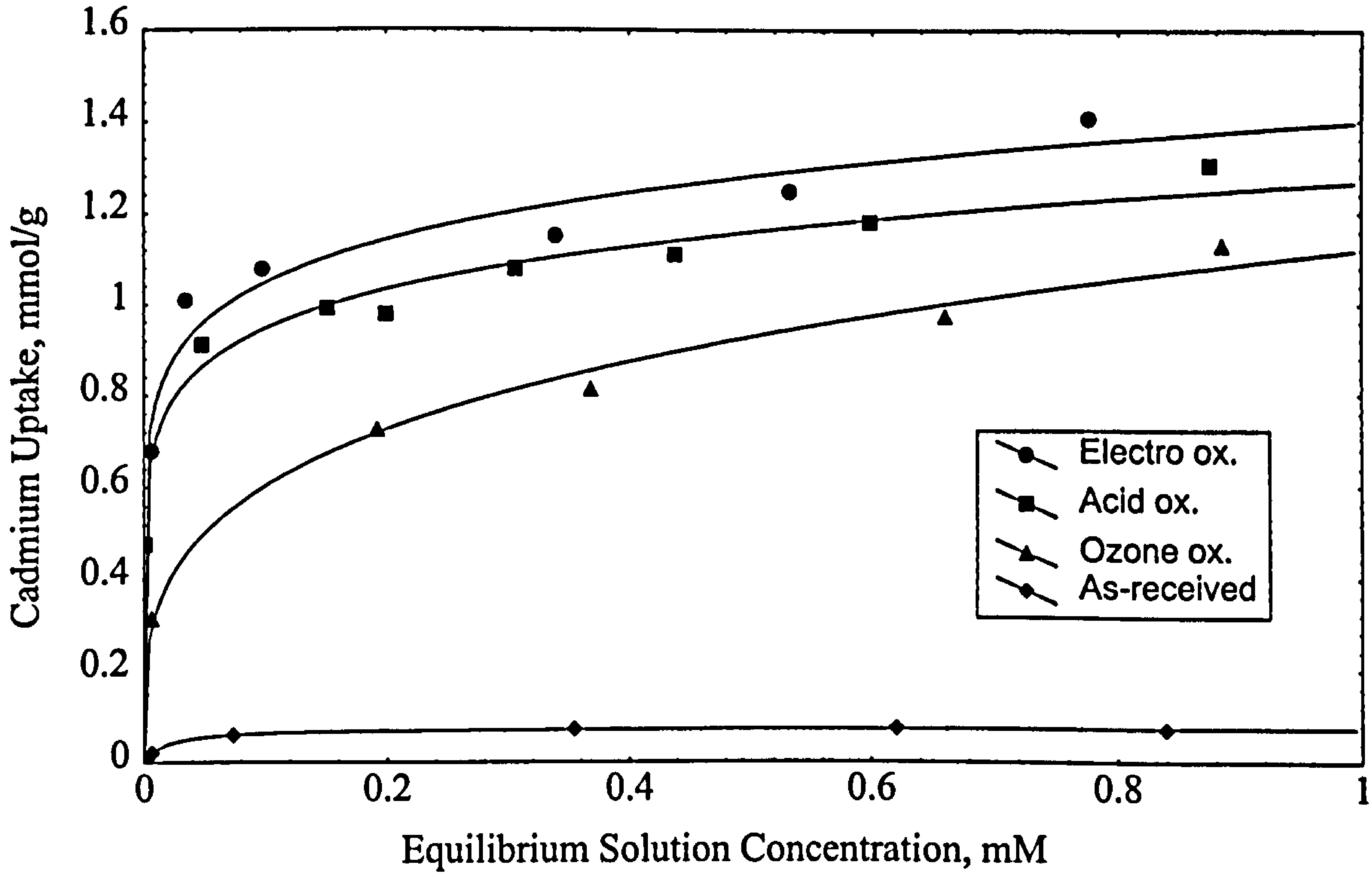


Fig 5.44. Equilibrium isotherms for cadmium using oxidised WHK (GAC), at pH 6 and room temperature

Table 5.14. Langmuir and Freundlich adsorption isotherms parameters for oxidised WHK (GAC)

Method of oxidation	q_mK [L/g]	K [L/mmol]	$R_{Langmuir}$	K $[L^{1/n}/mmol^{1-1/n}\,g^{-1}]$	n	$R_{Freundlich}$
Ozone	5.02	3.01	*0.90*	1.25	2.84	*0.96*
Acid	1978.93	1825.90	*0.87*	1.27	7.92	*0.99*
Electro.	200.40	160.53	*0.92*	1.40	8.04	*0.96*

Electrochemically modified granular carbon WHK and carbon cloth TC-66 C were compared, in terms of cadmium capacity, with a weak acid cation fibrous exchanger K-4 containing predominantly carboxylic groups. The equilibrium isotherms are reported in Fig 5.45. Ion exchange fibre shows a very high sorption capacity at about 1.86 mmol g^{-1} at an equilibrium concentration of 0.8 mM and pH 6. This means that K-4 has approximately 1.3 times higher cadmium capacity than electrochemically oxidised carbonaceous adsorbents WHK and TC-66 C at the conditions mentioned above. Polymeric ion exchangers usually posses a high density of functional groups hence very high sorption capacity compared to natural sorbents, e.g. zeolites and biosorbents, and conventional carbonaceous adsorbents, however their production cost is a limiting factor.

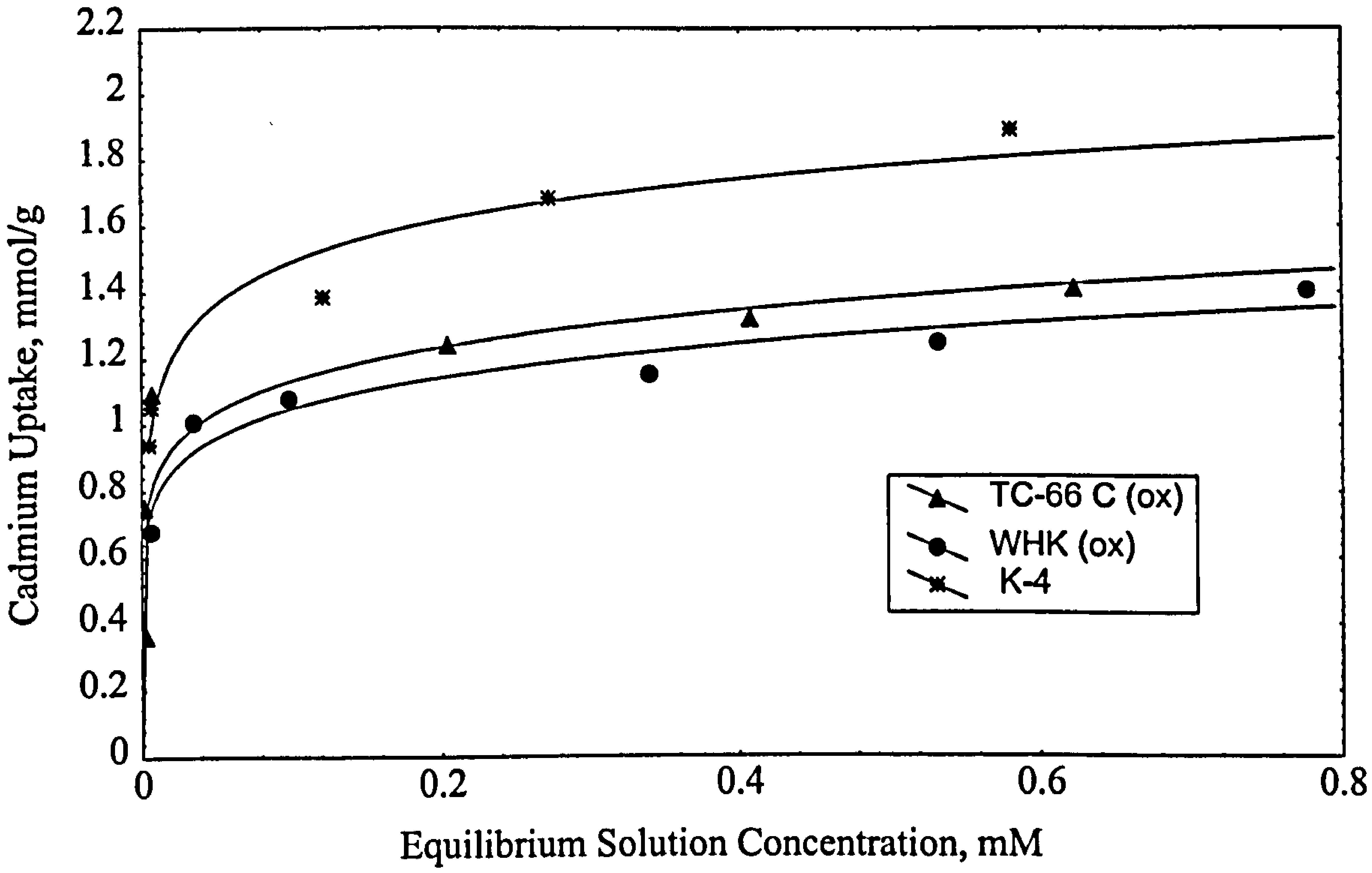


Fig 5.45. Adsorption of cadmium on electrochemically oxidised WHK (GAC) and TC-66 C (ACF), and ion exchange fibre K-4 at pH 6 and at room temperature

Knowledge of the relationship between the adsorbent surface chemistry and the species in solution helps to explain the metal sorption mechanisms. The speciation diagram for cadmium chloride in aqueous solutions is presented in Fig 5.46. This was calculated using the equilibrium constants reported by Stumm and Morgan[46]. The primary reactions of cadmium chloride in aqueous solution are as follows:

	Log K
$Cd^{2+} + H_2O \leftrightarrow Cd(OH)^+ + H^+$	-10.01
$Cd^{2+} + 2H_2O \leftrightarrow Cd(OH)_2(aq) + 2H^+$	-20.29
$Cd^{2+} + 3H_2O \leftrightarrow Cd(OH)_3^-(aq) + 3H^+$	-31.69
$Cd^{2+} + 2H_2O \leftrightarrow Cd(OH)_2(s) + 2H^+$	-13.65
$Cd^{2+} + Cl^- \leftrightarrow CdCl^+$	1.98

$Cd^{2+} + 2Cl^- \leftrightarrow CdCl_2(aq)$	2.60
$Cd^{2+} + 3Cl^- \leftrightarrow CdCl_3^-$	2.40

It can been seen that for a 0.1 M $CdCl_2$ solution, cadmium appears as Cd^{2+}, $CdCl^+$ and $CdCl_2(aq)$ below pH 7.6 in the approximate proportions 58, 39 and 3 % respectively. Precipitation as $Cd(OH)_2$ occurs just below pH 8. It is well known that the carbon surface charge depends on pH. For instance, the pH value of the point of zero charge for as-received granular activated carbon WHK is at pH of 4.5 (Fig 5.16). The surface is positively charged below the PZC, i.e. at pH<4.5. In this region the oxygen-containing groups are undissociated. The carbon surface becomes negative as the pH increases above 4.5 due to the dissociation of weakly acidic oxygen-containing groups. Since cadmium exists predominantly as Cd^{+2} and $CdCl^+$ in aqueous chloride solutions up to pH 7.6, cation exchange and/or complexation with surface functional groups is the most likely sorption mechanism.

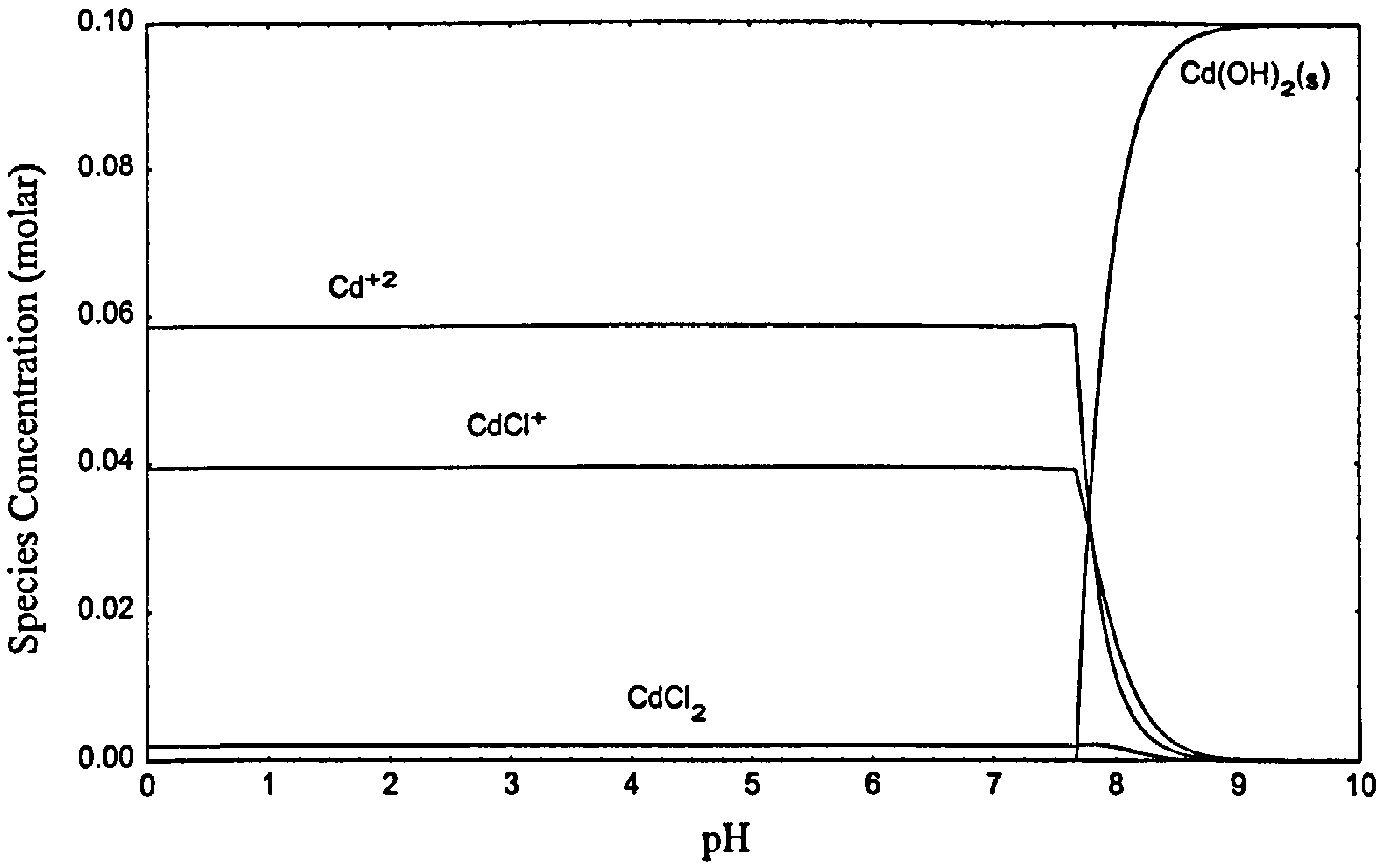


Fig 5.46. Speciation diagram of 0.1 M $CdCl_2$ in aqueous solution

5.3.1.1 *pH effect on the adsorption isotherm*

pH is one of the most important parameters in adsorption and ion exchange. For instance, the distribution and nature of the species in solution depend on pH as shown on the speciation diagram presented in Fig 5.46. Alternatively, the surface charge can be positively or negatively charged depending on the pH of the aqueous medium surrounding the adsorbent (see sections 5.1.6 and 5.1.7). Different researchers have reported the effect of pH on the adsorption of heavy metals from aqueous solutions [47,48,49,50]. These investigators have reported insignificant removal of heavy metals such as cadmium, zinc and lead at pH values below 3. This has been attributed to a low concentration of functional groups available for adsorption of cations at pH values close to the PZC. Therefore, the pH in contact with the adsorbent controls the metal sorption at the adsorbate-adsorbent interface.

In order to determine the sorption capacity at different acidic conditions, sorption of cadmium was carried out by modified granular and fibrous activated carbons, WHK and TC-66 C, at pH values of 4, 5 and 6. The data plotted in Figs 5.47 to 5.52 show the metal uptake at different pH using modified adsorbents. It is clearly seen that the sorption capacity increases with pH in all the cases. This suggests that the removal of cadmium from water is more effective at near-neutral pH, however adsorption of heavy metals at pH higher than 7 is normally not feasible due to hydrolysis. For instance, cadmium precipitates as $Cd(OH)_2$ at about pH 7.6 in a 0.1 M $CdCl_2$ solution. The increase in cadmium uptake with pH is attributed to the higher dissociation of oxygenated surface functional groups as pH rises. Hence, the concentration of negative surface charges increases giving rise to higher adsorption of cations. The latter has been analysed and discussed in previous sections (5.1.6 and 5.1.7).

The effect of pH on the adsorption of cadmium using a weak acid cation fibrous exchanger, K-4, containing predominantly carboxylic acid groups was also investigated. The equilibrium isotherms are reported in Fig 5.53. A big difference in cadmium uptake, about 1.2 mmol g^{-1}, was found between pH 4 and 5. However, the results obtained at pH 6 show almost the same cadmium capacity as those at pH 5. This means that the optimum is about pH 5 where the highest proportion of the functional groups, carboxylic, on K-4 are dissociated.

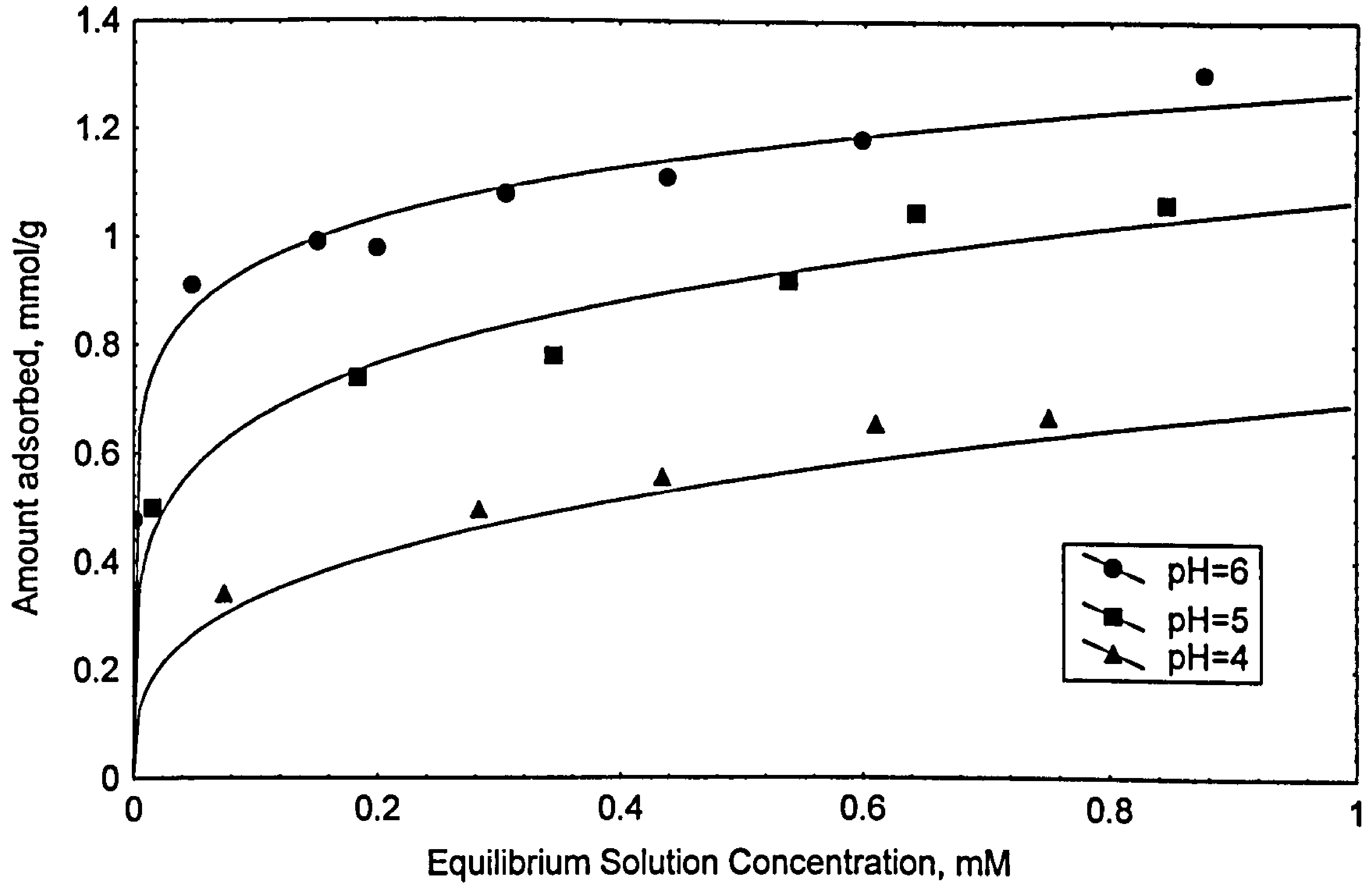


Fig 5.47. Equilibrium isotherms for cadmium using acid oxidised WHK, at different pH and at room temperature

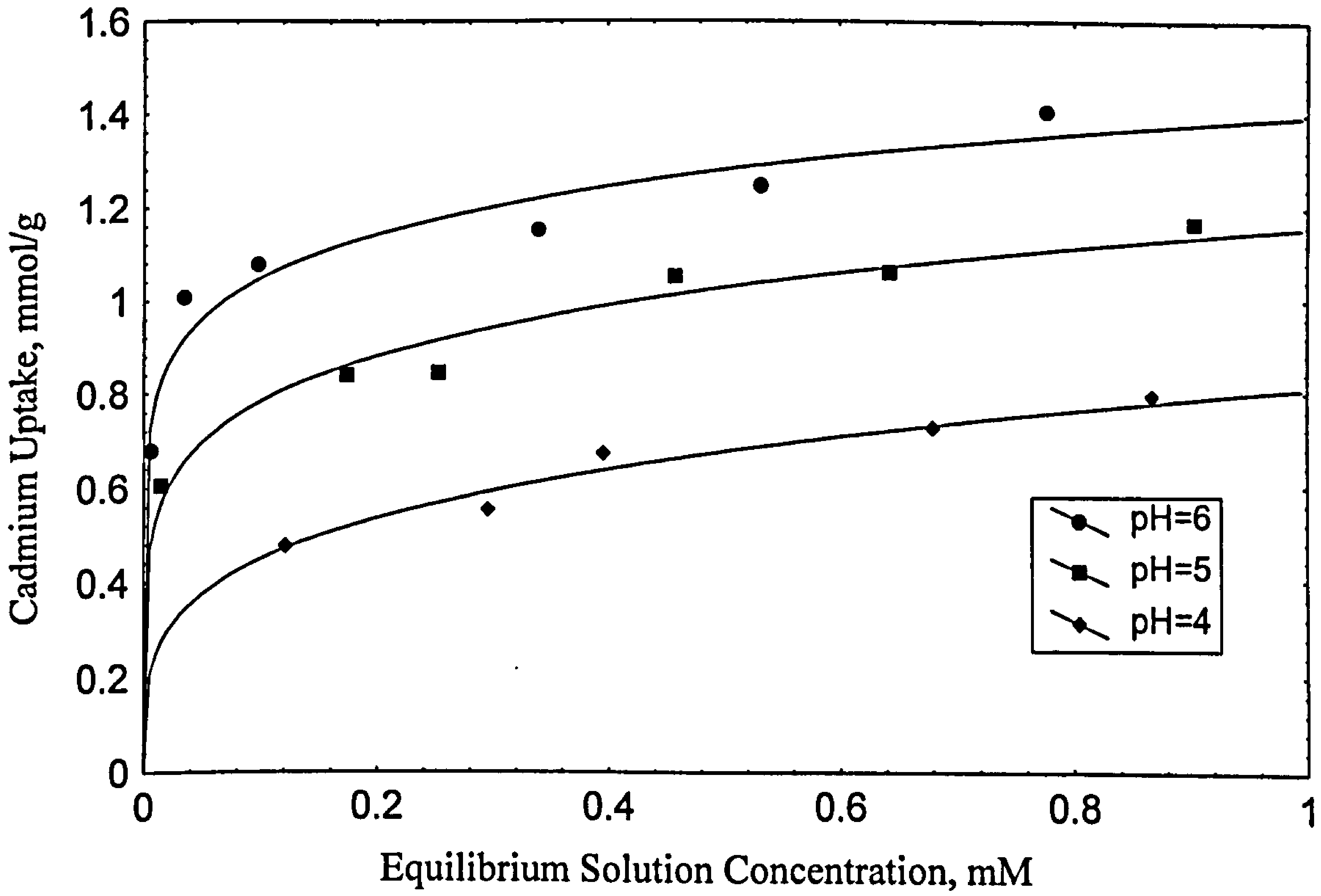


Fig 5.48. Equilibrium isotherms for cadmium using electrochemically oxidised WHK, at different pH and at room temperature

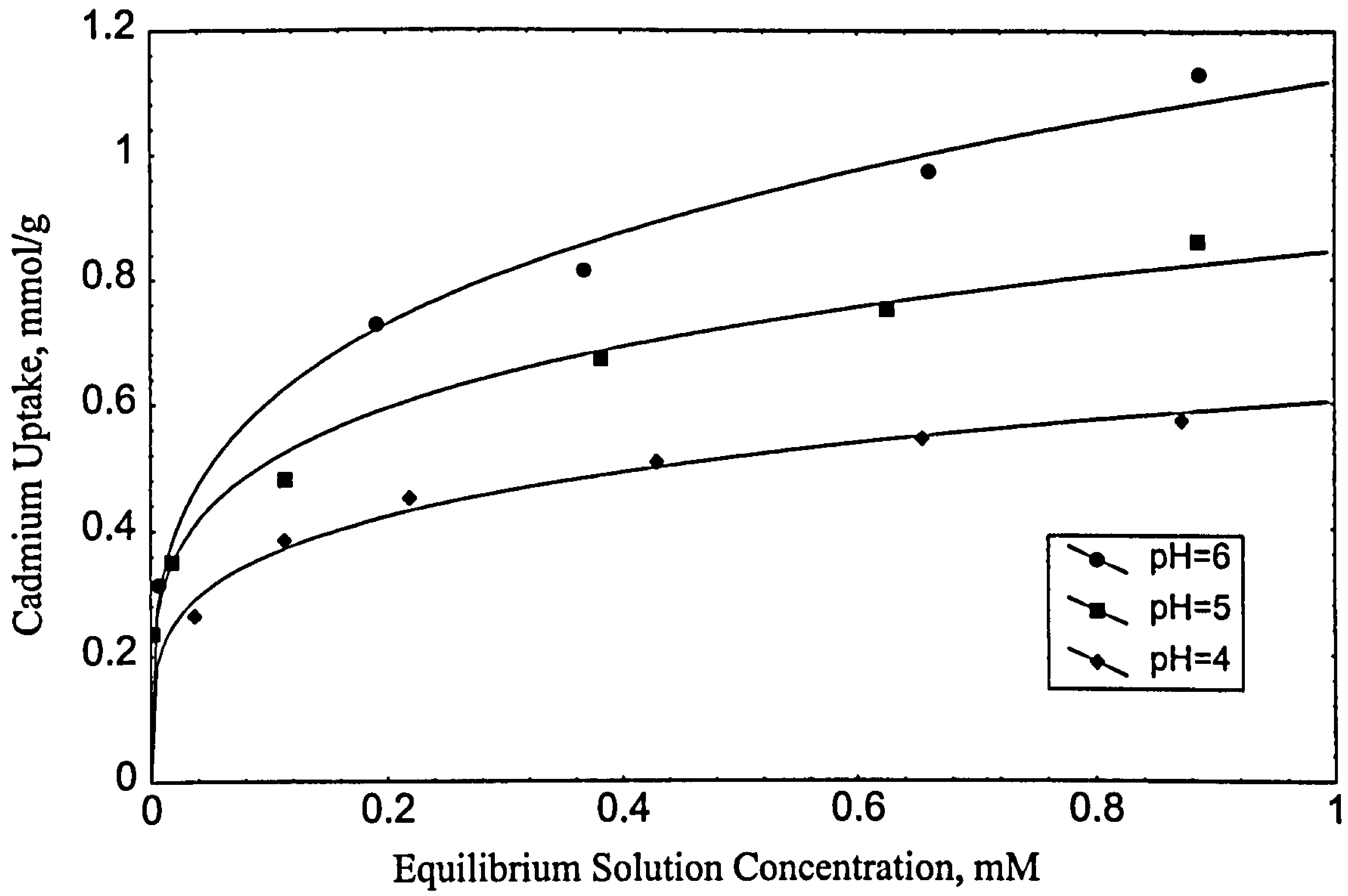


Fig 5.49. Equilibrium isotherms for cadmium using ozone oxidised WHK, at different pH and at room temperature

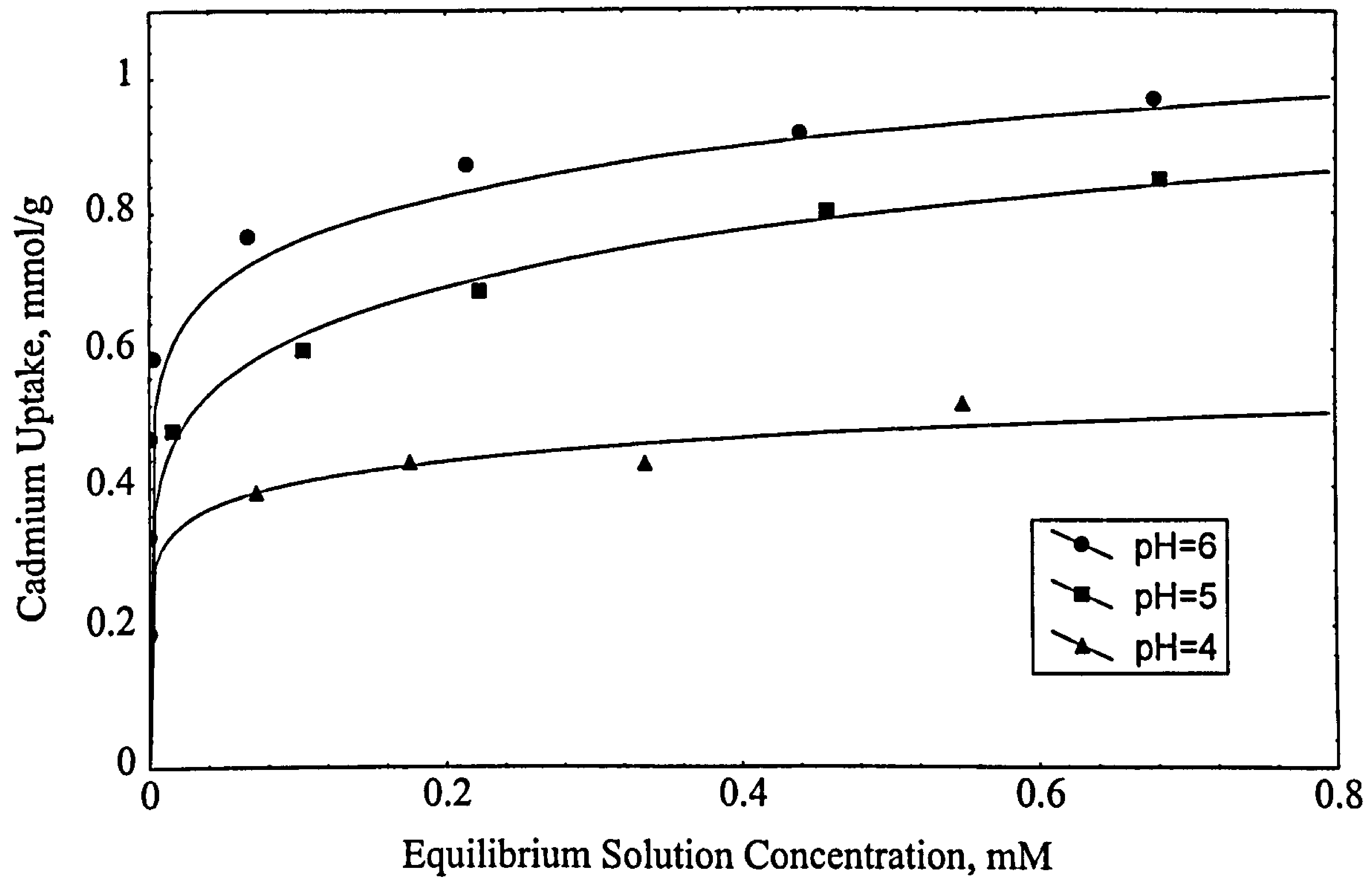


Fig 5.50. Equilibrium isotherms for cadmium using acid oxidised TC-66 C at different pH and at room temperature

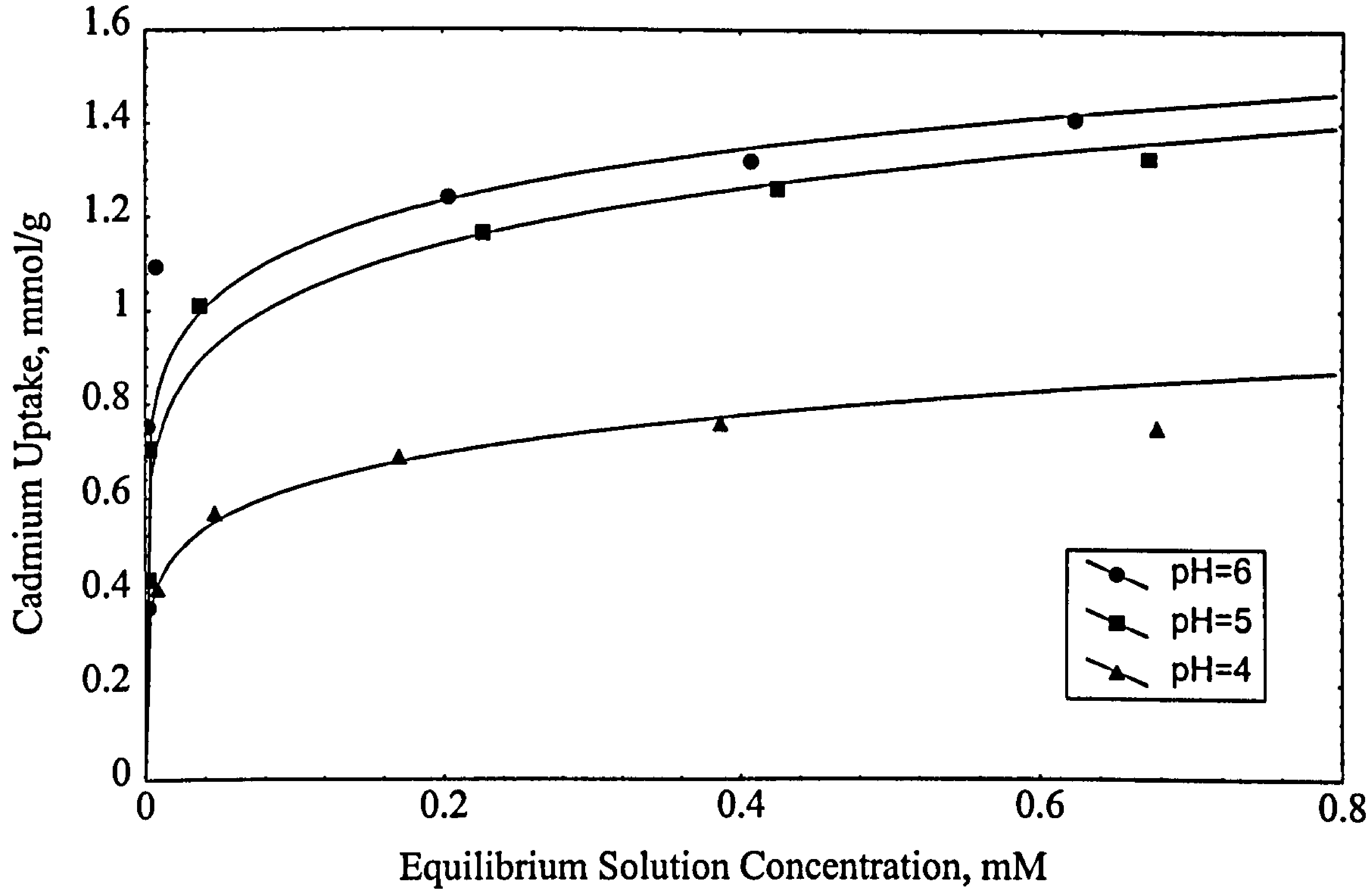


Fig 5.51. Equilibrium isotherms for cadmium using electrochemically oxidised TC-66 C at different pH and at room temperature

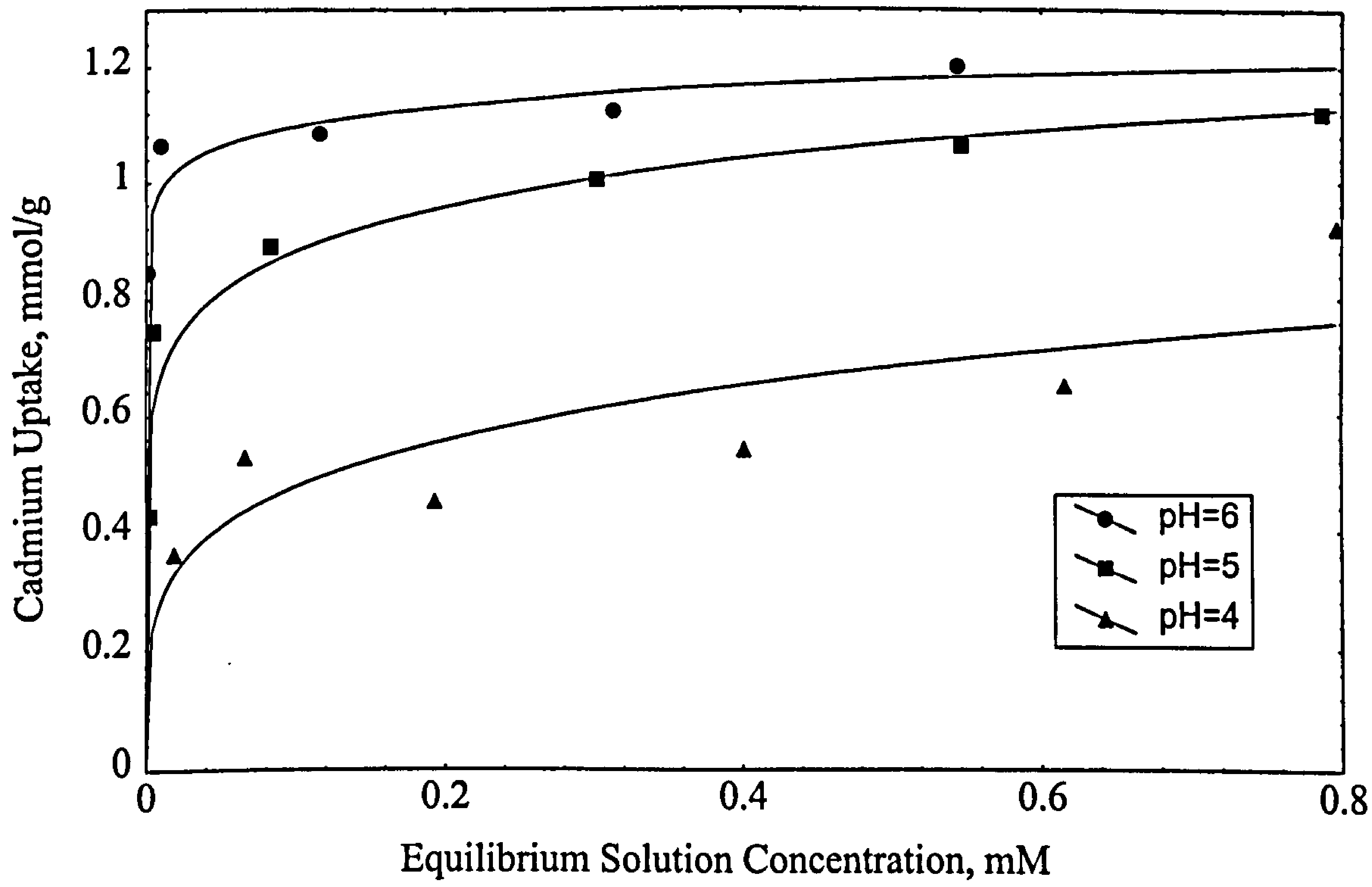


Fig 5.52. Equilibrium isotherms for cadmium using ozone oxidised TC-66 C at different pH and at room temperature

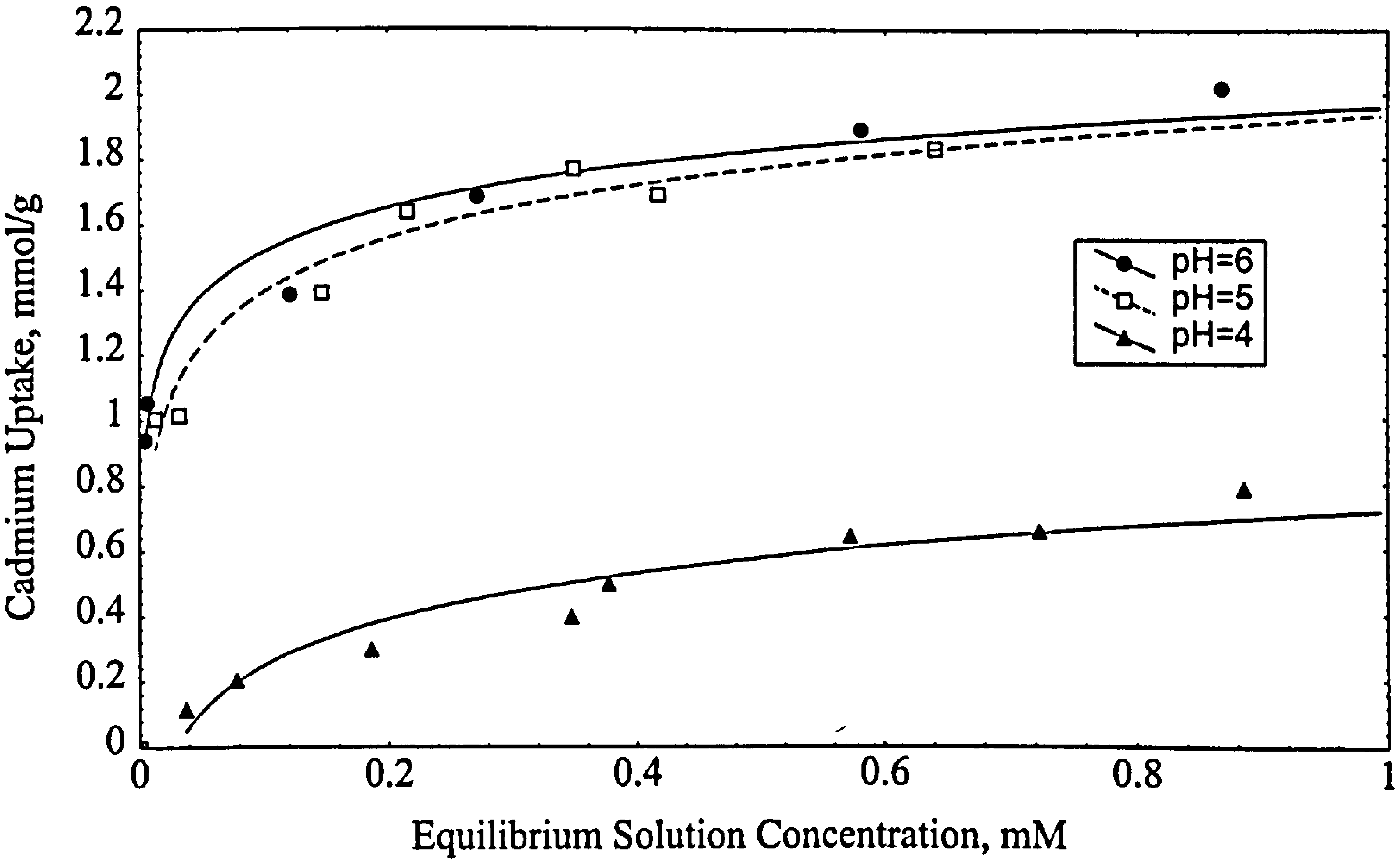


Fig 5.53. Equilibrium isotherms for cadmium using ion exchanger K-4 at different pH and at room temperature

Table 5.15. Langmuir and Freundlich adsorption isotherms parameters using acid oxidised WHK (GAC)

PH	q_mK [L/g]	K [L/mmol]	$R_{Langmuir}$	K $\left[L^{1/n}/mmol^{1-1/n}\,g^{-1}\right]$	n	$R_{Freundlich}$
6	1978.93	1825.90	*0.879*	1.27	7.92	*0.99*
5	55.33	57.83	*0.84*	1.07	4.85	*0.97*
4	6.32	8.20	*0.96*	0.72	3.41	*0.99*

Table 5.16. Langmuir and Freundlich adsorption isotherms parameters using acid oxidised TC-66 C (ACF)

PH	q_mK [L/g]	K [L/mmol]	$R_{Langmuir}$	K $\left[L^{1/n}/mmol^{1-1/n}\,g^{-1}\right]$	n	$R_{Freundlich}$
6	1599.19	1843.55	*0.95*	0.99	8.35	*0.96*
5	56.63	69.59	*0.86*	0.89	6.29	*0.99*
4	19.28	37.25	*0.88*	0.52	9.36	*0.92*

5.3.2 Sorption of Mercury

A wood based granular activated carbon WHK and a PAN based carbon fibre in the form of cloth TC-66 C were utilised to remove mercury from aqueous solution. These adsorbents were applied as-received and after electrochemical oxidation. Ozone and acid oxidised samples were not applied since their total ion exchange capacity is lower than the electrochemically modified samples. The effect of different oxidation methods has already been discussed in section 5.3.1 using cadmium as adsorbate. The isotherms reported in Fig 5.54 represent the removal of mercury using as-received granular carbon WHK and carbon fibre TC-66 C at pH 5 and room temperature. The mercury uptake by these materials was about 0.1 and 0.14 mmol g^{-1} for WHK and TC-66 C, respectively, at an equilibrium concentration of 0.8 mM. Carbon fibre showed about 0.04 mmol g^{-1} higher mercury sorption capacity at the conditions mentioned above. Different researchers have studied the removal of mercury(II) by conventional granular activated carbons. For instance, Karthikeyan and Chaudhuri[51] reported the highest sorption capacity of Filtrasorb 400 and GBC at 0.04 and 0.035 mmol g^{-1}, respectively, at initial pH 6.8 and 0.005 mM equilibrium concentration. On the other hand, Anirudhan and Sreedhar[52] report a high mercury removal, about 0.6 mmol g^{-1}, by a coconut husk based carbon at pH 5.5 and 2 mM initial concentration. It is obvious that the sorption capacity of different carbonaceous materials cannot be compared since it depends of many factors such as surface area, porosity, type and concentration of functional groups on the surface.

As-received adsorbents used in this investigation were chemically modified and tested to remove mercury. The corresponding equilibrium data are plotted in Fig 5.55. A significant increase in mercury uptake by a factor of approximately 10.7 and 14.5 for electrochemically oxidised TC-66 C and WHK was observed. This is attributed to the enhancement of oxygenated surface groups. These results were also compared with a weak acid cation fibrous exchanger, K-4, containing predominantly carboxylic acid groups. The isotherm generated by this ion exchange fibre, at pH 5, is shown in Fig 5.56 together with the equilibrium data obtained for as-received and electrochemically oxidised samples. The mercury uptake by K-4 was 1 mmol g^{-1} calculated at an equilibrium concentration of 0.8 mM, which is 65.3 and 68.9 % of the sorption capacity obtained by electrochemically oxidised carbon fibre TC-66 C and granular carbon WHK, respectively, calculated at the same conditions. It must be noted that the ion exchanger K-4 proved more effective for the removal of cadmium than modified adsorbents according to the results reported in section 5.3.1. The lines plotted in Figs 5.54 to 5.56 represent the fitting curves of the experimental data by the Langmuir model. This type of isotherm fitted the experimental data better than the Freundlich model. The corresponding parameters for each model and the correlation coefficients are reported in Table 5.17.

