

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, $\left[l^{1/n} / mg^{1-1/n} g^{-1} \right]$	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.

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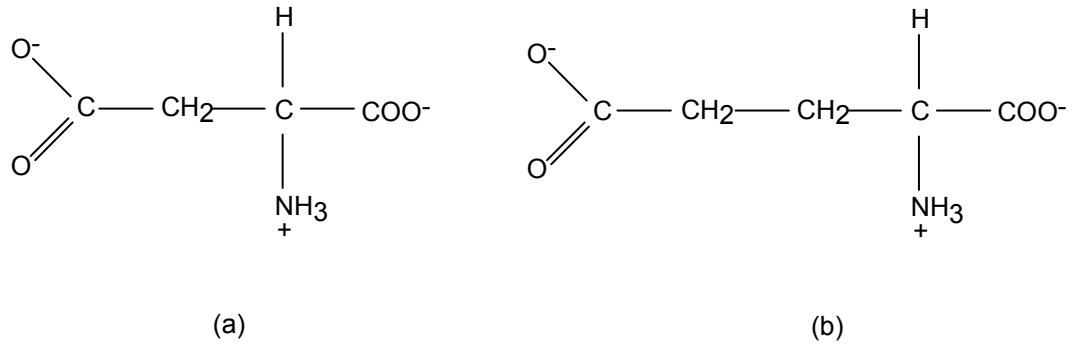