Table 5.17. Langmuir and Freundlich adsorption isotherm parameters for as-received adsorbents and electrochemically oxidised WHK and TC-66 C

Sample	q_mK [L/g]	K [L/mmol]	$R_{Langmuir}$	k $\left[L^{1/n}/mmol^{1-1/n}\,g^{-1}\right]$	n	$R_{Freundlich}$
TC-66 C	192.29	1888.69	*0.96*	0.12	9.43	*0.83*
WHK	39.01	264.20	*0.98*	0.17	7.18	*0.84*
TC-66 C ox.	277.16	179.16	*0.99*	1.90	4.82	*0.95*
WHK ox.	216.97	147.74	*0.99*	1.85	0.26	*0.98*
K-4	137.86	140.08	*0.95*	n/a	n/a	n/a

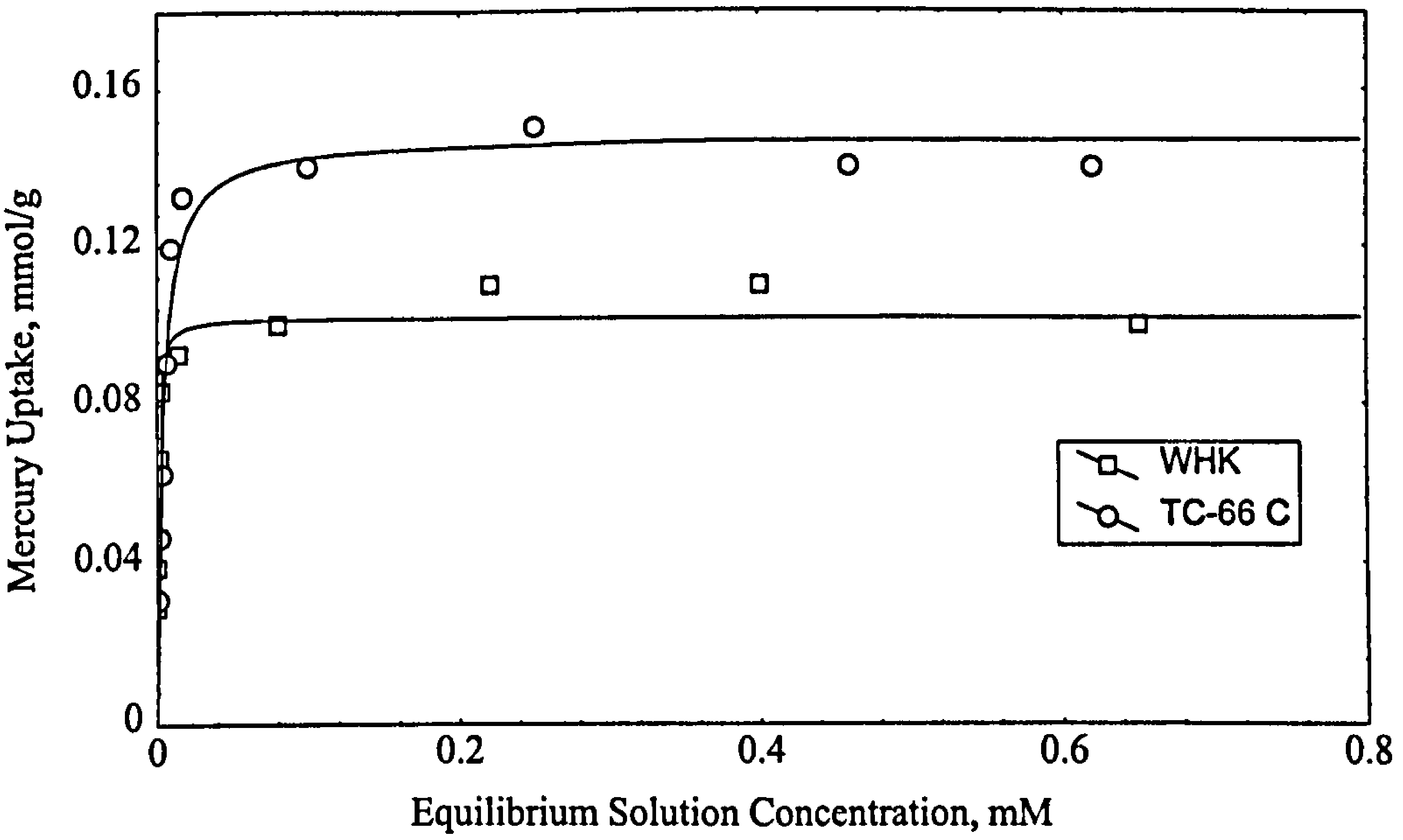


Fig 5.54. Mercury sorption isotherms using as-received granular carbon WHK and carbon fibre TC-66 C at pH 5 and room temperature

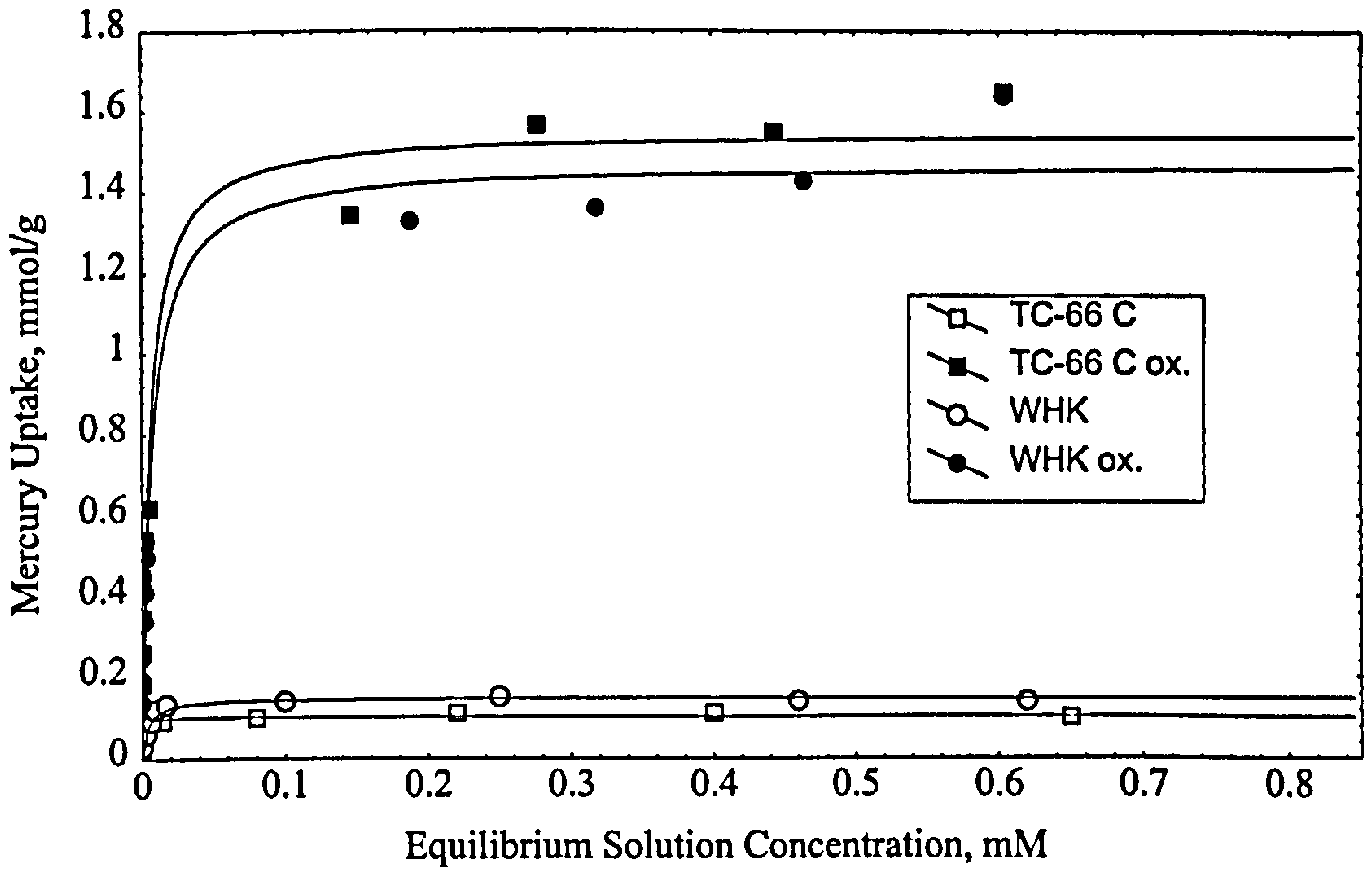


Fig 5.55. Mercury sorption isotherms using as-received and electrochemically oxidised granular carbon WHK and carbon fibre TC-66 C at pH 5 and room temperature

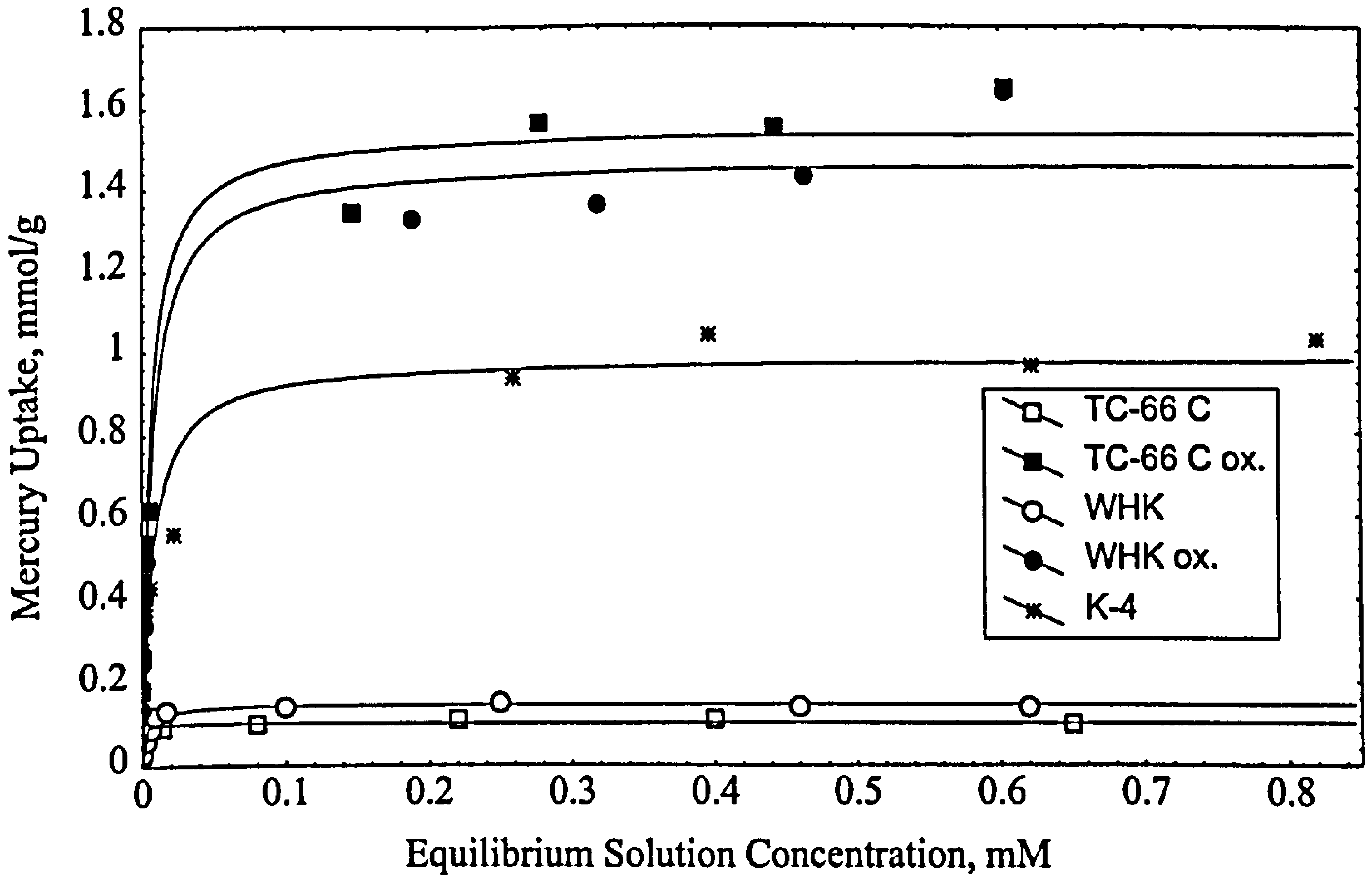


Fig 5.56. Mercury sorption isotherms using as-received and electrochemically oxidised granular carbon WHK and carbon fibre TC-66 C, and ion exchange fibre K-4 at pH 5 and room temperature

The sorption mechanism and species in solution are extremely important factors in deciding which adsorbent is the most appropriate for a particular sorption process. Unfortunately, the metals sorption mechanism is not always easy to elucidate. It has been mentioned that the adsorption of cations by carbonaceous adsorbents is due to electrostatic attraction at negative surface charges generated by the dissociation of oxygenated surface groups. Mercury sorption is more complicated than the mechanism described for cadmium in section 5.3.1. Mercury can exist as a cation, anion and/or neutral species. Obviously, the distribution of species depends on the concentration of $HgCl_2$ and pH. The speciation diagram for mercury chloride in aqueous solution is presented in Fig 5.57 and was calculated based on the following reactions and K values[53],

	K
$Hg^{2+} + H_2O \rightarrow Hg(OH)^+ + H^+$	3.98×10^{-4}
$Hg^{2+} + 2H_2O \rightarrow Hg(OH)_2 + 2H^+$	6.76×10^{-7}
$Hg^{2+} + 3H_2O \rightarrow Hg(OH)_3^- + 3H^+$	7.94×10^{-22}
$Hg^{2+} + Cl^- \rightarrow HgCl^+ + H^+$	2.69×10^{7}
$Hg^{2+} + 2Cl^- \rightarrow HgCl_2 + 2H^+$	1.78×10^{14}
$Hg^{2+} + 3Cl^- \rightarrow HgCl_3^- + 3H^+$	2.88×10^{14}
$Hg^{2+} + 4Cl^- \rightarrow HgCl_4^{2-} + 4H^+$	1.86×10^{15}

It can be seen in Fig 5.57 that $HgCl_2(aq)$ is the predominant species followed by $HgCl^+$ and $HgCl^-_3$ for 1×10^{-4}M $HgCl_2$ and pH<6. $Hg(OH)_2(aq)$ is the most important species at pH 6-10, but $HgCl_2(aq)$, $HgCl^+$ and $HgOH^+$ should also be taken in account. $Hg(OH)_2(aq)$ is most predominant species above pH 10 followed by $Hg(OH)_3^-$.

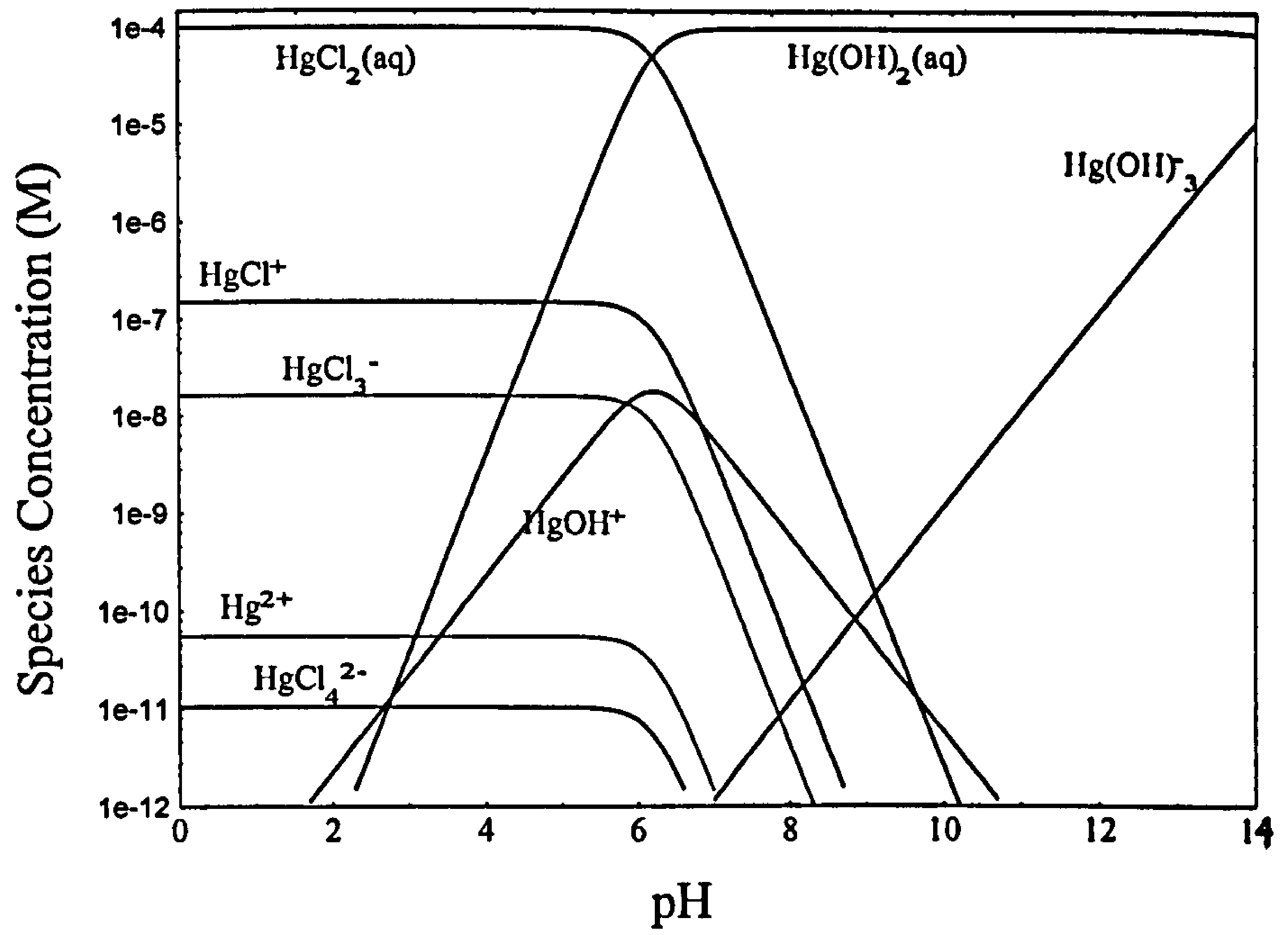


Fig 5.57. Speciation diagram for $1x10^{-4}$ M $HgCl_2$ in aqueous solution

Mercury can be removed from solution by two mechanisms; firstly by adsorption of cation species such as Hg^{2+}, $HgCl^+$ and $HgOH^+$ due to electrostatic attraction (ion exchange) and secondly by reduction of $HgCl_2$(aq) to Hg_2Cl_2(s). It has been reported that the phenolic and hydroquinonic groups on the surface of activated carbon are capable of reducing Hg(II) to Hg(I), according to the following reaction[54]

$$2(-OH) + 2HgCl_2(aq) \rightarrow 2(=O) + Hg_2Cl_2(s) + 2HCl \qquad \textbf{Reac. 5. 1}$$

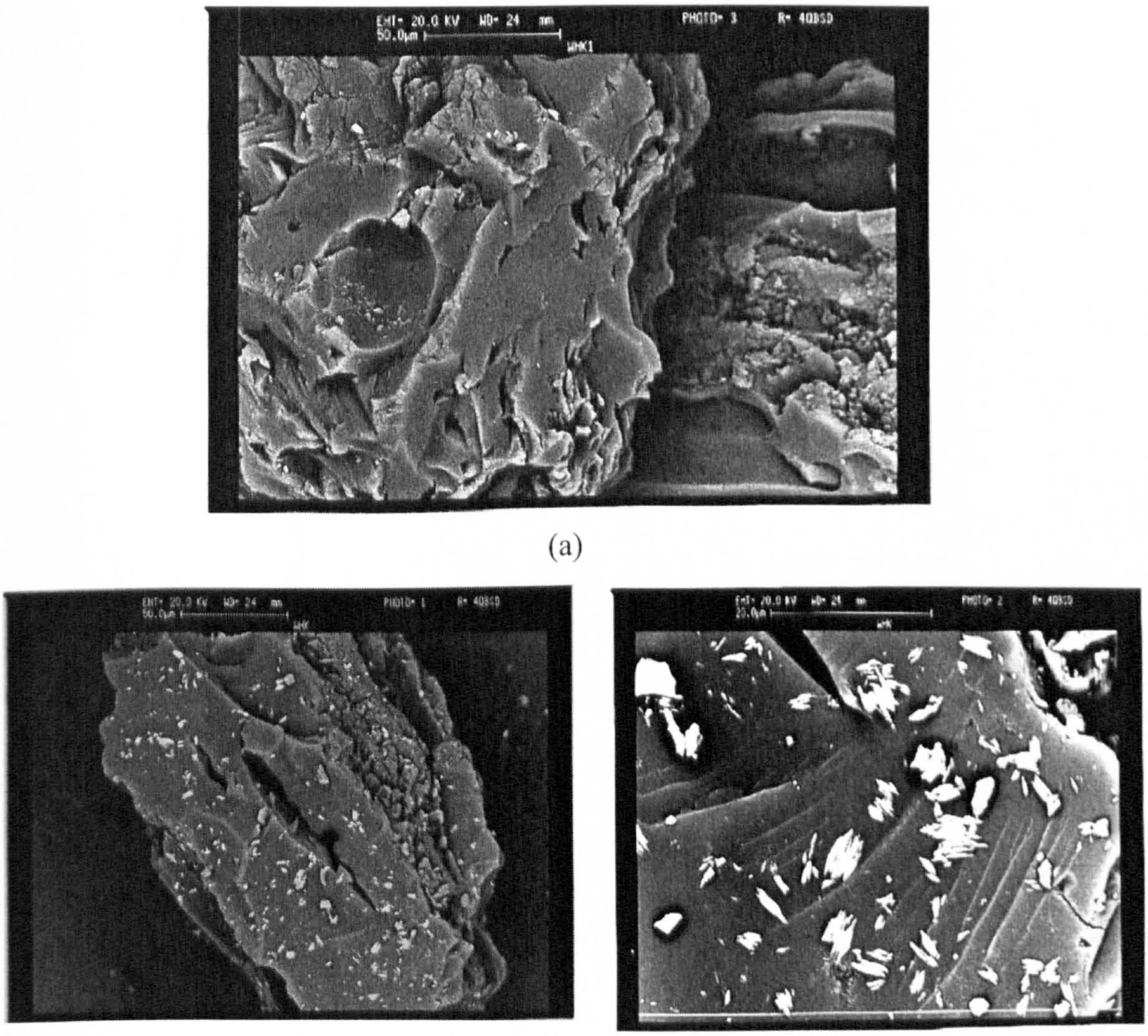
The speciation diagram shows that $HgCl_2$(aq) occurs to the extent of 99% in a solution containing 10^{-4} M $HgCl_2$ up to pH 5. Thus, reduction of Hg(II) to Hg(I) forming Hg_2Cl_2(s) as a colloidal precipitate might contribute to the removal of Hg from solution by activated carbon. At the beginning of the last decade, Adams[55] proposed that the removal of Hg(II) by activated carbon is possible by the reduction of Hg^{2+} to Hg_2^{2+} since this reaction has a much higher potential, +0.905 V, than that of activated carbon, +0.24 V. Therefore, mercury is removed by forming a precipitate, Hg_2Cl_2, through the following reactions,

$$2Hg^{2+} + 2e^- \leftrightarrow Hg_2^{2+} \qquad \textbf{Reac. 5.2}$$

$$Hg_2^{2+} + 2Cl \leftrightarrow Hg_2Cl_2(s) \qquad \textbf{Reac. 5.3}$$

It is possible that, in our case, mercury is mainly removed by the sorption mechanism proposed by Lopez Gonzales et al.[54] (Reac. 5. 1) since the concentration of $HgCl_2(aq)$ is almost 100% in the pH range of our experiments. On the other hand, mercury removal by cation exchanger K-4 should be solely due to an ion exchange mechanism between cations and H^+ ions at the carboxyl groups.

Fig 5.58 shows the scanning electron micrographs of granular activated carbon surfaces before and after the adsorbent was contacted with $HgCl_2$ solution. SEMs (b) and (c) clearly show the presence of a precipitate. Samples saturated with $HgCl_2$ solution were analysed by Energy Dispersive Spectroscopy (EDS). The results confirmed that the precipitate contains mercury and chloride.



(a)

(b)

(c)

Fig 5.58. SEMs of as-received granular carbon WHK, (a), and electrochemically oxidised WHK contacted with $HgCl_2$ solution, (b) and (c)

The spectra obtained by using EDS are presented in Figs 5.59 and 5.60. The spectrum for electrochemically oxidised WHK showed a small peak for chlorine, which may be attributed to contamination from the electrolyte (KCl) and/or hydrochloric acid, used to convert the sample to H^+ form after it was oxidised. An electro-oxidised sample equilibrated with a $HgCl_2$ solution showed a distinct peak for chlorine and mercury. The appearance of gold and silicon in the spectra is due to the fact that the samples were glued to aluminium platforms and sputter-coated with gold prior to analysis.

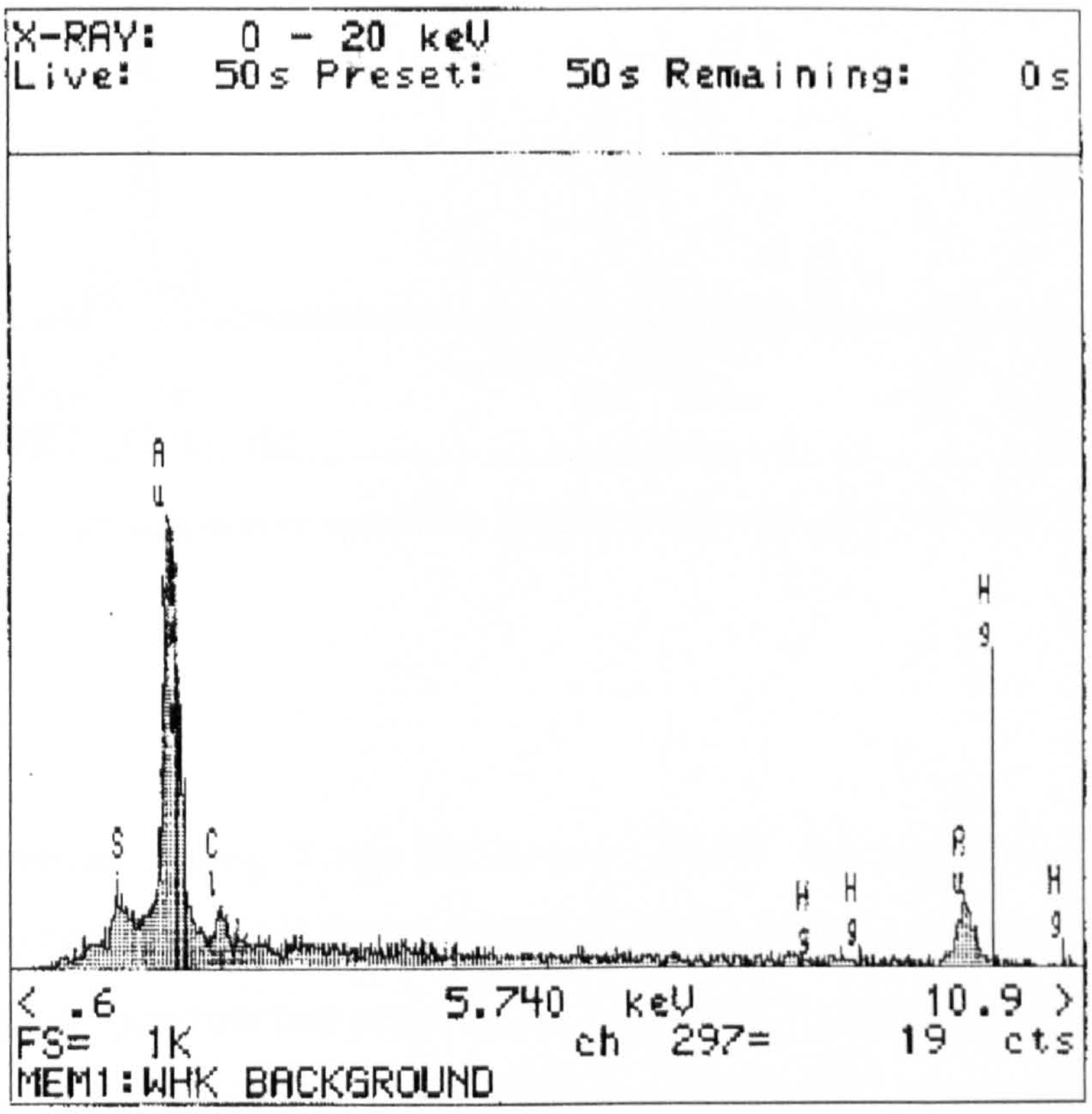


Fig 5.59. Energy dispersive spectrum for unsaturated electro-oxidised WHK

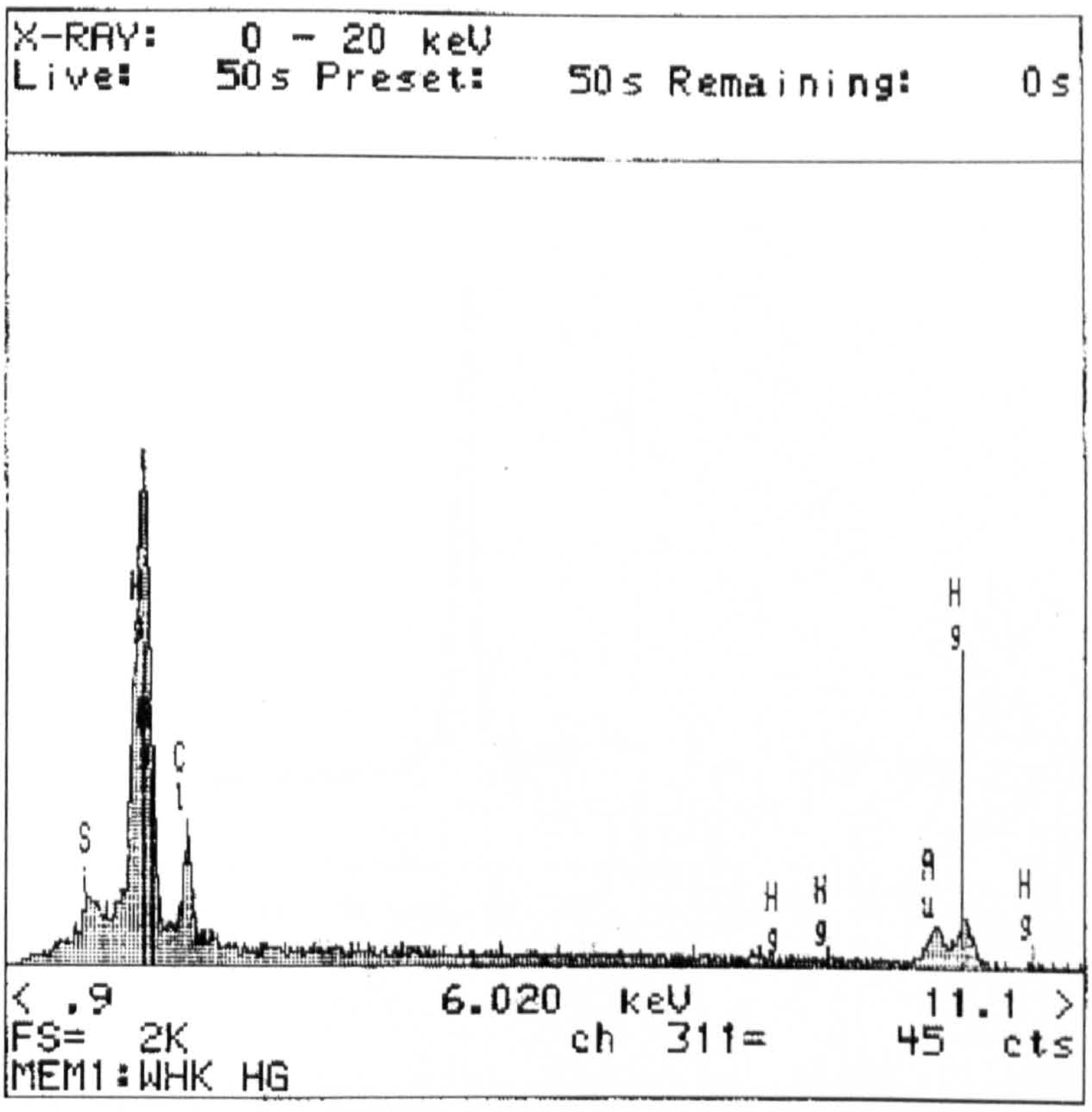


Fig 5.60. Energy dispersive spectrum for electro-oxidised WHK after Hg sorption

Further experiments using X-ray Diffraction (XRD) were carried out in order to elucidate the crystallographic form of the precipitate observed by SEM. The spectra shown in Fig 5.61 presents two peaks at 2θ angles of 21.4 and 28.2, which correspond to mercurous chloride (Hg_2Cl_2). Also, there is no evidence of a peak at 20.5 that would indicate that mercury is present as mercuric chloride ($HgCl_2$). These results confirm that mercury is in part removed by reducing Hg(II) to Hg(I) followed by Hg_2Cl_2 precipitation.

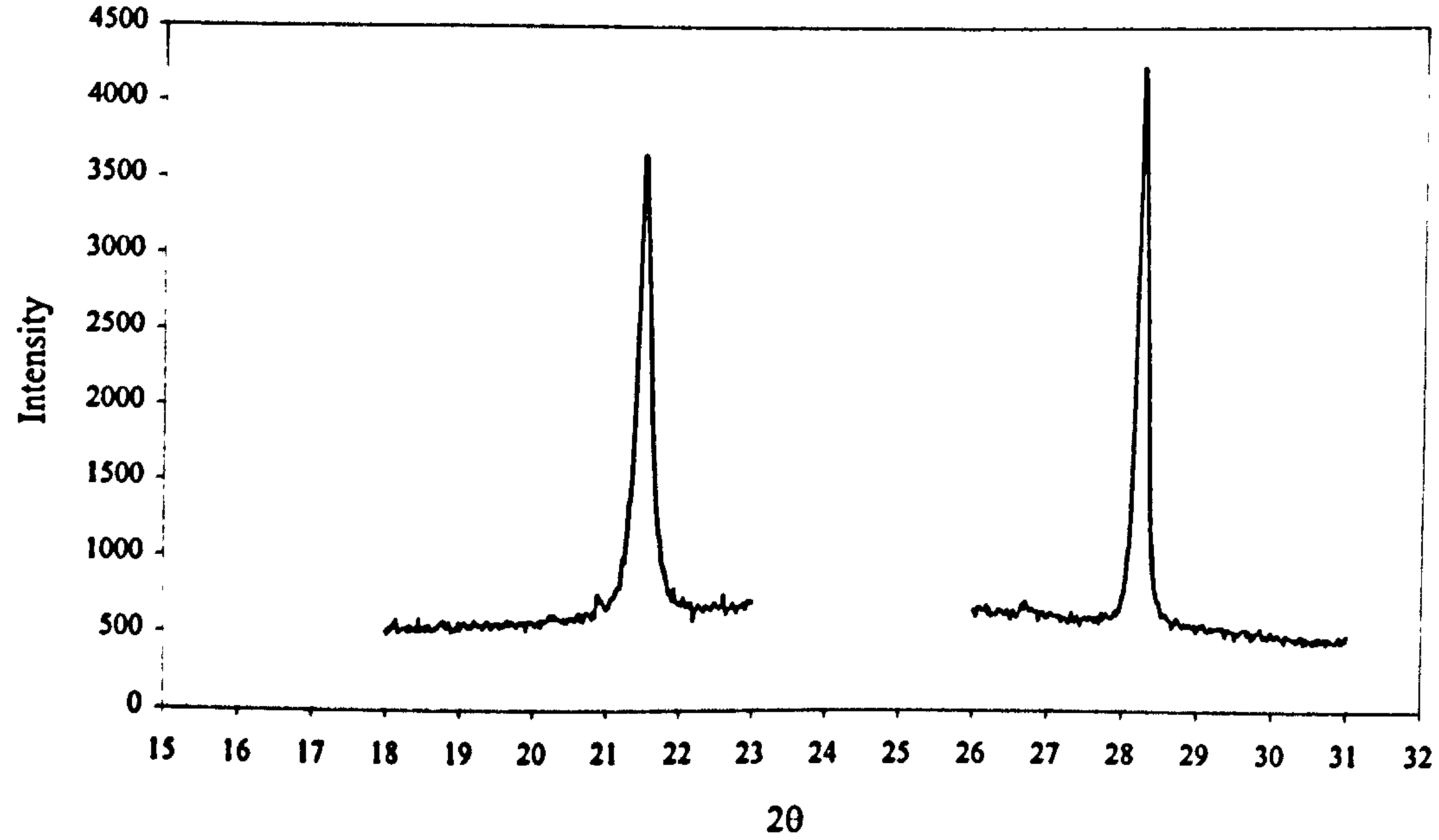


Fig 5.61. Combined XRD spectra for electro-oxidised WHK after Hg sorption

5.3.2.1 pH effect on the adsorption isotherm

The pH effect on the adsorption performance is related to the species in solution and chemical properties of the adsorbent. This has been discussed in more detail in section 5.3.1.1. In order to visualise the effect of pH on mercury uptake, complete isotherms were generated at pH 5 and 6 using ion exchanger K-4 and electrochemically oxidised granular carbon WHK. The equilibrium data are presented in Fig 5.62. The sorption capacity increases with pH. This behaviour is attributed to the higher amount of dissociated functional groups available for adsorption and ion exchange as pH rises. The increase in mercury uptake from pH 5 to 6 was almost in the same proportion for both K-4 and WHK.

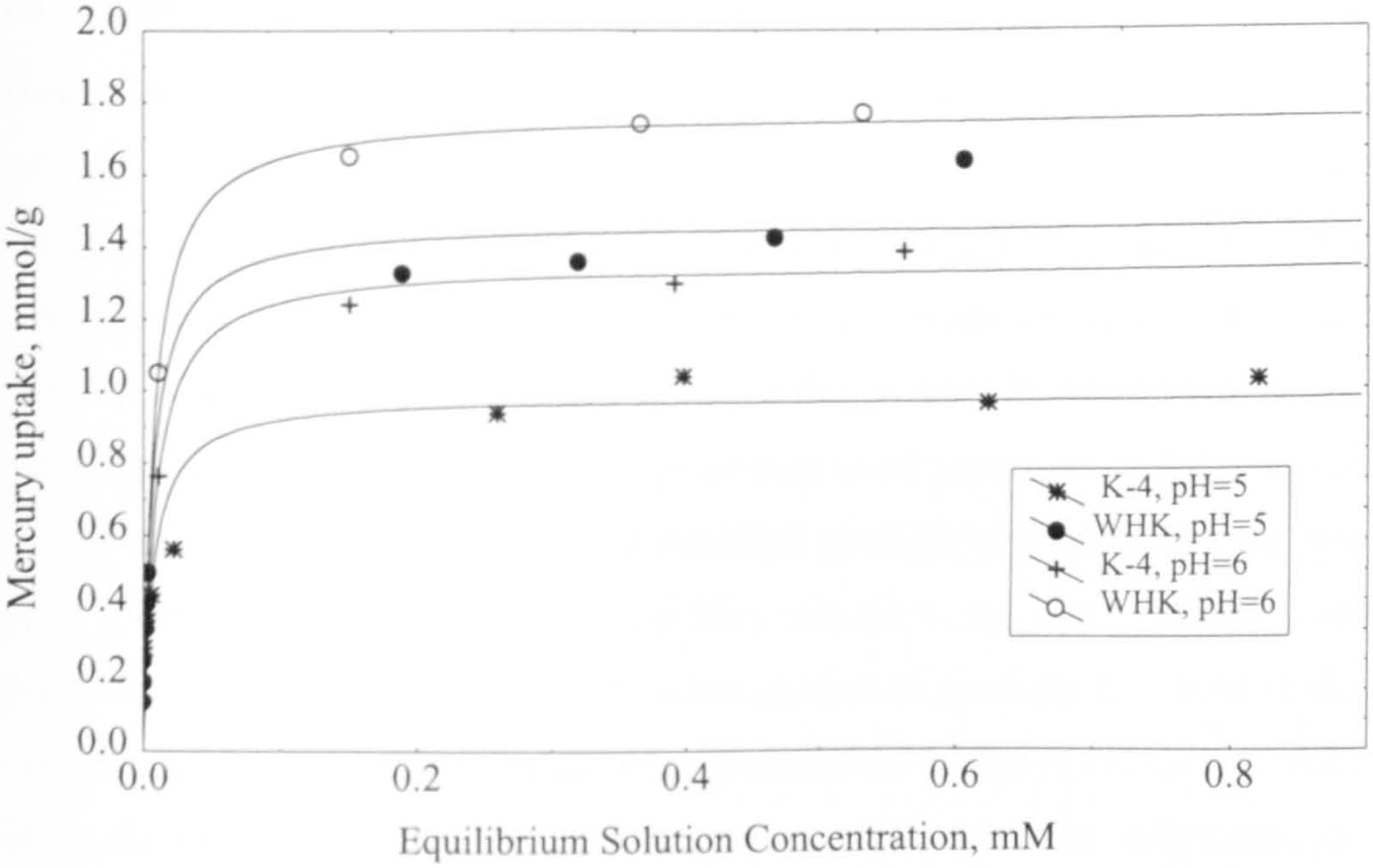


Fig 5.62. pH effect on the adsorption isotherm using ion exchanger K-4, as-received and electrochemically oxidised WHK at room temperature

Extra experiments were carried out at pH 3, 6 and 7 at the same initial concentration, i.e. 0.9 mM. The results are plotted in Fig 5.63 and the equilibrium concentration is included for each experimental point. The sorption of mercury by oxidised WHK increased by a factor of 2.46 from pH 3 to 6, and by a factor of 1.32 from pH 6 to 7. Moreover, mercury removal by ion exchange fibre K-4 drastically increased by a factor of 10 from pH 3 to 6 and just a small increase by a factor of 1.14 from pH 6 to 7.

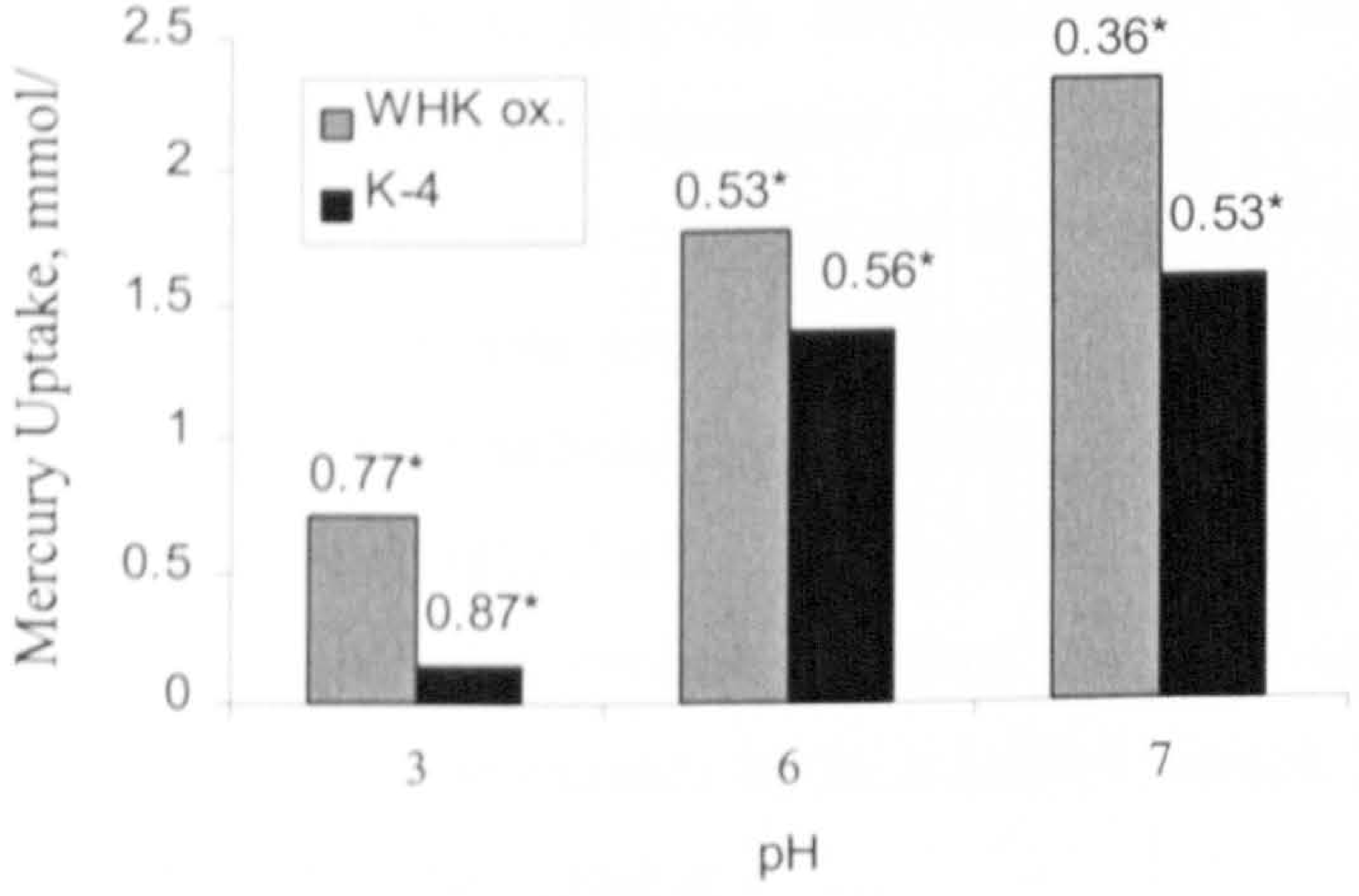


Fig 5.63. Sorption of mercury on electrochemically oxidised WHK and K-4 at room temperature. Initial concentration 0.9 mM. * Equilibrium concentration, mM

5.3.3 Mini-scale column trials to obtain breakthrough characteristics

Commercial granular activated carbons and ion exchange resins are normally used as fixed beds where a feed solution, containing the adsorbate, is normally passed in downflow. Column studies can give valuable information, such as sorption capacity, pH profile and kinetic performance. Studies in full-scale columns require a large amount of adsorbent, large quantities of feed solution and the whole process is time consuming. Therefore, breakthrough experiments were conducted in mini-columns, 3 cm^3 total volume, using as-received and modified granular carbons with a particle size rage of 170 to 210 μm. Activated carbon fibre was cut to the size of the mini-column internal diameter. A feed solution of cadmium and/or mercury was passed through the column at an initial concentration of approximately 1 mM at pH 6. The flow rate through the column was fixed at 10 bed volumes (BV) per hour, equivalent to 0.14 ml/min. The low flow rate allowed local equilibrium between adsorbent/adsorbate which ensures that the breakthrough and sorption capacity are more accurate. Strelko[56] recently studied the effect of flow rate on mini-columns containing granular carbon. He concluded that an increase in flow rate from 1 to 3.5 ml/min, bed volume of approx. 0.6 cm^3, reduces the efficiency of Pb removal by 25%.

The breakthrough curves presented in Fig 5.64 show a great difference in cadmium capacity between oxidised and as-received granular carbon WHK. Breakthrough for modified adsorbents occurred at about 130 BV whereas for as-received carbon it was almost instantaneous. The cadmium uptake for each sample at 5%, shows that the trend in sorption capacity is as follows; electrochemically ox.>acid ox.>ozone ox.>un-oxidised. These results are in agreement and confirm the trends reported for total ion exchange capacity presented in section 5.1.1. Activated carbon fibre in the form of cloth, TC-66 C, was also used in mini-columns to obtain breakthrough characteristics. About 50 BV of cadmium solution were passed through acid oxidised TC-66 C before breakthrough (Fig 5.65). The sorption capacity at 5% was 0.022 mmol g^{-1} for as-received material whereas for oxidised fibre it increased to 0.16 mmol g^{-1}. The enhancement in sorption capacity of the modified sample is attributed to the introduction of oxygenated surface groups.

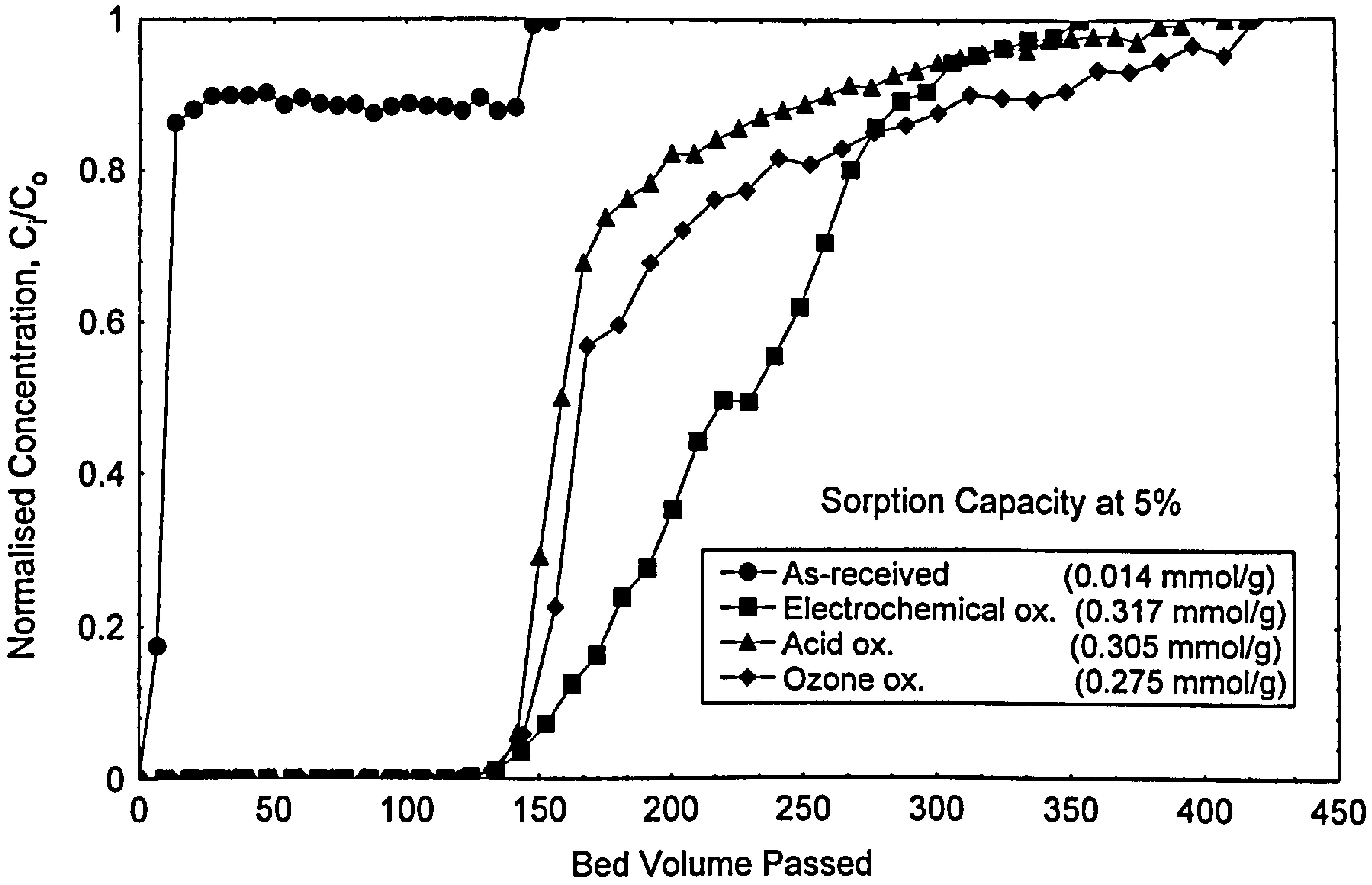


Fig 5.64. Cadmium normalised breakthrough curves for as-received and modified WHK. 1 mM cadmium feed solution at pH 6

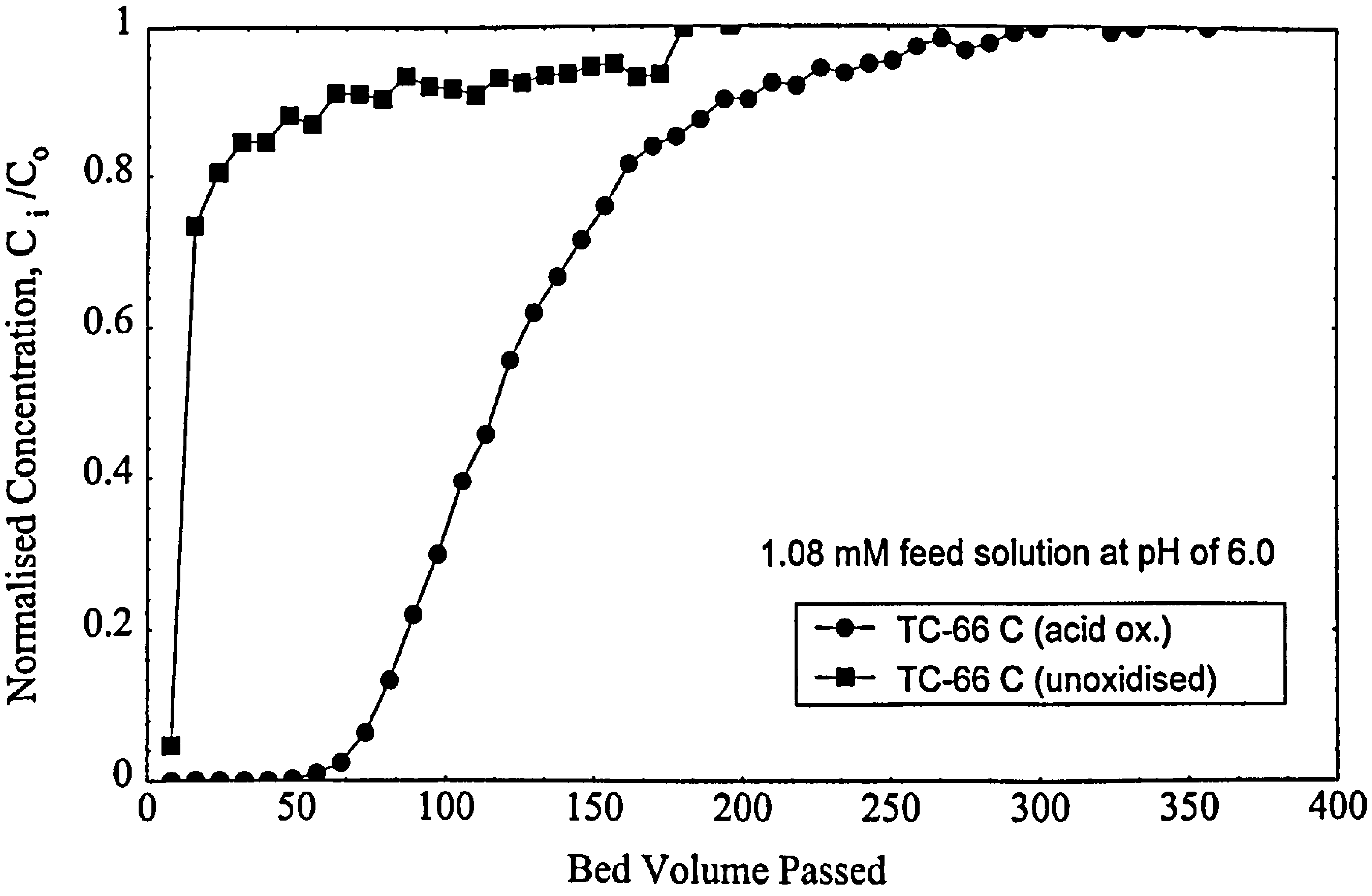


Fig 5.65. Cadmium normalised breakthrough curves for acid oxidised and as-received TC-66 C

The use of commercial granular activated carbon columns for removal of cadmium has been studied by Huang et al.[57] and Youseef et al.[58]. The latter group of researchers (ref. 58) also performed mercury breakthrough experiments using activated carbon made from Maghara coal. The effect of flow rate at a constant concentration of 0.0075 mM was investigated. A decrease in sorption capacity was observed as the flow rate was increased from 2.5 to 10 ml/min. The low sorption capacity obtained by mini-column studies compared to that achieved by equilibrium experiments was attributed to the deterioration of local equilibrium.

Electrochemically oxidised granular carbons WHK, in H^+ and Na^+ form, were used in mini-columns to study mercury breakthrough characteristics. Figs 5.66 and 5.67 show mercury breakthrough curves for modified WHK in H^+ and Na^+ form, respectively. Mercury sorption capacity with adsorbent in the acid form was very low, 0.026 mmol g^{-1} at 5% of the total metal uptake, compared to the sample in sodium form, 1.82 mmol g^{-1}. The big difference in sorption capacity between the H^+ and Na^+ form is due to the pH at which the sorption process takes place. The pH profile plotted in Fig 5.66 shows that the feed solution (pH 6) dropped to pH 2.93 in the column and remained constant for the first 12.5 BV passed during which time most of the mercury was removed. Thereafter, the pH started increasing continuously as the adsorbent became exhausted. The pH eventually rises steadily to reach the feed pH value when the adsorbent is completely saturated. The sorption of cadmium and mercury under acidic conditions is very low because the oxygen-containing surface groups are undissociated, hence ion exchange is unlikely to occur.

Alternatively, high mercury removal was obtained, 1.82 mmol g^{-1}, in alkaline conditions (see Fig 5.67). The pH profile shows that the pH is approximately constant at pH 7.4 until the breakthrough occurs and then starts to decrease rapidly as the carbon saturates, finally reaching the pH of the feed solution when the adsorbent is exhausted. At near-neutral pH, some of the oxygenated surface groups dissociate and ion exchange occurs thus explaining the high sorption capacity.

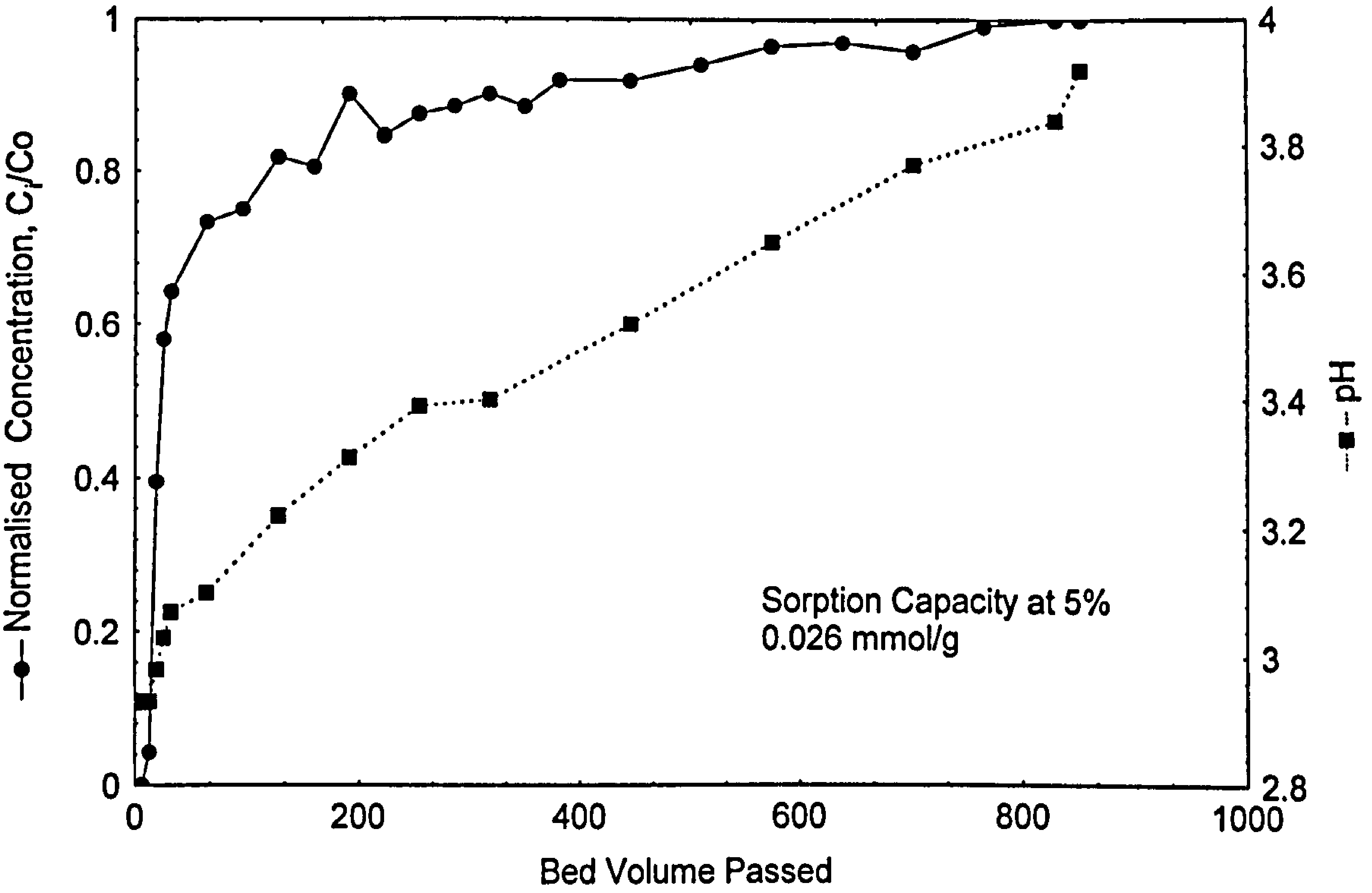


Fig 5.66. Mercury normalised breakthrough curves for electrochemically oxidised WHK in H form. 0.1 mM feed mercury concentration at pH 6

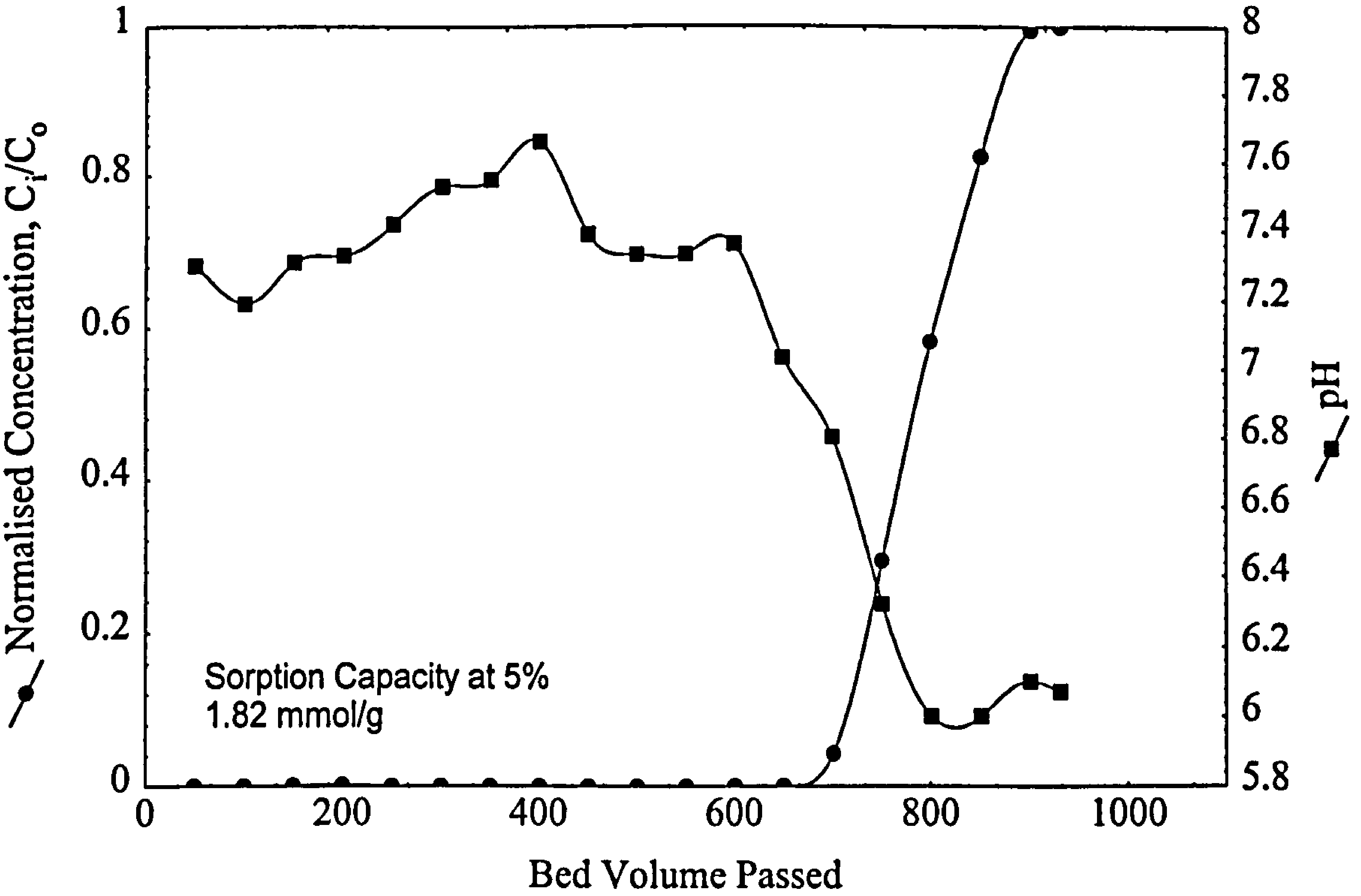


Fig 5.67. Mercury normalised breakthrough curves for electrochemically oxidised WHK in Na form. 0.1 mM feed mercury concentration at pH 6

The adsorption of a mixed cadmium/mercury solution using electrochemically oxidised granular carbon WHK in mini-columns was also investigated and the results have recently been published by Rangel-Mendez and Streat[59]. Breakthrough occurred at approximately 20 and 75 bed volumes for mercury and cadmium, respectively (see Fig 5.68). Hence, the uptake of cadmium is 72.9% greater than for mercury under these operating conditions. Breakthrough curves also indicate selectivity. This experiment was performed at pH 2.5 - 3.5, and according to the electrophoretic mobility measurements (Fig 5.21) the carbon surface is negatively charged in this region. It appears that WHK is more selective for cadmium than for mercury. The sorption mechanisms and the relative concentration of species in solution may in part explain this phenomenon. Mercury can be removed by two mechanisms; firstly by adsorption of cation species such as Hg^{2+}, $HgCl^{+}$ and $HgOH^{+}$ due to electrostatic attraction (ion exchange) and secondly by reduction of $HgCl_2$(aq) to Hg_2Cl_2(s). Alternatively cadmium exists as Cd^{+2} (about 60%) and $CdCl^{+}$ (about 40%) in solution up to pH 7.5 (see Fig 5.46). Consequently, adsorption is likely to be by cation exchange due to electrostatic attraction. Cadmium and mercury sorption mechanisms have been explained more in detail in sections 5.3.1 and 5.3.2, respectively.

The pH profile shows that the effluent pH was initially about 2.7. It remained roughly constant until cadmium breakthrough occurred, and then started increasing gradually as the adsorbent saturates. The reduction of pH during the adsorption process suggests that metal uptake is due to ion exchange, cations replacing protons at oxygenated surface groups. After breakthrough, the pH starts increasing as less hydrogen ions are released.

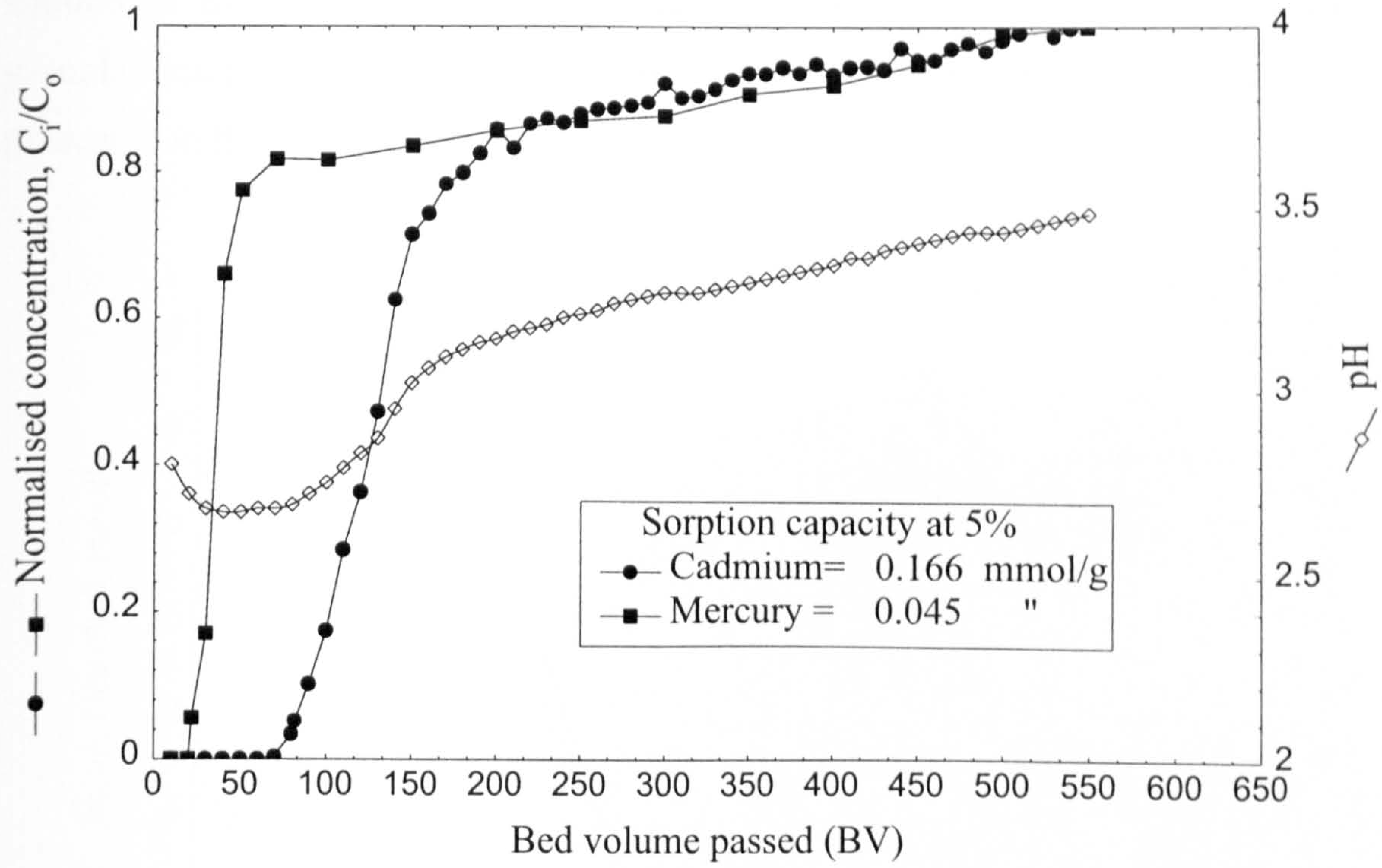


Fig 5.68. Cadmium and mercury normalised breakthrough curves for electrochemically oxidised WHK in H form. 0.1 mM feed mercury concentration at pH 6

5.4 Elution Experiments

The good performance of a granular activated carbon packed column is dependent on high sorption capacity and easy and fast regeneration of the sorptive material after a loading cycle. These factors make the column operation successful. Metal-saturated sorbents are usually regenerated in acid medium. However, if chemical reaction occurs during the sorption process, e.g. oxidation-reduction and chelation, regeneration is likely to be inefficient. For instance, Reed et al.[60] studied the removal of cadmium and lead using activated carbon packed columns. The metal recovery experiments showed that only 70 to 80 % was recovered after the first cycle, but metal recovery improved after subsequent adsorption/desorption cycles. Tai et al.[61] also conducted column experiments to remove metal ions such as copper, nickel and zinc by activated carbon. Saturated sorbents were regenerated with 0.1 M HCl. These authors reported that only 90% of the ions were recovered from the column after the first cycle.

Elution of metal ions, such as cadmium and mercury, from exhausted modified granular and fibrous activated carbons was carried out using HCl and the results are presented in this section.

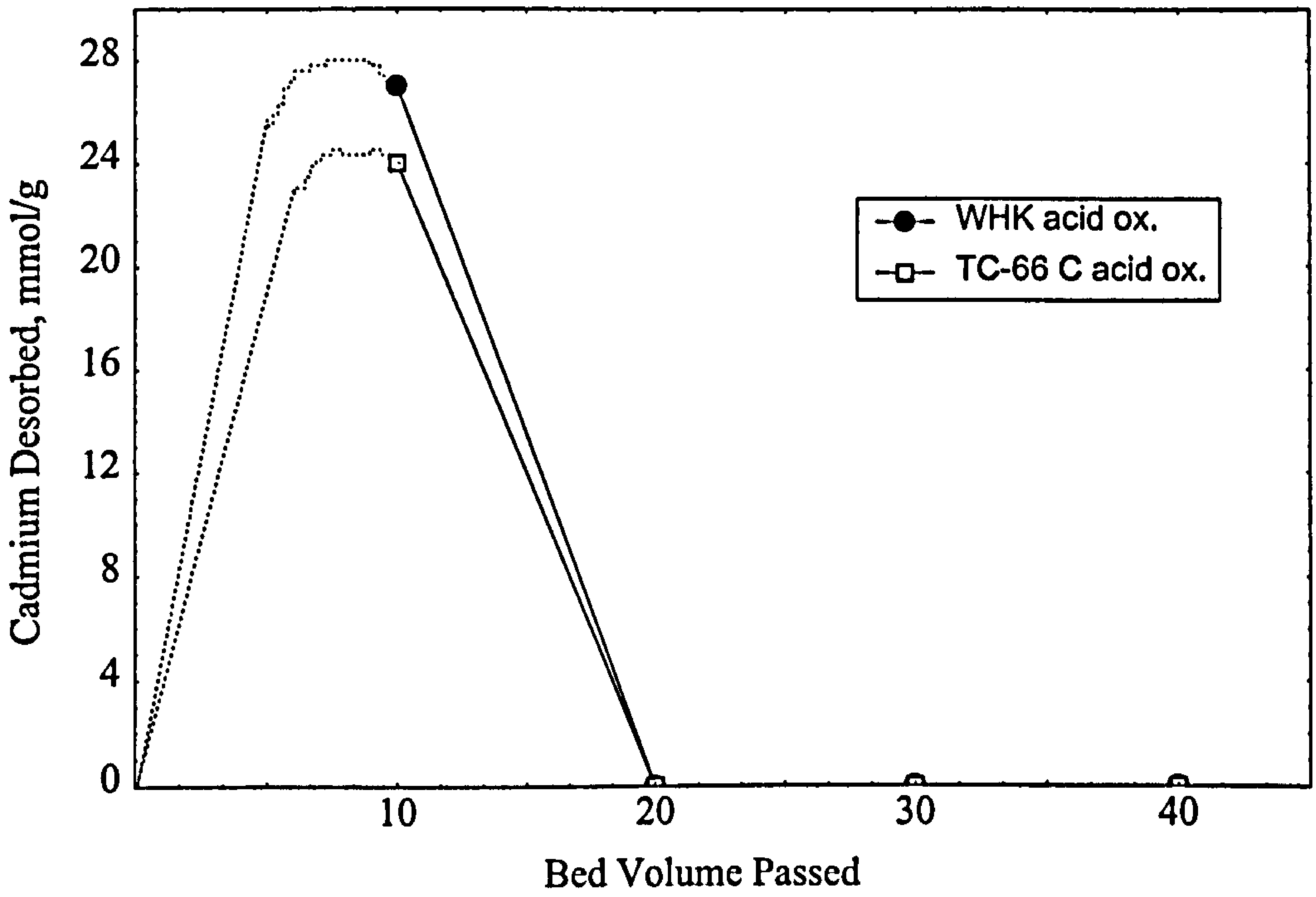


Fig 5.69. Cadmium elution profile for acid oxidised WHK and TC-66 C using 0.2 M HCl

A cadmium mass balance shows that 98.3 and 97.2 % was recovered after 20 BV (see Fig 5.69) from carbon fibre TC-66 C and granular carbon WHK, respectively. The small percentage of residual metal could be due to strongly bound cadmium complexes with oxygenated surface groups. Tai et al.[61] also concluded that metal uptake by activated carbons involves both ion exchange and the formation of strong complexes with oxygen-containing surface functional groups. Reed and Arunachalam[62] have mentioned that metal sorption by activated carbons may be related to speciation in solution and to the physico-chemical properties of the carbon surface. These authors concluded that sorption involves different mechanisms, e.g., surface or pore precipitation, and in some cases this can dominate the mechanism.

Elution of mercury from electrochemically modified carbons was also investigated. Mercury was desorbed using different concentrations of HCl and NaCl at 10 BV h^{-1}.

These two regenerants were selected bearing in mind that Cl^{-1} ions form strong complexes with Hg^+. The sorption/desorption reaction was carried out in acidic conditions when the adsorbent was in H-form and regenerated with HCl, or at near-neutral pH when the adsorbent used was in Na-form and regenerated with NaCl. This enabled the effect of pH on metal elution to be studed.

A mass balance for mercury shows that the maximum metal recovered, using 0.2M NaCl, after 100 BV was 44%. Most of the metal eluted, 92.6 % of the total mercury recovered, was obtained in the first 20 BV passed (see Fig 5.70).

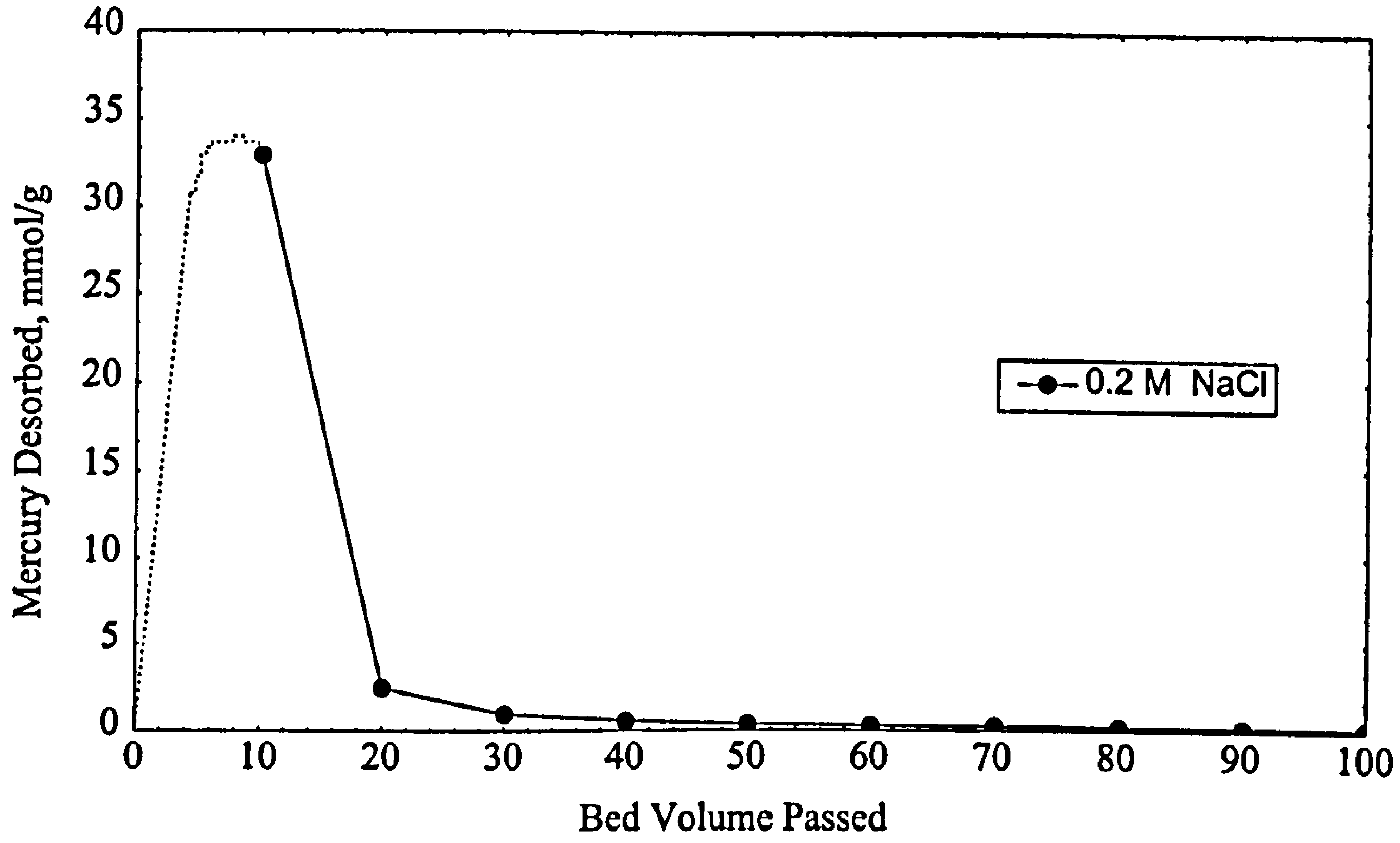


Fig 5.70. Mercury elution profile for electrochemically oxidised WHK using 0.2 M NaCl

A more concentrated regenerant, 0.5 M NaCl, was used to increase the desorption of mercury. However, the results plotted in Fig 5.71 show the same trend as those obtained at 0.2 M NaCl. The maximum mercury eluted after 100 BV was 47 %. The poor elution of mercury, even using concentrated regenerants, suggests that mercury uptake is not a simple adsorption or ion exchange process.

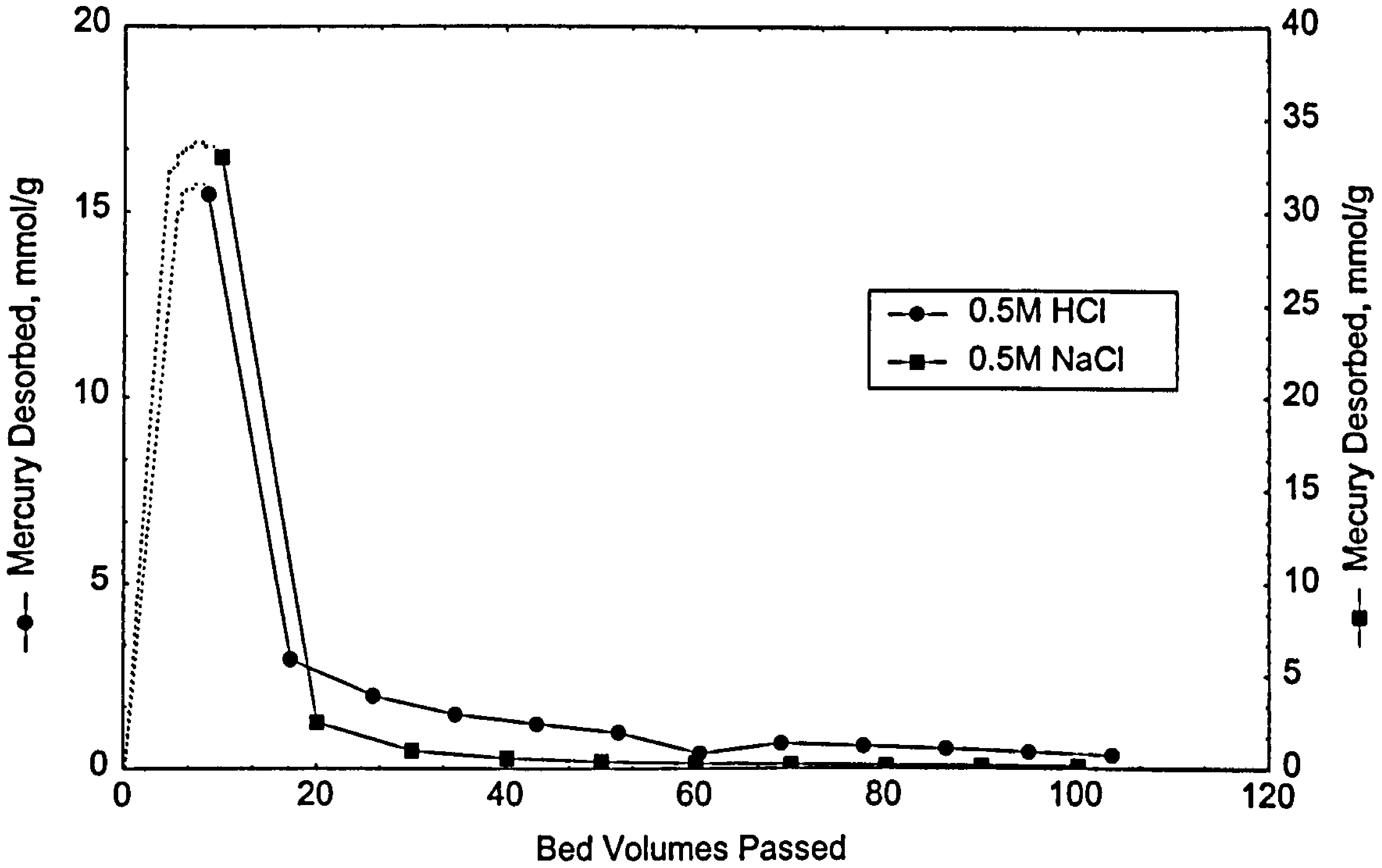


Fig 5.71. Mercury elution profile for electrochemically oxidised WHK

The elution of mercury was also studied with 0.5 M HCl, which was conducted at about pH 1.5. The results are plotted in Fig 5.71. It seems as if the carbon is regenerated more slowly with HCl than with NaCl. However, 86.1 % of mercury was recovered after 100 BV. This suggests that the desorption of mercury is easier under acidic conditions; where H^+ ions replace Hg^+ by ion exchange.

Namasivayan and Kadirvelu[63] studied the desorption of Hg(II) using 0.5 M hydrochloric acid and 2 % potassium iodide solution. These researchers found that the maximum mercury recovery was 63 and 84 % using HCl and KI, respectively. Anirudhan and Sreedhar[64] have carried out similar work using a coconut husk based carbon. In this research 1 M HCl was used to regenerate the adsorbent saturated with mercury. The maximum mercury desorbed was 95%.

The results reported in this section have shown that the elution of mercury is more efficient under acidic conditions. This may be due to the fact that a mixture of neutral, positive and negative mercury species are present at acidic pH, 2- 4 (see Fig 5.57). Therefore, adsorption and chemical reaction, followed by precipitation, can occur simultaneously. On the other hand, mercury sorption/desorption in sodium form was conducted at neutral pH, i.e. around 7. Under these conditions, mercury is mainly present as a neutral species, $Hg(OH)_2(aq)$ and $HgCl_2(aq.)$, which means that chemical reaction, e.g. reduction, is most likely to occur. Hence, mercury elution under these conditions is clearly lower than compared to that under acidic conditions.

The adsorption/desorption of mixed cadmium-mercury using electrochemically oxidised granular carbon WHK was also studied. A solution of 0.2M HCl was used as a regenerant. The elution profiles presented in Fig 5.72 show that cadmium was almost completely eluted after 20 BV, indicating that the adsorption/desorption process is predominantly due to an ion exchange mechanism. In contrast, only a small percentage of mercury is desorbed indicating that mercury is more tightly bound. It has been mentioned (section 5.3.2) that mercury removal can occur by reduction, forming an insoluble precipitate [$Hg_2Cl_2(s)$], and thus mercury uptake is only partially reversible.

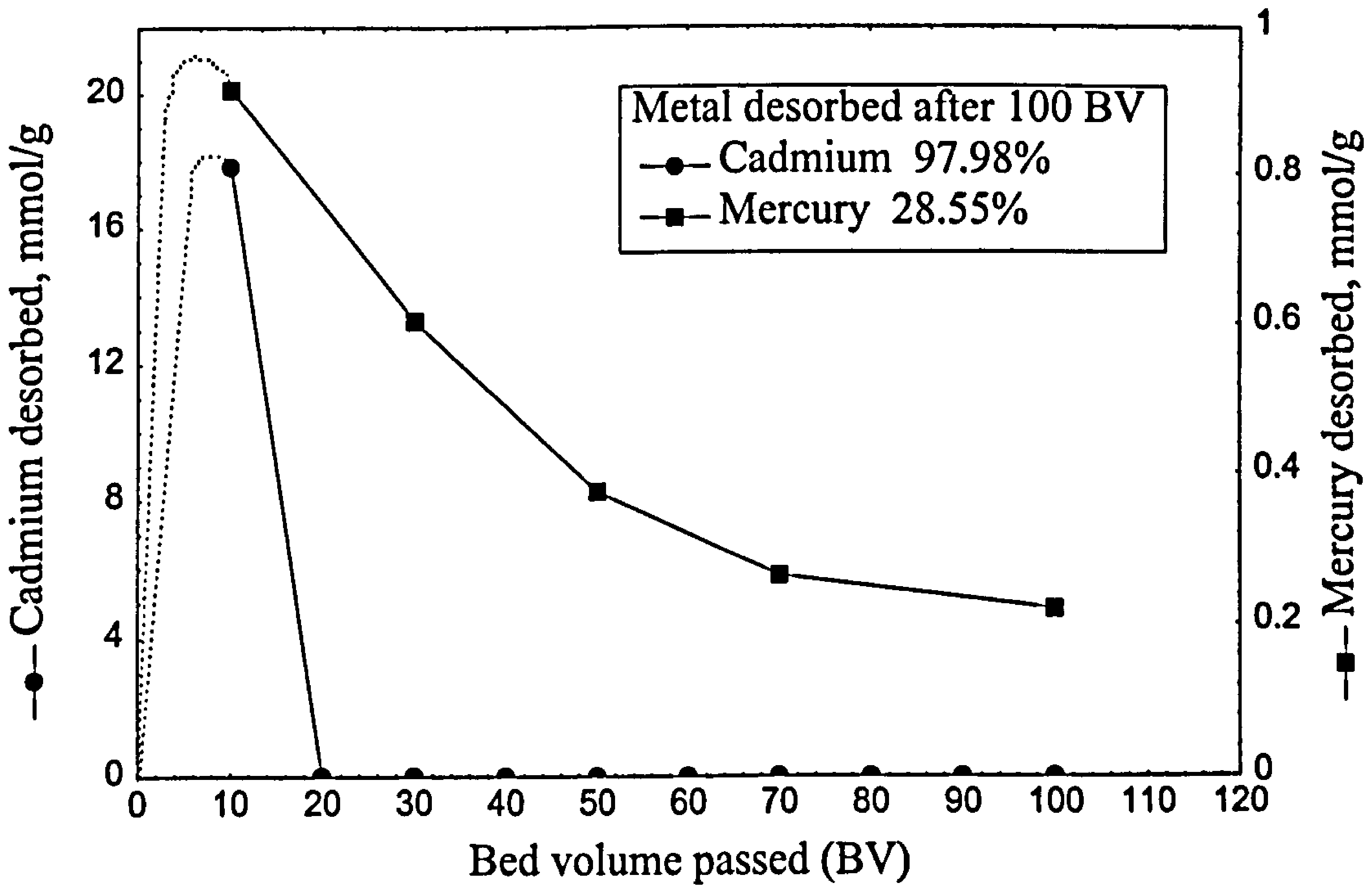


Fig 5.72. Cadmium and mercury elution profile for electrochemically oxidised WHK using 0.2M HCl as regenerant

5.5 Kinetic Experiments

Sorption rate is a crucial factor that has to be taken into consideration when a sorption process is designed. The micro-pollutant transport mechanism is more complicated when porous materials are used as adsorbents. The mechanism usually proceeds in three consecutive steps[65],

i). Transport of solute from the bulk solution to the outer surface of the film surrounding the particle (bulk transport).

ii). Transport of solute within the film (film transport).

iii). Transport in the interior of the particle (intraparticle transport).

This can also be represented in schematic form (see Fig 5.73).

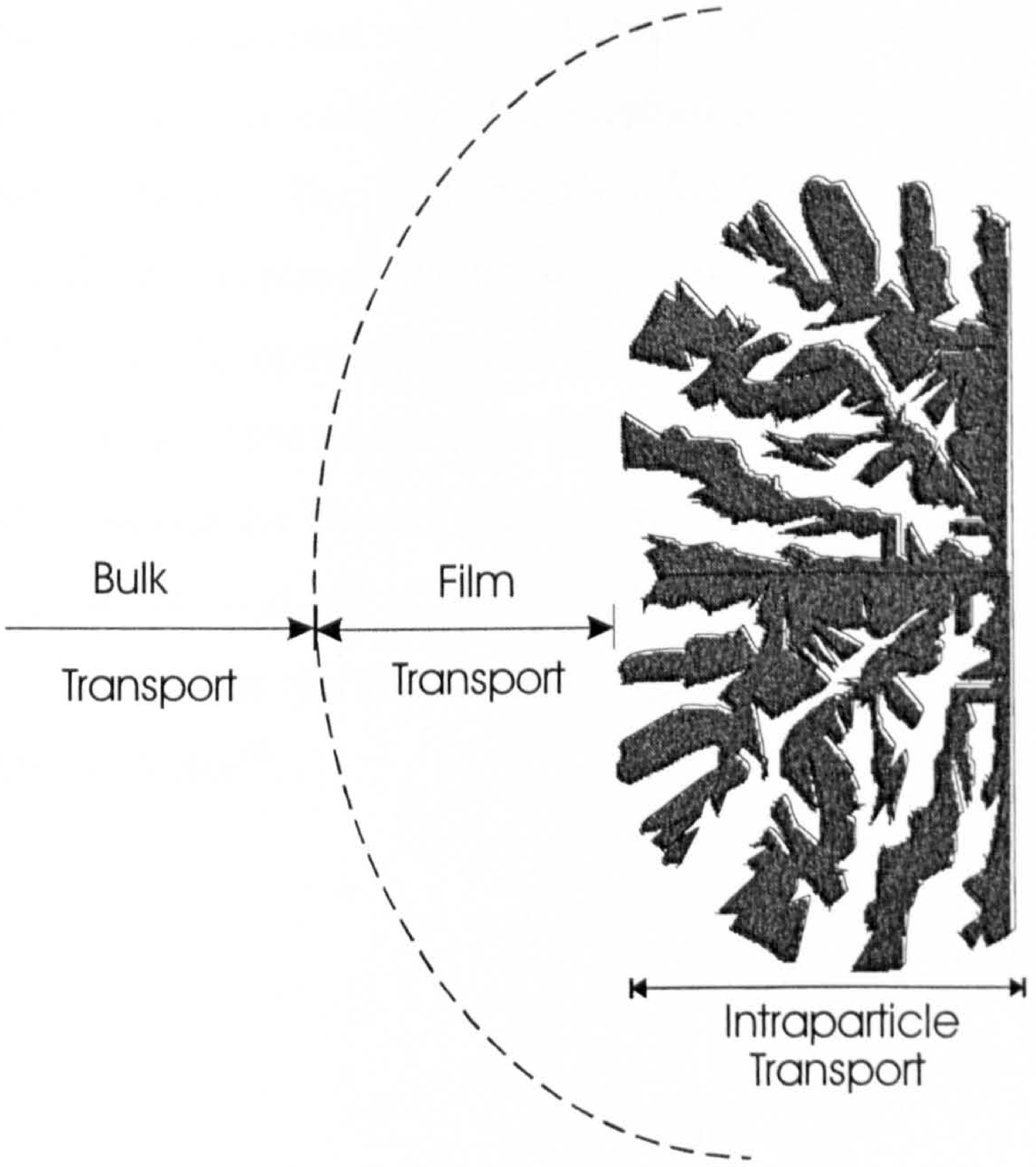


Fig 5.73. Schematic representation of the series of resistance to adsorption

Many researchers are interested in the theoretical prediction of sorption rate and the controlling transport mechanisms. Mathematical models that simulate sorption rate in porous media have, therefore, been extensively developed. Tien[65] has included several of these models in his textbook. Helfferich[66] has reported several mathematical expressions to determine sorption rate and calculate the diffusion coefficients in ion exchangers. Slater[67] has also recently published a useful monograph that discuses the sorption rate in ion exchangers.

Many factors must be taken into account when kinetic experiments are performed. Firstly, experiments have to be conducted using the appropriate equipment in order to obtain realistic results. Secondly, the solution pH should be controlled and the adsorbent particles should not fracture or crack during the experiment. Moreover, uniform particle size and preferably spherical particles are recommended when diffusion coefficients are to be computed.

Kinetic experiments for cadmium were conducted using conventional and modified granular and fibrous activated carbons. The sorption rate of cadmium was measured by two different methods. The first involved batch experiments using granular carbons. The adsorbent was placed into a rotating basket "centrifugal stirrer" made of Perspex and plastic mesh, opening 50μm, (see Fig 5.74). The centrifugal force presses the particles against the walls of the cage when the basket rotates. Solution is forced out radially through the layer of particles and fresh solution is sucked in at the centre through the bottom and top of the basket. Hence, a rapid circulating flow of solution passes through the particles. This system is often referred to as the Kitchener-Kressman reactor[68].

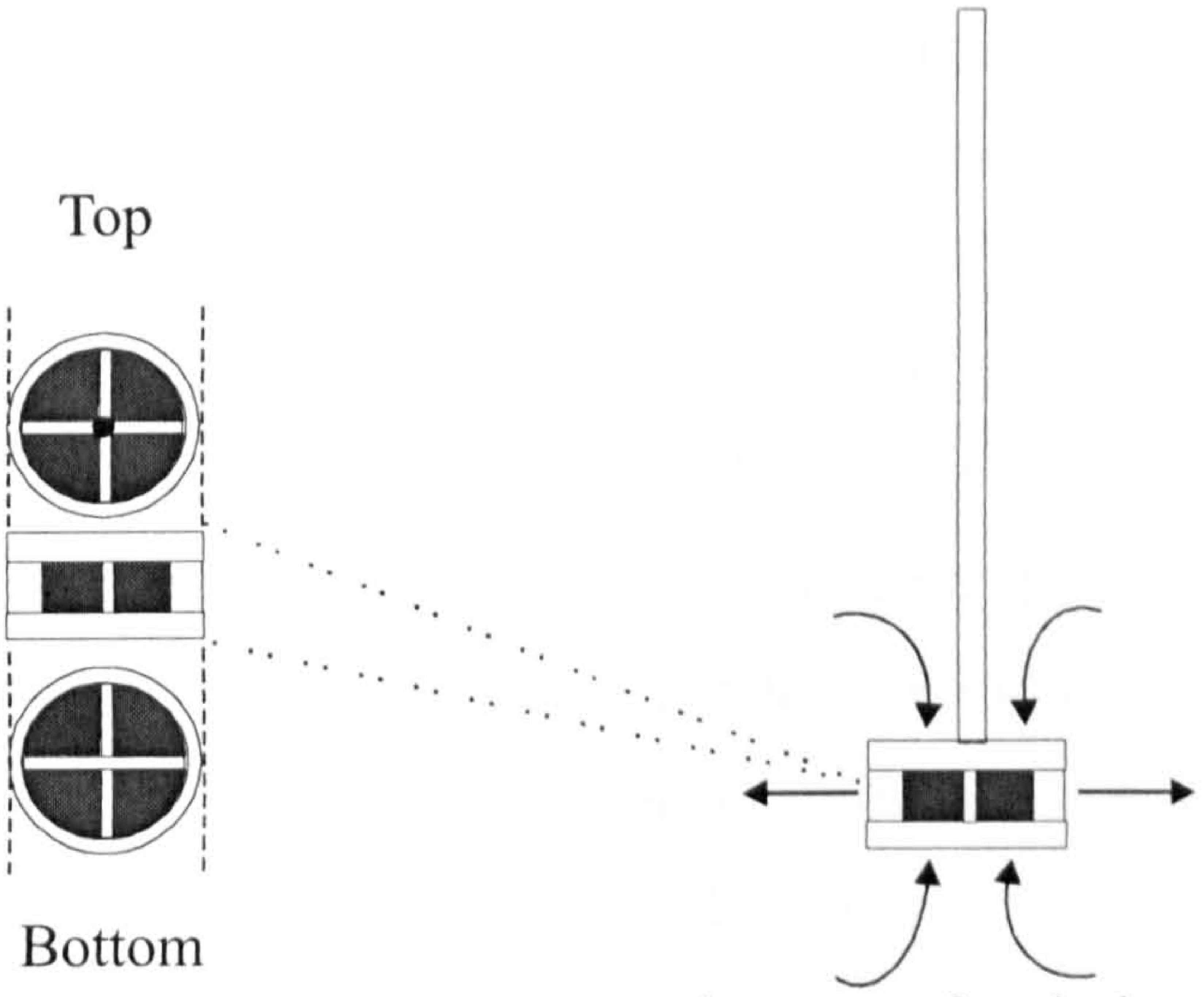


Fig 5.74. Stirrer used to determined the sorption rate of cadmium using as-received and modified granular carbon WHK

The centrifugal stirrer was also tested using activated carbon fibre. However, the cloth type structure of this carbonaceous material is not suitable for this kind of stirrer device since the fibres tend to agglomerate. Hence, an alternative shallow bed[66] method was used (see Fig 5.75). In this case a rapid stream of solution is passed through a layer of ion exchange particles or other sorbtive material, e.g. fibrous type. This method was used to study the kinetics of cadmium sorption using conventional and oxidised carbon fibre TC-66 C.

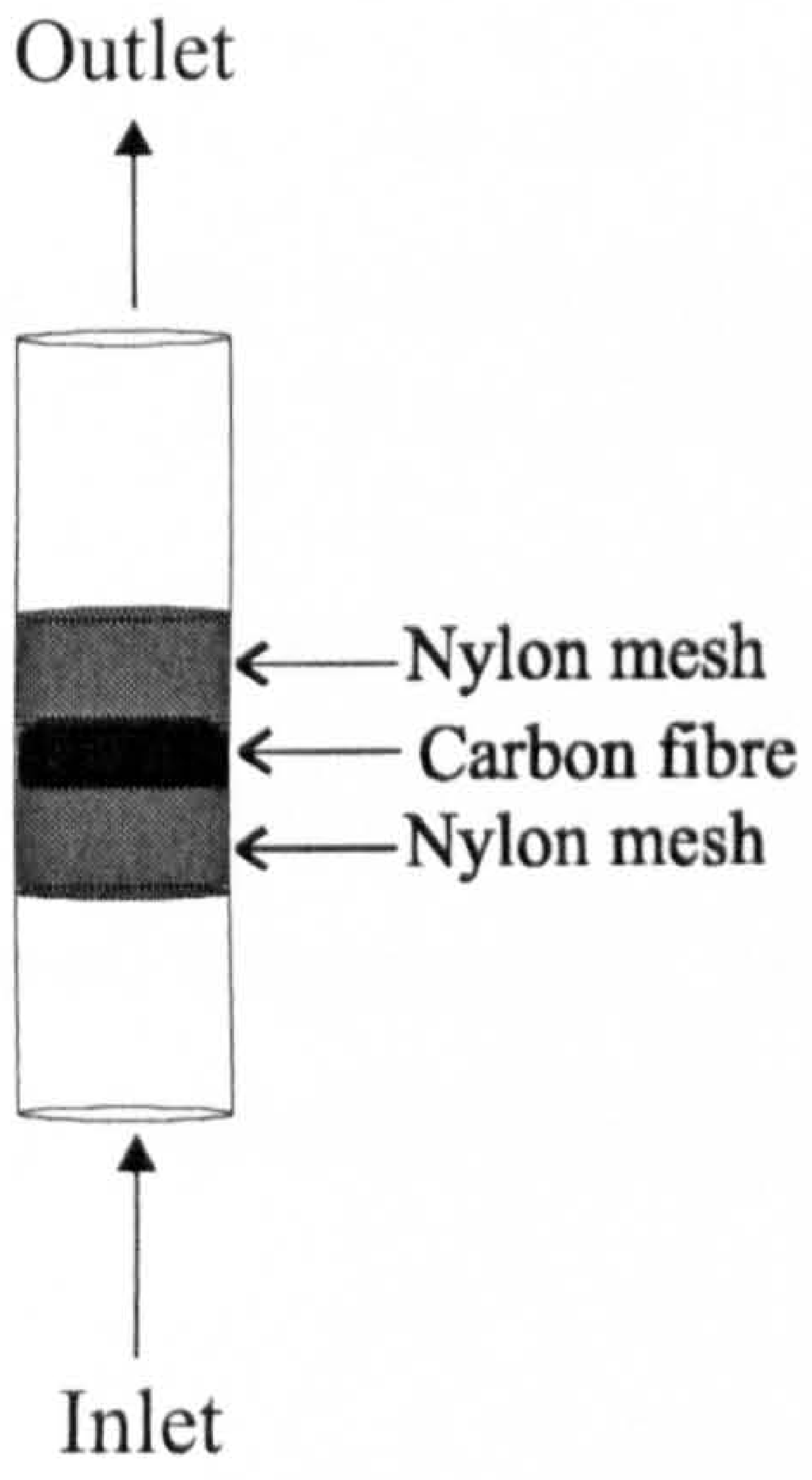


Fig 5.75. Column used to study cadmium sorption rate using activated carbon fibre, TC-66 C

It is surprising that many researchers have carried out kinetic studies using a very simple technique. For instance, adding the adsorbent particles to the solution in a reactor, stirring with an impeller and taking samples at different intervals of time is completely inappropriate for kinetic studies. In order to corroborate data, two experiments were carried out using as-received granular carbon WHK at the same conditions, but using a centrifugal stirrer and an impeller. The results are reported in Fig 5.76. It is clear that the sorption rate is much higher when the centrifugal stirrer was used. Approximately 58% of the fractional approach to equilibrium was attained in the first 2 minutes whereas only 12% was obtained using an impeller.

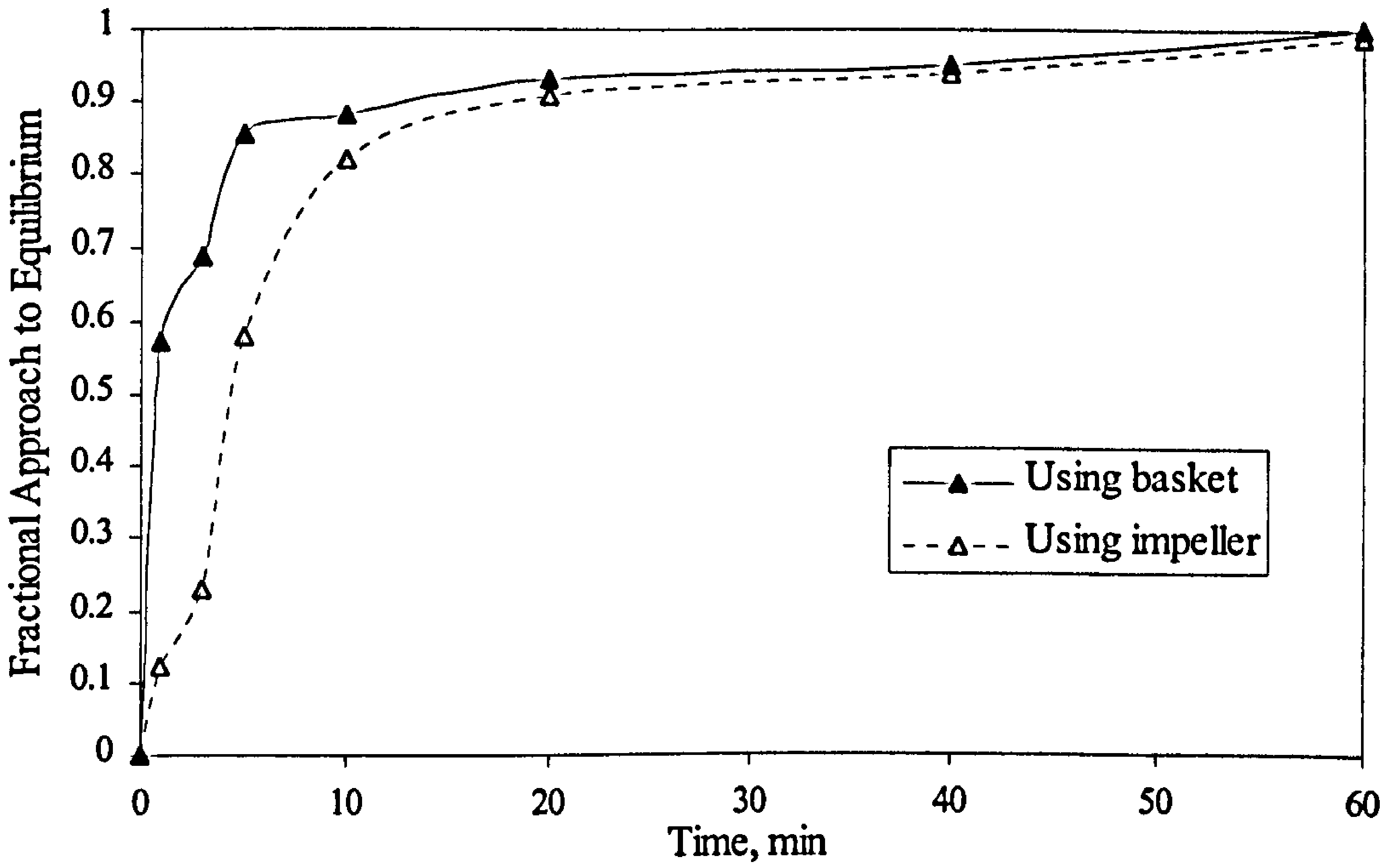


Fig 5.76. Comparison between using a centrifugal stirrer and an impeller in the cadmium sorption rate at 250 min^{-1}, 25 °C and 10 mg L^{-1} initial concentration

The significant difference in sorption rate may be due to the fact that an impeller moves particles within the flow field of the solution, therefore, film transport contributes significantly to the total sorption rate. Alternatively, mass transfer in the liquid film is much faster at high interstitial velocity through a bed of static particles in the rotating basket reactor.

Cadmium uptake rate was studied using three kinds of granular activated carbon, 207EA, 207C and WHK under the same experimental conditions. The kinetic curves presented in Fig 5.77 show that cadmium is removed much faster by WHK, followed by 207C and 207EA. Only 33% of the fractional approach to equilibrium was attained after a duration of 10 minutes for 207EA, whereas 70% and a maximum of 90% of the fraction uptake was presented by 207C and WHK, respectively. Leyva-Ramos et al.[69] have reported the intraparticle diffusion of cadmium in granular activated carbon F-400. The results reported by these researchers indicate that approximately 60% of the total cadmium uptake was achieved in an hour. Periasamy and Namasivayam[70] prepared an activated carbon from peanut hulls and cadmium uptake rate was studied. It was reported that about 50% of the total cadmium removed was accomplished in 10 min.

The difference in sorption rate can be directly related to porosity, external mass transfer and intraparticle diffusion [71,72]. It has been mentioned in the literature that metal sorption occurs in two stages. The first stage involves fast sorption in macropores and large mesopores (approximately 70 to 90% of metal ions are removed) where the controlling step is film diffusion. The second stage is slow and may require several days to reach equilibrium, since sorption occurs in micropores where intraparticle diffusion is the controlling step[73,74,75]. These two steps have been explained on the basis of the electrochemical theory of Frumkin. Fast initial kinetics are attributed to the exchange of metal ions with protons in the electrical double layer of the carbon, and the slow sorption process is due to chemical interactions between functional surface groups and metal ions. Different researchers[76] have related the sorption rate to an inhomogeneous carbon surface that contains a variety of functional surface groups. These active sites may vary with respect to the strength metal sorptive bond and sorption rate.

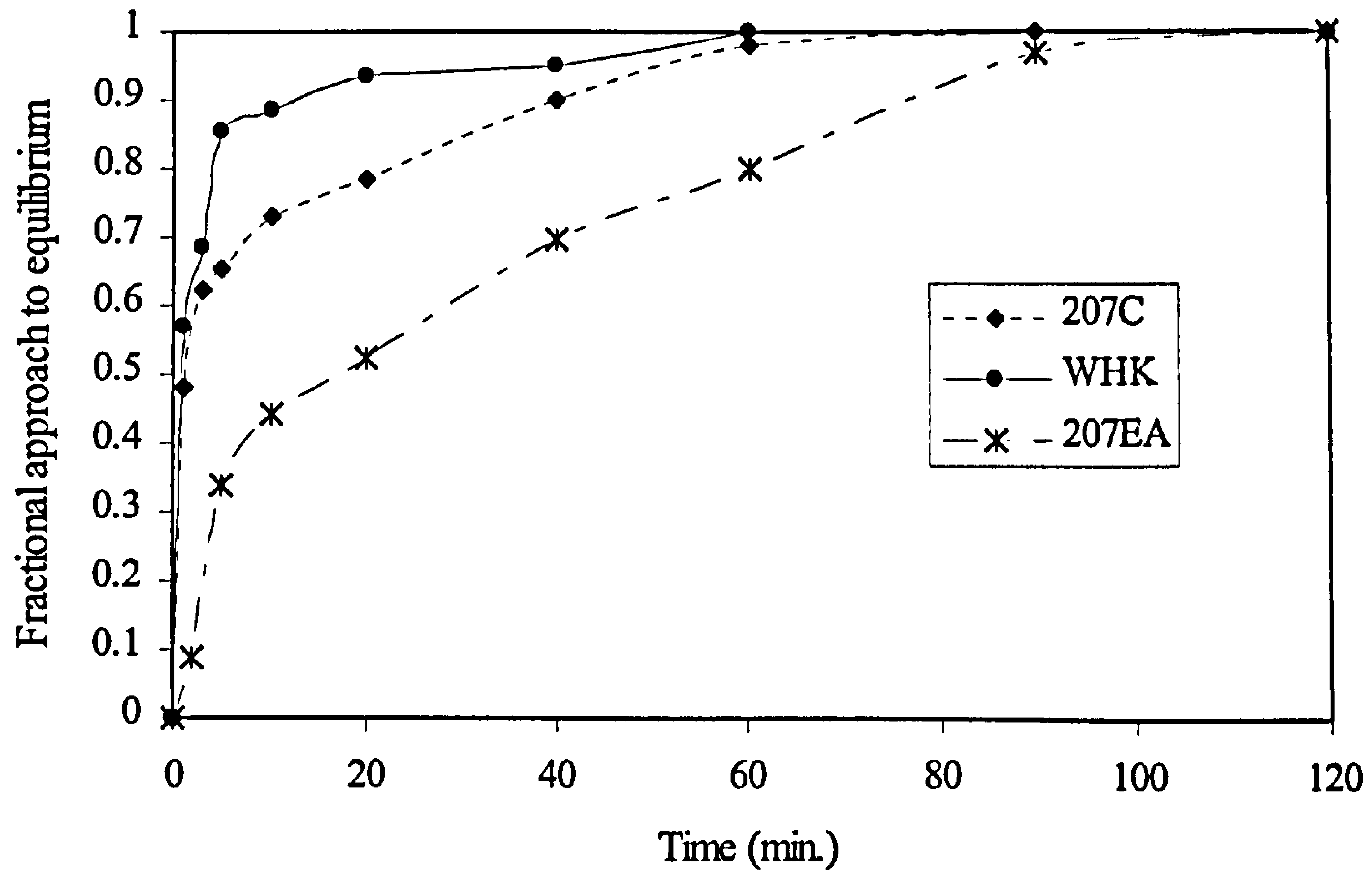


Fig 5.77. Cadmium sorption rate for different carbons at 250 rpm, 25 °C and 10 mg L^{-1} initial concentration

The effect of stirrer speed on cadmium uptake rate was also investigated using granular carbon. The kinetic curves obtained at various stirring speeds are presented in Fig 5.78. Increased stirring results in 64, 77 and 85 % of the fractional approach to equilibrium in 150, 200 and 250 min^{-1}, respectively, after a duration of 5 minutes. Similar experiments were conducted using carbon fibre TC-66 C, but applying the shallow bed method. In this case, the cadmium sorption rate was determined by flow rate through the carbon fibre bed. Fig 5.79 shows the kinetic curves generated by these experiments. A marked increase in metal uptake rate of 36% was observed when the flow rate was increased from 0.5 to 3.4 ml s^{-1}.

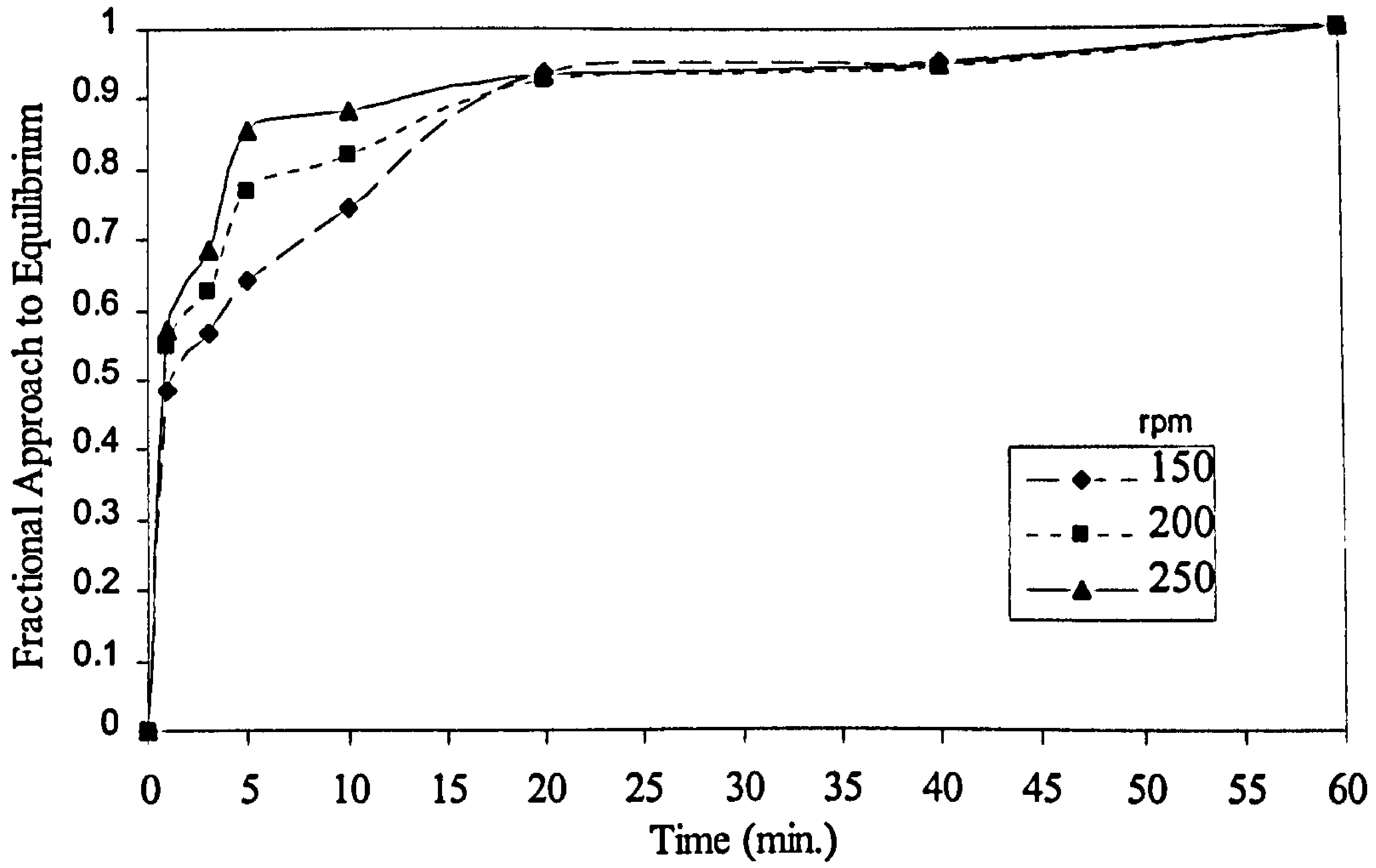


Fig 5.78. Influence of stirring rate in the cadmium sorption rate using granular carbon WHK at 25 °C and 10 mg L^{-1}initial concentration

The results presented above show that sorption rate increases as the flow rate passing through the adsorbent particles increases. This is because the liquid film thickness surrounding the sorbent beads or fibres decreases. Consequently, film diffusion is negligible and cadmium adsorption is controlled by intraparticle diffusion at stirring rate of 250 min^{-1} and above.

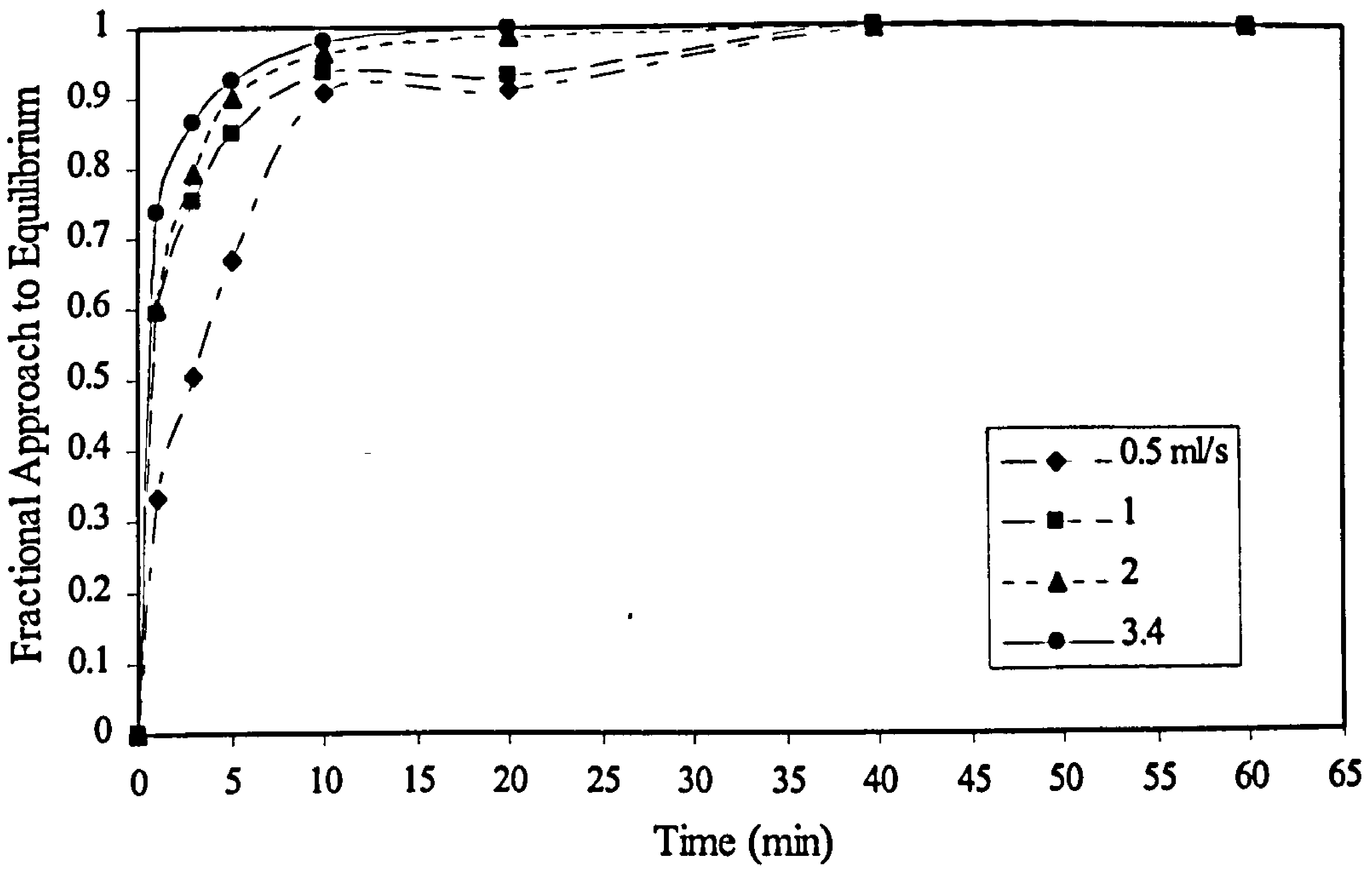


Fig 5.79. Influence of flow rate through carbon fibre TC-66 C in the cadmium sorption rate at 25 °C and 10 mg L^{-1}initial concentration

Kinetic properties where compared between granular carbon and carbon fibre by applying the Adam-Bohart-Thomas relation as represented by Brasquet et al.[77,78,79]. This mathematical expression has been applied to the sorption of organic compounds onto adsorbents and is represented as follows,

$$\frac{dq}{dt} = K_1 C(q_m - q) - K_2 q \qquad \textbf{Eq. 5.6}$$

Where:

q = Adsorption capacity(mg g^{-1})
C = Solution concentration(mg L^{-1})
K_1 = Adsorption kinetic constant(L mg^{-1} s^{-1})
K_2 = Desorption kinetic constant(s^{-1})
q_m = Maximal surface concentration(mg g^{-1})
t = Time (s)

When t→0, q→0 and $C \to C_o$. Then Eq. 5.6 can be rewritten as follows:

$$\left(\frac{dq}{dt}\right)_{t\to 0} = \left[\frac{d(C - C_o)}{dt}\right]_{t\to 0} \frac{V}{m} = K_1 C_o q_m \qquad \textbf{Eq. 5.7}$$

Where C_o represents the initial concentration (mg L^{-1}), V the solution volume (L) and m the adsorbent weight (g). It is then possible to calculate the *initial adsorption kinetic coefficient* "γ" represented as,

$$\gamma = -K_1 q_m = -\frac{V}{C_o m}\left(\frac{dC}{dt}\right)_{t\to 0} \qquad \textbf{Eq. 5.8}$$

The differential term $(dC/dt)_{t\to 0}$ was calculated using the concentration decay after one minute of the start of the experiment. The values of γ are calculated by the model described above and reported in Tables 5.18 and 5.19 for granular carbon WHK and carbon fibre TC-66 C, respectively.

Table 5.18. Initial adsorption kinetic coefficient of cadmium using as-received WHK

rpm	γ x10^4(L/mg min)
150	0.66
200	0.86
250	0.87

Table 5.19. Initial adsorption kinetic coefficients of cadmium using as-received TC-66 C

Flow rate (ml/s)	$\gamma \times 10^4$(L/mg min)
0.5	0.55
1.0	1.14
2.0	1.22
3.4	1.26

The kinetic coefficients γ for activated carbon fibre TC-66 C were approximately 1.4 times higher than those for granular activated carbon WHK. This may be due to the fact that micropores in carbon fibres are directly connected to the external surface (section 5.2.2). Therefore the mass transfer resistance and migration distances decrease. In contrast, the adsorbate has to diffuse first through the mesopores and macropores in granular carbons causing a decrease in sorption rate. Suzuki[80] has mentioned that adsorbates reach adsorption sites through micropores without the additional diffusion resistance of macropores, which is usually the rate-controlling step in granular adsorbents. Baudu et al.[81] have pointed out that the small diameter of carbon fibres results in a large external surface area exposed to the flowing fluid, hence, this fibrous material provides much faster adsorption kinetics compared with granular adsorbents. Brasquet and Le Cloirec[78] have reported initial adsorption kinetic coefficients, γ, for aromatic compounds, such as phenol and toluene. γ values were 5 to 10 times greater for carbon fibre compared with those obtained with granular carbon.

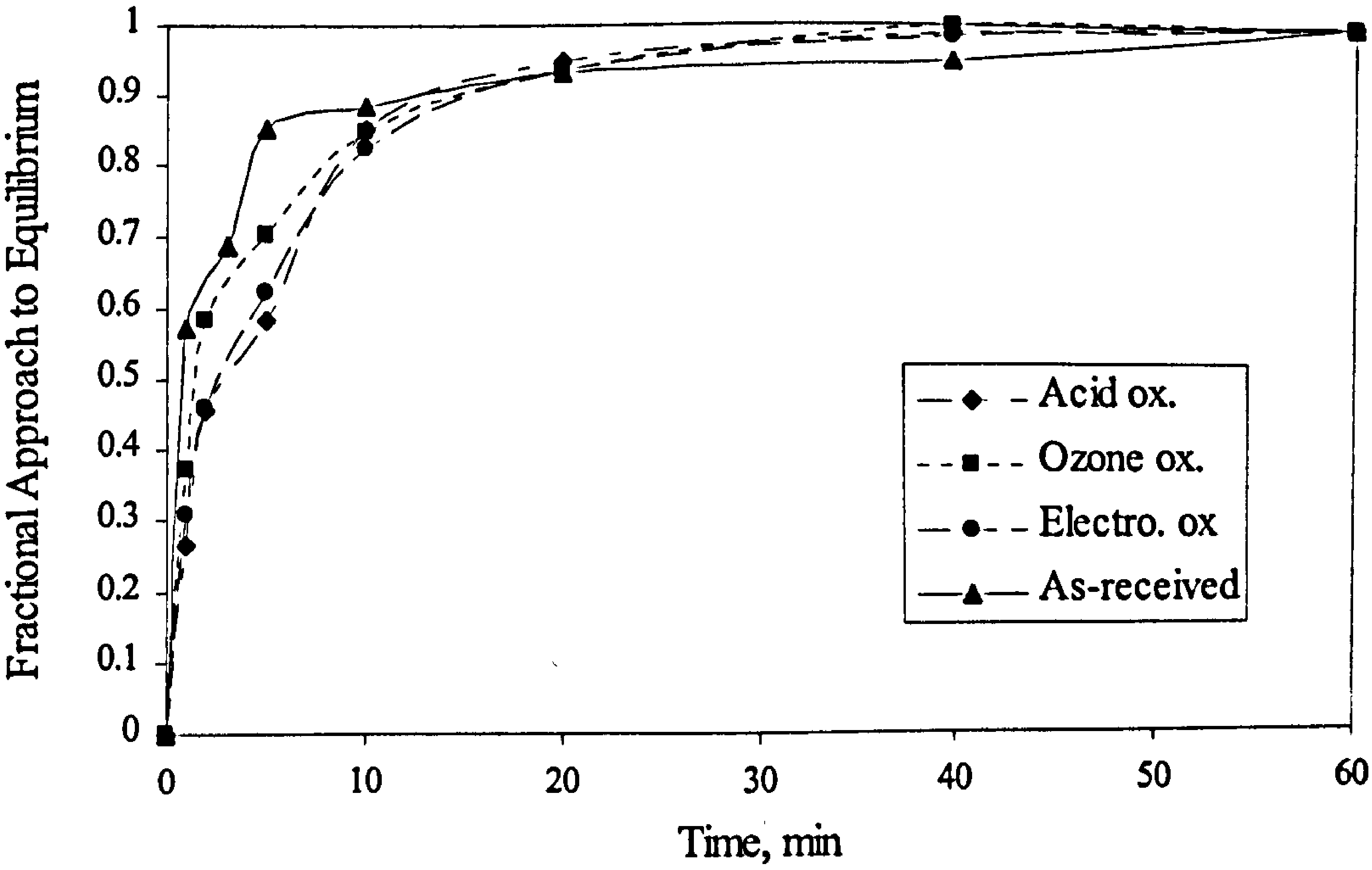


Fig 5.80. Cadmium sorption rate using oxidised WHK at 250 min^{-1} and 25 °C

Kinetic studies were also carried out using oxidised granular and fibrous activated carbons. The kinetic curves generated by modified granular carbon WHK (see Fig 5.80) showed that the sorption rate decreased compared to the as-received materials. This same behaviour was observed, Fig 5.81, for oxidised carbon fibre TC-66 C. Kinetic coefficients, γ, were computed and are reported in Table 5.20. γ decreased by a maximum of 46.5 and 37 % for TC-66 C and WHK, respectively. Values of γ showed that carbon fibre presented faster kinetics than granular carbon even after chemical modification.

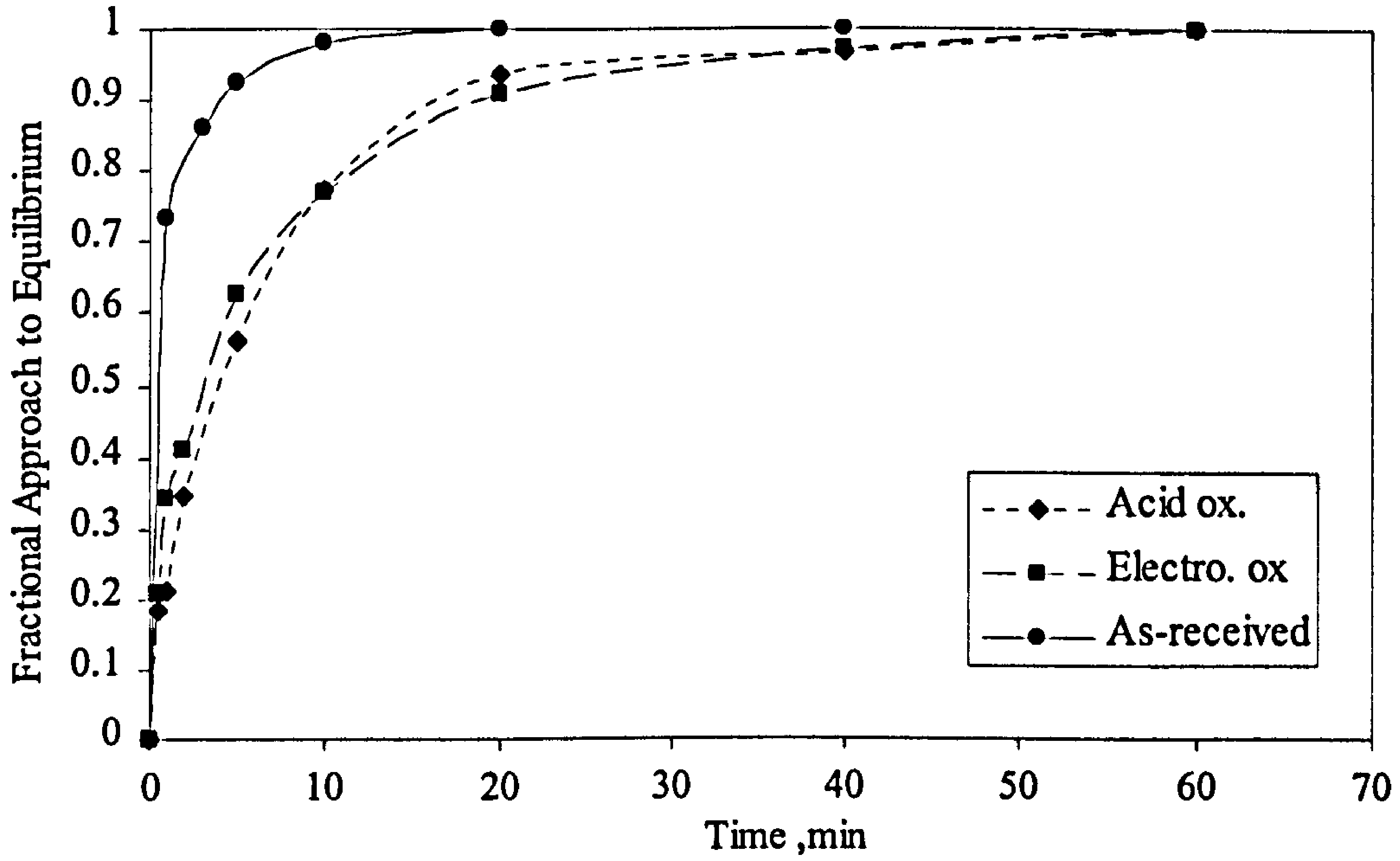


Fig 5.81. Cadmium sorption rate using oxidised TC-66 C at 3.4 ml s^{-1} and 25 °C

Table 5.20. Initial adsorption kinetic coefficient of cadmium using oxidised WHK and TC-66 C

Sample	γ x10^4(L/mg min)	
	TC-66 C	WHK
As-received	1.29	0.87
Acid ox.	0.86	0.63
Ozone ox.	-	0.55
Electro. Ox	0.69	0.60

The slower sorption rate of oxidised carbons may be attributed to a decrease in the intraparticle diffusivity of cadmium in the adsorbent pore volume due to erosion and blockage of the pores by degradation products produced during chemical reaction.

The Adam-Bohart-Thomas relation was applied in this research to compare the initial sorption rate for granular carbon and carbon fibre. However, this empirical equation is limited to some extent, since it does not take into account film and intraparticle diffusion. A comprehensive mathematical model still needs to be developed that takes diffusional parameters into account in order to determine the mechanism of sorption accurately for fibrous materials.

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Chapter 6:

CONCLUSIONS

6.1 Conclusions

Commercial granular and fibrous activated carbons have been successfully applied to the removal of heavy metals, e.g. cadmium and mercury, from aqueous solutions, however, their sorption capacity is rather limited. The ion exchange capacity of these conventional carbonaceous materials is higher for those materials with high surface area.

A significant increase in ion exchange capacity is obtained by oxidation and it increases with the extent of treatment. This is due to the introduction of oxygen-containing functional groups, such as carboxylic, lactonic, phenolic and carbonyl, as confirmed by direct titration, XPS and elemental analysis. The results also prove that the level of oxygen content follows the sequence: electrochemical>ozone>acid oxidation for carbon fibre TC-66 C and electrochemical>acid>ozone oxidation for granular carbon WHK.

The difference between PZC and IEP shows that commercial granular carbons have a more homogeneous surface charge distribution than modified materials. This is due to the introduction of oxygenated functional groups mainly on the external surface of the adsorbents. The PZC and IEP is shifted to lower pH values, as the degree of oxidation increases, due to the increase of acidic surface groups.

The sorption capacity of oxidised adsorbents for cadmium and mercury increases by a factor of approximately 16.5 and 10 (at pH 6), respectively, compared with conventional carbonaceous materials. This is directly related to the increase of oxygen-containing groups. Cadmium adsorption isotherms are best fitted by a Freundlich isotherm, whereas the Langmuir model gives a better fit to the equilibrium data for mercury sorption.

The removal of cadmium and mercury is pH dependent; it increases with increasing pH. This is due to the higher amount of dissociated functional groups available for adsorption and ion exchange as pH rises. At pH values above the PZC, surface charge becomes negative and therefore positively charged cadmium and mercury species can ion exchange and/or complex with the surface functional groups.

Carbon is more selective for cadmium than for mercury. This was found by breakthrough experiments. Mercury breakthrough occurs after about 70 BV of 1 mM cadmium and mercury feed solution, at pH 6, when passed through electrochemically oxidised WHK, whereas cadmium breakthrough occurs at 20 BV. Alternatively, cadmium adsorption is highly reversible, which indicates that the mechanism of cadmium adsorption/desorption is conventional adsorption and/or ion exchange. Mercury, on the other hand, is more tightly bound to the carbon surface and this suggests that the sorption mechanism is due not only to adsorption and ion exchange, but also to chemical reaction followed by precipitation. This has been confirmed by energy dispersive spectroscopy.

Kinetic coefficients, γ, show that carbon fibres present faster kinetics than granular carbons even after the samples are oxidised. This may be due to the fact that micropores in carbon fibres are directly connected to the external surface, therefore, mass transfer resistance and the migration distance decrease. The adsorbate has to diffuse through mesopores and macropores in granular carbons, thereby causing a decrease in sorption rate.

Some surface area is lost during oxidation due to erosion and blockage of the pores by degradation products produced during chemical reaction although this does not adversely affect cadmium and mercury sorption at the levels investigated. Moreover, adsorbents with a surface area of about 700 m^2 g^{-1} are perfectly applicable in water treatment. There is clear evidence of physical damage to ozone oxidise carbons, however, there is no change in surface morphology for acid and electrochemically oxidised samples.

The results obtained in this project indicate the considerable potential for oxidised carbonaceous adsorbents for large-scale removal of trace metal pollutants from water and aqueous effluents at neutral or near-neutral pH values.

It has been proven that oxidation of granular carbon and carbon fibre by ozone, nitric acid and electrochemical process significantly improves the sorption capacity for heavy metals. Therefore, these three methods are alternatives to the common practices for modifying carbonaceous materials. Results obtained from batch adsorption, kinetic experiments and mini-column studies would be useful to scale up the sorption process to pilot plant and even further to industrial scale. Activated carbon cloth is a new carbonaceous material and not much information of its application is available yet. The good sorption performance of carbon fibres, similar or better than granular carbons, found in this research make them suitable for its application in water treatment. The fast adsorption/desorption kinetics presented by as-received and oxidised granular and fibrous activated carbons make these carbonaceous materials an excellent alternative to remove and/or concentrate cations, i.e. toxic metals, from potable water and wastewater.

6.2 Recommendations for further work

The adsorption studies could be extended to investigate the removal of organic mercury, such as methyl mercury, since these species are also highly toxic and are often predominant in wastewaters.

The sorption mechanism of cadmium and mercury could be studied in more detail. For instance, the reactions involved in the removal of mercury; adsorption, reduction and precipitation, could be fully investigated.

The effect of particle size of adsorbent, in the case of granular carbons, concentration and temperature in kinetics could be investigated. Moreover, a mathematical model (including external and internal diffusivity) might be developed and applied to determine the rate controlling step in the sorption process.

Carbonaceous adsorbents could be chemically modified by using other methods, for instance, impregnation with sulphur, to enhance their sorption capacity without affecting surface area and porosity.

The mechanical strength of both granular and fibrous activated carbons, with different level of oxidation, could be studied. Mechanical properties of adsorbent materials are important when used in columns, filters, etc.

Finally, the electrochemical oxidation of carbonaceous materials could be optimised by varying current density. Moreover, the introduction of specific oxygen-containing groups by using different electrolytes and changing the experimental parameters could be explored.

APPENDIX A

List of publications and papers presented in congresses

I. **J. R. Rangel-Mendez**, M.H. Tai and M. Streat., (2000), "Removal of cadmium using electrochemically oxidized activated carbon". *Trans. IChemE 2000*; 78, part B: 143-148.

II. P. J. Lloyd Jones, **J. R. Rangel-Mendez** and M. Streat., (2001), "Sorption of cadmium using a natural biosorbent and activated carbon", To be published in *Trans. IchemE.*

III. **J. R. Rangel-Mendez** and M. Streat., (2001), "Adsorption of cadmium by activated carbon cloth: influence of surface oxidation and solution pH", Accepted for publication in *Water Research.*

IV. **J. R. Rangel-Mendez** and M. Streat. "Sorption of cadmium on modified and conventional granular and fibrous activated carbon", 12/07/1999, *Carbon*, Charleston, USA.

V. **J. R. Rangel-Mendez** and M. Streat. "Cadmium sorption from aqueous solutions: enhancement of surface groups on activated carbon cloth by nitric acid, ozone and electrochemical oxidation", 14/07/2000, *Carbon*, Berlin, Germany.

VI. **J. R. Rangel-Mendez** and M. Streat. "Mercury and cadmium adsorption by conventional and modified granular activated carbon", 14/07/2001, *Carbon*, Lexington, Kentucky, USA.

VII. **J. R. Rangel-Mendez** and M. Streat. "Removal of cadmium using electrochemically oxidised activated carbon", 06/01/2000, *IchemE*, University of Bath, England.

PUBLICATIONS

IChem^E

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REMOVAL OF CADMIUM USING ELECTROCHEMICALLY OXIDIZED ACTIVATED CARBON

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A wood-based activated carbon, AUG WHK, was oxidized electrochemically to enhance its metal binding capacity and subsequently studied for the removal of cadmium ions from aqueous solution. Treated adsorbents were characterized by N_2 adsorption at 77 K before and after oxidation, and a quantitative determination of weak-acid surface groups was carried out by direct titration. The BET surface area decreased considerably after oxidation; however, the total amount of oxygen-containing surface groups was 3.36 times higher compared to the untreated adsorbent. Batch equilibrium tests indicated that the oxidized material has 16.5 times higher sorption capacity for cadmium than conventional activated carbon. Equilibrium isotherms were determined at pH 4, 5 and 6 and showed that there was a slight increase in cadmium uptake with increase in pH. The experimental data were fitted by Langmuir and Freundlich isotherms and it was found that the Freundlich isotherm fitted better in all the cases. Overall, the results indicated a rapid adsorption rate with over 96% fractional uptake of metal occurring in the first 12 minutes.

Small-scale mini-column experiments were performed and indicated that breakthrough occurred after about 140 bed volumes (BV) of feed solution, containing 1 mM Cd at pH 6, was passed at 10 BV h^{-1} for oxidized WHK, whereas breakthrough was instantaneous for the unoxidized sample.

Keywords: sorption; cadmium; adsorption; breakthrough; pH; kinetics.

INTRODUCTION

The presence of heavy metals in effluents is a matter of primary environmental concern due to toxicity. Cadmium is one of the most toxic elements, which can seriously affect human health. Dispersion of cadmium into the environment results from industrial processes, domestic activities, agricultural practices (use of fertilizers), use of cadmium-containing goods, and disposal of wastes.

Adsorption has been widely applied for the removal of trace contaminants from potable water, domestic water and industrial effluents. Sorption of heavy metals on activated carbon is not a simple process because it depends on several factors such as metal speciation, water chemistry and chemistry of the carbon surface. Activated carbons are extensively used in wastewater treatment for the removal of a wide range of contaminants. They offer extensive surface area for sorption of metal ions from aqueous solutions and have been investigated for treatment of solutions bearing inorganic species. By far the most extensively developed large-scale application of activated carbon is the recovery of gold from dilute cyanide leach solutions. A detailed study of this process is reported by Bailey[1]. The metal binding ability of conventional activated carbon is very limited. However, this can be significantly enhanced by chemical modification. These modifications can be carried out by addition of oxygen, nitrogen, sulphur and phosphorus onto the surface of the original precursor. Oxidation is commonly used to increase the number of weakly acidic groups on the carbon surface, e.g. carboxylic, carbonic, phenolic and lactonic. Hence, metal ions can interact directly with these mainly oxygen-containing groups and are thereby removed from solution. The groups added during the oxidation affect acidity, porosity and the adsorption performance of modified carbons[2].

Oxidation has been carried out mostly by using air at high temperature or nitric acid solutions[3]. Other oxidants such as ozone and hydrogen peroxide have also been used[4]. Electrochemical oxidation of carbon fibres has been carried out mainly to increase tensile strength as well as improving metal binding capacity[5]. However, only a limited amount of work has been carried out on electrochemical oxidation of granular activated carbons.

Some preliminary studies of the adsorption and kinetics of cadmium uptake on conventional and modified granular activated carbon are reported in this work.

EXPERIMENTAL

Materials

Granular activated carbon, designated WHK, was supplied by AUG, Germany. This material was sieved to a particle size fraction of 170–210 μm, washed carefully with distilled water and then dried in an oven at 378 K until no change in weight was observed. Cadmium solution was prepared using $CdCl_2 \cdot H_2O$ laboratory grade purchased from May & Baker Ltd, Dagenham, England. Sodium hydroxide, nitric acid, hydrochloric acid and potassium chloride were prepared from analytical reagents supplied by Fisher, UK. Sodium hydrogen carbonate and sodium ethoxide solutions were prepared from analytical reagents purchased from Aldrich Chemicals, USA. Volumetric standard solutions of sodium hydroxide and sodium carbonate, and HPLC grade ethanol were supplied by Aldrich Chemicals, USA.

Electrochemical Oxidation

The electrochemical oxidation of granular activated carbon was carried out by applying a current of 3 mA m^{-2} for 3 hours in the presence of 0.5 M KCl as electrolyte. The current applied during the oxidation and the duration of the process were chosen on the basis of the studies conducted by several researchers in recent years[5-7]. Current is normally applied in the range 0.01–3 mA m^{-2} for different periods of time depending on sample characteristics, such as surface area and conductivity. In this study, the BET surface area was taken into account to determine the total current applied during the oxidation.

Several batches of granular activated carbon were oxidized under the same conditions and then thoroughly mixed to obtain only one sample. The procedure was as follows: 0.3 g of granular activated carbon was placed into a plastic column and contacted with electrolyte for 1 hour prior to the start of the experiment. The experimental rig can be seen in Figure 1. The bed depth of granular carbon inside the column was approximately 2 mm, which reduces the possibility of inhomogeneous oxidation. During the experiment the temperature was maintained between 293 and 295 K. In order to maintain the temperature within this range, the electrolyte was recirculated through a convoluted pipe, which was in contact with water at 278 K. In order to remove humic substances produced during oxidation, the adsorbent was washed in a column with 0.1 M sodium hydroxide solution until the outlet solution was colourless. This was followed by washing with 0.1 M hydrochloric acid solution. The carbon was then washed with distilled water until the solution pH in the column inlet and outlet was identical. Finally, the adsorbent was dried in an oven at 378 K for 24 hours. The drying of activated carbon was continued until no change in the weight was observed.

Characterization

Surface area was obtained by nitrogen adsorption and desorption at 77 K using a Micromeritics ASAP2010 automatic surface area analyser. The samples were outgassed for 24 hours at 378 K.

Direct Titration

In order to determine the amount and type of oxygen-containing groups[8], samples of conventional and oxidized granular activated carbon WHK were contacted with 0.1 M solutions of NaOH, $NaCO_3$, $NaHCO_3$ and $NaOC_2H_5$ (dissolved in HPLC grade ethanol). Approximately 0.1 g of adsorbent was placed in a 50 ml conical flask and then contacted with 20 ml of each alkali solution. The flask was sealed and stirred using an orbital shaker at 300 oscillations/min for seven days. The solution was filtered using a 0.2 μm PTFE syringe top filter to remove adsorbent particles. Finally a 5 ml aliquot was titrated with 0.1 M volumetric standard solution of HCl using methyl red as indicator.

Batch Sorption Experiments

A pre-determined amount of granular activated carbon was added to 50 ml of cadmium solution, of known initial concentration and pH, in a 100 ml conical flask and agitated by an orbital shaker. The cadmium solution pH was adjusted regularly by addition of 0.1 M HNO_3 or 0.1 M NaOH until a constant pH was attained. The equilibrated samples were filtered using a 0.2 μm PTFE syringe top filter to remove the adsorbent particles and then analysed for cadmium concentration.

Mini-column Experiments

Small plastic columns of 3 ml were packed with 0.5 g of unoxidized or oxidized granular activated carbon. Approximately 1 mM feed cadmium solution of pH 6 was passed through the columns, at 10 BV h^{-1}, to obtain the breakthrough curves. The samples were collected automatically by a fraction-collector and each test tube collected solution for 50 minutes. Samples were analysed for cadmium concentration and pH.

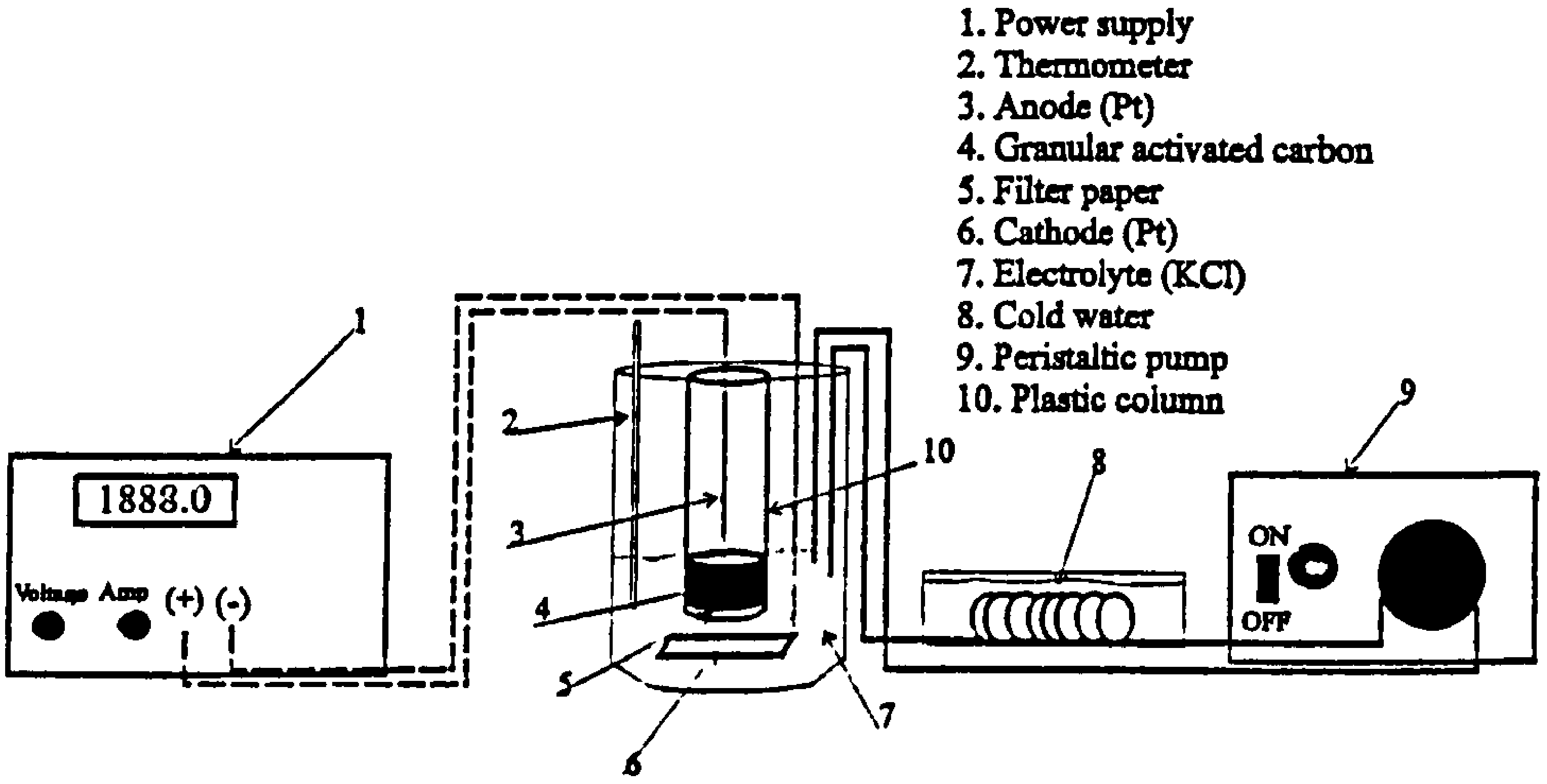

Figure 1. Equipment used in electrochemical oxidation of granular activated carbon.

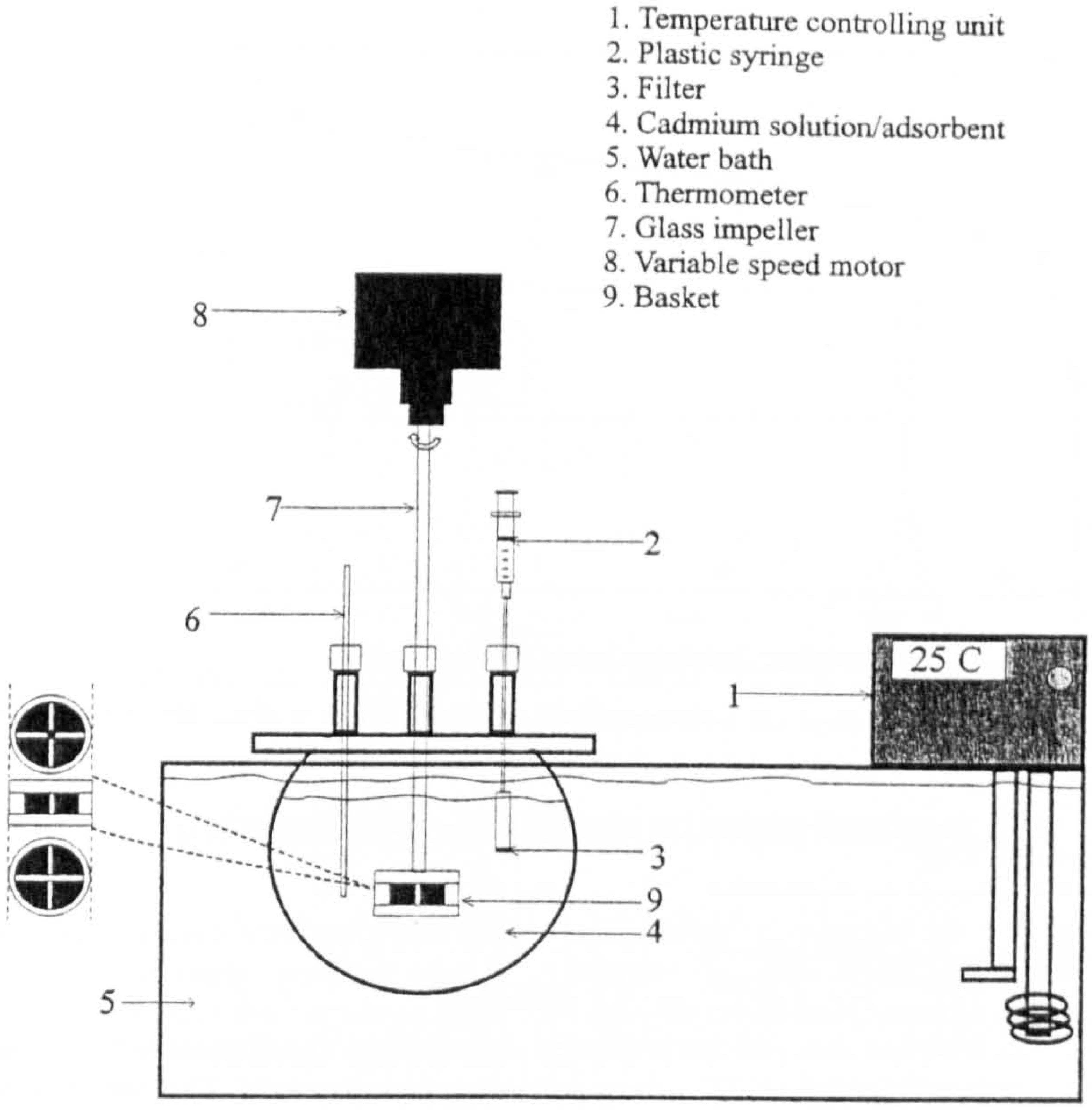

Figure 2. Equipment used in kinetic experiments.

Kinetic Experiments

Kinetic experiments were conducted in the rig shown in Figure 2. 1990 ml of distilled water was added to a round-bottomed flask, and 1 g of adsorbent was placed into a rotating basket made of perspex and plastic mesh (opening 50 μm). The basket containing activated carbon was placed in the reactor and connected to a stirrer. The adsorbent was contacted with distilled water for 1 hour prior to the start of the experiment. 10 ml of cadmium solution, of known initial concentration, was added to the reactor and the timer and the stirrer motor (set at 250 rpm) started immediately. This was noted as the zero-time of the experiment. Samples were collected at certain time intervals and analysed for cadmium concentration. The experiments were conducted for 2 hours and the temperature was kept at 298 K by a temperature control unit.

Analysis

The analysis of the samples was carried out using an atomic absorption spectrophotometer (Varian SpectrAA-200) in flame mode. Conditions of the spectrometer were: acetylene-air flame under oxidizing conditions at 228.8 nm wavelength for cadmium concentrations from 0.02 to 3.0 mg l^{-1}, and 326.1 nm wavelength for cadmium concentrations from 20 to 1000 mg l^{-1}. The solution pH was measured using a Mettler Toledo 340 pH meter.

RESULTS AND DISCUSSION

Surface Area and Direct Titration

The BET surface area of granular activated carbon WHK decreases from 1935 to 702 $m^2 g^{-1}$ upon electrochemical oxidation as indicated in Table 1. This reduction in surface area is significant although a surface area of about 700 $m^2 g^{-1}$ is entirely adequate for most water treatment applications. More significant is the increase in total oxygen-containing functional groups. This has increased by a factor of 3.36 resulting in a weakly acidic ion exchange capacity of 7.29 meq g^{-1}. Metal uptake is highly dependent on solution pH and the accessibility of weakly acidic sites within the activated carbon matrix. The enhancement of oxygen-containing functional groups in electrochemically oxidized WHK activated carbon will significantly increase the sorption of cadmium from water and wastewater at near-neutral pH.

Table 1. Concentration of oxygen-containing groups.

WHK	BET surface area, $m^2 g^{-1}$	Carboxyl	Lactonic	Phenolic meq g^{-1}	Carbonyl	Total capacity
Untreated	1935.39	0.24	0.49	0.26	1.17	2.17
Oxidized	702.28	1.39	2.45	1.11	2.34	7.29

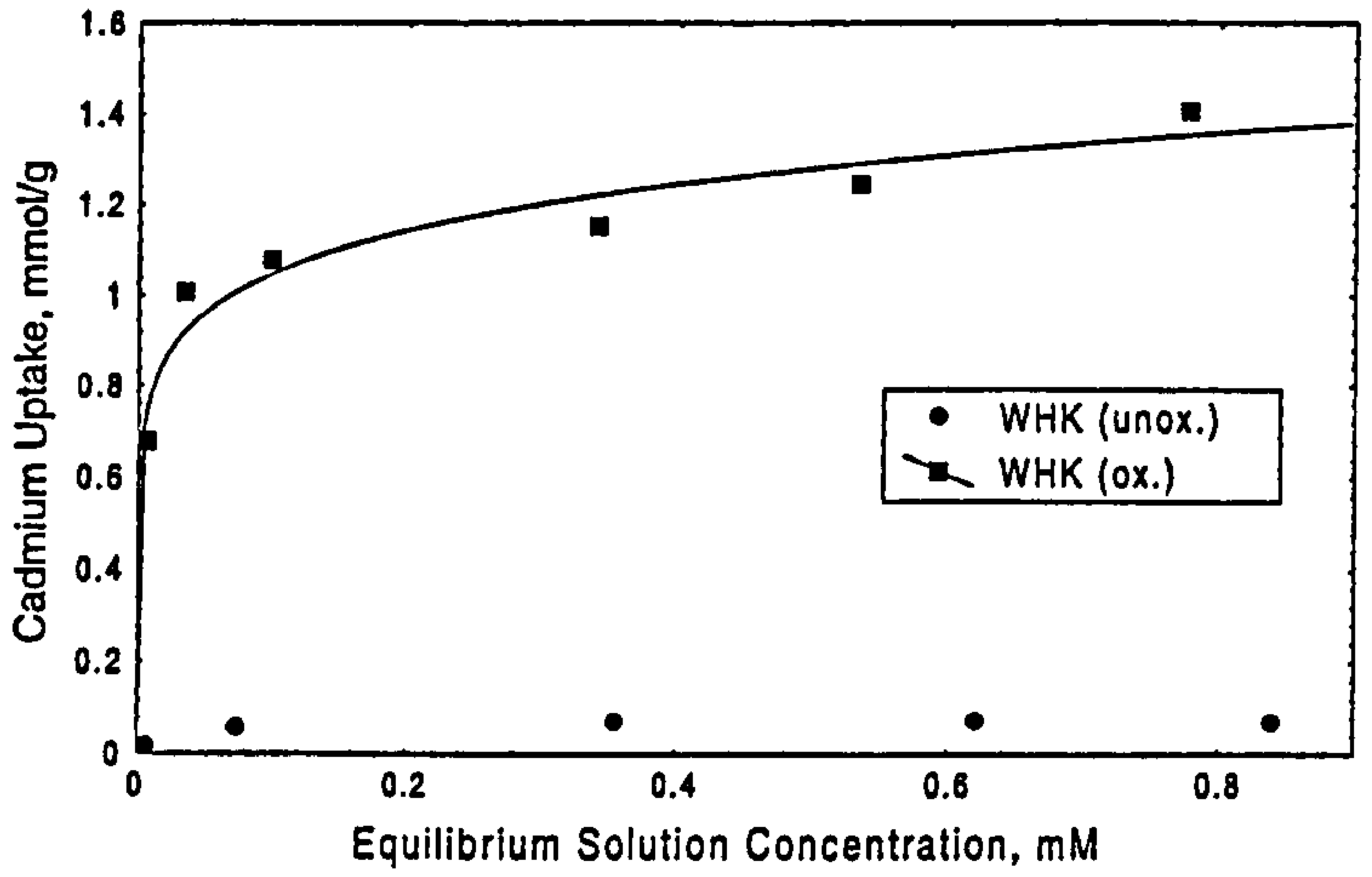

Figure 3. Adsorption of cadmium on unoxidized and electrochemically oxidized WHK, at pH 6 and room temperature.

Table 2. Freundlich isotherm parameters for the adsorption of cadmium on electrochemically oxidized WHK.

pH	k, $[l^{1/n}/mg^{1-1/n} g^{-1}]$	n	R
4	0.809	0.255	0.983
5	1.157	0.169	0.977
6	1.396	0.124	0.962

Adsorption Isotherm

Figure 3 shows a significant increase in cadmium uptake with oxidized WHK. The adsorption capacity has increased by a factor of 16.5 in comparison with the unoxidized material. The equilibrium capacity of modified WHK was 1.4 mmol g^{-1} at a solution concentration of about 0.8 mmol l^{-1} whereas negligible cadmium uptake was observed for conventional as-received WHK (0.08 mmol g^{-1}). The large increase in adsorption capacity is attributed to the enhancement of oxygen-containing groups during electrochemical oxidation.

The adsorption isotherms were fitted by Langmuir and Freundlich isotherm models which are represented by equations (1) and (2) respectively:

$$q = \frac{q_m KC}{1 + KC} \qquad (1)$$

$$q = kC^{1/n} \qquad (2)$$

It was found that the Freundlich isotherm fitted the experimental data very well. The parameters of this model were calculated using the method of least squares and are shown in Table 2. Predicted isotherms using these parameters are given in Figures 3 and 4.

pH Effect on Adsorption Isotherm

Cadmium uptake increased as pH increased (see Figure 4). Adsorption of cadmium ions strongly depends on metal speciation and the chemistry of the carbon surface. A speciation diagram for 0.1 M $CdCl_2$ solution is shown in Figure 5. This was constructed using the equilibrium constants reported by Stumm and Morgan[9]. Cadmium appears as Cd^{2+}, $CdCl^+$ and $CdCl_2$ below pH 7.5 in the approximate proportions 65, 33 and 2% respectively. Precipitation as $Cd(OH)_2$ occurs just below pH 8.

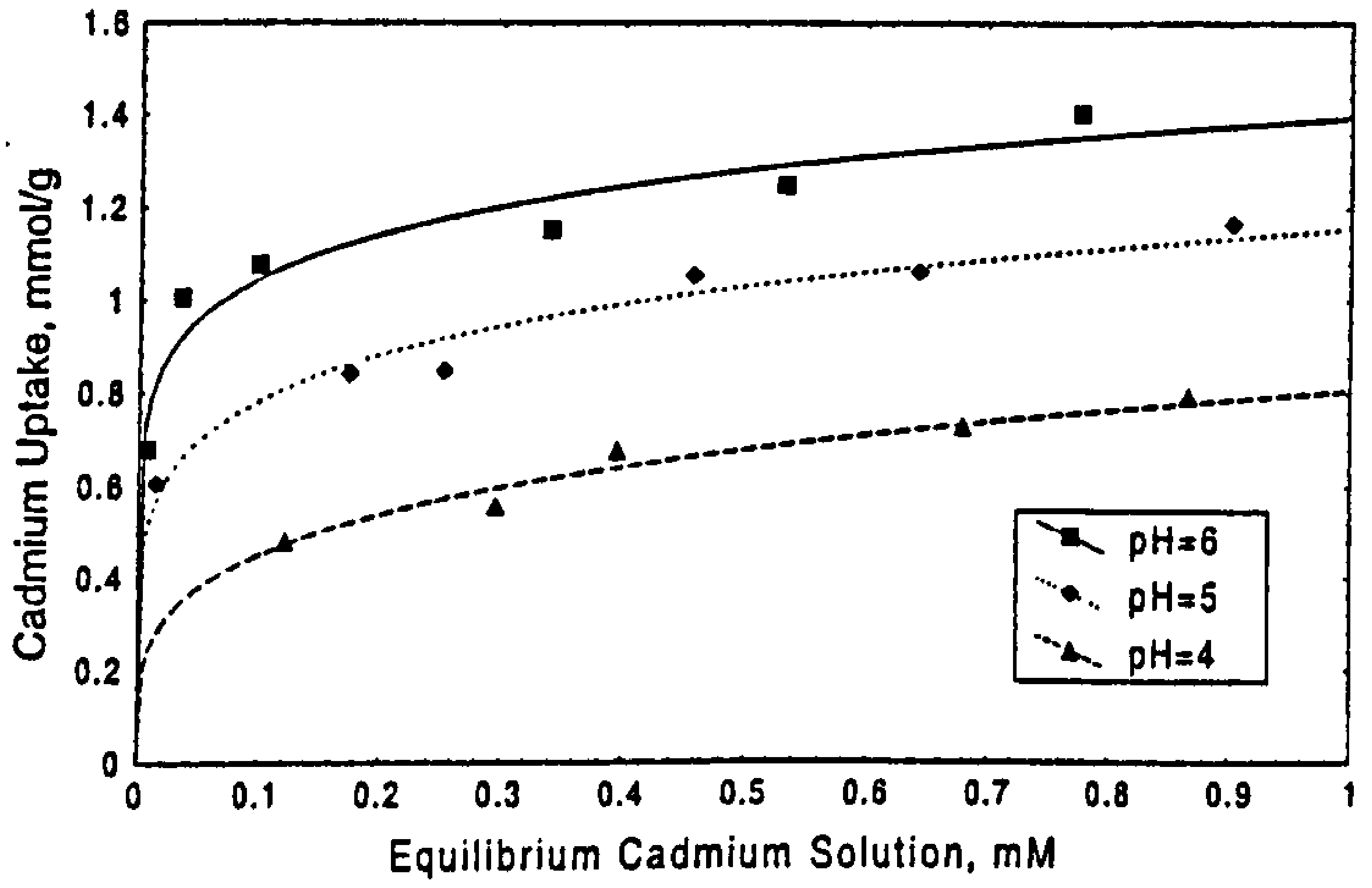

Figure 4. Equilibrium isotherms for cadmium using electrochemically oxidized WHK, at different pHs and room temperature.

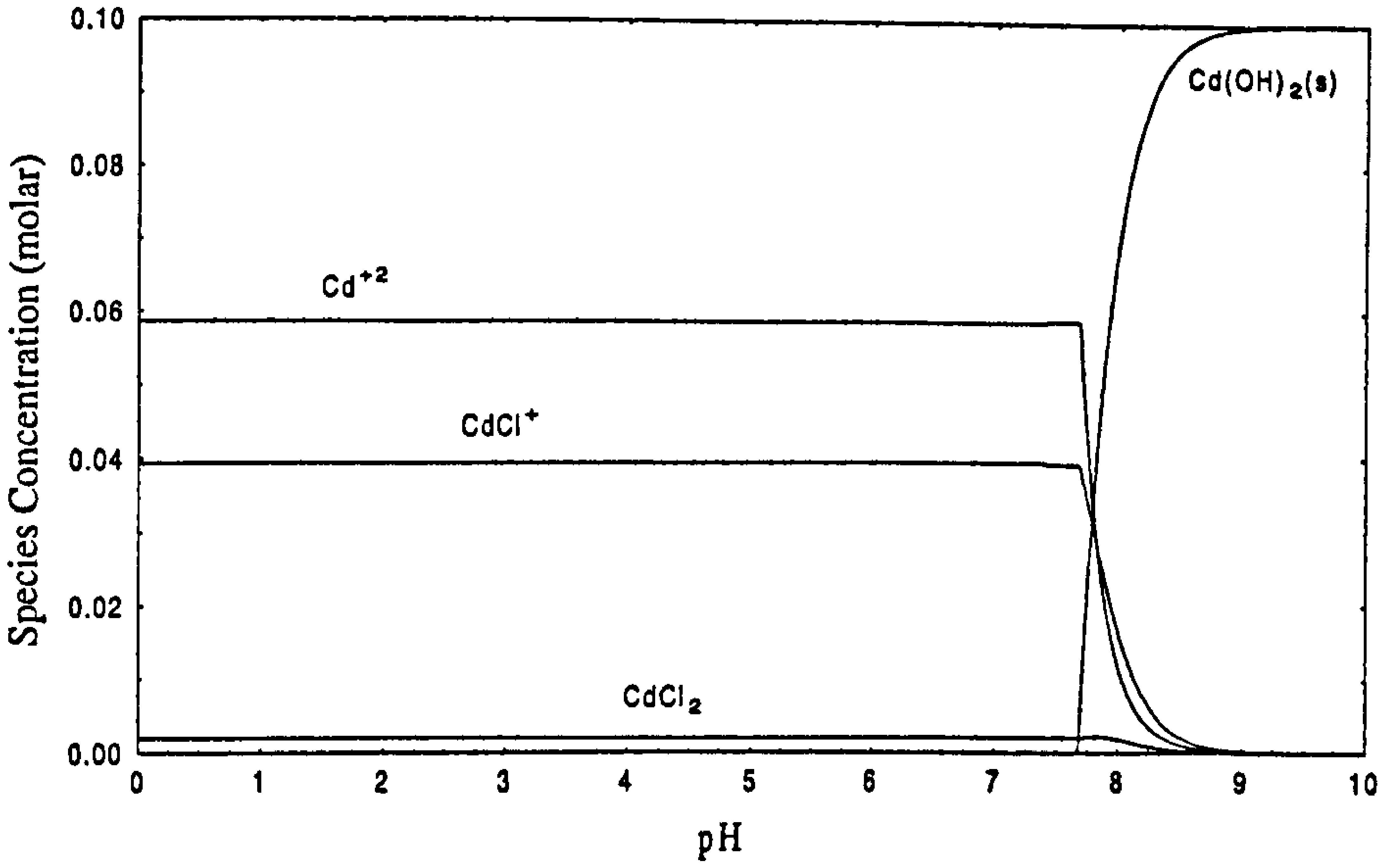

Figure 5. Speciation diagram of $CdCl_2$ 0.1 M in aqueous solution.

The pH value of the point of zero charge (PZC) for activated carbon WHK was previously reported as 2.5 by Saha *et al*[10]. It is well known that the carbon surface charge depends on solution pH. The surface is positively charged below the PZC, i.e. at pH<2.5. In this region the oxygen-containing groups are undissociated. The carbon surface becomes negative as the pH increases above 2.5 due to the dissociation of weakly acidic oxygen-containing groups. Since cadmium exists predominantly as Cd^{+2} and $CdCl^{+}$ in aqueous chloride solutions up to pH 7.5, cation exchange and/or complexation with surface functional groups is the most likely sorption mechanism.

Kinetics

Kinetic data are plotted in Figure 6 and this shows that the adsorption rate for cadmium is extremely fast in both unoxidized and modified granular activated carbon, WHK. About 96% of the fractional approach to equilibrium is attained in 12 minutes. Rapid sorption kinetics in these experiments can be attributed to the relatively small and close size distribution of particles, well-defined surface area and pore size distribution.

Breakthrough Curves

Results of mini-column trials are shown in Figure 7. This graph gives a comparison of cadmium uptake by unoxidized and electrochemically oxidized WHK and confirms the significant improvement in performance of the oxidized material. The breakthrough capacity at 5% is 0.014 and 0.317 mmol g^{-1} for conventional and modified WHK respectively. Breakthrough occurs at about 140 BV for modified WHK whereas it is almost instantaneous for unoxidized adsorbent.

CONCLUSIONS

Granular activated carbon, WHK, has been modified

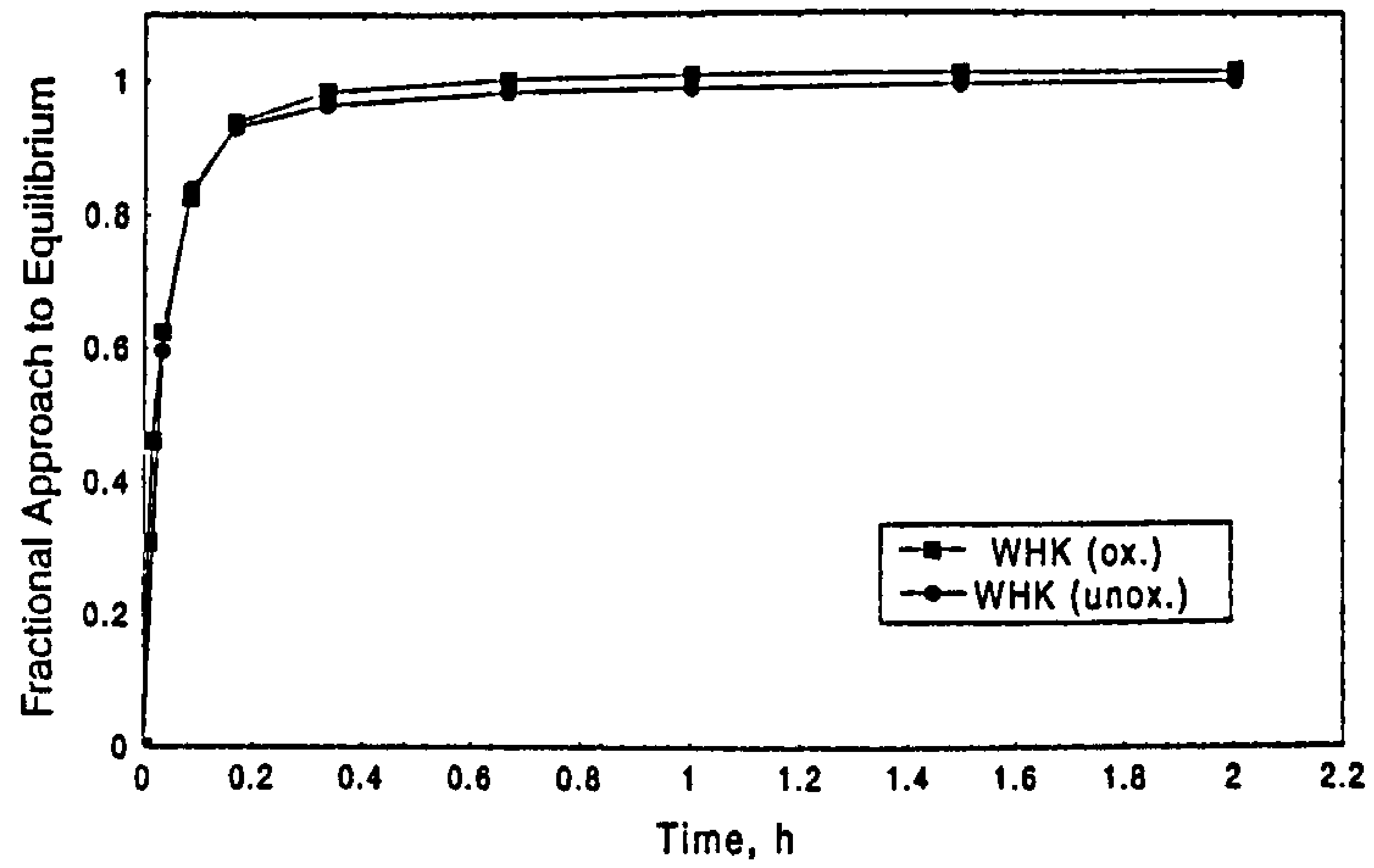

Figure 6. Sorption rate for cadmium using unoxidized and modified granular activated carbon WHK, at 298 K and 250 rpm.

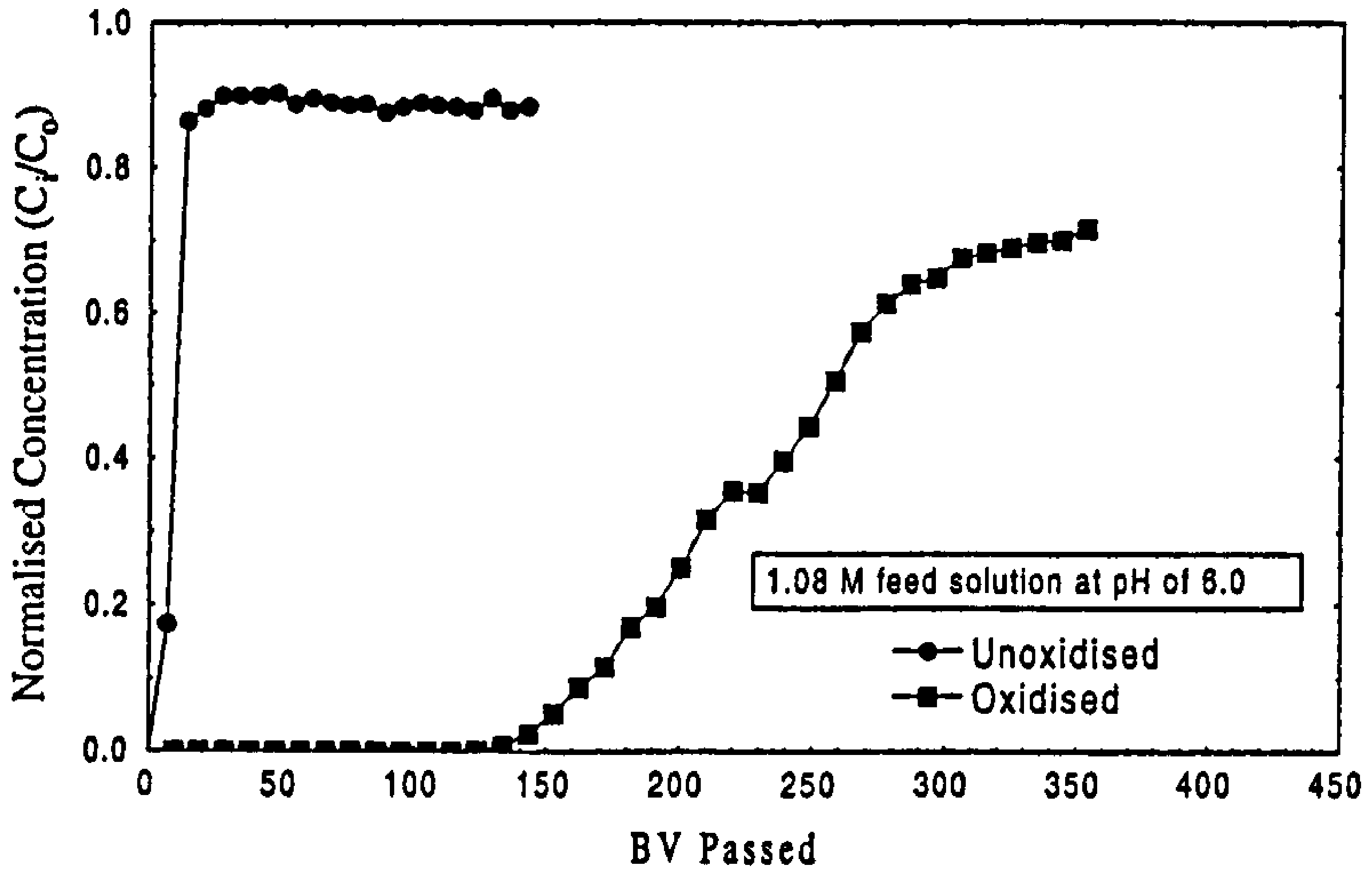

Figure 7. Cadmium breakthrough results for unoxidized and electrochemically oxidized WHK.

by electrochemical oxidation to enhance ion exchange properties. The equilibrium capacity of oxidized WHK was 16.5 times greater than the unoxidized form at a cadmium concentration of 0.8 mmol l^{-1} in solution, which is mainly attributed to the introduction of surface acidic functional groups during oxidation. Cadmium adsorption is pH dependent and a slight increase in cadmium uptake was observed as pH increased from 4 to 6. Kinetic experiments showed that the adsorption rate for cadmium was rapid and 96% of the fractional approach to equilibrium was attained in 12 minutes using both unoxidized and electrochemical oxidized WHK. Some surface area is lost during electrochemical oxidation but this does not adversely affect cadmium sorption at the levels investigated.

NOMENCLATURE

C	cadmium concentration in solution, mg l^{-1}
k	Freundlich isotherm parameters, $l^{1/n}/mg^{1-1/n}\,g^{-1}$
K	Langmuir isotherm parameters, l mg^{-1}
n	Freundlich isotherm parameters
q	cadmium uptake, mg g^{-1}
q_m	amount adsorbed of a mono-layer, mg g^{-1}
R	correlation coefficient

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ADDRESS

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SORPTION OF CADMIUM USING A NATURAL BIOSORBENT AND ACTIVATED CARBON

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This paper investigates the use of commercially available and modified activated carbon and a natural biosorbent for the removal of cadmium from water. A wood based activated carbon, AUG WHK, was acid oxidised to enhance its metal binding capacity. The leaves of a water fern, Azolla filiculoides were separated from the roots and ground into particles and acid washed to create a uniform hydrogen form adsorbent. These materials were subsequently studied for the removal of cadmium ions from aqueous solution. The sorption performance of these materials for cadmium is compared. The physical structure of the adsorbents has been investigated using scanning electron microscopy, nitrogen and amino acid content and BET surface area. Carbon adsorbents were characterised by N2 adsorption at 77K before and after oxidation, and a quantitative determination of weak-acid surface groups was carried out by direct titration. The BET surface area decreased considerably after oxidation, however, the total amount of oxygen-containing surface groups was 3.3 times higher compared to the untreated adsorbent. Cadmium adsorption isotherms were performed at pH values of 4, and 6 showing an increase in capacity as pH increases. The maximum capacity for the sorbents was 0.08, 0.33, 1.40 mmol/g for the three adsorbents: unoxidised WHK, Azolla filiculoides and acid oxidised WHK, respectively. Kinetic experiments showed that the materials were all rapid adsorbents of cadmium, with 80% of capacity reached in 0.2 hours for all three materials.

Keywords: cadmium, biosorbent, activated carbon, granular carbon, adsorbents, kinetics, oxidation.

INTRODUCTION

The presence of heavy metals in effluents is a world-wide environmental problem. There are a wide range of industries that produce heavy metal waste, therefore efficient and cost effective methods of water treatment are essential. Cadmium is prominent on the EU Black List of priority pollutants that are highly toxic and a serious threat to life. It is a carcinogen and causes damage to the kidneys. Cadmium is used extensively in electroplating due to its corrosion resistance and is a component in the expanding market for rechargeable batteries. Concentrations of the metal can reach 100ppm in surrounding areas adjacent to mines, smelters and Ni-Cd battery plants. Therefore, cost-effective methods of removing this trace metal are in great demand. At present a number of technologies, such as chemical precipitation, electroplating, evaporation, adsorption and ion exchange, are used to treat heavy metal containing wastewaters. Conventional chelating ion exchange resins can be effective but their production costs are a limiting factor. The above methods, other than adsorption and ion exchange, are not efficient or cost effective when the concentrations of metal ions are as low as 100ppm and the required concentration in the treated water is almost at the limit of detection [1].

Adsorption has been widely applied for the removal of trace contaminants from potable water, domestic water and industrial effluents. Sorption of heavy metals on activated carbon is not a simple process because it depends on several factors such as water chemistry and the surface reactivity of the adsorbent material. Granular activated carbons are extensively used in wastewater treatment for the removal of a wide range of contaminants. They possess high mechanical rigidity, well defined pore size distribution and offer extensive surface area for sorption of metal ions from aqueous solutions.

The use of naturally occurring plants as biosorbents for the removal of trace toxic metals is extensively studied on the laboratory scale but has not yet found widespread industrial application. Biosorption defines processes that remove contaminants from wastewater by either metabolic or physico-chemical pathways [2]. Many biological materials have been investigated for their ability to remove cadmium ions from solution. These include bacteria [3], fungi [4] and most commonly algae [5,6,7]. When considering biomass as a commercial process, the abundance and availability of the material are important considerations. In the case of algae, seaweeds can be harvested directly or received as recycled waste from the algin production industry. *Azolla filiculoides* is a fast free-growing "weed" that re-produces prodigiously, covering and blocking many waterways around the world. Biosorbents generally have a lower capacity than commercial ion exchange resins and modified activated carbons, however, they are regenerable and low-priced. *A. filiculoides* has already been shown to be very effective in repeatedly removing many pollutants from waste waters [8,9,10], including cadmium [11].

It is the aim of this work to compare the cadmium sorption capacity abilities of a commercial and modified granular activated carbon and a natural biosorbent. Sorption isotherms and kinetic experiments were performed to describe their performance. Samples were characterised, chemically and physically, by acid/base titration, pH titration, nitrogen and amino acid content, BET surface area and Scanning Electron Microscopy.

EXPERIMENTAL

MATERIALS

A. filiculoides was received from The University of Liverpool, Department of Biological Sciences. This was frozen in liquid nitrogen and the leaves separated from the roots. The leaves were then selected as they had shown a significantly greater cadmium sorption capacity than the roots. These were then ground into particles using a mortar and pestle. The particles were dried and sieved to 170-210μm. A wood based granular activated carbon WHK, supplied by AUG Germany, was sieved to a particle size fraction of 170-210μm, washed carefully with distilled water and then dried in an oven at 378K until no change in weight was observed. Cadmium solution was prepared using $CdCl_2{\cdot}H2O$ laboratory grade purchased from May & Baker Ltd., Dagenham, England. Sodium hydroxide, nitric acid, hydrochloric acid and potassium chloride were prepared from analytical reagents supplied by Fisher, UK. Aldrich Chemicals, USA, supplied volumetric standard solutions of sodium hydroxide, sodium carbonate, and HPLC grade ethanol. Sodium hydrogen carbonate and sodium ethoxide solutions were prepared from analytical reagents purchased from Aldrich Chemicals, USA.

CHARACTERISATION

Surface Area

The Surface area of granular activated carbons was obtained by nitrogen adsorption and desorption at 77 K using a Micromeritics ASAP2010 automatic surface area analyser. The samples were outgassed for 24 hours at 378 K under a vacuum of <10 μmHg.

Scanning Electron Microscopy (SEM)

Scanning Electron Microscopy pictures of granular carbons and *A. filiculoides* were taken using a Cambridge Stereoscan 360 operated at an accelerating voltage of 10 kV.

Nitrogen Analysis

Nitrogen analyses for biosorbent were conducted using the Kjelhdahl Method [12]. Duplicate 1g samples of *A. filiculoides* and native and dealginated seaweeds: *Ascophyllum nodosum* and *Lessonia flavicans* (both supplied gratis by Kelco, UK) were weighed on filter paper and placed into digestion vessels on a Buchi B435 digestion unit. The nitrogen control sample was a known weight of ammonium sulphate (to calculate process efficiency). The samples were then heated for 45 minutes at 623 K with sulphuric acid and catalyst pellets, to complete the hydrolysis stage. The hydrolysed product was steam distilled for 3 minutes using a Buchi 323 Kjeldahl distillation unit. The resulting distillate was titrated against a 0.1M hydrochloric acid solution, using screened methyl red indicator in a 2% boric acid solution.

Amino Acid Analysis

Samples of *A. filiculoides* were hydrolysed in order to liberate the amino acids. This was achieved by adding 0.5ml of 0.1M phenol (to reduce oxidation) and 4.5ml of 6.6M HCl to 100mg of the sample. The samples were heated at 383 K for 24 hours and then allowed to desiccate until dryness. Distilled water was twice added and evaporated to ensure removal of all HCl. The amino acids were then obtained as hydrochlorides. The samples were analysed by ion exchange High Performance Liquid Chromatography (HPLC) using a Kontron Analytical Chromakon 500. The results were compared against standards and quantities of each amino acid were ascertained.

pH Titration

15 ml of a 0.1M NaCl solution was added to 25ml Erlenmeyer flasks. The solution pH was varied by adding, a total volume of 5 ml, 0.1M NaOH, HCl and/or distilled de-ionised water. Then, 10mg of neutrally buoyant adsorbent particles, <90 μm, were added to the flasks. The samples were stirred for 48 hours at room temperature to allow them to reach equilibrium. The initial (before the addition of adsorbent) and final pH were measured. Blank samples, under the same conditions, were titrated at the same time for comparison. The electrophoretic mobility of the equilibrated samples was measured using a Malvern Instruments Zetasizer 3000HSA.

Acid/Base Titration

The distribution of oxygen-containing groups was analysed by direct titration using the Boehm method [13]. The samples were contacted with bases of different strength, NaOH, $NaCO_3$, $NaHCO_3$ and $NaOC_2H_5$ (dissolved in HPLC grade ethanol). A pre-determined amount of adsorbent was placed in a 50 ml conical flask and then contacted with 20 ml of each alkali solution. The flask was sealed and stirred using an orbital shaker at 300 min^{-1} for seven days. The solution was filtered using a 0.2 μm PTFE syringe top filter to remove adsorbent particles. Finally a 5 ml aliquot was titrated with volumetric standard solution of

HCl, using a glass burette (tolerance ± 0.02ml), with methyl red as indicator. A simple mass balance was used to determine the ion exchange capacity of each oxygen-containing group.

Batch Sorption

A pre-determined amount of adsorbent was added to a 100ml conical flask containing 50ml of cadmium solution, of known initial concentration and pH. Samples were agitated by an orbital shaker at 300 min^{-1} at room temperature. The cadmium solution pH was checked and adjusted daily by addition of 0.1M NaOH or HCl until a constant pH was attained. The samples were deemed to have achieved equilibrium when no significant change in pH was observed (± 0.1 units) in a 24-hour period. The equilibrated samples were filtered using a 0.2μm PTFE syringe top filter to remove the adsorbent particles and then analysed for cadmium concentration, using a Varian SpectraAA-200 atomic adsorption spectrophotometer in flame mode at 228.8nm wavelength. Blank samples using the same solutions under the same conditions without adsorbent were prepared for comparison.

Kinetic Experiments

990ml of distilled water was added to a round-bottomed flask. Then, 1 g of adsorbent was placed into a rotating basket made of perspex and plastic mesh (opening 50 μm) [14]. The basket containing adsorbent was placed in the reactor and connected to a stirrer. The adsorbent was contacted with distilled water for 1 hour prior to the start of the experiment to allow trapped air to diffuse out and in the case of the biomass for particle swelling. 10ml of cadmium solution, of known initial concentration, was added to the reactor and the timer and the stirrer motor (set at 250 min^{-1}) started immediately. This was noted as the zero-time of the experiment. Samples were collected at certain time intervals and analysed for cadmium concentration. The experiments were run for up to 3 hours and the temperature was kept at 298 K by a temperature control unit.

RESULTS AND DISCUSSION

NITROGEN CONTENT AND AMINO ACID ANALYSIS

Previous metal sorption experiments on seaweed algae have attributed metal removal to functional groups present as part of the polysaccharide algin [15]. However, a significant residual metal sorption capacity remains after the alginates have been chemically removed [16]. It was suggested that this residual capacity can be attributed to functional groups associated with protein in the material. Protein is composed of a polymer of amino acids joined by primary amine and carboxyl groups. It is the functionality of the side chain that is of importance in metal binding. Amino acids contain a wide variety of side chains but only two are ionised in the pH range of interest i.e. the carboxylic groups on aspartic and glutamic acid (see Figure 1).

Table 1 Nitrogen content of several biomaterials

Material	Percent Nitrogen	Estimated Percent Protein*
Azolla filiculoides	3.80	23.76
De-alginate *Lessonia flavicans*	3.20	20.02
Lessonia flavicans	1.90	11.86
De-alginate *Ascophyllum. nodosum*	1.66	10.38
Ascophyllum nodosum	0.79	4.94

* Using AOAC international protein factor of 6.25

The biomaterials were analysed for nitrogen and this value was converted to a protein concentration using the general Association of Official Analytical Chemists (AOAC) factor of 6.25, which assumes the nitrogen content of the protein is 16%. Table 1 shows a high nitrogen content per unit mass for the dealginated seaweeds. *A. filiculoides* contains more than twice the nitrogen content of native *L. flavicans* and *A. nodosum*.

Figure 2 shows that *A. filiculoides* has a high concentration of the useful amino acids that may be involved in metal binding. 14.2% of the amino acids were aspartic acid and 10.2% glutamic acid.

OXYGEN-CONTAINING GROUPS

Figure 3 shows the concentration and type of functional groups on activated carbons. It can be seen that the concentration of oxygen-containing groups increases considerably after acid oxidation, but not in equal proportion. As-received granular activated carbon (WHK) contains carbonyl surface groups in the highest concentration. Acid oxidation results in an increase of 2, 3, 5 and 9 times higher for carbonyl, lactonic, phenolic and carboxyl groups, respectively. It is clear that carboxyl groups are introduced in the highest concentration, which will render acid oxidised carbon (WHK) more efficient in the treatment of drinking water since carboxyl groups are completely dissociated at near-neutral pH [17].

PH TITRATION

The surface chemistry of the adsorbents is extremely important in the sorption of metal ions and has to be studied in detail. The point of zero charge (PZC) is a useful parameter and can be determined by pH titration. PZC is the pH at which the net surface charge (internal and external) is zero [18]. This point can be deduced in Figure 4. The PZC for commercial granular carbon is at pH 4.5 whereas after acid oxidation it is shifted to pH 3.5. This behaviour is attributed to an increase in acidic surface groups, e.g. carboxyl, phenolic and carbonyl. The increase of these functional groups is also reflected in high concentration of ions released, H^+, with increasing pH (see Figure 4). The surface is positively charged in conventional and modified granular carbon WHK at pH values below the PZC where the oxygen-containing groups are undissociated and the adsorbent is able to remove anionic species. On the other hand, at pH values greater than the PZC, the sorbent surface becomes increasingly negative due to the dissociation of weakly acidic oxygen-containing groups. Hence, the adsorbent surface is able to attract and exchange cations in solution.

Alternatively, *A. filiculoides* has a proton binding curve that does not show a PZC within the experimental range (above pH 2). This means that the charge on the surface is always negative which is characteristic of a weak acid cation exchanger.

ELECTROPHORETIC MEASUREMENTS

The zeta potential (ZP) obtained by electrophoretic measurements at different pHs is reported in Figure 5. ZP is an index of the magnitude of interaction between colloidal particles. Colloidal suspensions/dispersions of fine particles in a liquid phase possess an electric charge that depends on the nature of the solid surface and the surrounding medium [19]. The point of zero net external surface charge is defined as the isoelectric point (IEP), which is located at the crossover point shown in Figure 5. The IEP for commercial and modified granular carbon is at pH 2.19 and 0.90 respectively, whereas for *A. filiculoides* it is at a pH of 1.42. The surface charge below and above the IEP can be explained in terms of the protonation and dissociation of oxygen-containing groups. It has already been mentioned that the PZC relates to the internal and external surface, whereas the IEP refers only to the external surface of the adsorbent. Hence, it can be deduced that the distribution of acidic surface groups is not homogeneous since the IEP is located at lower pH values. This indicates that the concentration of acidic groups is higher at the external surface as compared to the interior of the adsorbent.

SCANNING ELECTRON MICROGRAPHY

The SEMs presented in Figure 6 show the surface morphology of commercial and modified carbons, respectively. Un-oxidised carbon shows a well-defined and regular distribution of pores, whereas the oxidised sample shows irregular openings and roughness produced by chemical erosion. This is reflected in the loss of surface area. In comparison, the SEM of *A. filiculoides* leaves shows no sign of porosity.

BATCH EXPERIMENTS

Natural biosorbent, *A. filiculoides*, commercial and oxidised granular activated carbons, WHK, were tested for the removal of cadmium from aqueous solution. The sorption of cadmium at an equilibrium concentration of 0.8mM and pH 6 was 3.7 times higher for *A. filiculoides* than for commercial WHK (see Figure 7). Under the same conditions acid oxidised WHK showed 4 times higher cadmium capacity than *A. filiculoides*. This was expected since the concentration of oxygen-containing groups, found by acid/base titration, increased after chemical modification. However, BET surface area of the oxidised carbon decreased from 1912 to 714m^2/g due to the chemical reaction. An adsorbent with this surface area is entirely suitable for water treatment. The tendency for cadmium uptake is also reflected in the proton binding curves and electrophoretic mobility measurements. The concentration of ions released and zeta potential *versus* pH increases in the following order: commercial WHK, *A. filiculoides* and acid oxidised WHK. These results are in total agreement with the amount of cadmium removed by the adsorbents investigated in this research.

The effect of pH on adsorption was investigated and is reported in Figure 8. An increase of 53.12 and 58.33 % in cadmium uptake at 0.8mM was found when the solution pH was increased from 4 to 6 for *A. filiculoides* and oxidised granular carbon WHK, respectively. This is attributed to increased dissociation of acidic surface groups as the pH increases. For example the pK values of carboxylic groups lies between 2 and 5 [20,17].

Table 2 Freundlich isotherm parameters for the adsorption of cadmium

Material	pH	k, $\left[1^{1/n} / mg^{1-1/n} g^{-1}\right]$	n	R
A. filiculoides	4	0.161	2.915	0.995
A. filiculoides	6	0.350	5.495	0.989
Acid-ox. WHK	4	0.726	3.401	0.995
Acid-ox. WHK	6	1.267	7.937	0.988
Un-ox. WHK	6	0.081	5.208	0.919

The isotherms (Figures 7 and 8) were fitted using the Freundlich adsorption model, which had the best correlation of the experimental data compared with the Langmuir model. The parameters are shown in Table 2.

It has been mentioned that the surface chemistry and the metal speciation in solution are essential parameters to an understanding of the sorption mechanism. The speciation diagram for 0.1M $CdCl_2$ in aqueous solution (see Figure 9) was calculated using the equilibrium constants reported by Stumm and Morgan [21]. Cadmium appears as Cd^{2+}, $CdCl^+$ and $CdCl_2(aq)$ below pH 7.6 in the approximate proportions of 58, 39 and 3 %, respectively. Cadmium precipitates above pH 7.6 as $Cd(OH)_2$. Therefore cation exchange and/or complexation with surface functional groups is the most likely sorption mechanism.

The results presented in this section show that natural biosorbent, *A. filiculoides*, has 3.7 times higher cadmium capacity than commercial granular carbon WHK. Biosorbents are potentially useful for water treatment since they possess satisfactory capacities for metal ions and have a distinct economic advantage. However, it is shown that by oxidising the granular carbon WHK it is possible to obtain a cadmium sorption capacity greater than *A. filiculoides*. The drawbacks are that this process incurs extra cost and reduces the mechanical strength of the material. Oxidised carbons may also leach humic substances during subsequent use in water treatment.

KINETICS

Kinetic data are plotted in Figure 10 and this shows that the adsorption rate for cadmium is extremely fast for all the adsorbents. A significant difference is observed after 0.2 hours, when 94% capacity is reached with activated carbons compared to 82% for the biosorbent. Rapid sorption kinetics in these experiments can be attributed to the relatively small and close size distribution of particles and well-defined pore size distribution for the carbons. It has been shown that there is little or no porosity in the biosorbent, hence there are no internal diffusion constraints in the sorption mechanism.

CONCLUSIONS

The capacity of biomass for cadmium is 4 times greater than as-received commercial granular carbon WHK. The oxidation of commercial activated carbon increases sorption capacity for cadmium by a factor of 15 compared with the as-received material. There is, however, a subsequent loss in surface area due to the chemical reaction. Biosorbents are potentially useful for water treatment since they possess satisfactory capacities for metal ions and have a distinct economic advantage. All the materials displayed fast sorption kinetics, more than

80% capacity was reached in 0.2 hours, making them suitable for conventional column techniques.

ACKNOWLEDGEMENTS

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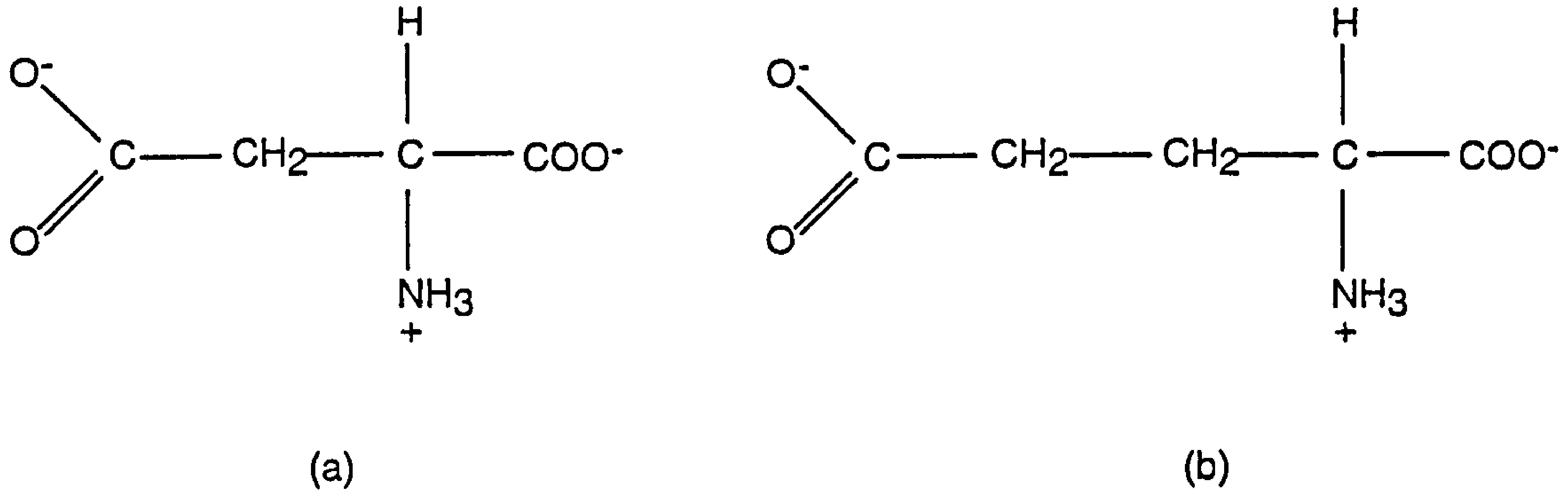


(a) (b)

Fig. 1 Amino acids, (a) aspartic acid and (b) glutamic acid

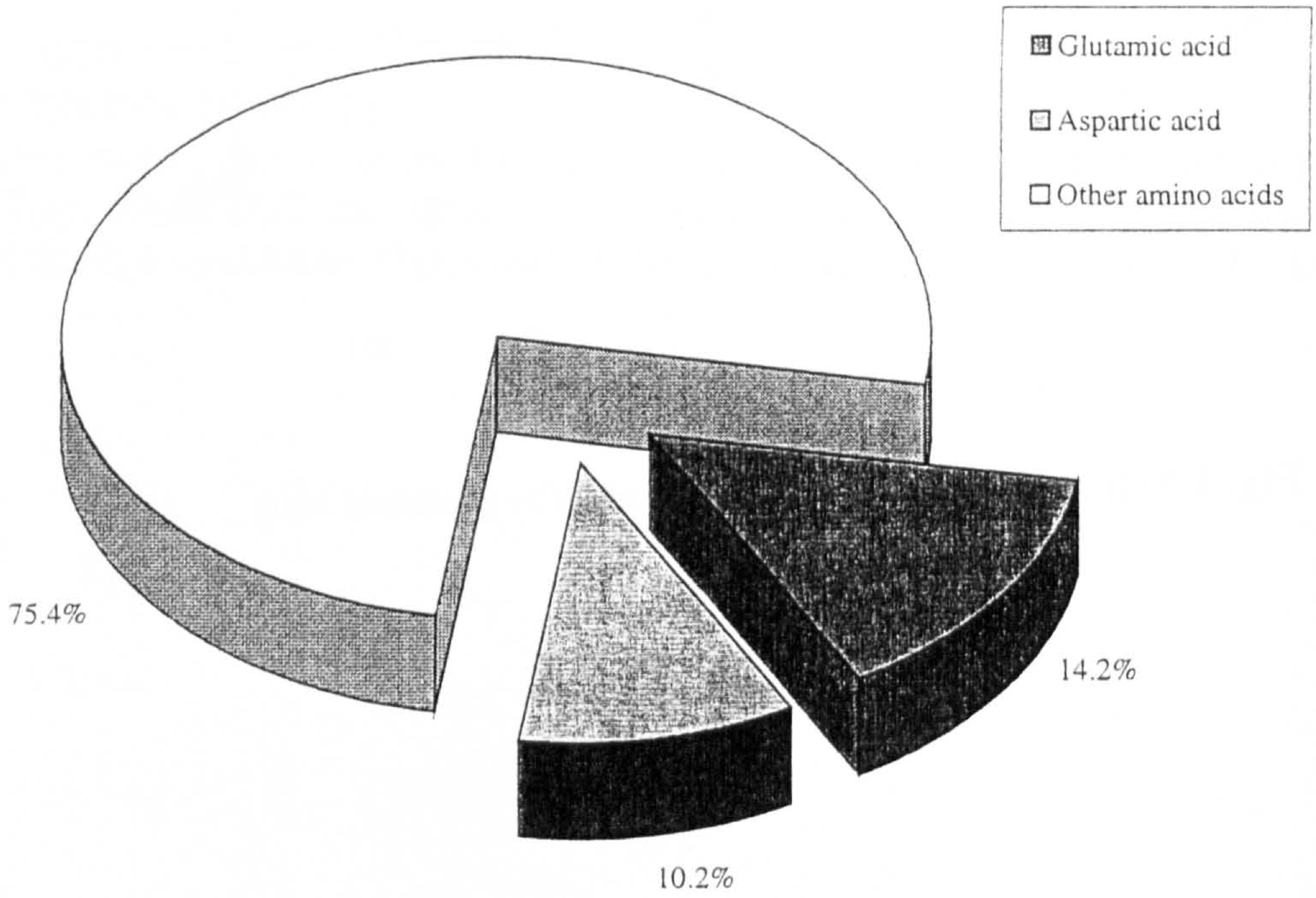


Fig. 2 Amino acid profile of *A. filiculoides*

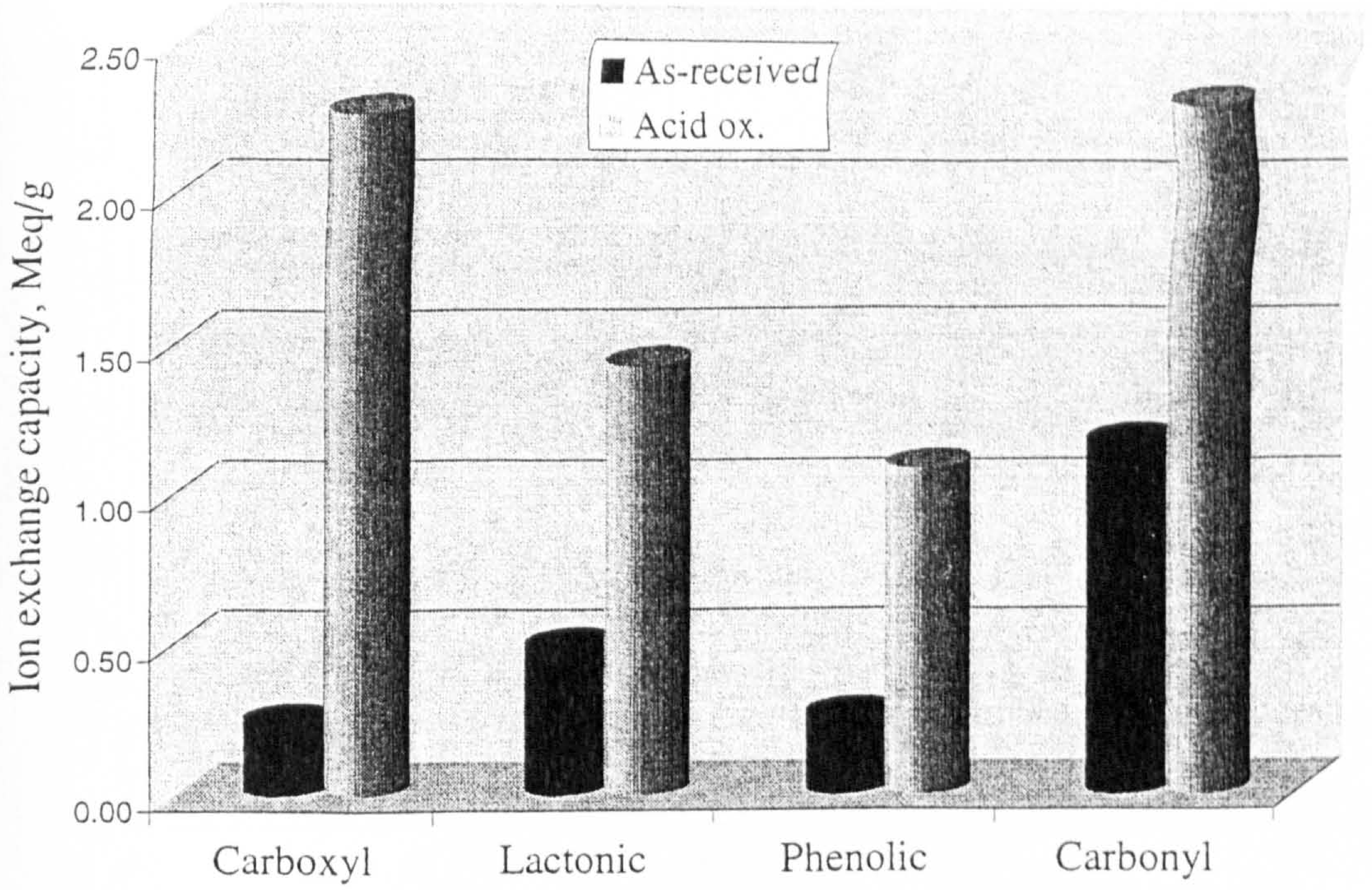


Fig. 3 Oxygen containing groups on conventional and modified granular carbon WHK

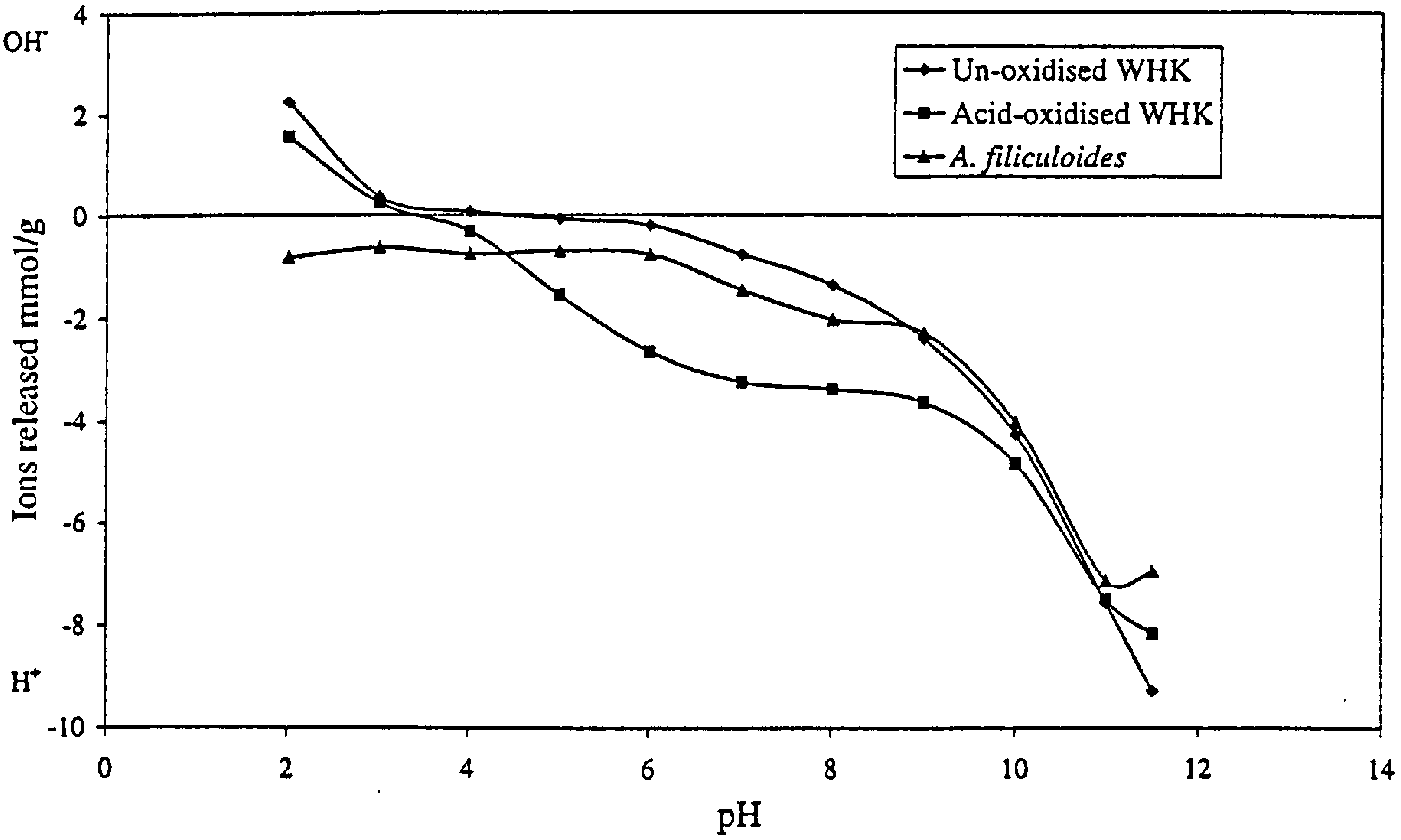


Fig. 4 Proton binding curves for granular carbon WHK and *A. filiculoides*

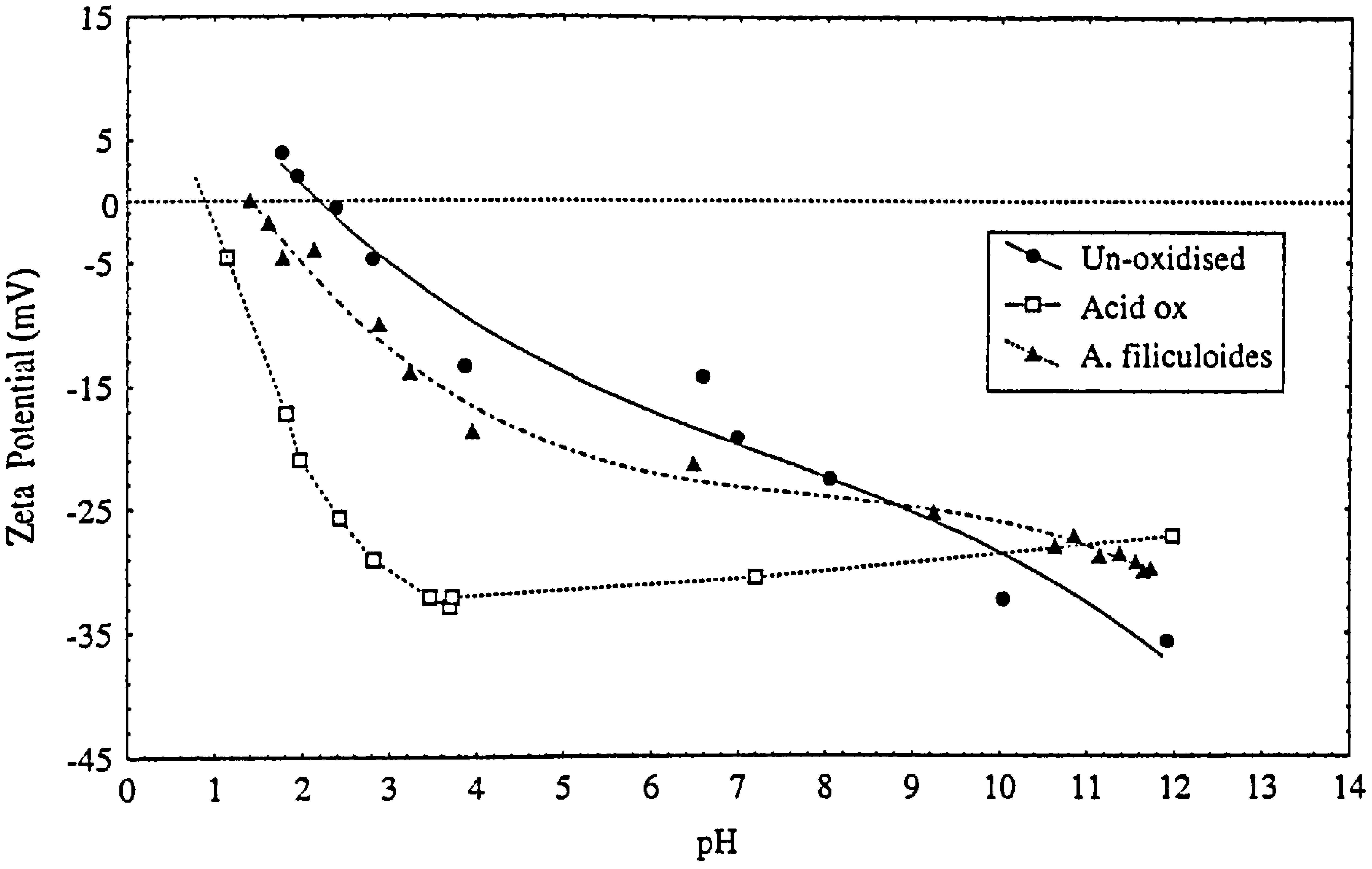
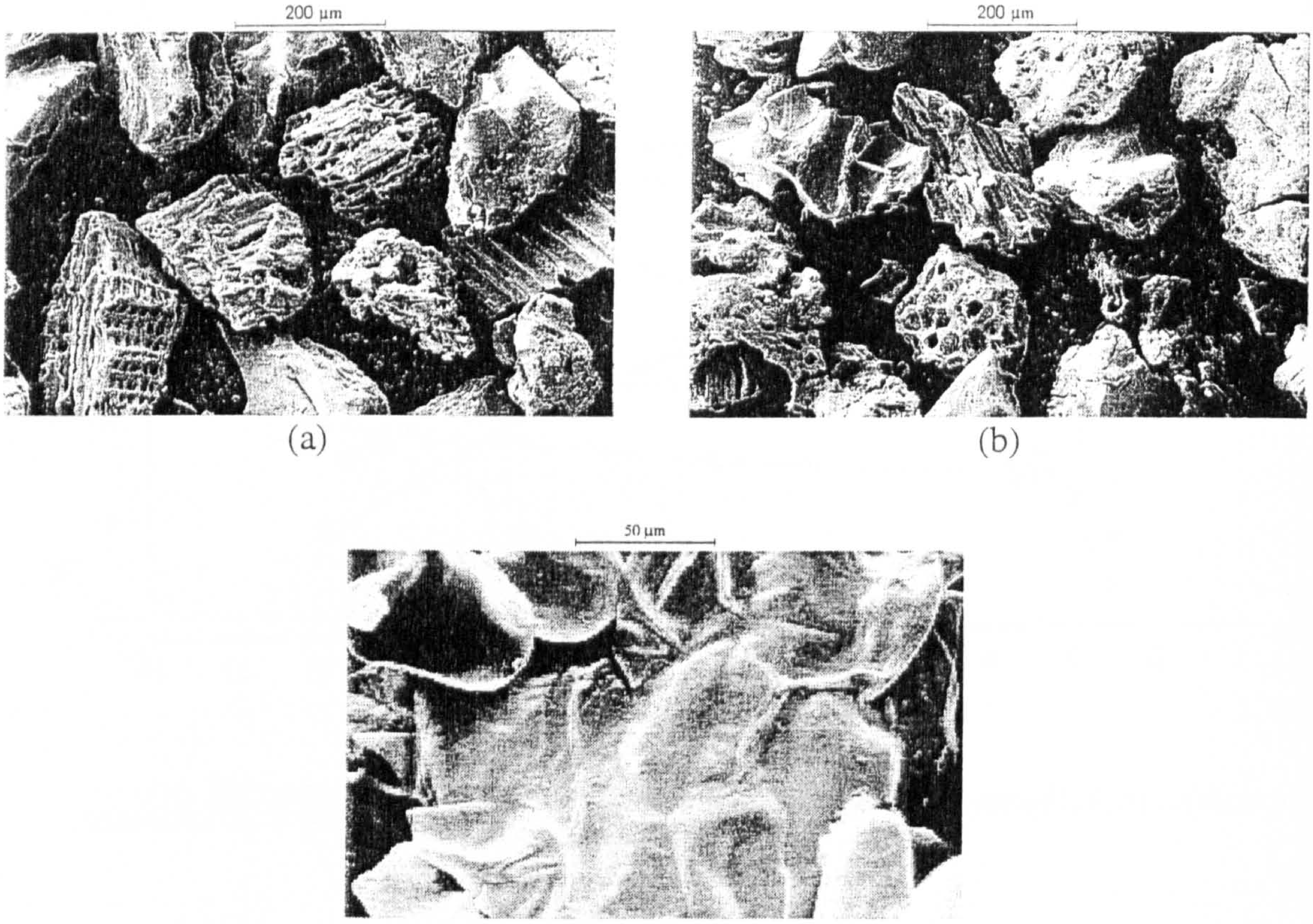


Fig. 5 Electrophoretic mobility measurements using granular carbon WHK and *A. filiculoides*



(a) (b) (c)

Fig. 6 Scanning Electron Micrographs of: (a) conventional WHK, (b) Acid oxidised WHK, (c) *A. filiculoides*

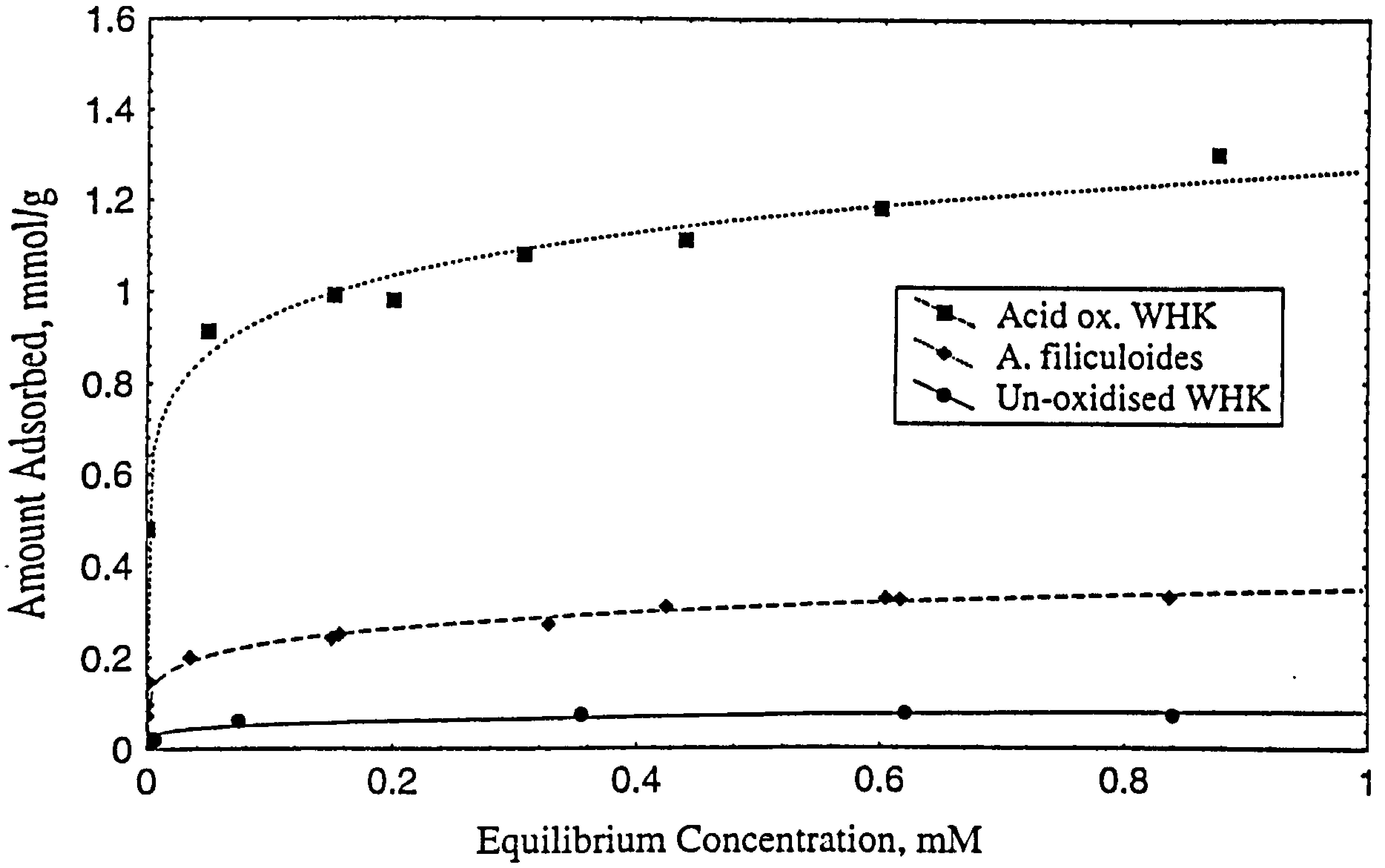


Fig. 7 Equilibrium cadmium sorption isotherms for granular carbon and *A. filiculoides* at pH 6 and room temperature.

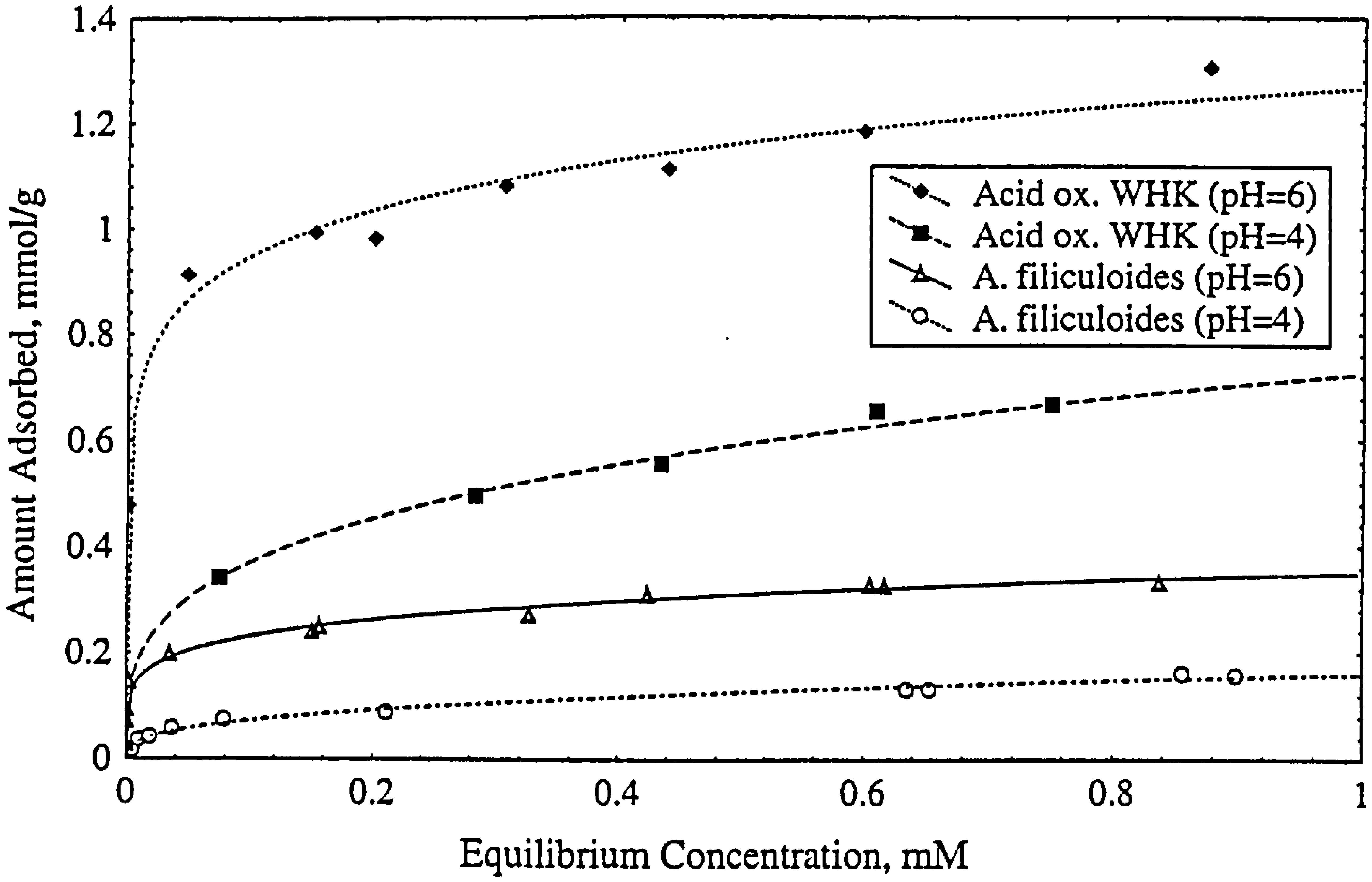


Fig. 8 Equilibrium cadmium sorption isotherms for oxidised granular carbon and *A. filiculoides* at pH 4 and 6, and room temperature.

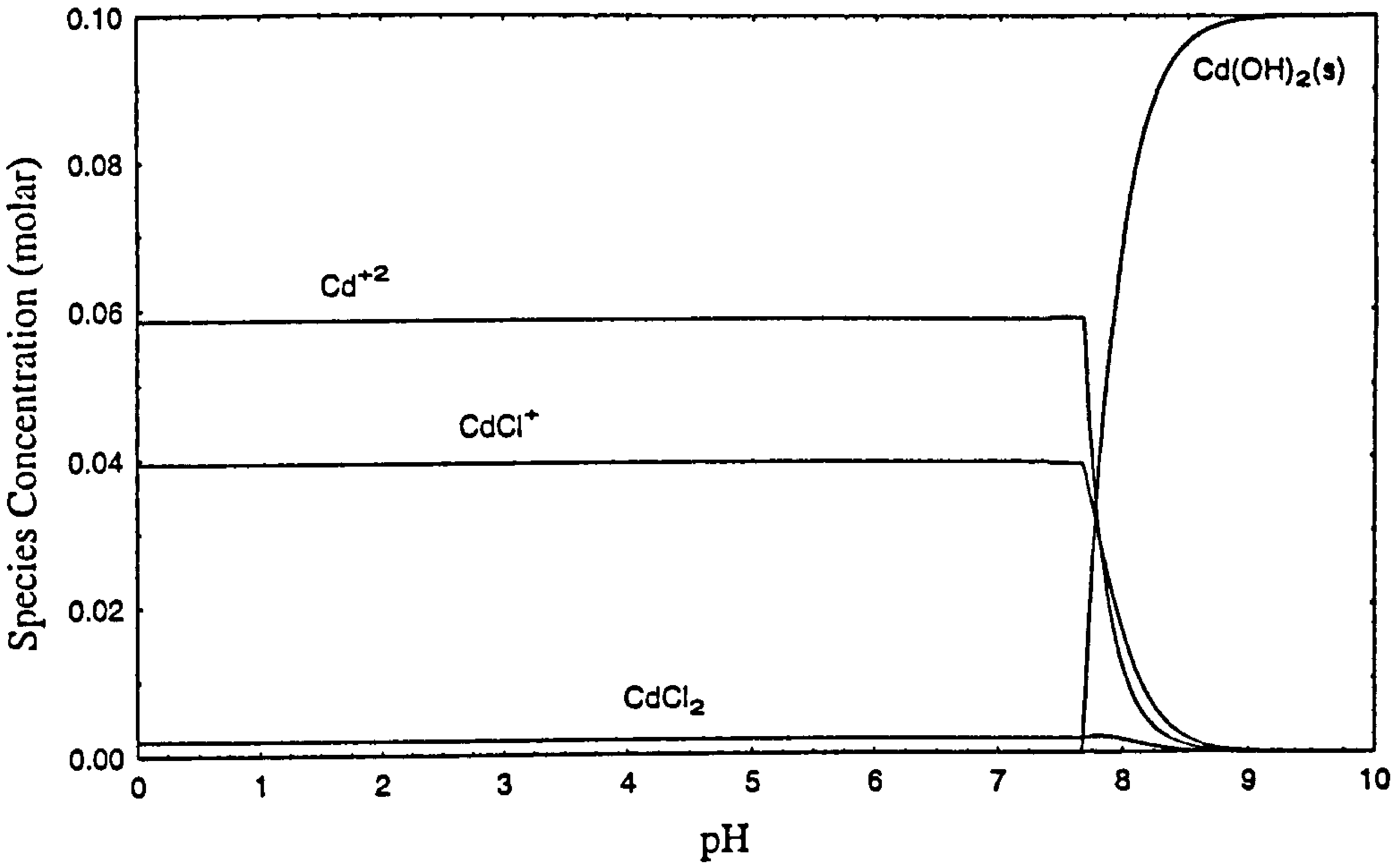


Fig. 9 Speciation diagram of 0.1 M $CdCl_2$ in aqueous solution at 298.15 K

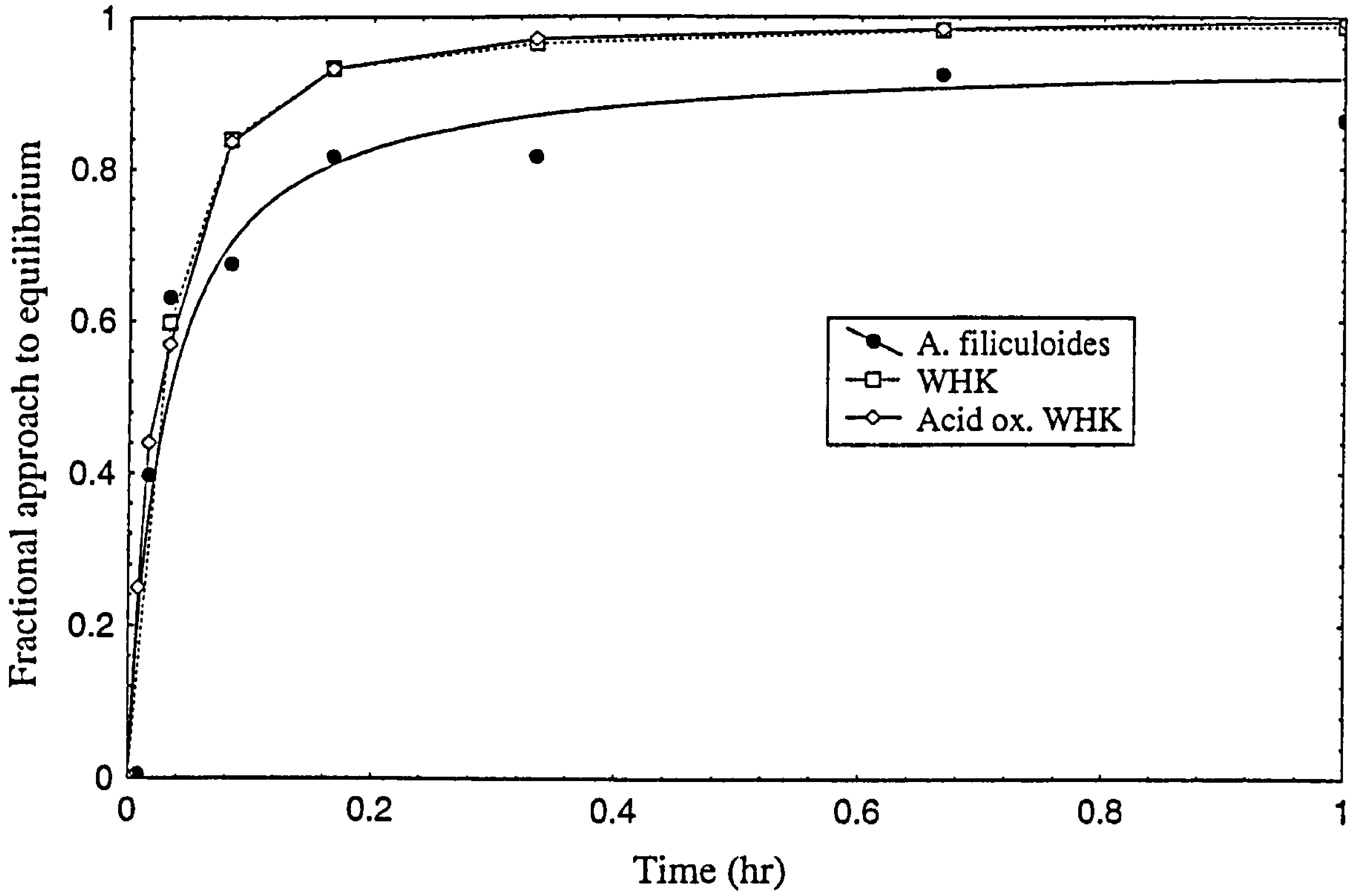


Fig. 10 Comparison of kinetics for granular carbons and the biosorbent

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Adsorption of cadmium by activated carbon cloth: influence of surface oxidation and solution pH

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Abstract

The surface of activated carbon cloth (ACC), based on polyacrylonitrile fibre as a precursor, was oxidised using nitric acid, ozone and electrochemical oxidation to enhance cadmium ion exchange capacity. Modified adsorbents were physically and chemically characterised by pH titration, direct titration, X-ray photoelectron spectroscopy, elemental analysis, surface area and porosimetry, and scanning electron microscopy. BET surface area decreased after oxidation, however, the total ion exchange capacity increased by a factor of approximately 3.5 compared to the commercial as-received ACC. A very significant increase in cadmium uptake, by a factor of 13, was observed for the electrochemically oxidised ACC. Equilibrium sorption isotherms were determined at pH 4, 5 and 6 and these showed that cadmium uptake increased with increasing pH. There was clear evidence of physical damage to ozone-oxidised fibre, however, acid and electrochemically oxidised samples were completely stable. © 2001 Published by Elsevier Science Ltd.

Keywords: Activated carbon cloth; Oxidation; Surface groups; Adsorption; Cadmium

1. Introduction

Activated carbon materials are versatile adsorbents that can be applied in both gas and liquid phase applications due to their excellent physical and chemical properties. In recent years, a variety of conventional granular activated carbons and ion exchange resins have been used in water treatment and to treat a wide range of domestic and industrial effluents containing organic and inorganic pollutants. It is well known that oxidation of granular carbons by reagents such as nitric acid, air, hydrogen peroxide and ozone introduces weakly acidic surface groups such as carboxylic, carbonyl, phenolic and lactonic [1–3]. Hence, these modified materials posses high sorption capacity, high selectivity for trace metal ions in solution and in certain cases are more effective than conventional ion exchange resins [2]. However, the application of granular activated carbons in water treatment can result in slow intraparticle diffusion and more complicated handling and regeneration procedures [4].

More recently, activated carbon fibre in the form of cloth (ACC) has been developed and has received considerable attention as a potential adsorbent for water treatment applications. The ACC can be prepared from synthetic and natural precursors, possesses a surface area between 1000 and 2100 $m^2 g^{-1}$, is robust and compact and therefore offers opportunities for the design of novel intensified water treatment systems [5]. The material is highly microporous; approximately 90% of the total pore volume is attributed to micropores. These micropores are directly accessible, thereby increasing intraparticle diffusion so that the overall sorption rate is faster than granular activated carbons that possess a combination of micropores, mesopores and macropores [4,6].

The ACC based on polyacrylonitrile fibre, i.e. KoTHmex TC-66 C, was modified using nitric acid, ozone and electrochemical oxidation to enhance cation sorption capacity. In order to characterise the commercial as-received and modified TC-66 C, techniques such

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as pH titration, direct acid/base titration, X-ray photoelectron spectroscopy (XPS), elemental analysis, surface area and porosimetry, and scanning electron microscopy were used.

The European Community has published a list of the most toxic organic and inorganic pollutants present in drinking water [7]. Metal ions such as arsenic, cadmium, copper, lead, mercury and nickel appear prominently in this list. Cadmium is one of the most toxic elements that can seriously affect human health. The concentration of this element in the environment is increasing rapidly due to its intensive use in industrial processes, e.g. fertilisers, and for many domestic purposes [8]. The maximum permissible concentration in water for human consumption has been set at 5 μg l^{-1}.

Cadmium sorption experiments for commercial and surface modified adsorbents are described here. Metal concentration and pH effects on the adsorption isotherm are investigated.

2. Materials

Activated carbon cloth TC-66 C was supplied by KoTHmex, Taiwan. This material was washed with distilled water to remove impurities and then dried in an oven at 378 K for 24 h prior to use.

Cadmium solution was prepared using laboratory grade $CdCl_2 \cdot H_2O$ purchased from May & Baker, Dagenham, England. Aldrich Chemicals, USA, supplied volumetric standard solutions of sodium hydroxide, sodium carbonate and HPLC grade ethanol, and the analytical reagents sodium hydrogen carbonate and sodium ethoxide. Nitric acid, hydrochloric acid and potassium chloride were prepared from analytical reagents purchased from Fisher, UK.

The modified TC-66 C was contacted with 1 M NaOH in a conical flask, sealed with Parafilm and agitated at 100 min^{-1} for 1.5 h to remove humic substances that form as by-products of oxidation. Excess sodium hydroxide was extracted with distilled water in a Soxhlet apparatus for 48 h. Finally, the modified samples were converted to hydrogen form by contacting them with 0.1 M HCl and then rinsed with deionised water. All samples were dried in an oven at 378 K for 24 h until no change in the weight was observed.

3. Analysis

A Varian SpectrAA 200 atomic absorption spectrophotometer in flame emission mode was used to determine the cadmium concentration. The spectrophotometer conditions were: acetylene–air flame under oxidising conditions at a wavelength of 228.8 nm for cadmium concentrations from 0.02 to 3.0 mg l^{-1}, and 326.1 nm for cadmium concentrations from 20 to 1000 mg l^{-1}. The solution pH was measured using a Mettler Toledo 340 pH meter.

4. Experimental

4.1. Acid oxidation

A three-necked round-bottomed flask was placed in a constant temperature water bath at 363 K (Fig. 1). Quantities of 2 g of TC-66 C and 80 ml of 8 M nitric acid was placed into the reactor. The oxidation reaction was carried out for 1, 2 and 3 h at 360 ± 1 K. A condenser was fitted to the reactor to prevent liquid loss by evaporation, and nitrogen was injected through a glass tube to agitate the sorbent/acid mixture. Fresh nitric acid was used in each experiment. The reactor containing the ACC/acid mixture was cooled immediately after chemical oxidationwas completed. The modified sample was removed from acidic solution and rinsed with distilled water.

4.2. Ozone oxidation

Air at the rate of 1000 cm^3 min^{-1}, measured by a rotameter, was passed through a column of silica gel to remove moisture. The dry air was then passed through an ozone generator with the voltage set at 9 V. The outlet of the ozone generator was connected to a horizontal glass reactor containing 1 g of the ACC (see Fig. 2). Teflon tubing was used to direct the air/ozone mixture from the ozonator to the reactor. Ozone

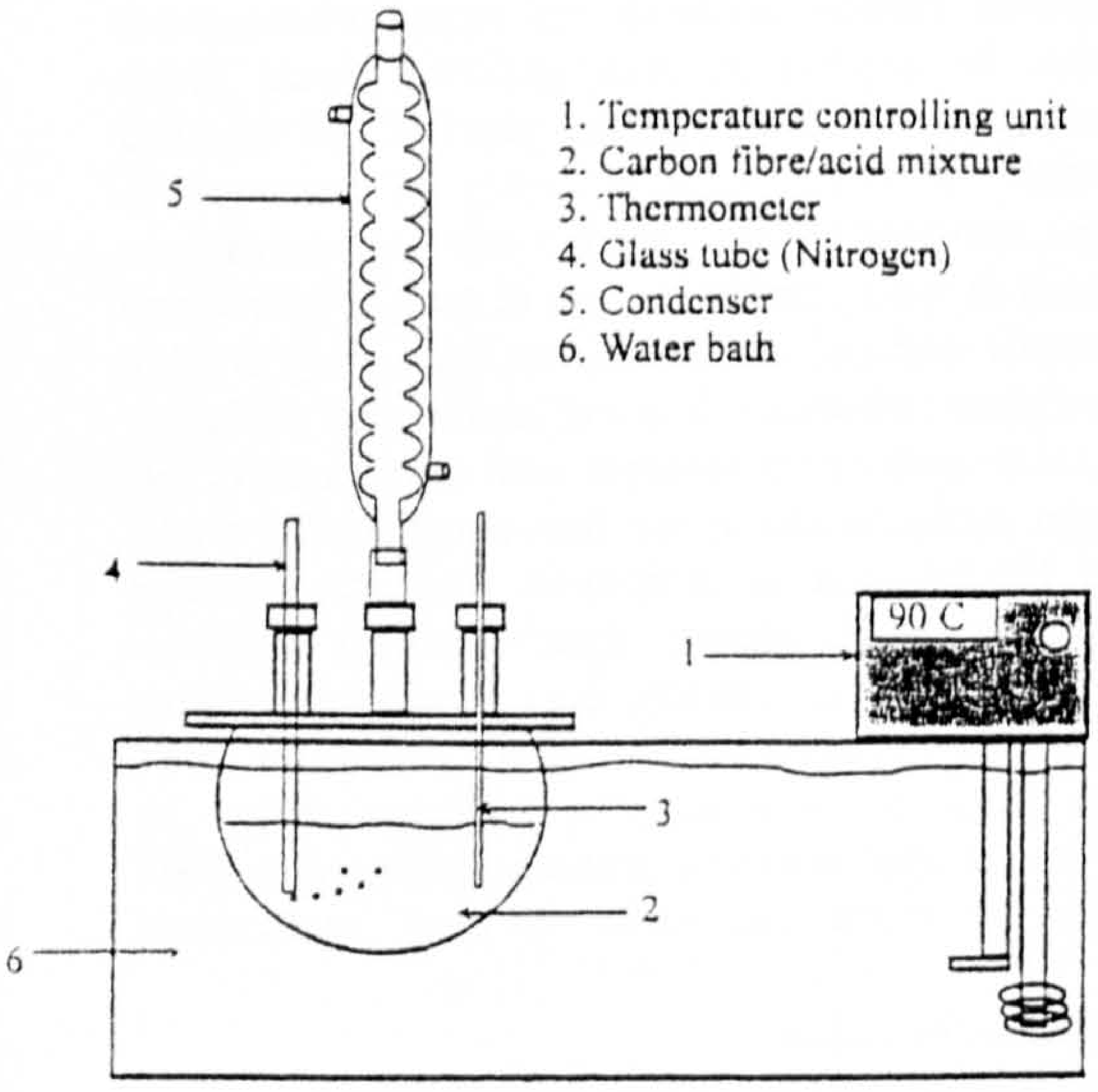

Fig. 1. Equipment used to oxidise TC-66 C using nitric acid.

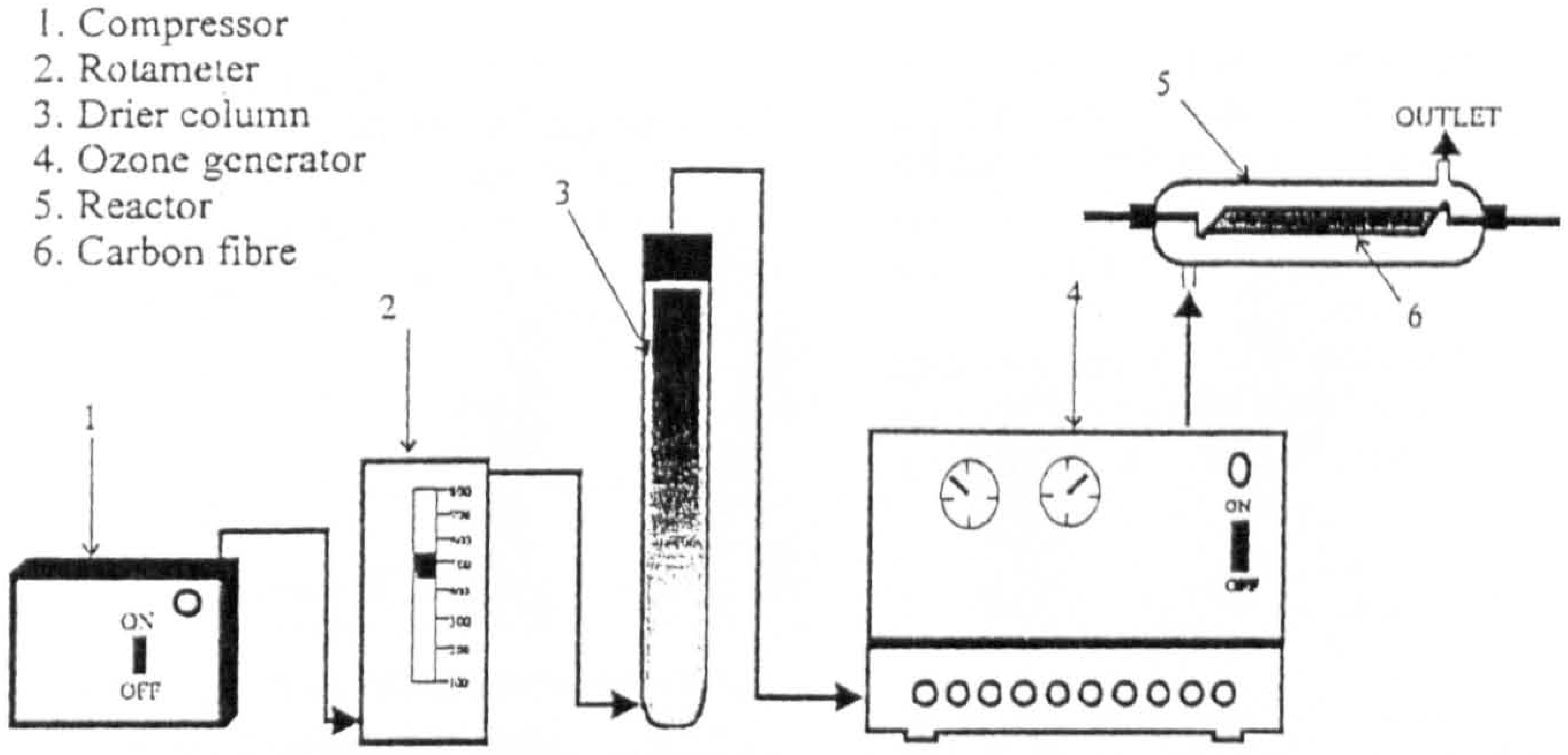

Fig. 2. Equipment used to oxidise TC-66 C using ozone.

oxidation was carried out for 1, 2 and 3 h at room temperature, approximately 293.15 ± 1 K.

4.3. Electrochemical oxidation

The electrochemical cell was immersed in a thermostatically controlled water bath at 298 K. A 20 cm^2 sample of commercial ACC was attached to the anode (platinised titanium) and immersed in 0.5 M KCl for 1 h prior to the start of the experiment. Oxidation was carried out by applying a current of 3 $mA\,m^{-2}$ for 1, 2 and 3 h. Several experiments were performed under the same conditions using fresh electrolyte each time. The current normally applied in the oxidation of carbonaceous material is between 0.01 and 3 $mA\,m^{-2}$ and depends on the characteristics of the sample, i.e. conductivity and surface area [9,10]. In this research, BET surface area was used as the criterion to determine the experimental conditions. The current density used throughout the experiments was high in order to introduce as many oxygen-containing groups as possible in the minimum period of time.

In order to identify oxidised samples of the ACC, the abbreviations UO, AO, OO and EO are used to denote unoxidised, acid, ozone and electrochemically oxidised samples, respectively, throughout the text.

4.4. Batch sorption studies

A volume of 50 ml of cadmium solution of known initial concentration, 0.05–1 mM, and pH, 4–6, was agitated in a 100 ml conical flask with a predetermined mass of conventional or modified ACC using an orbital shaker at 300 min^{-1}. The solution pH was adjusted daily by addition of 0.1 M NaOH or 0.1 M HNO_3 until a constant pH was reached. Equilibrium was attained in approximately 7 days. The equilibrated samples were filtered using 0.2 μm PTFE syringe top filters to remove the adsorbent particles and the adsorbate concentration was subsequently determined.

4.5. Direct acid/base titration

In order to determine the amount and type of oxygen-containing groups [11], samples of conventional and oxidised carbon cloth TC-66 C were contacted with 0.1 M solutions of NaOH, $NaCO_3$, $NaHCO_3$ and $NaOC_2H_5$ (dissolved in HPLC grade ethanol). Approximately 0.1 g of adsorbent was placed in a 50 ml conical flask and then contacted with 20 ml of each alkali solution. The flask was sealed and stirred using an orbital shaker at 300 min^{-1} for 7 days. The solution was filtered using a 0.2 μm PTFE syringe top filter to remove adsorbent particles. Finally, a 5 ml aliquot was titrated with 0.1 M volumetric standard solution of HCl, by using a glass burette (tolerance ± 0.02 ml), with methyl red as indicator. A simple mass balance was used to determine the ion exchange capacity of each oxygen-containing group.

4.6. Determination of sodium capacity

A series of experiments was conducted to determine the total sodium capacity of the adsorbents. A quantity of 0.5 g of adsorbent was placed into a conical flask containing 25 ml of 0.1 M volumetric standard sodium hydroxide. This was agitated at 300 min^{-1} for 48 h. The solution was filtered and a 10 ml aliquot was back titrated with 0.1 M volumetric standard HCl using methyl red as indicator.

4.7. X-ray photoelectron spectroscopy (XPS) and elemental analysis

Conventional and modified ACC was analysed by XPS. This technique was carried out on a VG

ESCALAB MK I spectrometer under a vacuum of 10^{-7} Torr. The study scan spectra was recorded using a pass energy of 100 eV. A curve-fitting program (PeakFit software version 4) that uses a Gaussian function was used to deconvolute the XPS peaks. The samples were dried for 24 h prior to analysis.

A Perkin-Elmer series II elemental analyser was used to determine the percentage of oxygen, nitrogen and hydrogen present in commercial and oxidised carbon fibres.

4.8. Scanning electron micrography (SEM)

A Cambridge Instrument 360 scanning electron microscope was used at an accelerating voltage of 10 kV to visualise the surface morphology and structure of commercial and modified ACC.

4.9. pH titration

Samples of 100 mg adsorbent were weighed using a Sartorius BP210D balance, (accuracy ± 0.0005 g), and placed into 25 ml conical flasks. A volume of 20 ml of 0.1 M NaCl was used in each experiment. A determined volume of 0.1 M sodium hydroxide or hydrochloric acid (between 0.1 and 5 ml) was used to obtain the shape of the curve over the entire pH range. The flasks were sealed with Parafilm and agitated by an orbital shaker at 300 min^{-1} for 48 h. Finally, the equilibrium pH of the solution was measured. Blank experiments without adsorbent were also performed.

4.10. Surface area and porosimetry

The surface area of commercial and chemically modified carbon fibres was determined by nitrogen (99.99% purity) adsorption/desorption at 77 K using a Micromeritics ASAP 2010 surface analyser. The adsorbents were outgassed at 378.15 K under a vacuum of <10 µm Hg for a minimum period of 24 h. Porosity distribution was calculated using density functional theory (DFT) [12].

5. Results and discussion

5.1. Surface area and porosimetry

Commercial ACC TC-66 C has a BET surface area of 973 $m^2 g^{-1}$. This was reduced after 3 h of chemical oxidation to 730 and 627 $m^2 g^{-1}$ for the AO and EO samples, respectively. The reduction in surface area can be attributed to erosion and blockage of pores by degradation products produced during chemical reaction.

The DFT pore size distribution of conventional and modified TC-66 C is shown in Fig. 3. These adsorbents are highly microporous with an average pore size of 17.9, 18.3 and 16.5 Å for the UO, AO and EO samples, respectively. Acid oxidation slightly enlarges the pores whereas electrochemical oxidation causes a slight reduction. A decrease in pore volume after chemical oxidation clearly corresponds with the loss in surface area.

5.2. Oxygen containing groups

The concentration and type of oxygen containing groups on the surface of conventional and oxidised adsorbents are shown in Fig. 4. The total ion exchange capacity is a factor of 3.5, 3.4 and 2.6 times higher than commercial ACC for the EO, OO and AO, respectively.

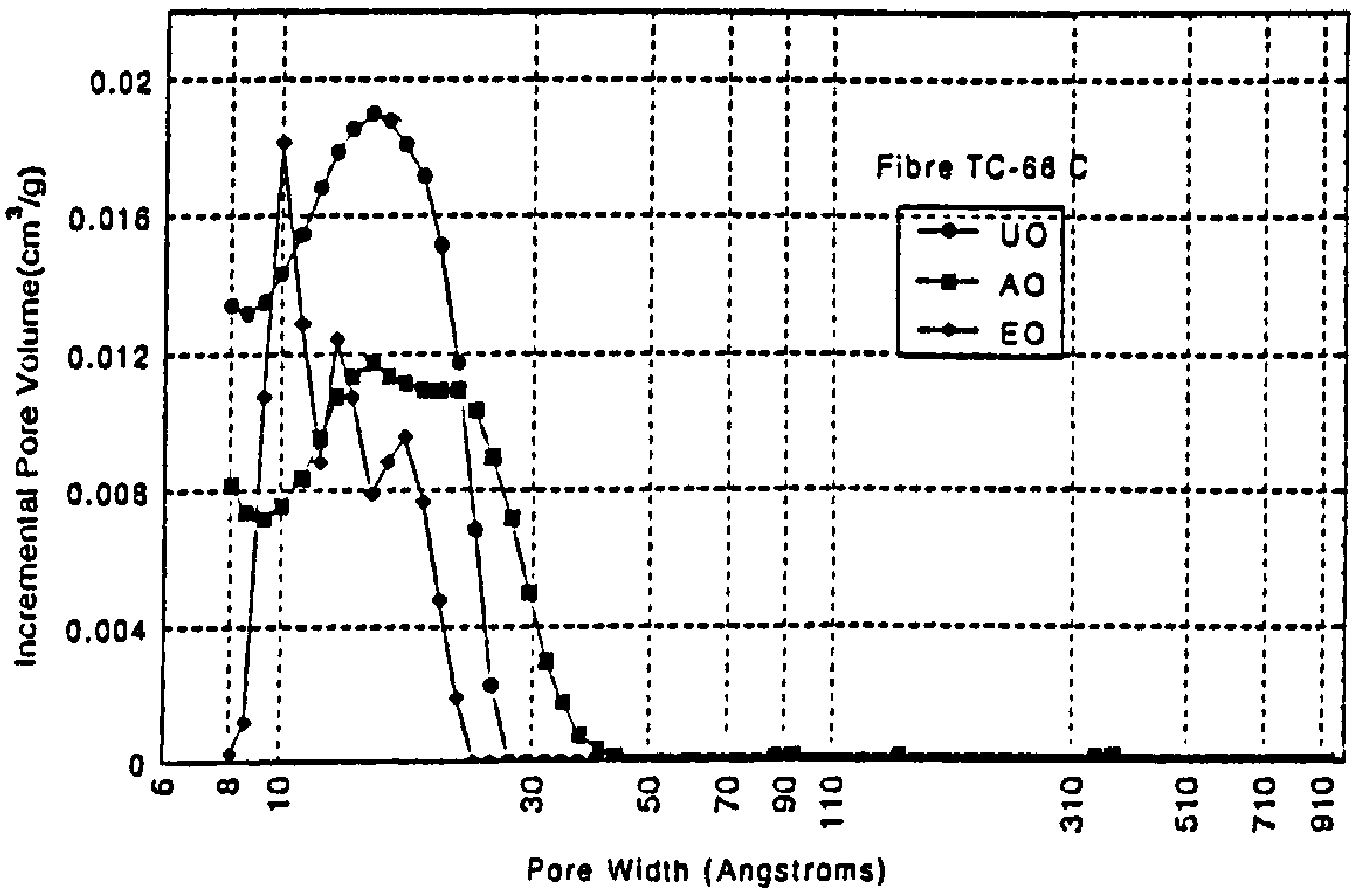

Fig. 3. Pore size distribution of the UO and oxidised TC-66C.

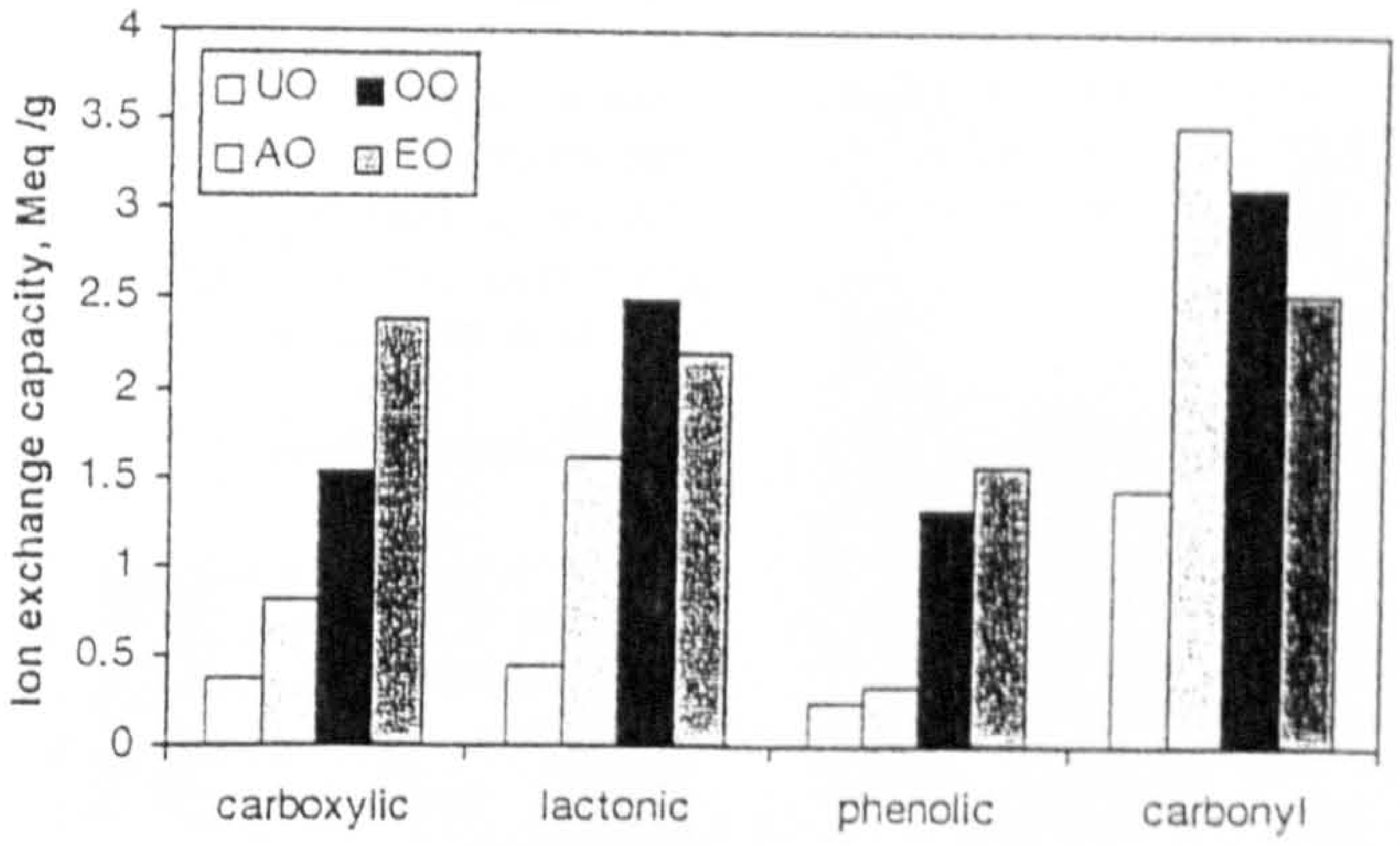

Fig. 4. Oxygen-containing groups present in the UO and oxidised TC-66 C.

The enhancement of oxygen-containing groups will significantly increase the cation sorption capacity at near-neutral pH due to the dissociation of the weakly acid groups; e.g. carboxylic groups dissociate between pH 3 and 6 [13].

5.3. X-ray photoelectron spectroscopy and elemental analysis

Figs. 5 and 6 show the spectra obtained by the XPS for conventional and modified TC-66 C. The high-energy resolution studies of carbon fibre show a major peak at an approximate binding energy of 284.6 eV, that can be attributed to a carbon ring structure (C – C) and CH_n. Other peaks detected at a shift of 2.9 and 4.18–4.33 eV from the main peak can be attributed to C = O (carbonyl), and COOH (carboxylic), respectively [14,15]. A more obvious shoulder appears at a binding energy of 287.6 in the modified sample and this may be attributed to carbonyl groups. Table 1 gives the percentage of carbon, nitrogen and oxygen in each sample. The results show a significant increase in oxygen content between the commercial and modified adsorbents. This is directly related to the increase in oxygen-containing surface groups that was confirmed by direct acid/base titration. These results also confirm that the oxygen content in TC-66 C follows the sequence electrochemical > ozone > acid oxidation.

The elemental analysis data (Table 2) shows the same trends as obtained by the XPS. The amount of oxygen estimated by elemental analysis is higher than that estimated by the XPS. Both techniques have limitations. The XPS analyses only a few atomic layers (5–10 nm) on the ACC surface; consequently, the composition reported corresponds only to the irradiated area. Elemental analysis, on the other hand, gives the average

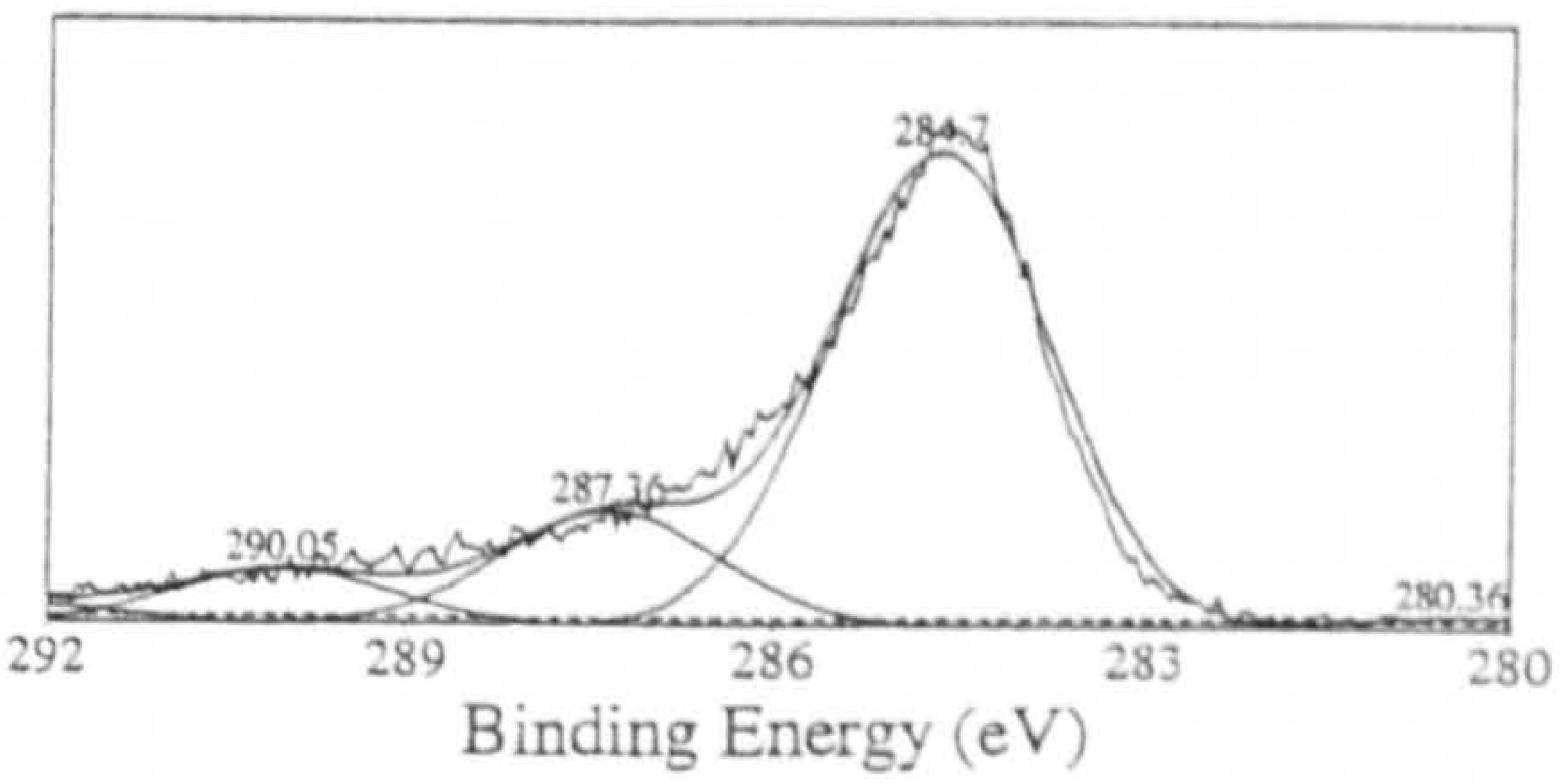

Fig. 5. The XPS spectra of TC-66 C.

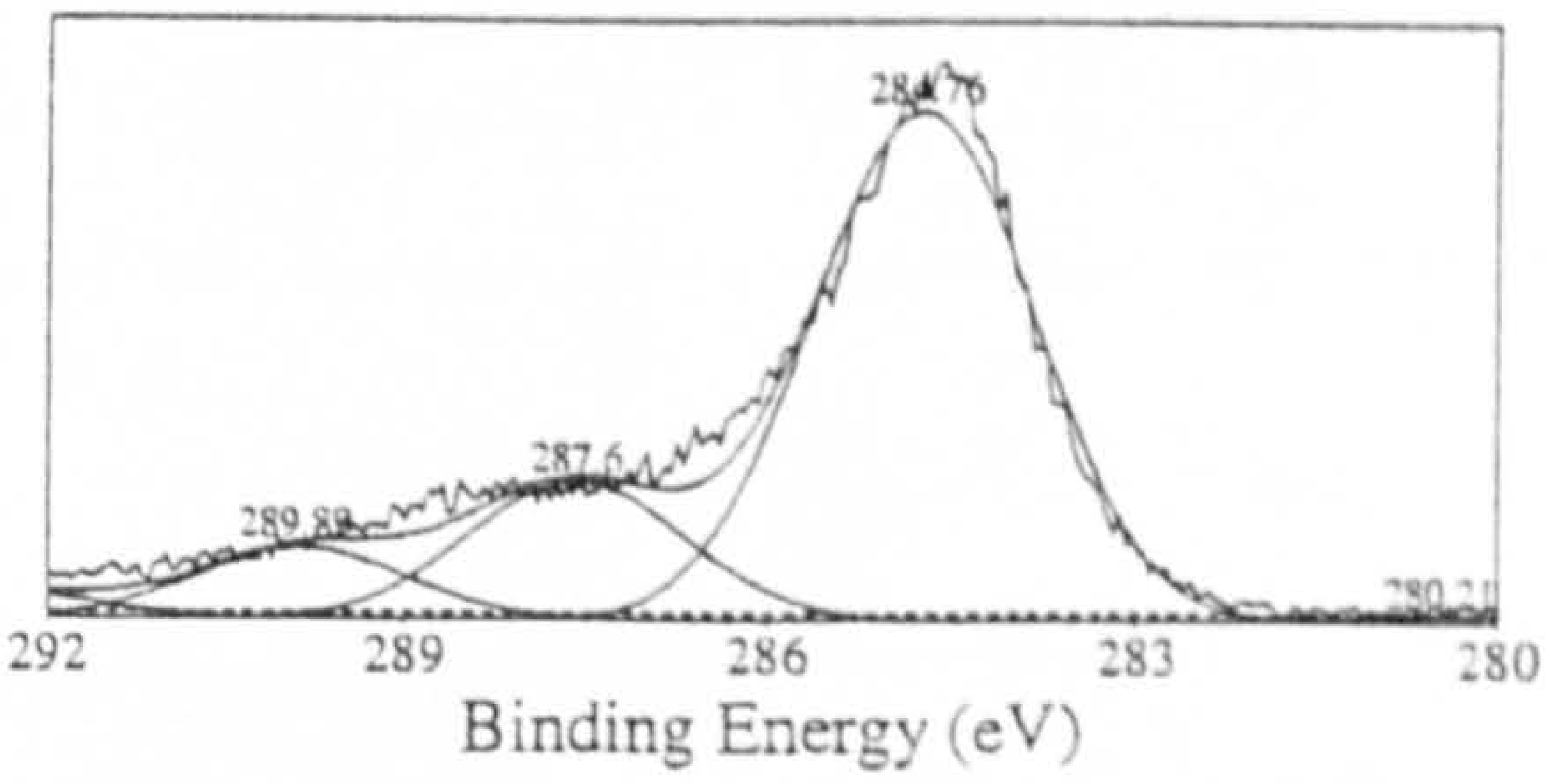

Fig. 6. The XPS spectra of AO TC-66 C.

Table 1
The XPS results for the UO and oxidised TC-66 C

Sample	C (%)	N (%)	O (%)
UO	82.8	3.4	12.1
AO	81.5	2.8	15.7
OO	77	2.5	19.3
EO	80.2	0.5	20.4

composition of the entire sample, but the oxygen composition is calculated by difference. Therefore, the results shown in Tables 1 and 2 should be treated with caution.

3.4. pH titration

Fig. 7 shows the point of zero charge (PZC) for the UO and modified TC-66 C. This is defined as the pH value at which surface charge is zero at a particular ambient temperature, applied pressure, and aqueous solution composition [16]. The PZC will change depending on the level of oxidation. It is shifted to lower pH values as the degree of oxidation increases due to the introduction of acidic groups such as carboxyl, phenolic, carbonyl and lactonic [17]. For instance, the PZC of the UO TC-66 C is at pH 4.2 whereas it is at pH 2.8 for the OO, at 2.4 for the AO and at 2.25 for the EO. It is well known that the sorption of metal ions strongly depends on the chemistry of the carbon surface [18]. The surface is positively charged at pH values below the PZC, since the oxygen-containing groups are undissociated and the adsorbent will remove anionic species from solution under these conditions. On the other hand, at solution pH values greater than the PZC, the carbon surface becomes more negative due to dissociation of weakly acidic oxygen-containing groups. Thus, the adsorbent surface is able to attract and exchange cations in solution. This renders the ACC capable of adsorbing trace metal ions from aqueous solution at pH values in excess of about 3.

Table 2
Elemental analysis for the UO and oxidised TC-66 C

Sample	C (%)	H (%)	N (%)	O (%)
UO	64.21	2.84	3.63	29.32
AO	60.97	2.81	3.9	32.32
OO	58.71	1.73	3.02	36.54
EO	56.34	2.07	2.29	39.3

3.5. Sodium capacity

The total sodium capacity for the conventional and modified TC-66 C is shown in Fig. 8. It is observed that the sodium capacity increases with time of oxidation for all samples. However, electrochemical oxidation is most effective and yields the highest ion exchange capacity. The sodium capacity does not increase much beyond 2 h of oxidation for the AO sample whereas for the OO and EO it continues to increase.

3.6. Scanning electron micrography

Figs. 9 and 10 show the SEMS for the commercial and OO carbon fibres TC-66 C, respectively. There is clear evidence of physical damage to the OO fibre when compared with the UO sample. However, there is no visual change in surface morphology for the AO and EO samples over periods of up to 3 h.

3.7. Sorption studies

The cadmium sorption capacity is increased by a factor of 13 when oxidised ACC is used (see Fig. 11). The highest sorption capacity is obtained with the EO fibre though the cadmium uptake by the OO and AO samples is also significantly enhanced. This is directly related to the increase of oxygen-containing groups, as detected by direct acid/base titration and confirmed by the XPS and elemental analysis. The effect of pH on cadmium adsorption is shown in Fig. 12. Cadmium

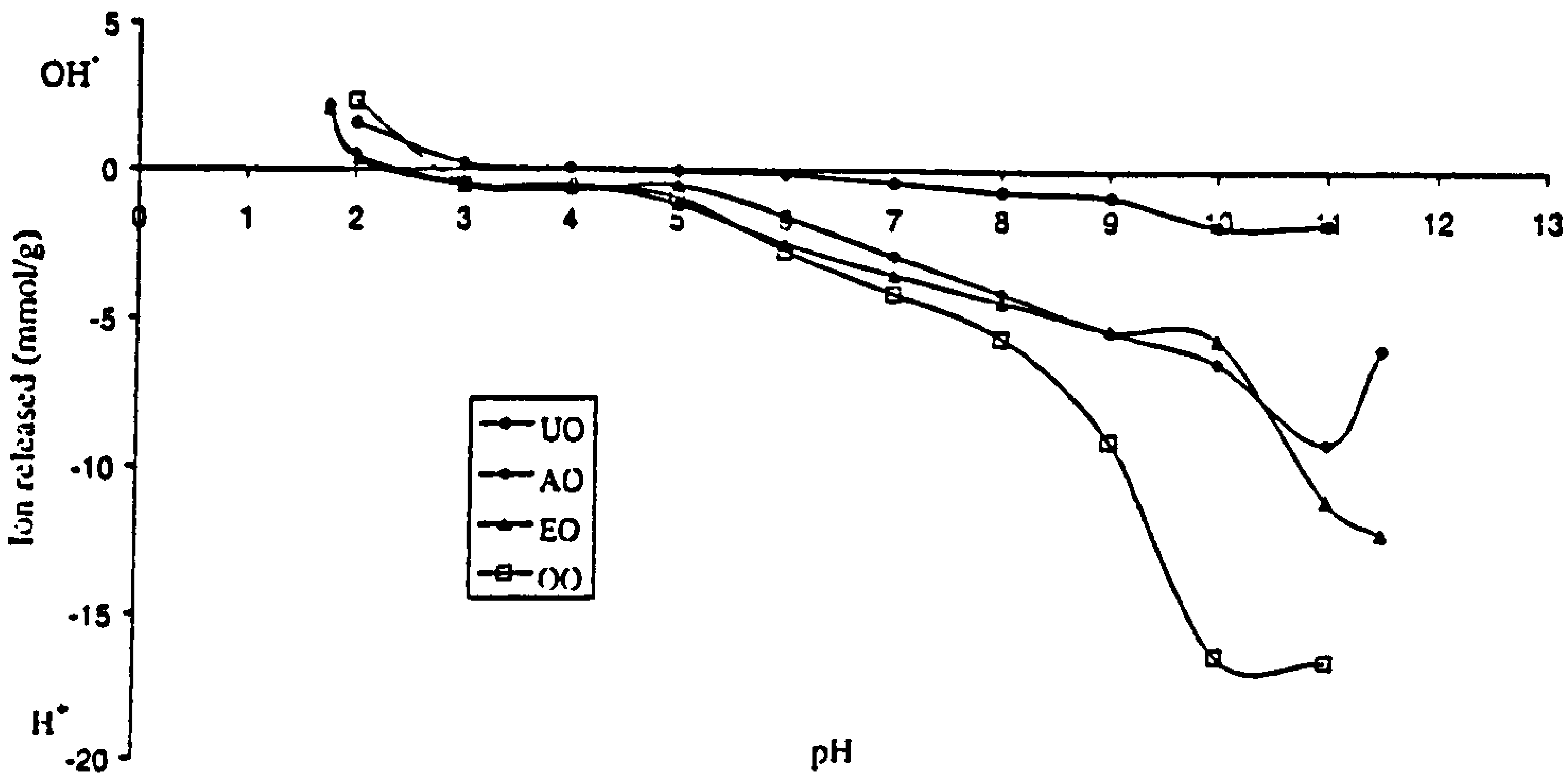

Fig. 7. The PZC of the UO and oxidised TC-66 C.

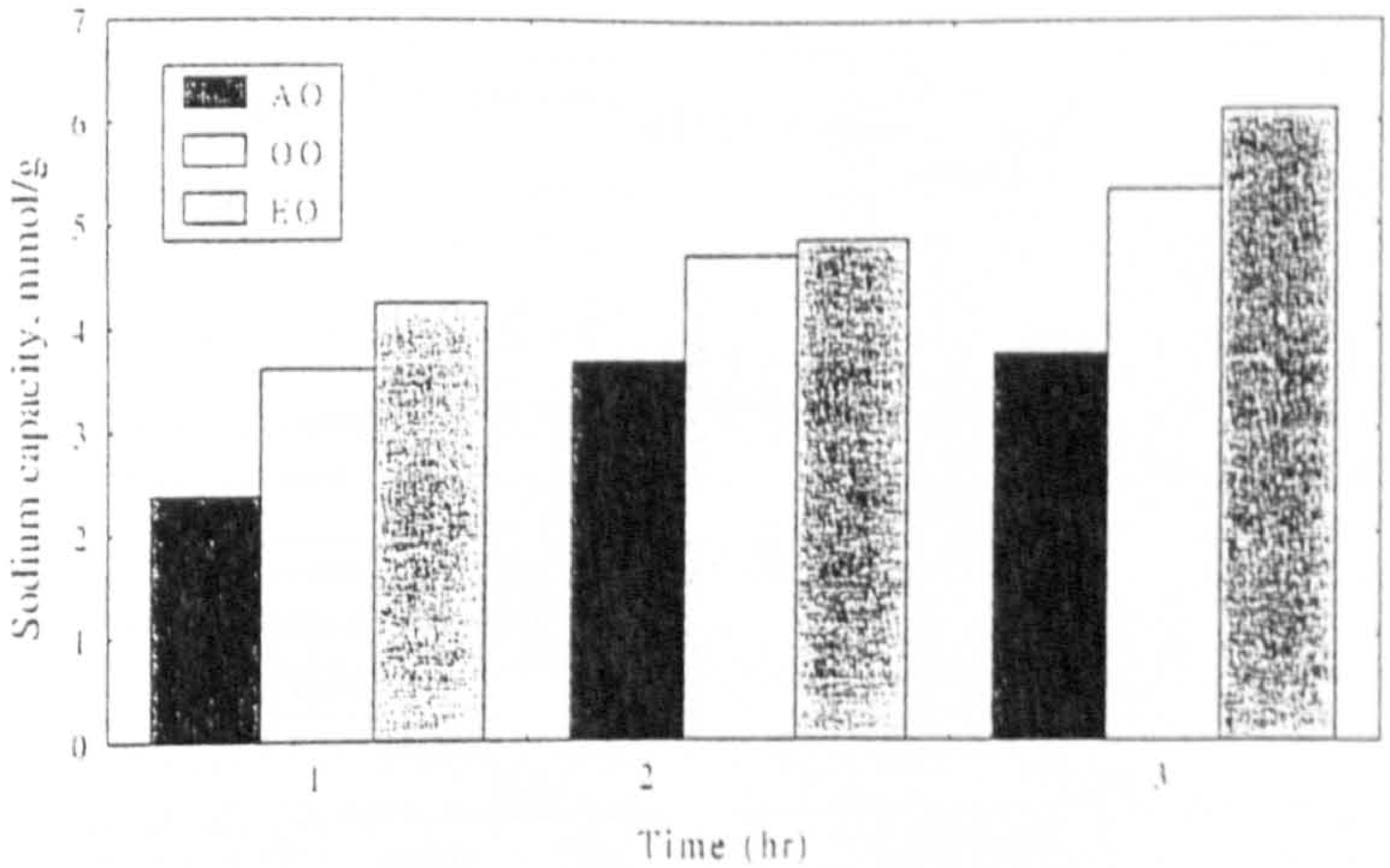

Fig. 8. Sodium capacity of the oxidised TC-66 C.

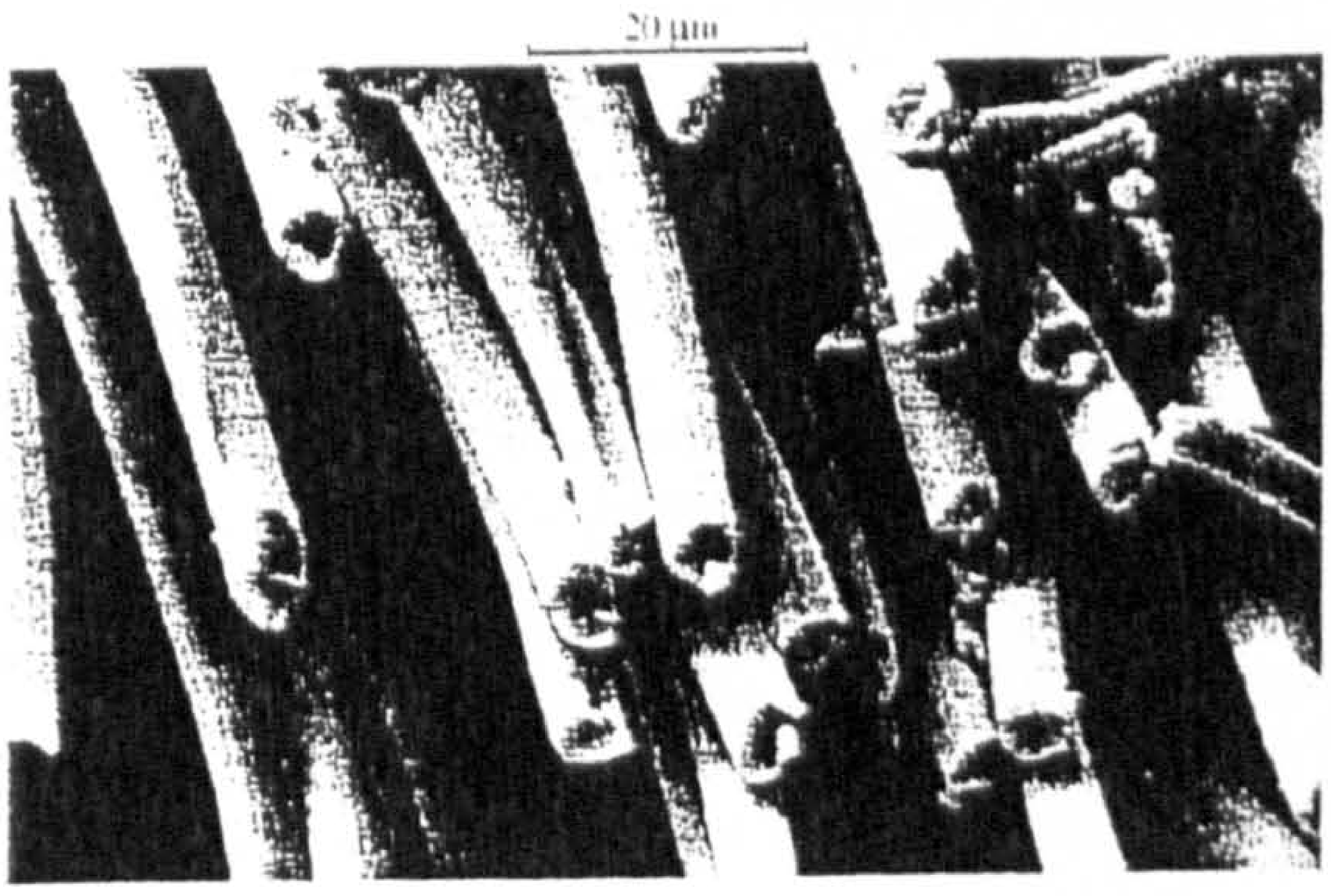

Fig. 9. The SEM of UO TC-66 C.

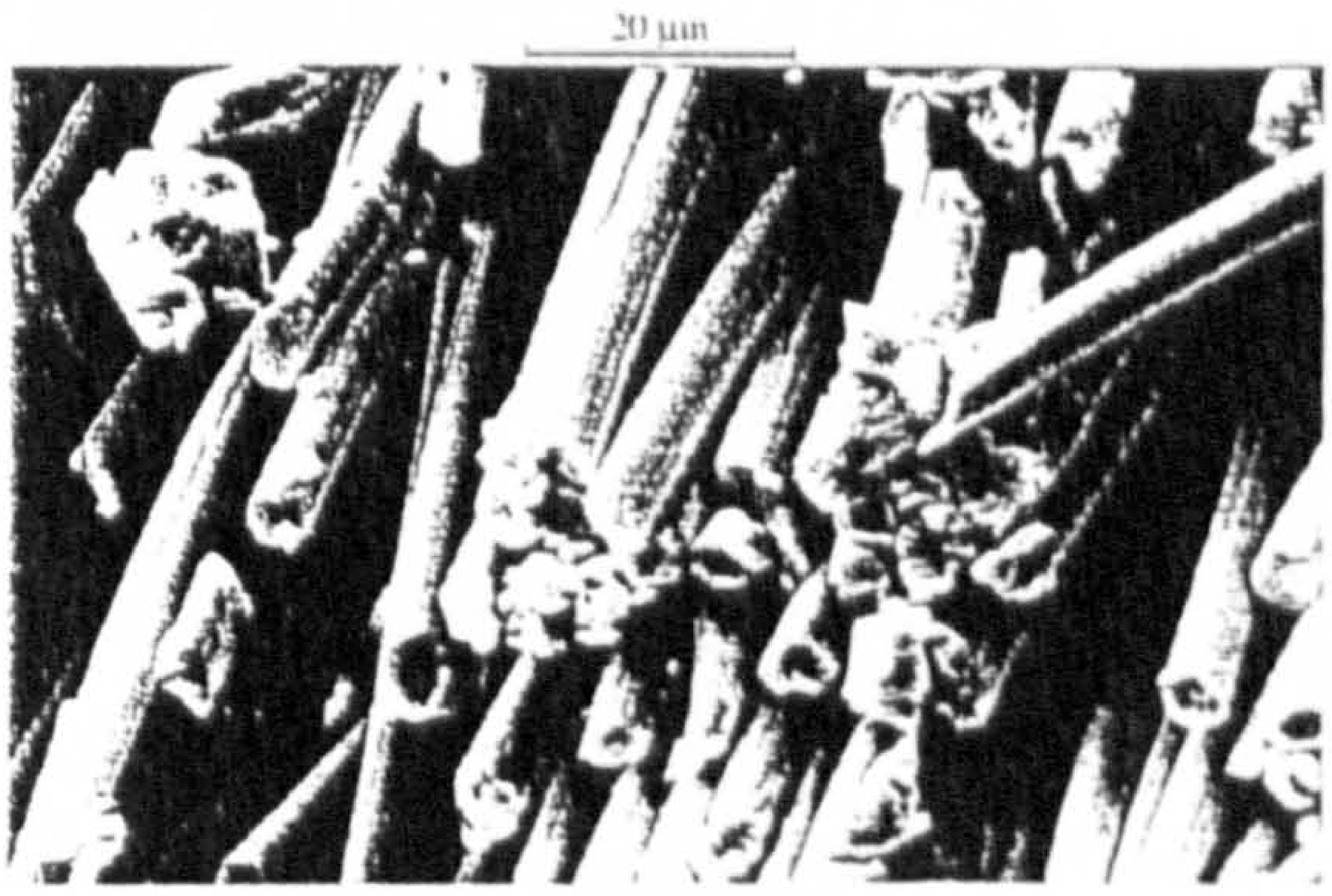

Fig. 10. The SEM of OO TC-66 C.

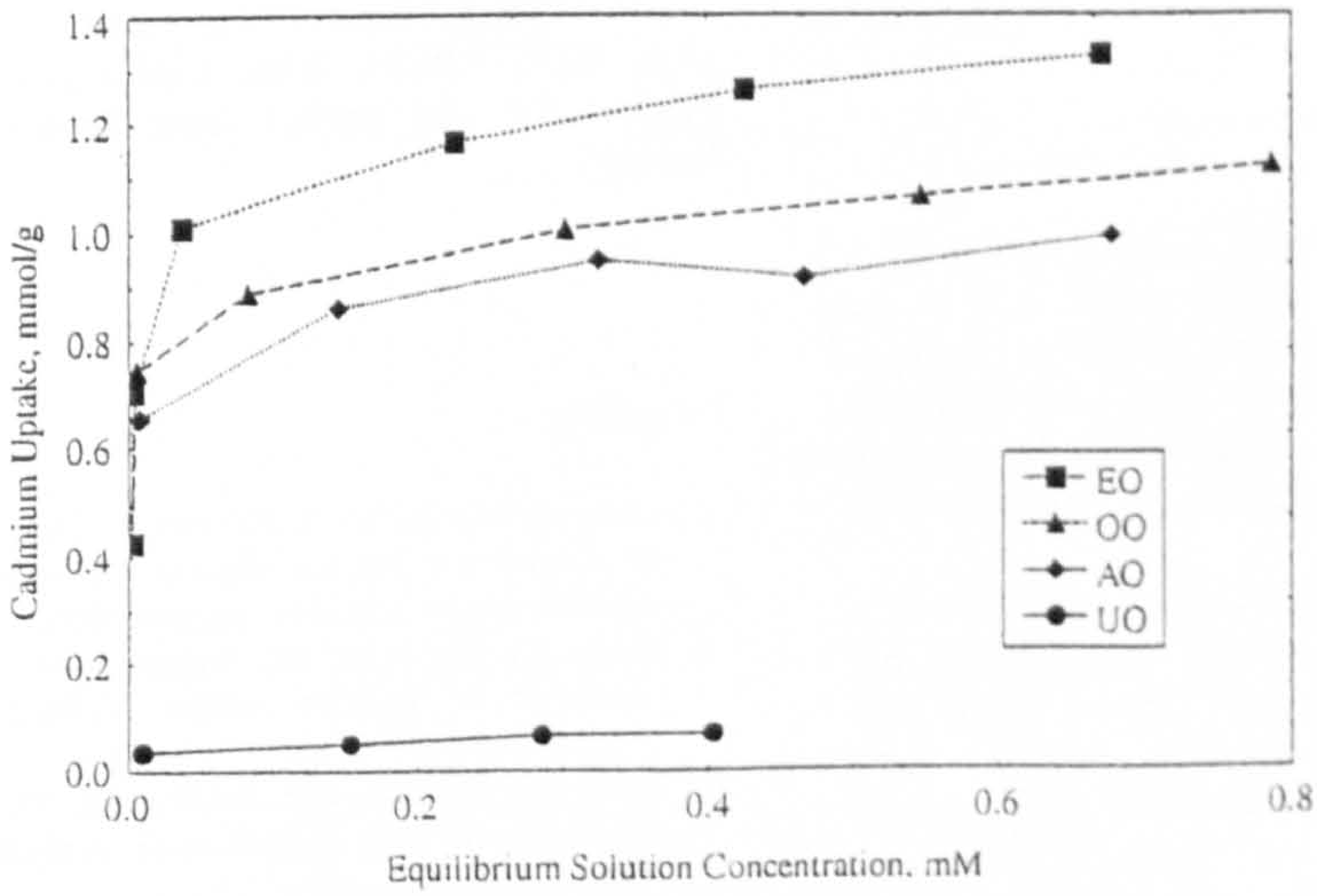

Fig. 11. Cadmium adsorption isotherms of the UO and oxidised TC-66 C at pH 5 and room temperature.

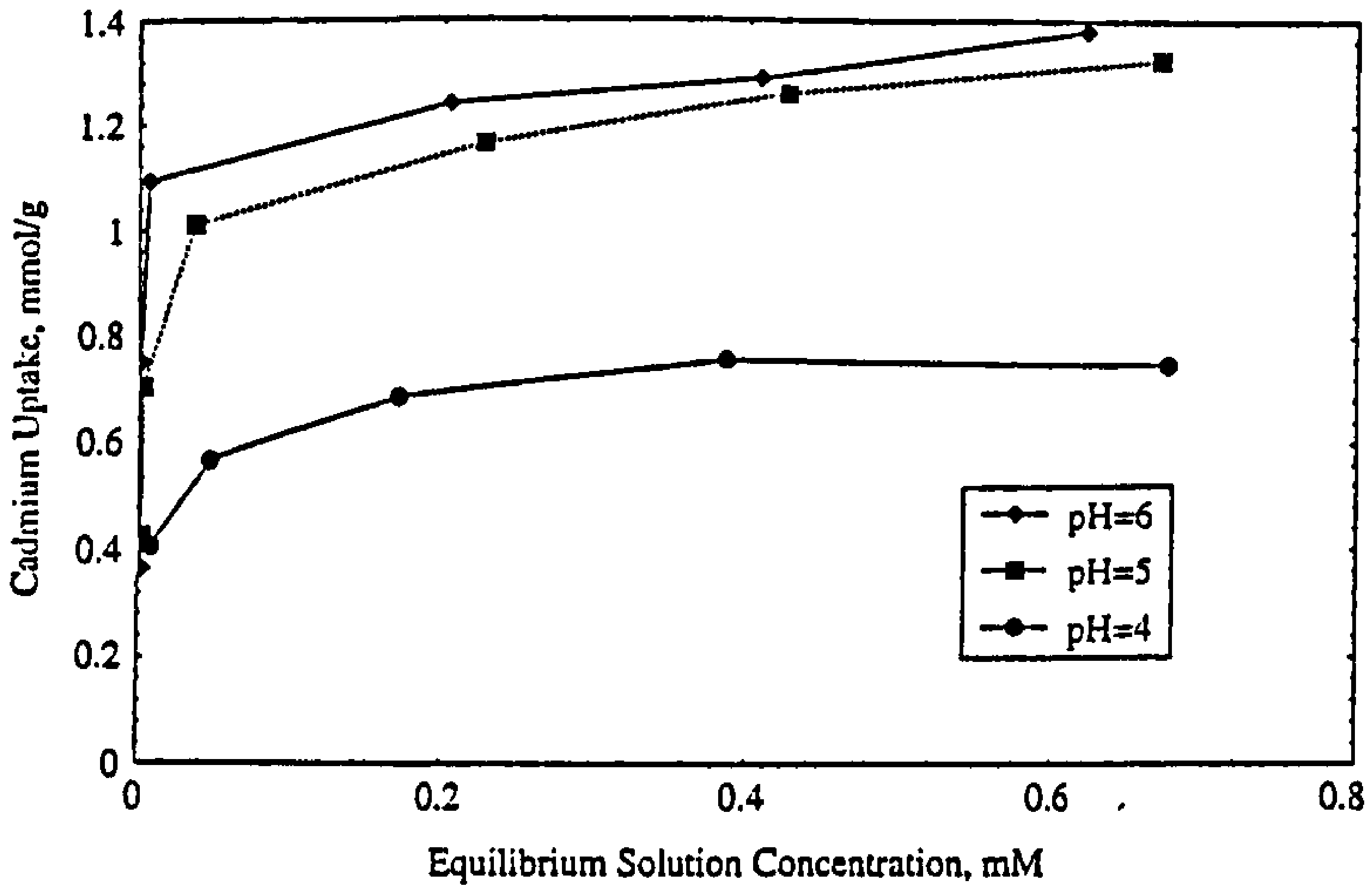

Fig. 12. Cadmium adsorption isotherms for the EO TC-66 C at different pHs and room temperature.

uptake increases as pH increases. The speciation of cadmium in aqueous solution at 298 K has been previously reported by us [19]. It was found that cadmium exists predominantly as Cd^{+2} and $CdCl^{+}$ in aqueous chloride solutions up to pH 7.5 and precipitates as $Cd(OH)_2$ just below pH 8. It has already been pointed out that the adsorbent surface is negatively charged at pH values higher than the PZC and becomes more negatively charged as the pH increases due to the dissociation of weakly acidic oxygen-containing groups (Fig. 7). Hence, positively charged cadmium species will ion exchange and/or complex with oxygenated surface functional groups at pH values in the region 4–6. Ion exchange is therefore the most likely adsorption mechanism.

6. Conclusions

A significant increase in ion exchange capacity is obtained during oxidation of the ACC due to the introduction of oxygen-containing functional groups as confirmed by direct titration, XPS and elemental analysis. The results also prove that the oxygen content follows the sequence: electrochemical > ozone > acid oxidation.

Cadmium capacity increases by a factor of 13 for the EO ACC. Also, cadmium uptake increases as pH increases. This is due to the dissociation of weakly acid groups such as carboxyl, phenolic, carbonyl and lactonic. At pH values greater than the PZC, surface charge becomes negative and therefore positively charged cadmium species can ion exchange and/or complex with the surface functional groups.

There is clear evidence of physical damage to the OO fibre. However, there is no change in surface morphology for the AO and EO oxidised samples. Some surface area is, however, lost due to erosion and blockage of the pores by degradation products produced during chemical reaction.

These results indicate the considerable potential for the oxidised ACC as an adsorbent for large-scale removal of trace metal pollutants from water and aqueous effluent at neutral or near-neutral pH values.

Acknowledgements

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CONFERENCE PAPERS

SORPTION OF CADMIUM ON MODIFIED AND CONVENTIONAL GRANULAR AND FIBROUS ACTIVATED CARBON

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Introduction

The presence of heavy metals in wastewater and effluents is a matter of primary environmental concern due to toxicity. Adsorption and ion exchange are techniques that have been widely applied for treatment of metal bearing effluents. For example, studies of cadmium adsorption onto carbon based materials have been reported in recent years (1-3). Activated carbon is a widely used sorbent in water treatment and its sorption properties towards metal ions can be enhanced by surface modification.

Cadmium adsorption studies were conducted using a wood based conventional activated carbon, AUG WHK, and an activated carbon cloth based on polyacrylonitrile, KoTHmex TC-66 C. These were oxidised by concentrated nitric acid to enhance their cation sorption capacity. Physical characterisations and ion exchange studies of conventional and oxidised samples have been performed and are reported.

Experimental

The granular activated carbon (AUG WHK) was sieved to a particle size fraction of 170-210 µm. This was washed thoroughly with distilled water and then dried at 115 °C for 24 hours prior to use.

Cadmium solutions were prepared using $CdCl_2 \cdot H_2O$ and distilled water. The solution pH was adjusted by addition of 0.1M HNO_3 and 0.1M NaOH.

Acid Oxidation. Granular and fibrous activated carbons were oxidised using nitric acid. Samples of the carbon based materials and nitric acid slution were placed into a flask and the oxidation reaction was carried out for 3 hours at 90 °C. Temperature was monitored by a thermometer placed in the reaction mixture. A condenser was fitted to the flask to prevent liquid loss by evaporation. Nitrogen was injected through a glass tube to stir the adsorbent/acid mixture. Samples were oxidised by using a mixture consisting of distilled water and 16M nitric acid in 1:1 ratio. The reaction mixture used for oxidation of TC-66 C was 40 ml of nitric acid and 40 ml of distilled water.

After oxidation, the adsorbents were separated from the acid solution and washed. The oxidised WHK was washed with 0.1M sodium hydroxide solution to remove brownish humic type substances. Washing was continued until the outlet solution was colourless. This was followed by washing with 0.1M hydrochloric acid to neutralise the sodium hydroxide. The carbon was then washed with distilled water until the solution pH in the column inlet and outlet was the same.

Oxidised TC-66 C was placed into a conical flask containing 1M sodium hydroxide for 1.5 hours. The excess of sodium hydroxide was extracted using distilled water in a Soxhlet equipment for 48 hours. The carbon cloth was converted to hydrogen form by contacting with 0.1M HCl solution. Finally the adsorbents were dried in an oven at 115 °C for 24 hours. The drying of activated carbon was continued until there was no change in weight.

Batch Sorption Experiments. A 100 ml conical flask was used as batch reactor to obtain adsorption isotherm data. A predetermined mass of adsorbent was contacted with 50 ml of cadmium solution of known initial concentration and pH. The solution pH was adjusted daily until a constant pH was obtained. The cadmium concentration was determined when the equilibrium pH reached a constant value.

Mini-column Experiments. Mini-columns were packed with 0.5 g of unoxidised or acid oxidised samples. 1.1 mM cadmium feed solution at pH 6 was passed through the columns to obtain the breakthrough curves. The flow rate was 10 BV h^{-1}.

Characterisation. Surface area and pore size distribution of the adsorbents were obtained by nitrogen adsorption/desorption at 77 K using a Micromeritics ASAP2010 surface analyser.

Analysis. The cadmium concentration was determined using a Varian SpectrAA 200 atomic absorption spectrophotometer in flame emission mode. The solution pH was measured using a Mettler Toledo 340 pH meter.

Results and Discussion

Figure 1 shows that there is a significant increase in cadmium adsorption when acid oxidised adsorbents are used. The cadmium adsorption capacity increased by a factor of 15.5 and 12 respectively when acid oxidised WHK and TC-66 C were used. This large improvement in adsorption capacity can be attributed to the enhancement of surface acidic functional groups introduced during chemical oxidation.

Table 1 shows that oxidised WHK has a slightly lower BET surface area than oxidised TC-66 C. However, modified WHK has a higher cadmium adsorption capacity. This can be attributed, in part, to a difference in pore size distribution (Figure 2). WHK has a combination of micropores (<20 Å) and mesopores (>20Å) which are more accessible and offer less resistance to intraparticle diffusion. TC-66 C, on the other hand, is highly microporous and this may impede diffusion and limit sorption of trace metals.

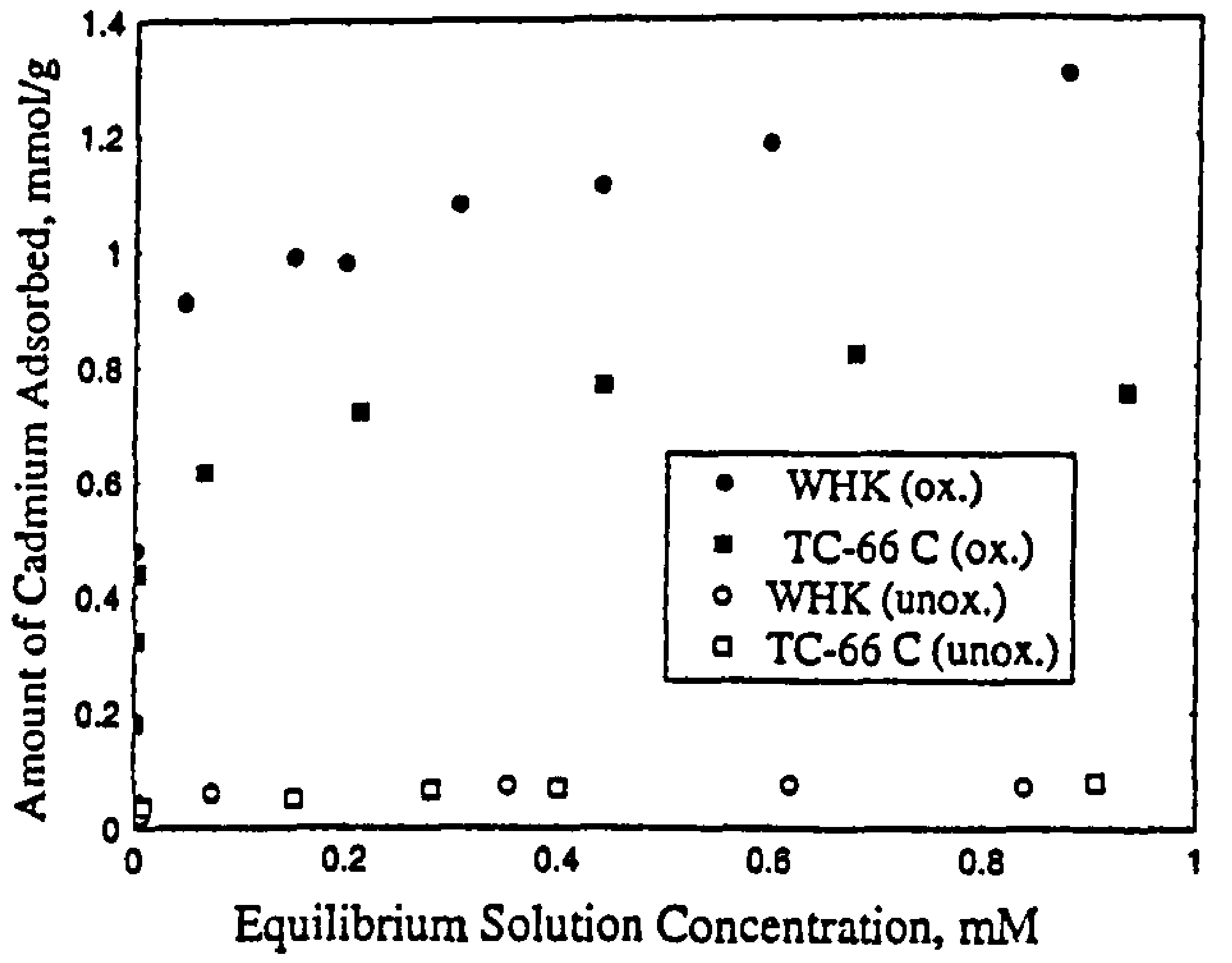

Figure 1. Cadmium adsorption isotherms for unoxidised and acid oxidised WHK and TC-66 C, at pH 6 and room temperature.

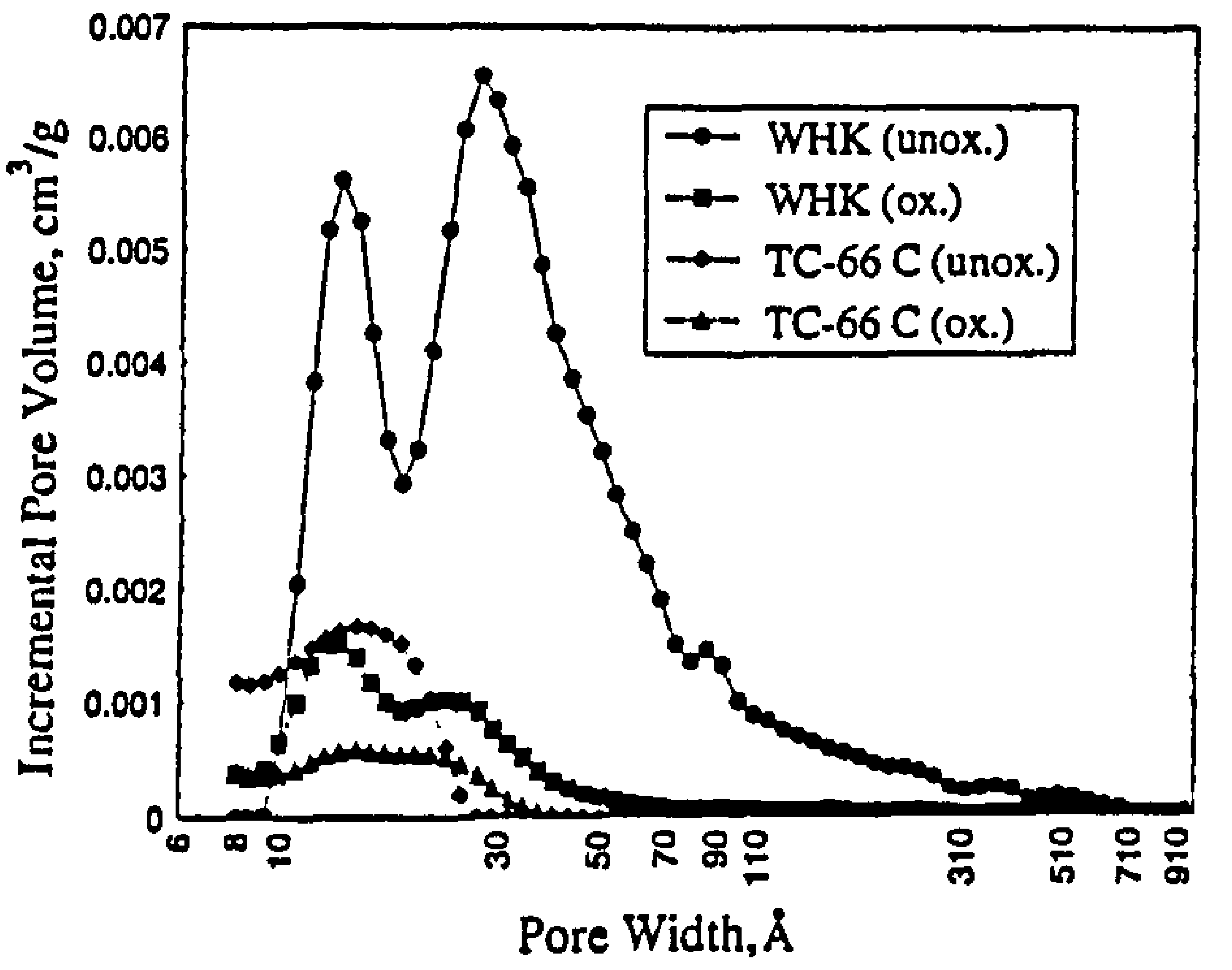

Figure 2. DFT pore size distribution of unoxidised and acid oxidised WHK and TC-66 C.

Results of mini-column trials are shown in Figure 3. The graph gives a comparison of cadmium uptake by unoxidised and acid oxidised WHK and TC-66 C and confirms the significant improvement of performance of oxidised materials. Breakthrough occurs at about 140 BV for oxidised WHK whereas it is almost instantaneous for the unoxidised sample.

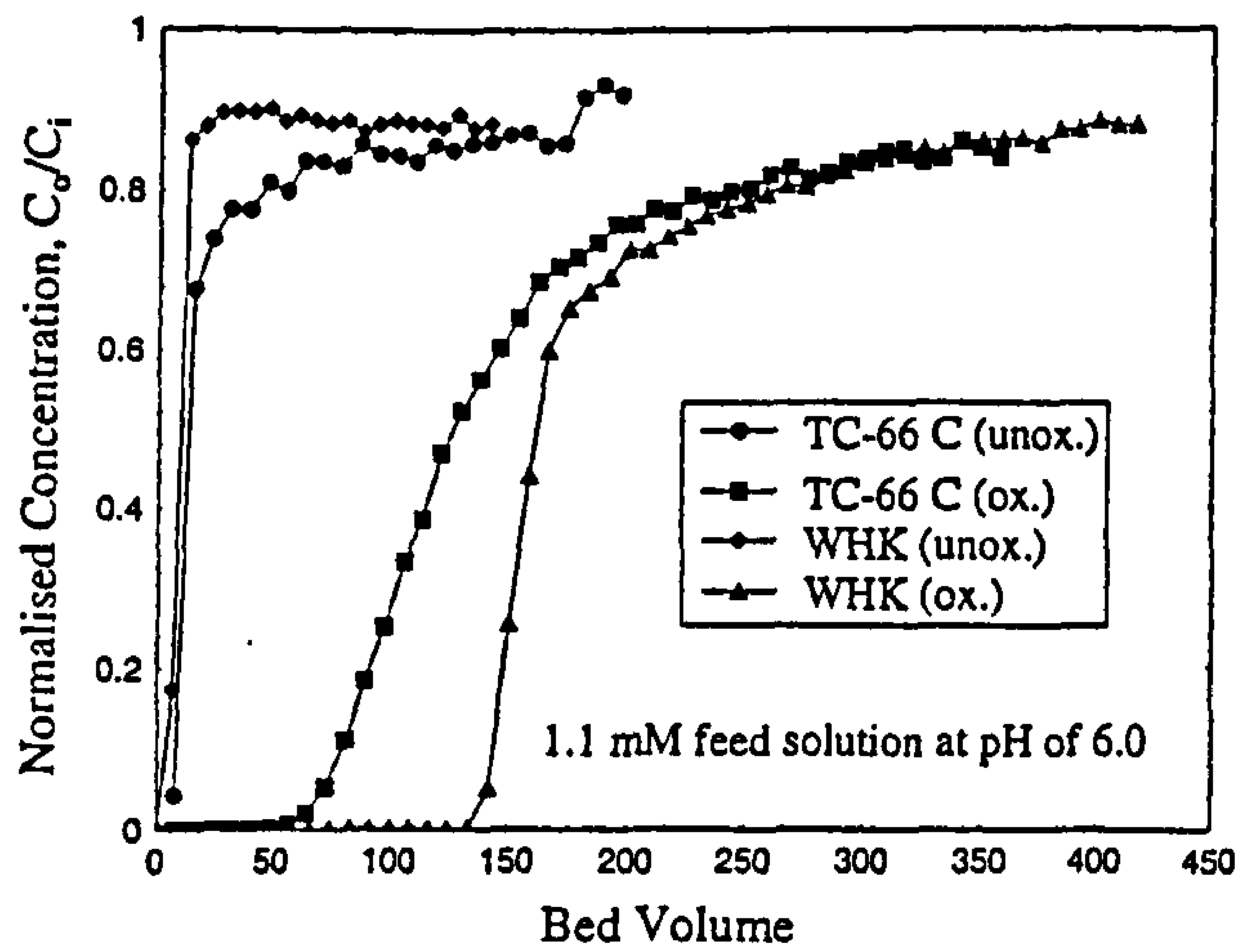

Figure 3. Cadmium breakthrough results for unoxidised and acid oxidised WHK and TC-66 C.

Table 1. Surface area of unoxidised and acid oxidised WHK and TC-66 C.

Adsorbent	BET Surface Area,[m²/g]
WHK (unox.)	1912.40
WHK (ox.)	714.34
TC-66 C (unox.)	972.73
TC-66 C (ox.)	730.19

Conclusions

A significant increase in cadmium uptake was obtained by acid oxidation. Acid oxidised WHK and TC-66 C have 15.5 and 12 times higher cadmium capacity compared to their unoxidised forms. Some surface area is lost during acid oxidation due to chemical reaction.

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CADMIUM SORPTION FROM AQUEOUS SOLUTIONS: ENHANCEMENT OF SURFACE GROUPS ON ACTIVATED CARBON CLOTH BY NITRIC ACID, OZONE AND ELECTROCHEMICAL OXIDATION

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KEYWORDS

Sorption, cadmium, oxidation, surface groups, kinetics.

INTRODUCTION

The presence of heavy metals such as cadmium in wastewater and aqueous environment is a matter of primary concern due to the risk that it may pose to human health. In recent years, a variety of granular activated carbons and ion exchange resins have been used to treat a wide range of domestic and industrial effluents containing heavy metals. For instance, the sorption of cadmium by conventional activated carbons has been previously reported[1,2]. Activated carbon cloth (ACC) has been developed in recent years and possesses high surface area and compactness that can lead to the design of intensified water treatment systems.

Sorption studies were conducted using an activated carbon cloth based on polyacrylonitrile, KoTHmex TC-66 C. This material was modified by nitric acid, ozone and electrochemical oxidation to enhance cation sorption capacity. Chemical and physical characterisations were compared before and after oxidation. Kinetic and batch experiments have been carried out and are reported.

EXPERIMENTAL

Activated carbon cloth TC-66 C was washed with distilled water and then dried in an oven at 105 °C for 24 hours prior to use. Cadmium solution was prepared using $CdCl_2 \cdot H_2O$ and distilled water, and the solution pH was adjusted using 0.1M nitric acid and sodium hydroxide.

Acid Oxidation. 2 g of TC-66 C and 80 ml of 8M nitric acid were placed into a three-necked round-bottomed flask. The oxidation reaction was conducted for 3 hours at 90 °C. A condenser was fitted to the reactor to prevent liquid loss by evaporation. Nitrogen was injected through a glass tube to stir the sorbent/acid mixture and the temperature was monitored.

Ozone Oxidation. Activated carbon was oxidised using ozone. 1000 cm^3 min^{-1} of dry air was passed through an ozone generator; the ozonization voltage was fixed at 9 volts. The outlet of the ozone generator was connected to a horizontal glass reactor containing 1 g of ACC. Ozone oxidation was carried out for 3 hours at room temperature.

Electrochemical Oxidation. The electrochemical cell was immersed in a water bath and the temperature was maintained at 25 °C using a temperature controller. A 20 cm^2 sample of ACC was attached to the anode, and the oxidation was carried out applying 40mA cm^{-2} for 3 hours. 0.5M KCl was used as electrolyte.

The oxidised TC-66 C was contacted with 1M NaOH in a conical flask for 1.5 hours. The excess sodium hydroxide was extracted with distilled water in a Soxhlet apparatus for 48 hours. Finally the modified samples were converted to hydrogen form by contacting them with 0.1M HCl and then dried in an oven at 105 °C for 24 hours.

Kinetic Experiments. 1.9 L of distilled water was added to a round-bottomed flask, and 1 g of adsorbent was placed into a rotating basket. The basket containing activated carbon was placed in the reactor and connected to a stirrer. 10 ml of cadmium solution, of known initial concentration, was added to the reactor and the timer and the stirrer motor (set at 250 rpm) started immediately. Samples were collected at certain time intervals for 2 hours.

Batch Sorption Studies. A predetermined mass of ACC was contacted with 50 ml of cadmium solution of known initial concentration and pH. The solution pH was adjusted daily until a constant pH value was obtained and then the cadmium concentration was determined.

Characterisation. 0.1g of ACC was contacted, for seven days, with 20 ml of 0.1M solutions of NaOH, $NaCO_3$, $NaHCO_3$ and $NaOC_2H_5$ (dissolved in HPLC grade ethanol) in order to determine the amount and type of oxygen-containing groups[3]. Finally a 5 ml aliquot was titrated with 0.1 M HCl using methyl red as indicator.

Surface area of the adsorbents was determined by nitrogen adsorption/desorption at 77K using a Micromeritics ASAP2010 surface analyser.

Analysis. A Varian SpectrAA 200 atomic absorption spectrophotometer in flame emission mode was used to determine the cadmium concentration. The solution pH was measured using a Mettler Toledo 340 pH meter.

RESULTS AND DISCUSSION

Oxidised samples of ACC show a significant increase of ion exchange capacity, from 2.48 to 8.66 meq g^{-1} (see Table 1). However, the surface area decreased from about 972-627 m^2 g^{-1} due to oxidation, but this is entirely adequate for water treatment.

Table 1. Oxygen containing groups and surface area

TC-66 C	Carboxyl	Lactonic	Phenolic	Carbonyl	Total capacity meq g^{-1}	BET surface area m^2 g^{-1}
Unoxidised	0.36	0.44	0.24	1.43	2.48	972.73
Acid-ox	0.82	1.61	0.54	3.48	6.46	730.19
Ozone-ox	1.53	2.48	1.32	3.14	8.47	-
Electro-ox	2.37	2.19	1.56	2.54	8.66	627.23

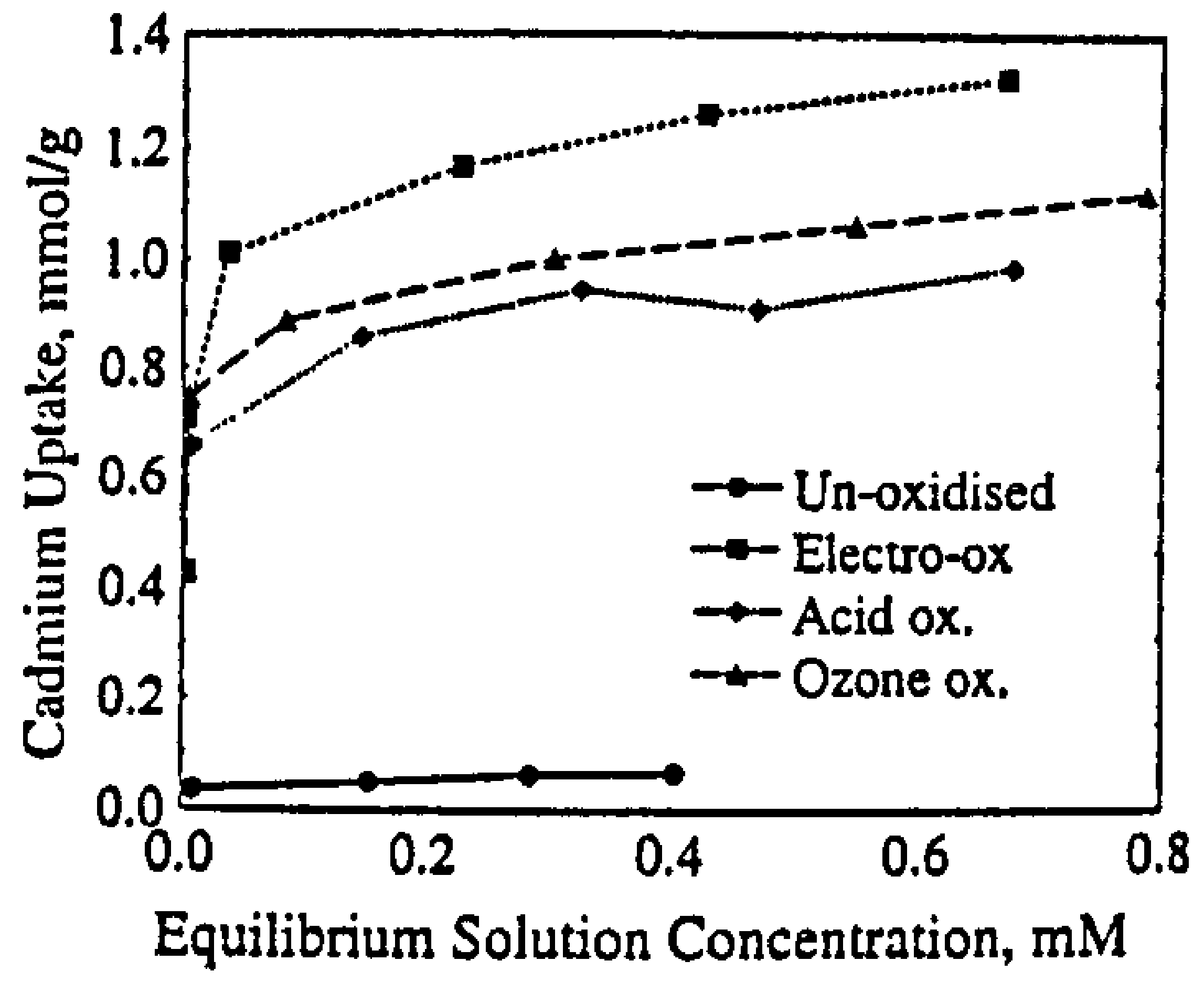

Fig 1. Cadmium adsorption isotherms for TC-66 C, at pH 5 and room temperature

The isotherms presented in Fig 1 are in agreement with the results presented above. An important increase, up to 13 times higher, in cadmium uptake is observed when oxidised ACC is used. The highest sorption capacity is obtained by electrochemical oxidation. This is directly related to the enhancement of oxygen-containing groups.

The data presented in Fig 2 show fast kinetics for both unoxidised and oxidised samples. About 90 and 96% of the total cadmium uptake was achieved in 18 minutes for unoxidised and oxidised ACC, respectively. The slight decrease in sorption rate may be due to a reduction in pore size as a result of chemical erosion.

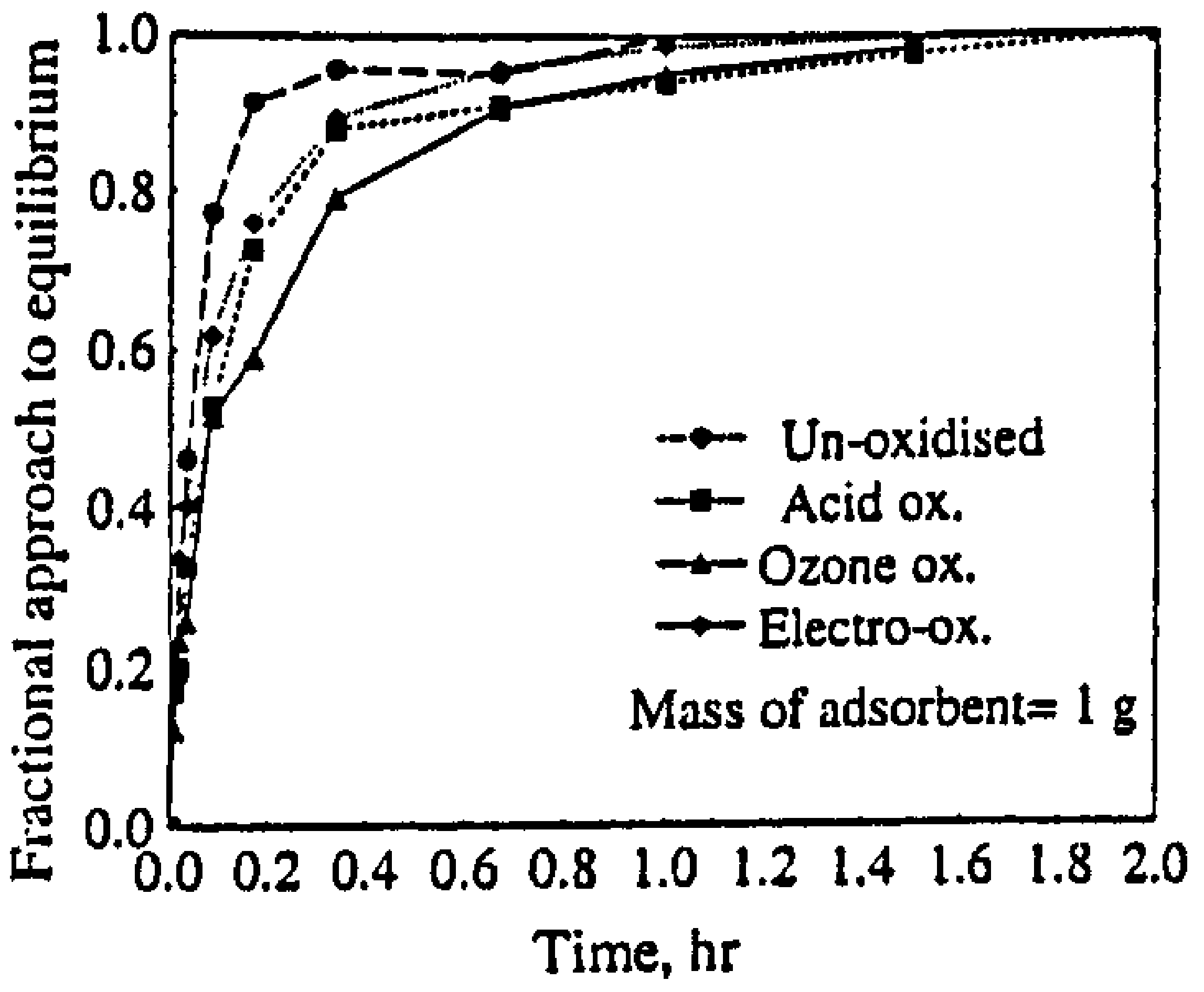

Fig 2. Sorption rate for cadmium using TC-66 C, at 25 °C and 250 rpm

CONCLUSIONS

A significant increase in ion exchange capacity is generated during oxidation. This enhances the cadmium sorption capacity by a factor of 13 compared to unoxidised ACC. The sorption rate of cadmium slightly decreases when oxidised samples are used. Some surface area is lost due to chemical reaction.

ACKNOWLEDGEMENTS

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MERCURY AND CADMIUM ADSORPTION BY CONVENTIONAL AND MODIFIED GRANULAR ACTIVATED CARBON

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Introduction

In the last few years, a number of adsorption and ion exchange techniques have been developed to treat a wide range of domestic and industrial effluents containing heavy metals. Carbonaceous materials have been extensively used to remove a wide range of contaminants from wastewater, especially organic micropollutants, and to a lesser extent toxic heavy metals. Conventional granular activated carbon can be modified by oxidation to enhance metal uptake. It is now well established that oxidation results in a significant increase in the proportion of weakly acidic groups present on the surface of the adsorbent.

A wood based activated granular carbon (WHK) was electrochemically modified to enhance cation sorption capacity. Modified adsorbents were physically and chemically characterised by direct titration, X-ray photoelectron spectroscopy (XPS), elemental analysis, surface area, electrophoretic mobility measurements, and scanning electron microscopy (SEM). Batch sorption experiments, breakthrough curves and desorption experiments were carried out to determine the sorption performance of the modified adsorbent. The effect of pH on the sorption process was also investigated.

Experimental

Mercury and cadmium solutions were prepared using $HgCl_2$ and $CdCl_2 \cdot H_2O$, respectively. The solution pH was adjusted using 0.1M HNO_3 and NaOH. Mercury was analysed at 575 nm against a reagent blank using a UV/VIS spectrophotometer (Perkin Elmer lambda 12) with 10 mm quartz cells. Rhodamine 6G was used in order to achieve these analyses[1]. A Varian SpectrAA 200 atomic absorption spectrophotometer in flame emission mode was used to determine cadmium concentration. The solution pH was measured using a Mettler Toledo 340 pH meter. Electrophoretic mobility was measured by using a Malvern Instrument Zetasizer model 3000HAS.

Granular activated carbon (WHK) was supplied by AUG, Germany. This material was sieved to a particle size fraction of 170-210 μm, washed carefully with distilled water and then dried in an oven at 378 K for 24 hours.

The commercial granular carbon was electrochemically oxidised for 3 hours to enhance the sorption capacity. It was modified by applying a current of 3 mA m^{-2} in the presence of 0.5 M KCl as electrolyte. The comprehensive oxidation procedure has been reported elsewhere[2]
The adsorbent was washed in a column with 0.1 M NaOH solution until the outlet solution was colourless in order to remove humic substances and by-products produced during oxidation. This was followed by washing with 0.1 M HCl solution. The carbon was then washed with distilled water until the solution pH in the column inlet and outlet was identical. Finally, the adsorbent was dried in an oven at 378 K for 24 hours.

Conventional and modified granular activated carbons were chemically analysed by XPS, elemental analysis, direct titration, and zeta potential. XPS studies were carried out on a VG ESCALAB MK I spectrometer under a vacuum of 10^{-7} torr. The study scan spectra was recorded using a pass energy of 100 eV. An elemental analyser (Perkin Elemer series II) was utilised to determine the percentage of O, N and H present in both commercial and modified samples. The distribution of oxygen-containing groups was analysed by direct titration using the Boehm method[3]. The samples were contacted with basic solutions of different strength, i.e. NaOH, $NaCO_3$, $NaHCO_3$ and $NaOC_2H_5$ (dissolved in HPLC grade ethanol). A pre-determined amount of adsorbent was placed in a 50 ml conical flask and then contacted with 20 ml of each alkali solution. The flask was sealed and stirred using an orbital shaker at 300 min^{-1} for seven days. The solution was filtered using a 0.2 μm PTFE syringe top filter to remove adsorbent particles. Finally a 5 ml aliquot was titrated with volumetric standard HCl solution using a glass burette (tolerance ± 0.02ml) with methyl red as indicator. A simple mass balance was used to determine the ion exchange capacity of each oxygen-containing group. Electrophoretic mobility measurements were conducted by contacting 10 mg of adsorbent, <90μm, with 0.1M NaCl solution. The solution pH was varied using 0.1M HCl and 0.1M NaOH. The samples were stirred for 48 hours prior to analysis.

Physical characterisation consists of surface area and SEM studies. Surface area analyses were carried out by nitrogen adsorption/desorption at 77K using a Micromeritics ASAP 2010 surface analyser. The surface morphology of the adsorbents was visualised by using a scanning electron microscope (Cambridge Instrument 360) at an acceleration voltage of 10kV.

Batch sorption experiments and column breakthrough experiments were performed in order to establish the sorption capacity of conventional and oxidised carbons,.

A fixed mass of WHK was contacted with 50 ml of cadmium solution of known initial concentration and pH. The solution pH was adjusted daily until a constant pH value was obtained and then the cadmium concentration was determined. Alternatively, a predetermined amount of carbon was placed in a mini-plastic column. A mixed solution of cadmium and mercury, at a known pH and concentration, was passed through the column. The flow rate was kept at 10 BV per hour (12 ml hr^{-1}). The carbon bed was regenerated with 0.2M HCl.

Results and Discussion

The results obtained by XPS and elemental analysis (Tables 1 and 2) show an increase in oxygen content in electro-oxidised samples. The amount of oxygen found by elemental analysis is higher than that reported by XPS. Both techniques have limitations. XPS analyses only a few atomic layers (5-10 nm) on the carbon surface, consequently the composition reported corresponds only to the irradiated area. Elemental analysis, on the other hand, gives the average composition of the entire sample, but the oxygen composition is calculated by difference. Therefore, the results reported in Tables 1 and 2 are not precise and should be treated with caution.

It has been found that oxidation introduces oxygen in the form of acidic oxygen-containing groups, such as carboxyl, lactonic, phenolic and carbonyl[4]. These functional groups determine the adsorption process and their reactivity will depend on their dissociation constant. It is very important to know the distribution and concentration of functional groups present on the carbon surface in order to understand the adsorption mechanism. The latter can be measured using acid/base titration following Boehm's method. Figure 1 shows the concentration of oxygen-containing groups in conventional and electrochemically oxidised carbon WHK. It is evident that the concentration of weak acidic groups increases with oxidation but not in the same proportion.

Table 1. Surface composition of granular activated carbon WHK determined by XPS

WHK	%		
	C	N	O
Un-oxidised	91.5	0.0	8.1
Electro-ox	79.4	0.0	17.2

Table 2. Composition of granular activated carbon WHK determined by elemental analysis

WHK	%			
	C	H	N	O
Un-oxidised	77.23	1.15	0.0	21.62
Electro-ox	64.88	2.28	0.0	32.84

Lactonic groups are present in highest concentration in modified carbon followed by carbonyl, carboxyl and phenolic groups. It has been reported that carboxyl groups dissociate at pH 3 - 6[5]. Hence a considerable increase in sorption capacity is expected at or near neutral pH, which makes granular carbon an excellent alternative medium for the treatment of drinking water.

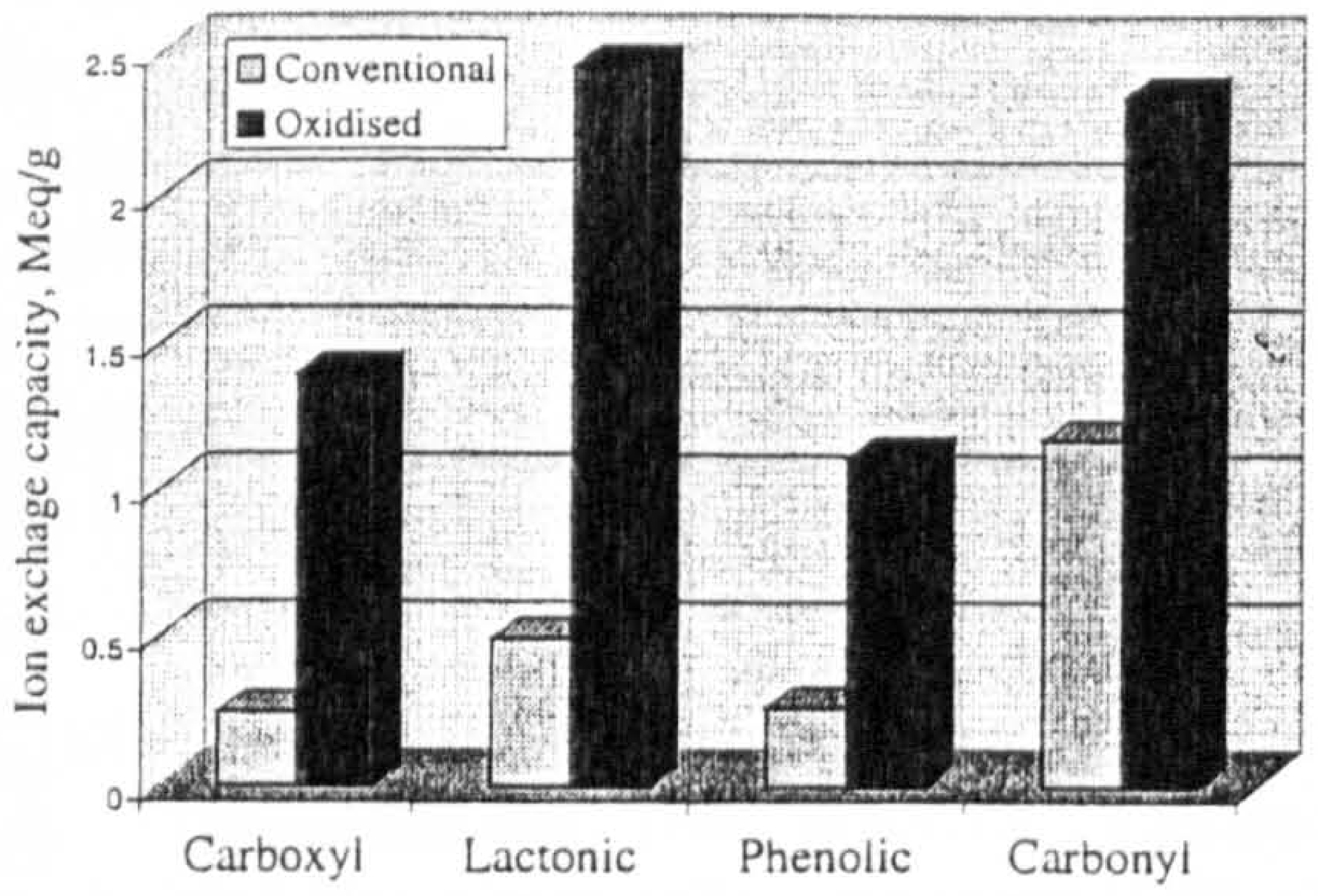

Fig 1. Oxygen containing groups on conventional and modified granular carbon WHK

The SEMs presented in Figures 2 and 3 show the surface morphology of commercial and modified carbons, respectively. Un-oxidised carbon shows a well-defined and regular distribution of pores, whereas the oxidised sample presents irregular openings and roughness produced by chemical erosion. This is reflected in loss of surface area. The BET surface area decreases from 1935 to 702 m^2 g^{-1}, however an adsorbent with these characteristics is perfectly applicable in water treatment.

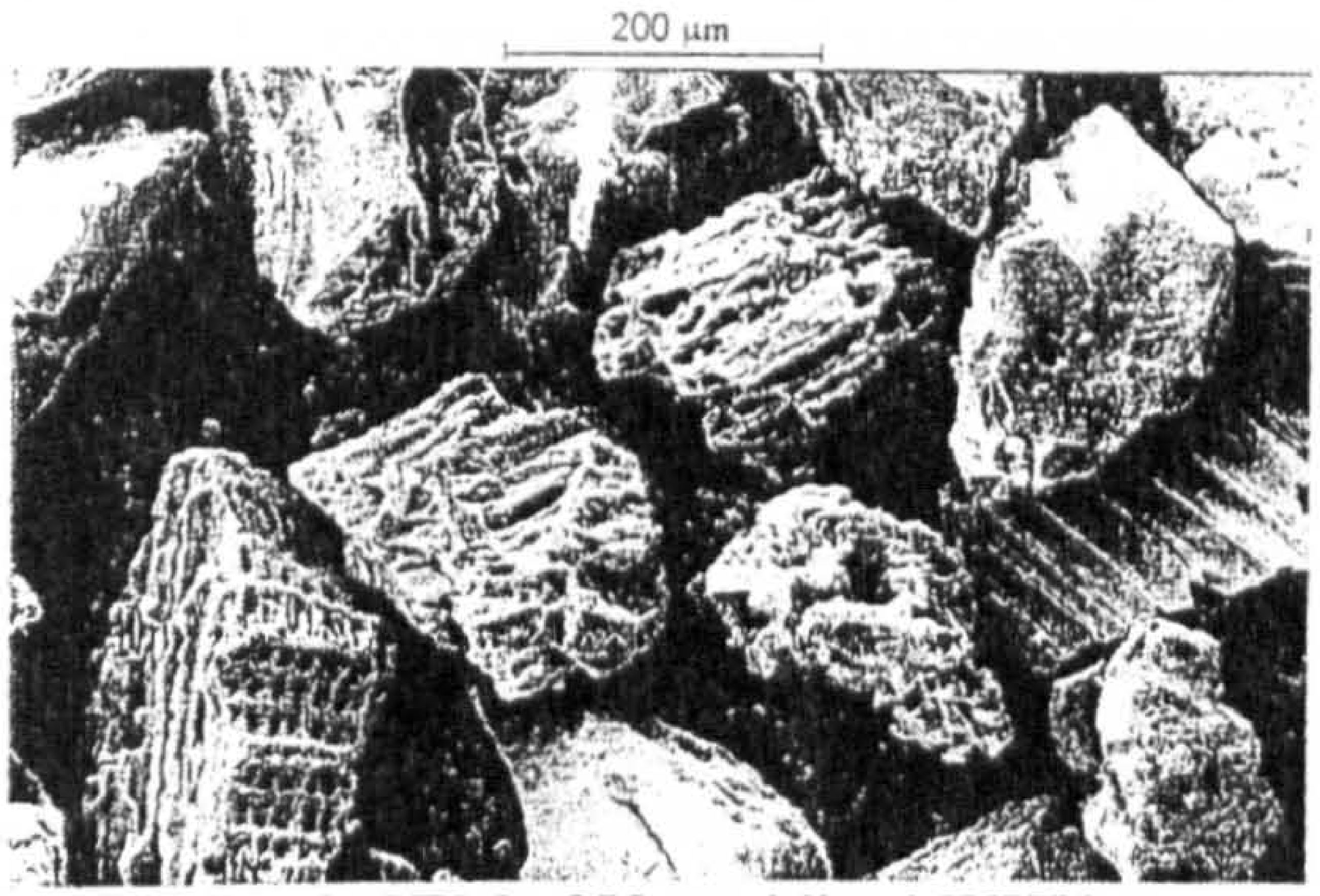

Fig 2. SEM of Un-oxidised WHK.

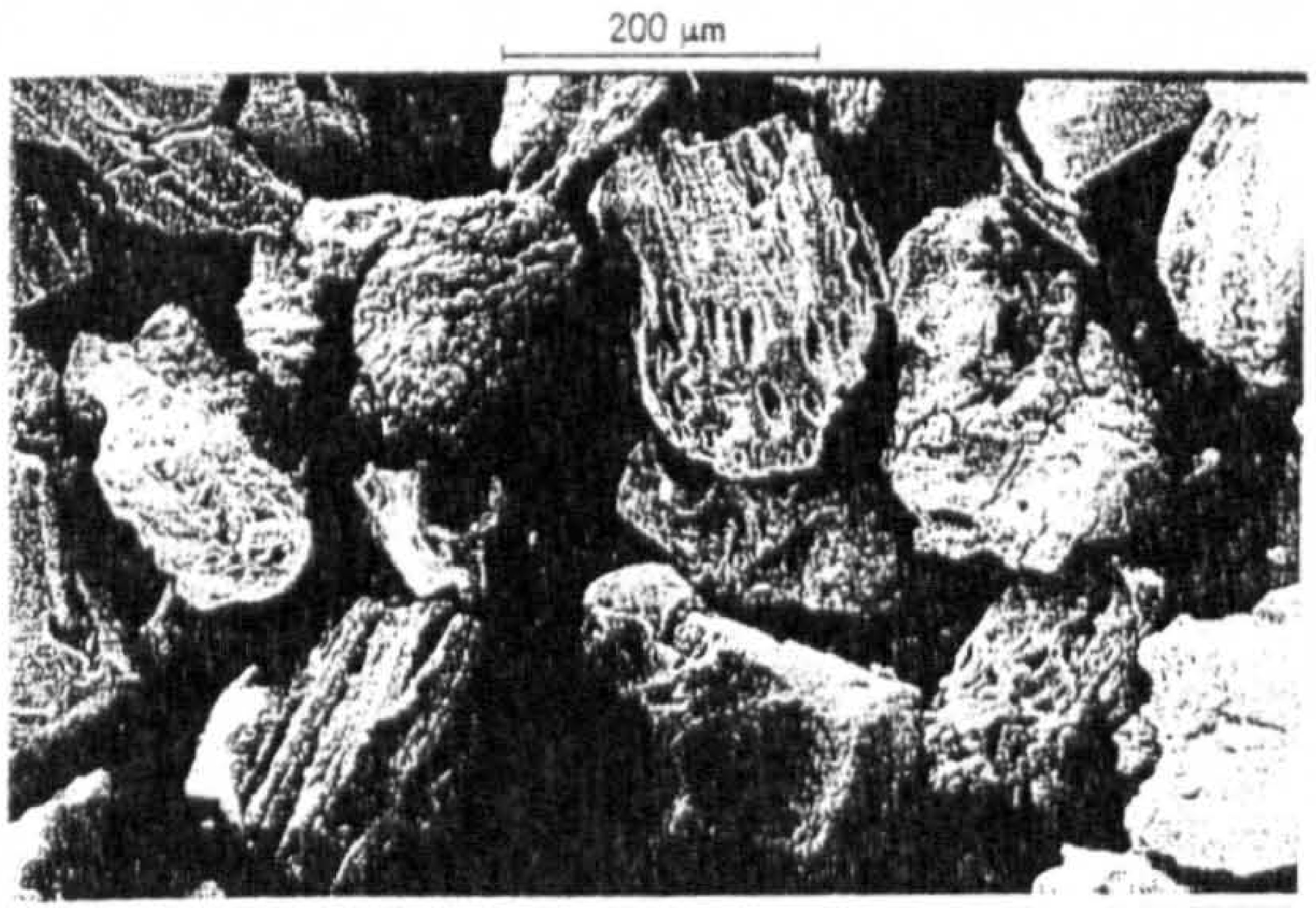

Fig 3. SEM of electrochemically oxidised WHK

The sorption capacity of granular carbon (WHK) was evaluated by using cadmium and mercury as adsorbate. The removal of mercury with oxidised carbon increases by a factor of 10 at pH 5 compared to the un-oxidised sample (see Fig 4). The same trend was observed for cadmium[2]. It must be noted that this refers to single component adsorption.

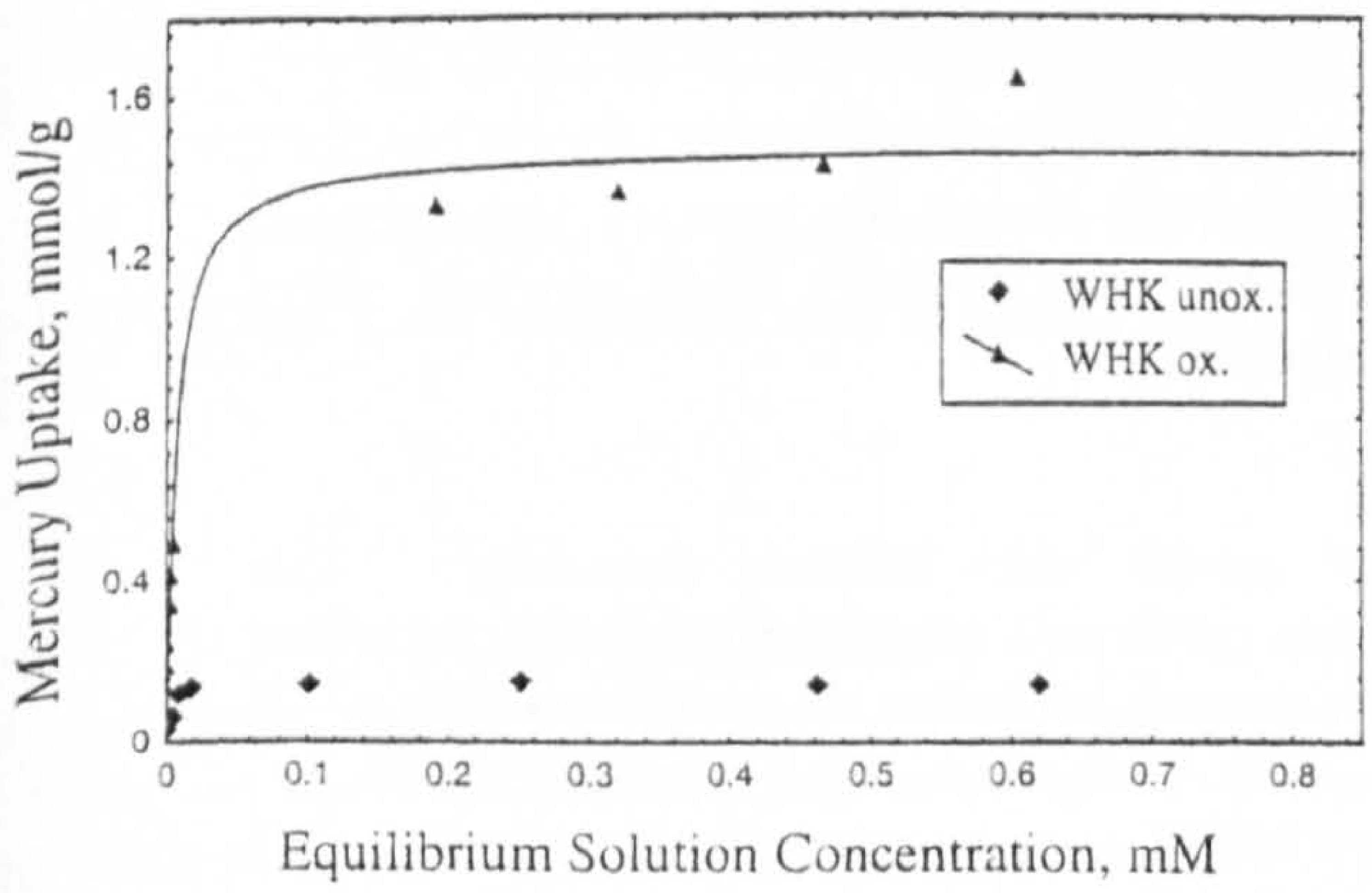

Fig 4. Sorption of mercury on conventional and modified WHK at pH 5 and room temperature

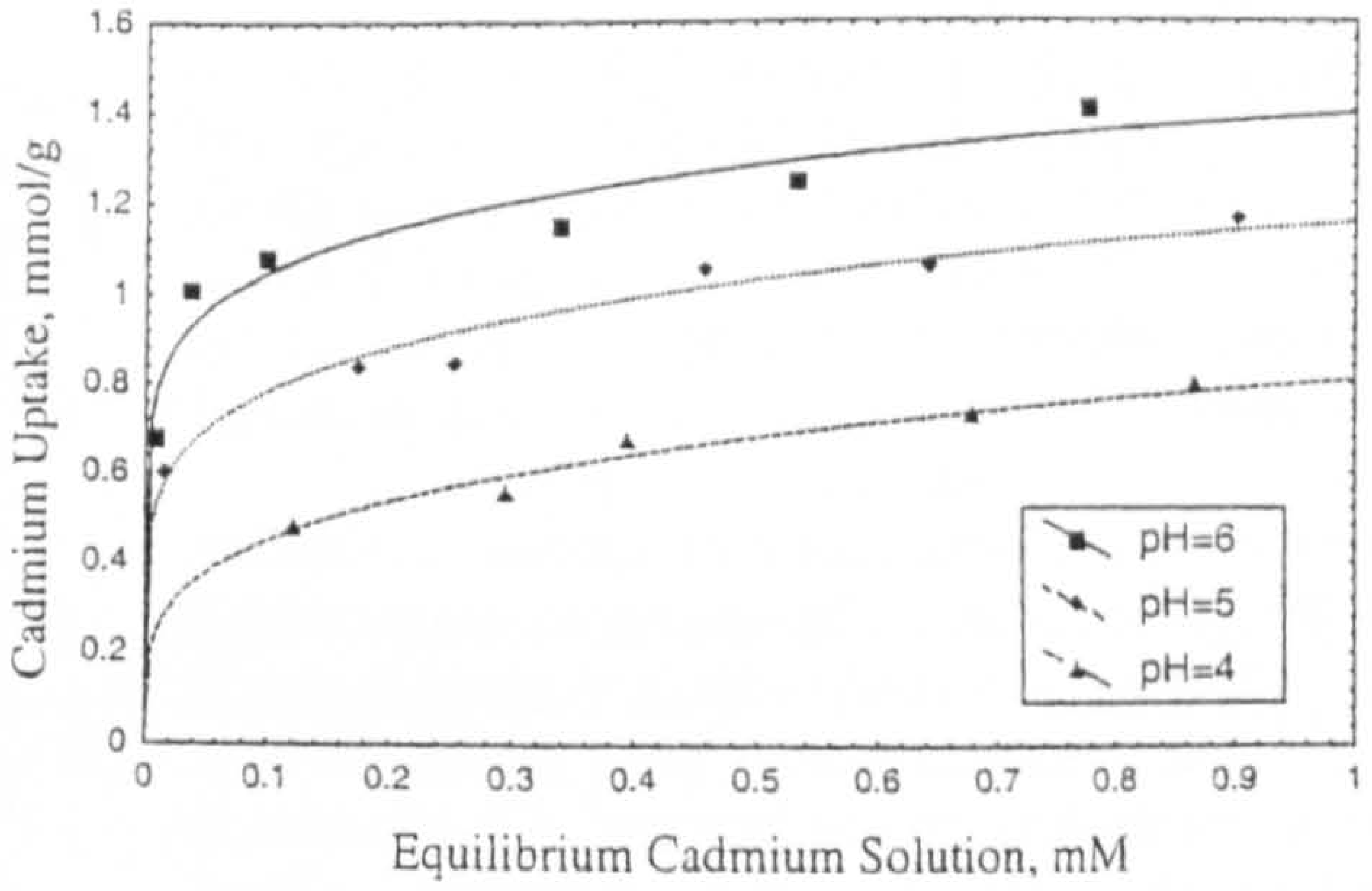

Fig 5. Sorption of cadmium on modified WHK at room temperature

The effect of solution pH was also investigated and the results are plotted in Figures 5 and 6 for cadmium and mercury, respectively. The sorption capacity increases with pH and approximately in the same proportion for both metals. This behaviour is attributed to the higher amount of dissociated functional groups available for adsorption and ion exchange as pH rises.

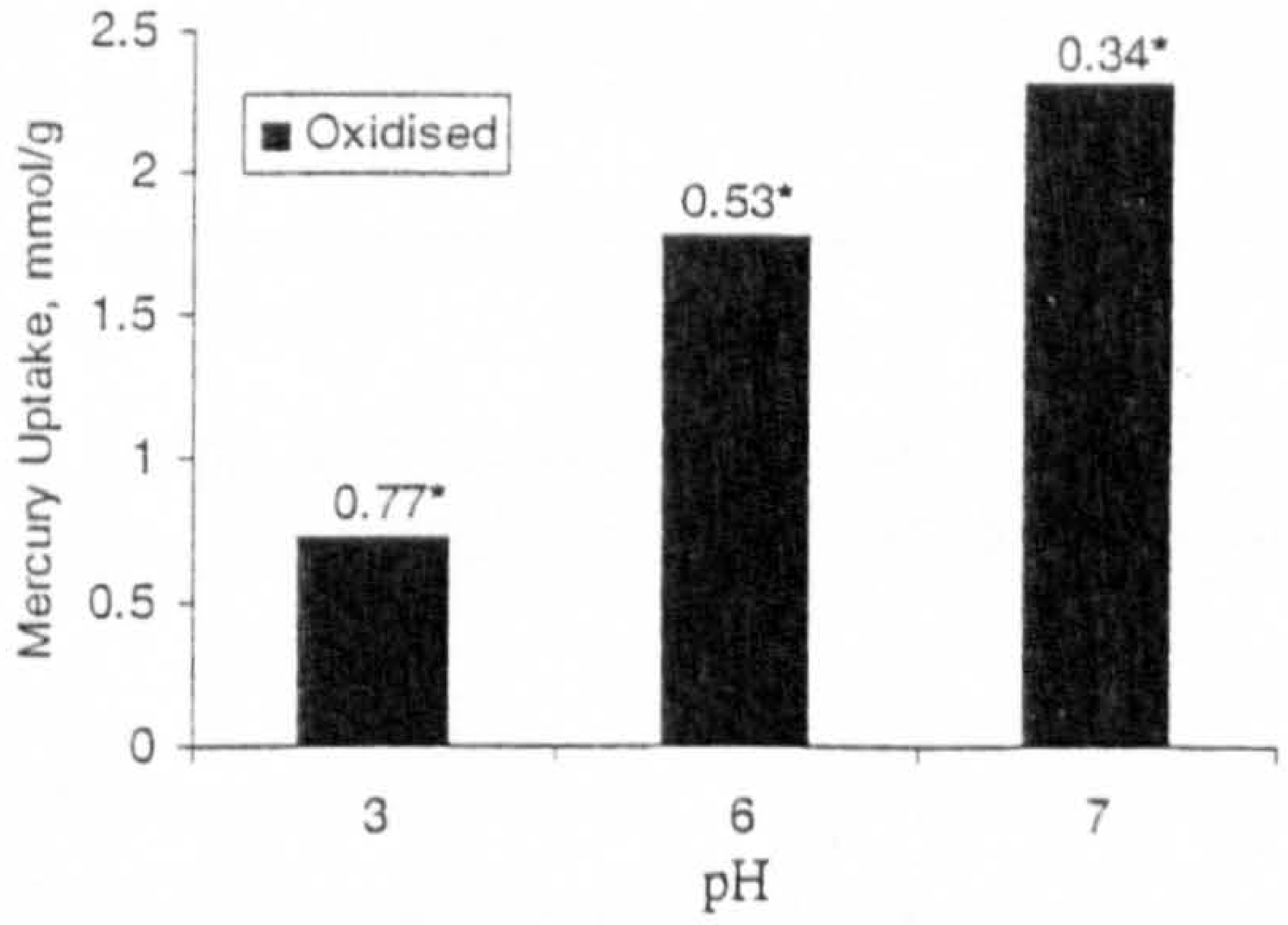

Fig 6. Sorption of mercury on oxidised WHK and room temperature. Initial concentration 0.9 mM mg L^{-1}. * Equilibrium concentration, mM.

Zeta potential (ZP) is related to electrophoretic mobility and is an index of the magnitude of interaction between colloidal particles. Colloidal suspensions/dispersions of fine particles in a liquid phase possess an electric charge that depends on the nature of the solid surface and the surrounding medium[6]. The dissociation of acid or basic surface groups and the solution pH alter the surface charge density. The isoelectric point (IEP) is defined as the point of zero net external surface charge and is detected at the crossover point shown in Figure 7. The IEP for conventional and oxidised carbons is at pH 2.19 and 0.96, respectively. The external surface is positively charged below the IEP since the acidic surface groups are protonated. The carbon surface becomes negative above the IEP due to the dissociation of oxygen-containing groups. Hence, adsorption of cations is promoted by electrostatic interaction of ions, i.e. by an ion exchange mechanism.

The distribution and concentration of species in solution depend on the solution pH. The speciation diagrams for cadmium and mercury are presented in Figures 8 and 9, respectively. These were calculated using the equilibrium constants reported by Stumm and Morgan[7]. A knowledge of the relationship between the adsorbent surface chemistry and the species in solution helps to explain the metal sorption mechanisms.

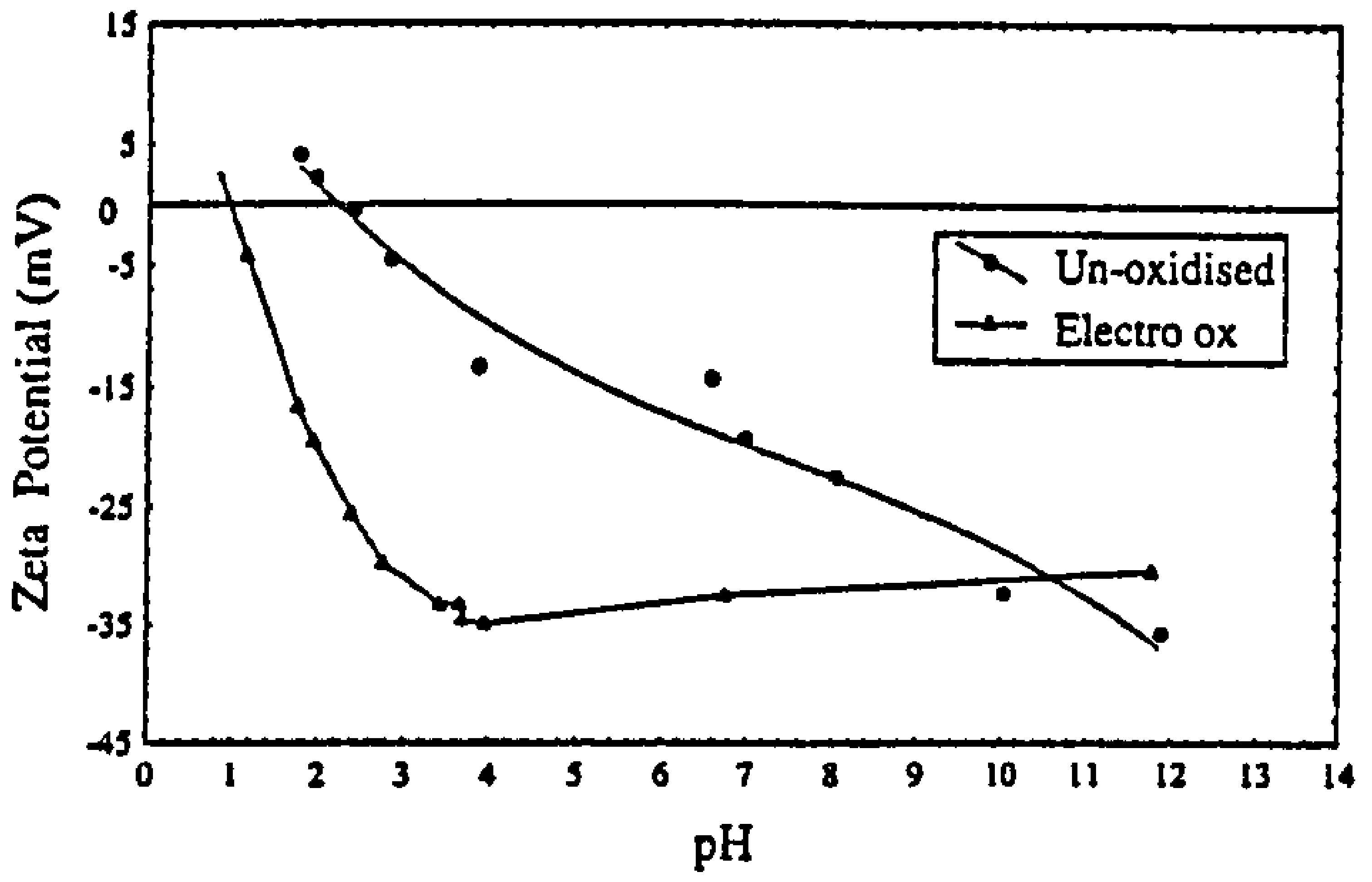

Fig 7. Electrophoretic mobility measurements using conventional and oxidised granular carbon WHK.

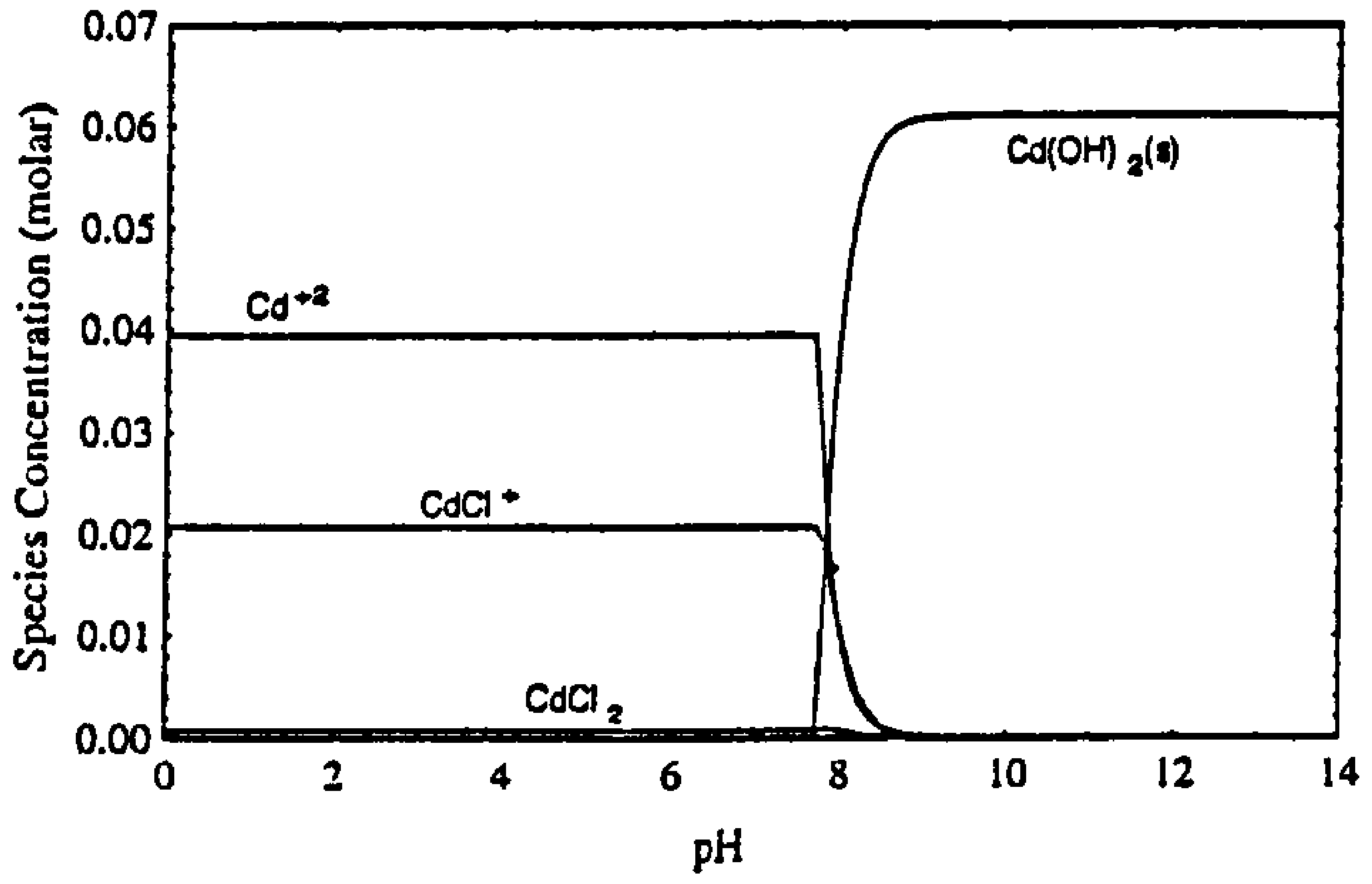

Fig 8. Speciation diagram of $CdCl_2$ 0.1 M in aqueous solution

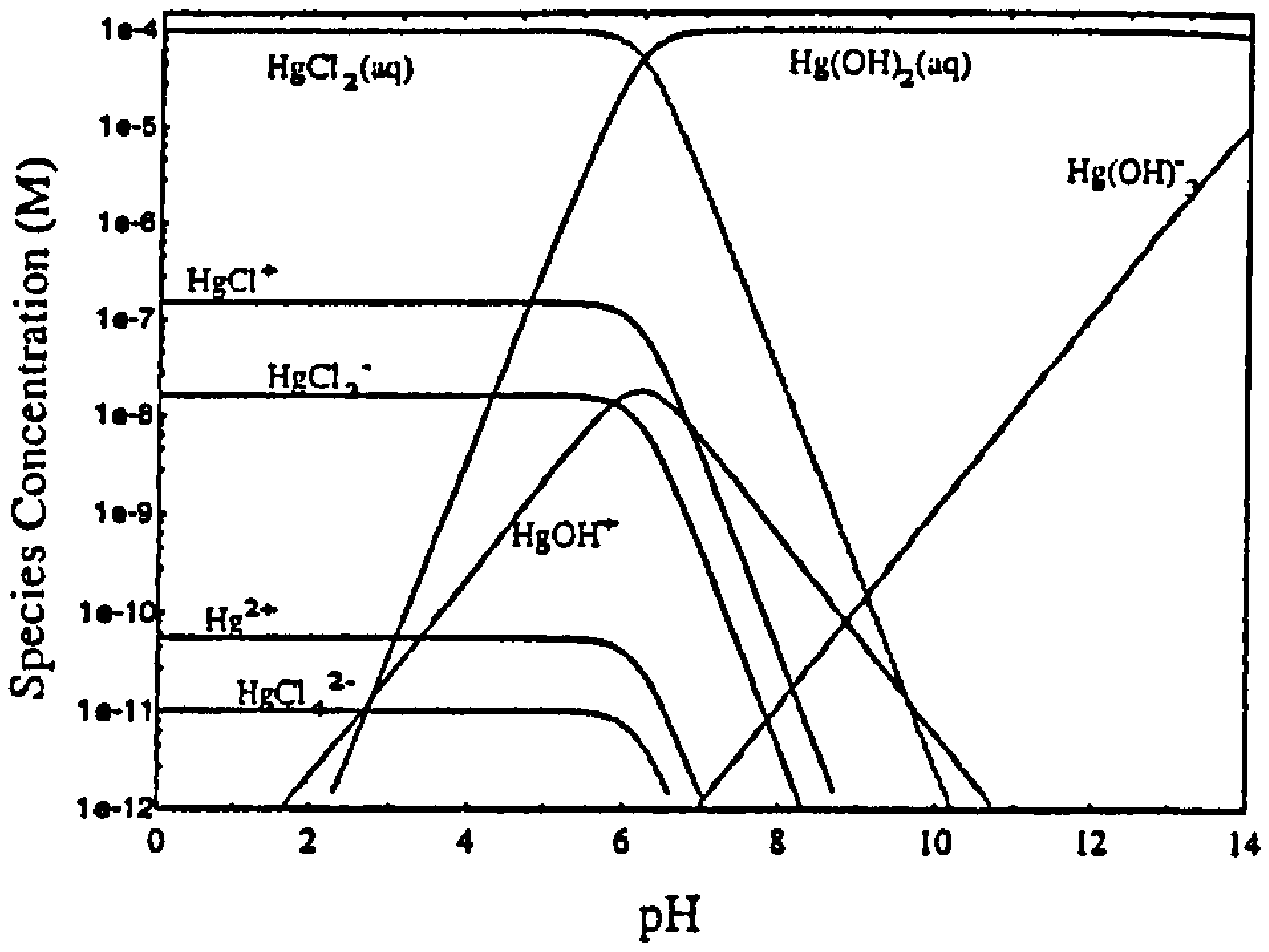

Fig 9. Speciation diagram for 1e-4 M $HgCl_2$ in aqueous solution

The breakthrough curves reported in Figure 10 were obtained using a mixed cadmium and mercury feed solution. Breakthrough occurred at approximately 20 and 75 bed volumes for mercury and cadmium, respectively. Hence the uptake of cadmium is 27% greater than for mercury under these operating conditions.

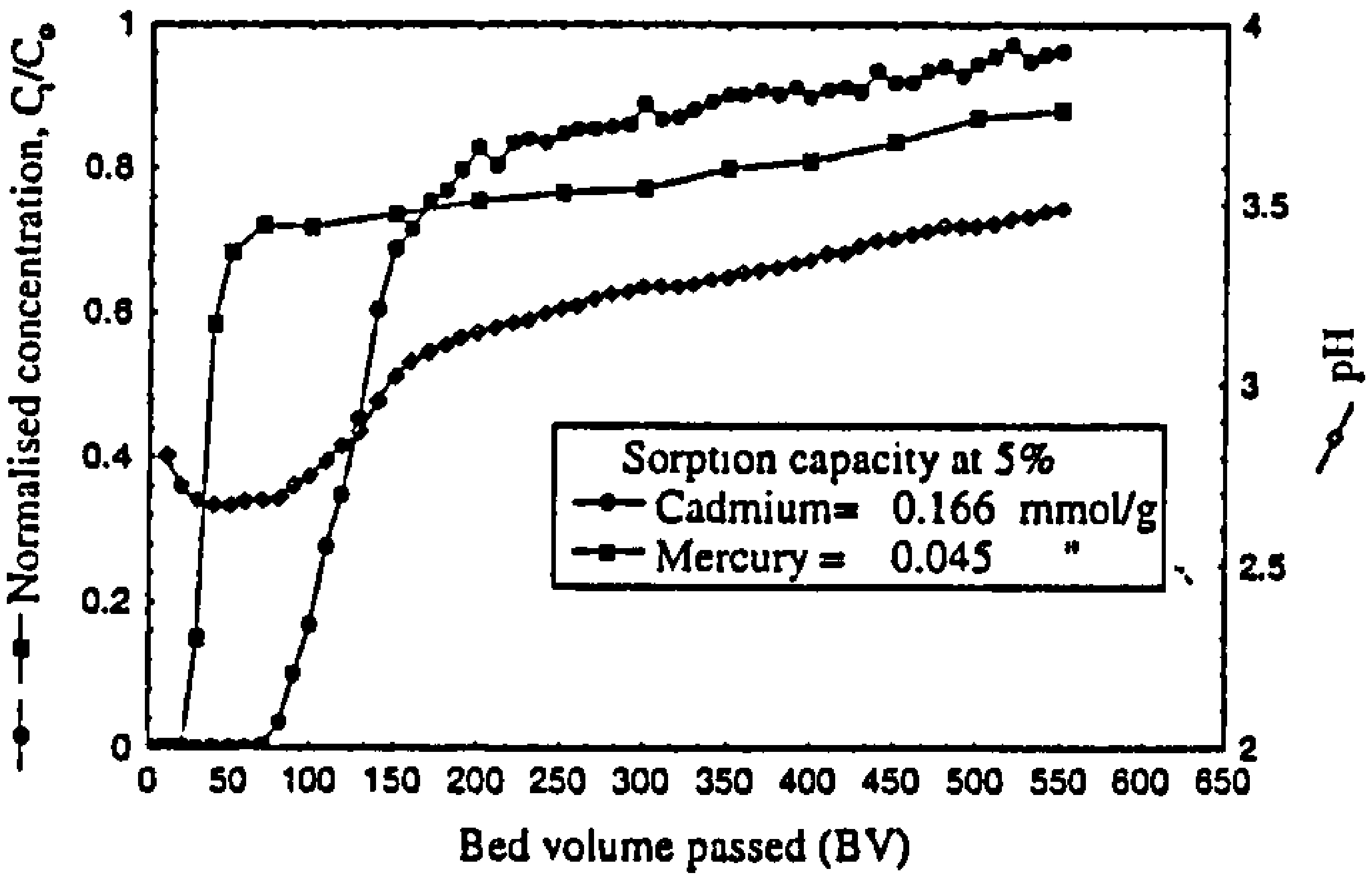

Fig 10. Breakthrough curves for mercury and cadmium using electrochemically oxidised WHK. 1 mM initial concentration at pH 6.

Breakthrough curves also indicate selectivity. This experiment was performed at pH 2.5 - 3.5, and according to the electrophoretic mobility measurements (Figure 7) the carbon surface is negatively charged in this region.

It appears that WHK is more selective for cadmium than for mercury. The sorption mechanisms and the relative concentration of species in solution may in part explain this phenomenon. Mercury can be removed by two mechanisms; firstly by adsorption of cation species such as Hg^{2+}, $HgCl^+$ and $HgOH^+$ due to electrostatic attraction (ion exchange) and secondly by reduction of $HgCl_2(aq)$ to $Hg_2Cl_2(s)$. It has been reported that the phenolic and hydroquinonic groups on the surface of activated carbon are capable of reducing Hg(II) to Hg(I), according to the following reaction[8]

$$2(-OH) + HgCl_2(aq) \rightarrow 2(=O) + Hg_2Cl_2(s) + 2HCl \quad (1)$$

Figure 9 shows that $HgCl_2(aq)$ occurs to the extent of 99% in a solution containing 10^{-4} M $HgCl_2$ up to pH 5. Thus reduction of Hg(II) to Hg(I) forming $Hg_2Cl_2(s)$ as a colloidal precipitate might contribute to the removal of Hg from solution by activated carbon.

Cadmium exists as Cd^{+2} (about 60%) and $CdCl^+$ (about 40%) in solution up to pH 7.5 (see Figure 9). Consequently, adsorption is likely to be by cation exchange due to electrostatic attraction.

Cadmium was almost completely eluted after passing 20 BV of 0.2M HCl indicating that the adsorption/desorption process is predominantly due to an ion exchange mechanism. In contrast, only a small percentage of mercury is desorbed (see Figure 11) indicating that mercury is more tightly bound. $Hg_2Cl_2(s)$ is insoluble and therefore mercury uptake by chemical reduction is only partially reversible.

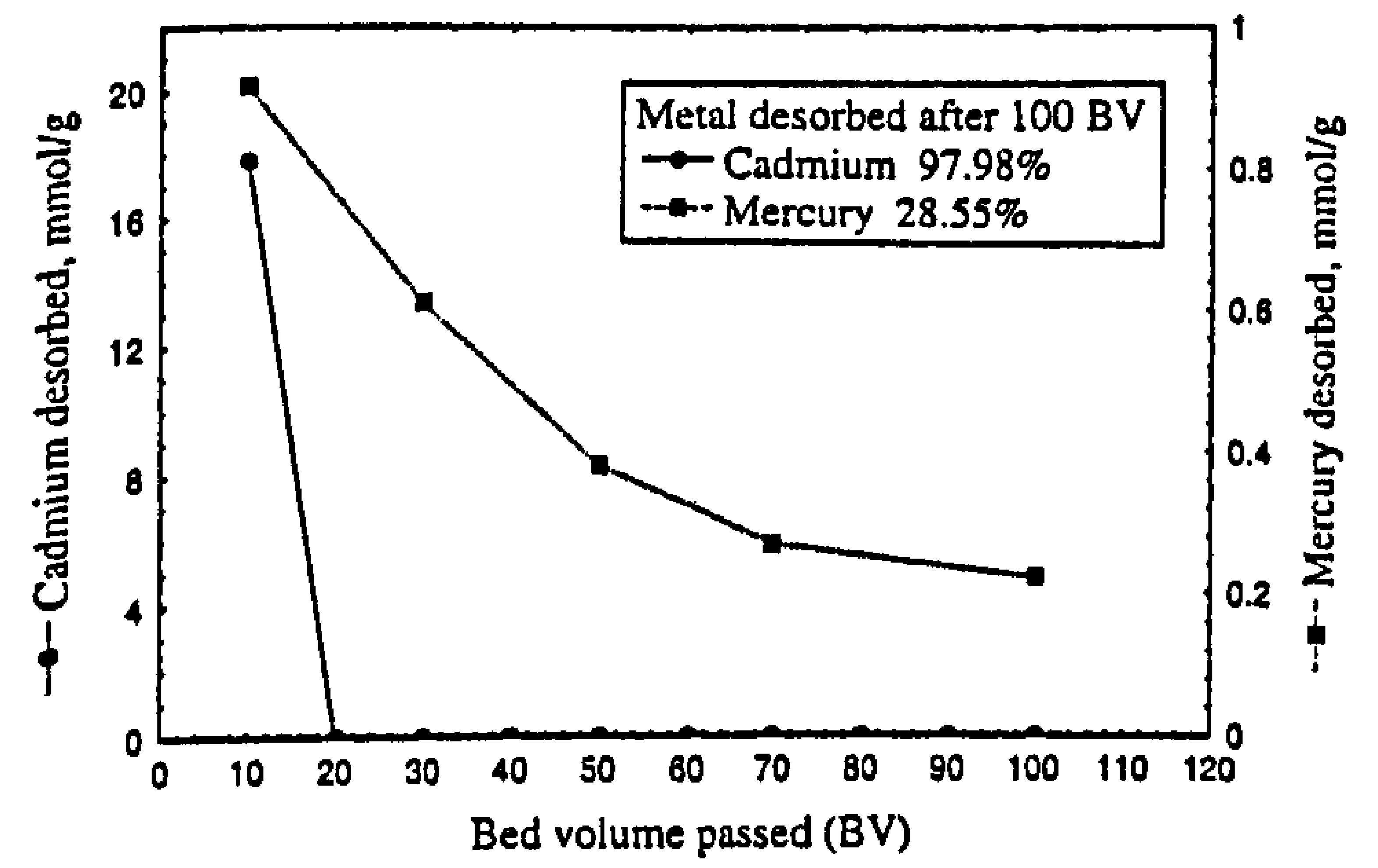

Fig 11. Desorption of mercury and cadmium with 0.2M HCl

Conclusions

The electrochemical oxidation of granular carbon WHK results in a marked increase in sorption capacity. Mercury sorption increased by a factor of 10 times at pH 5 for oxidised activated carbon. The adsorption process is dependent on solution pH and the uptake of cadmium and mercury increases with pH. Modified granular activated carbon is more selective for cadmium than for mercury. It is suggested that the overall sorption mechanism in the pH range 2.5 - 3.5 is controlled by ion exchange/adsorption rather than by chemical reduction. Some surface area was lost due to chemical reaction.

Acknowledgements

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REMOVAL OF CADMIUM USING ELECTROCHEMICALLY OXIDISED ACTIVATED CARBON

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ABSTRACT

Activated carbons are extensively used in wastewater treatment for the removal of a wide range of contaminants. They offer extensive surface area for sorption of metals from aqueous solutions and have been investigated for treatment of solutions bearing inorganic species. By far the most widely developed large-scale application of activated carbon in hydrometallurgy is the recovery of gold from dilute cyanide leach solutions. Metal binding ability of conventional activated carbon is very limited. However, this can be significantly enhanced by chemical modification.

Conventional activated carbons can be modified by oxidation to add weakly acidic groups on to the surface of these materials. Metal ions can ion exchange with these mainly oxygen-containing functional groups and thereby removed from solution. Oxidation has been carried out mostly by using air at high temperature or nitric acid solutions. Other oxidants such as ozone and hydrogen peroxide have also been used. Electrochemical oxidation of carbon fibres has been carried out to increase tensile strength as well as to improve metal binding capacity. However, only a limited amount of work has been carried out on electrochemical oxidation of granular activated carbons.

In the present work, a wood based activated carbon, AUG WHK, was oxidised electrochemically to enhance its metal binding capacity. Ion exchange studies of the conventional and the modified materials were carried out for the removal of cadmium ions from aqueous solution. Batch equilibrium isotherms were generated to determine equilibrium capacity. Breakthrough experiments were also carried out in mini-column experiments to examine the sorption performance of these materials. Overall, adsorbents are produced which possess similar metal sorptive capacities to those of polymeric ion exchange resins.

Results of batch equilibrium tests indicate that the oxidised material has 16.5 times higher sorption capacity for cadmium than the conventional activated carbon. The improvement of cadmium uptake was also observed in breakthrough experiments. Breakthrough in mini-columns occurred at about 140 bed volumes for oxidised WHK, whereas it was instantaneous for the unoxidised samples. The adsorption isotherms were obtained at pH 4, 5 and 6. It was observed that cadmium uptake increased slightly with an increase in pH. The experimental data were fitted by Langmuir and Freundlich isotherms and it was found that the Freundlich isotherm fitted better in all the cases. Kinetic experiments reveal a high adsorption rate for cadmium. Up to 96% of total metal ions were removed in 12 minutes for modified WHK.