Fig. 1 Amino acids, (a) aspartic acid and (b) glutamic acid

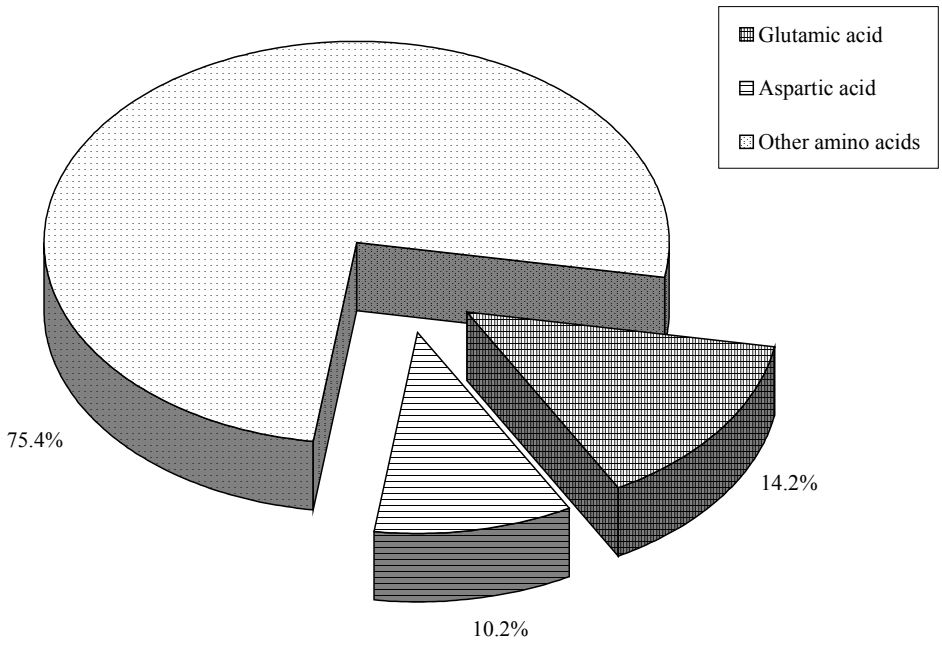


Fig. 2 Amino acid profile of *A. filiculoides*

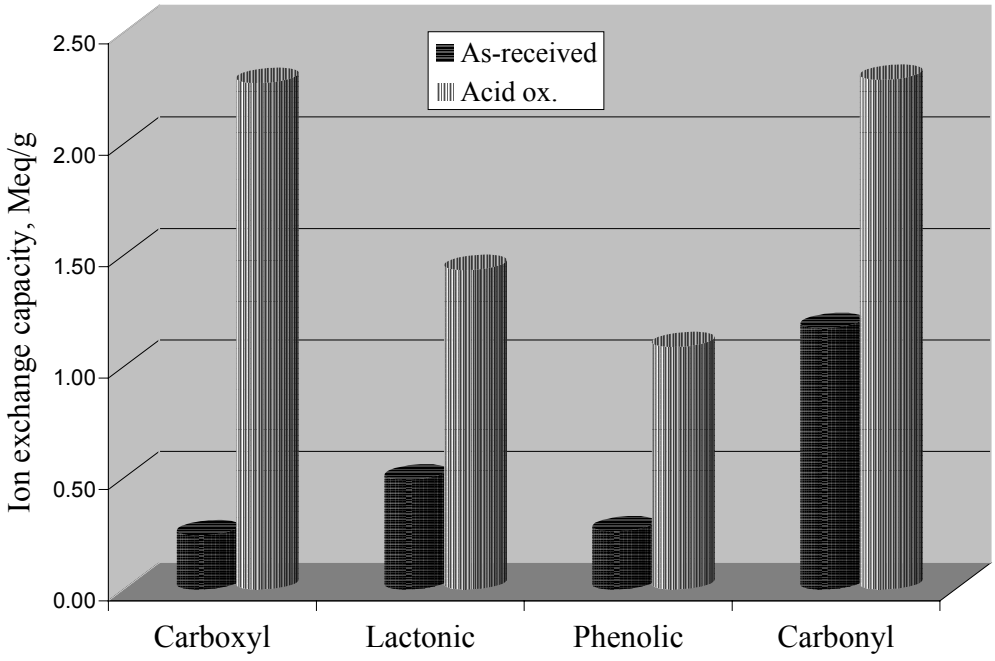


Fig. 3 Oxygen containing groups on conventional and modified granular carbon WHK

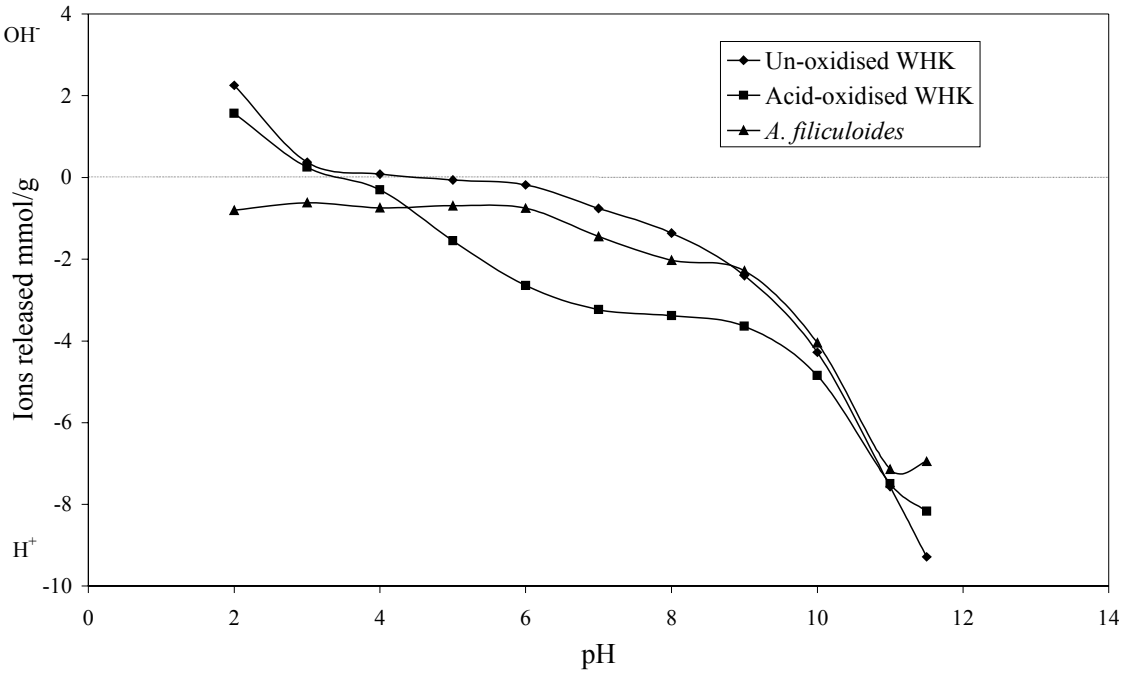


Fig. 4 Proton binding curves for granular carbon WHK and *A. filiculoides*

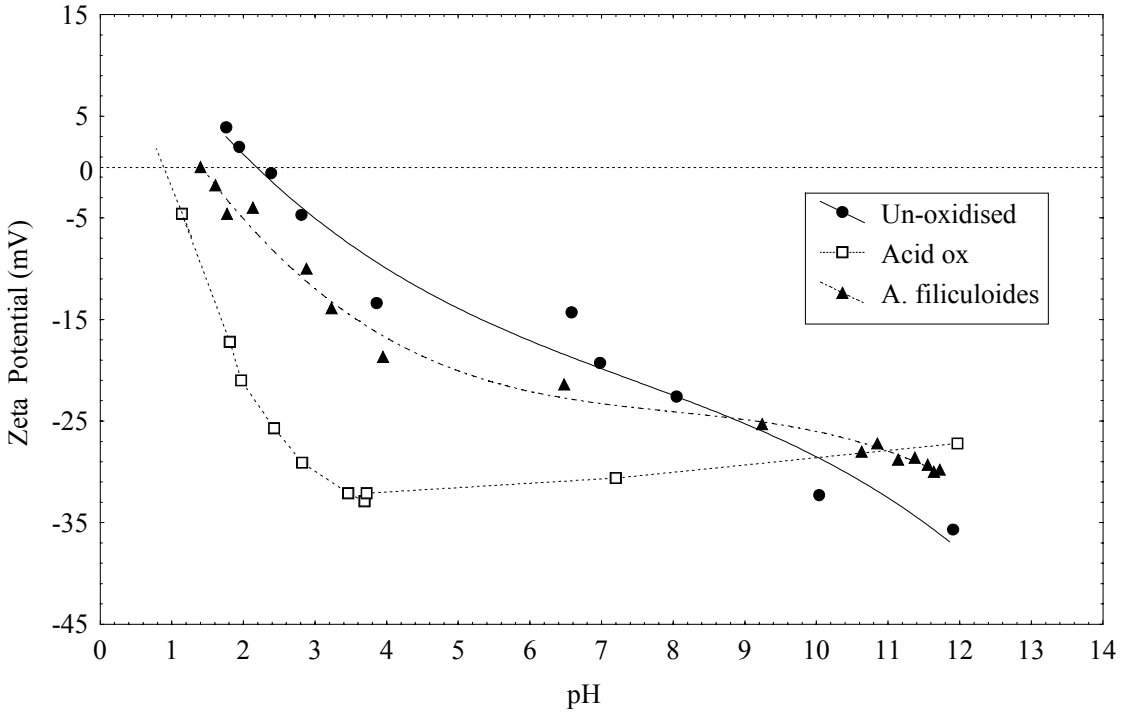
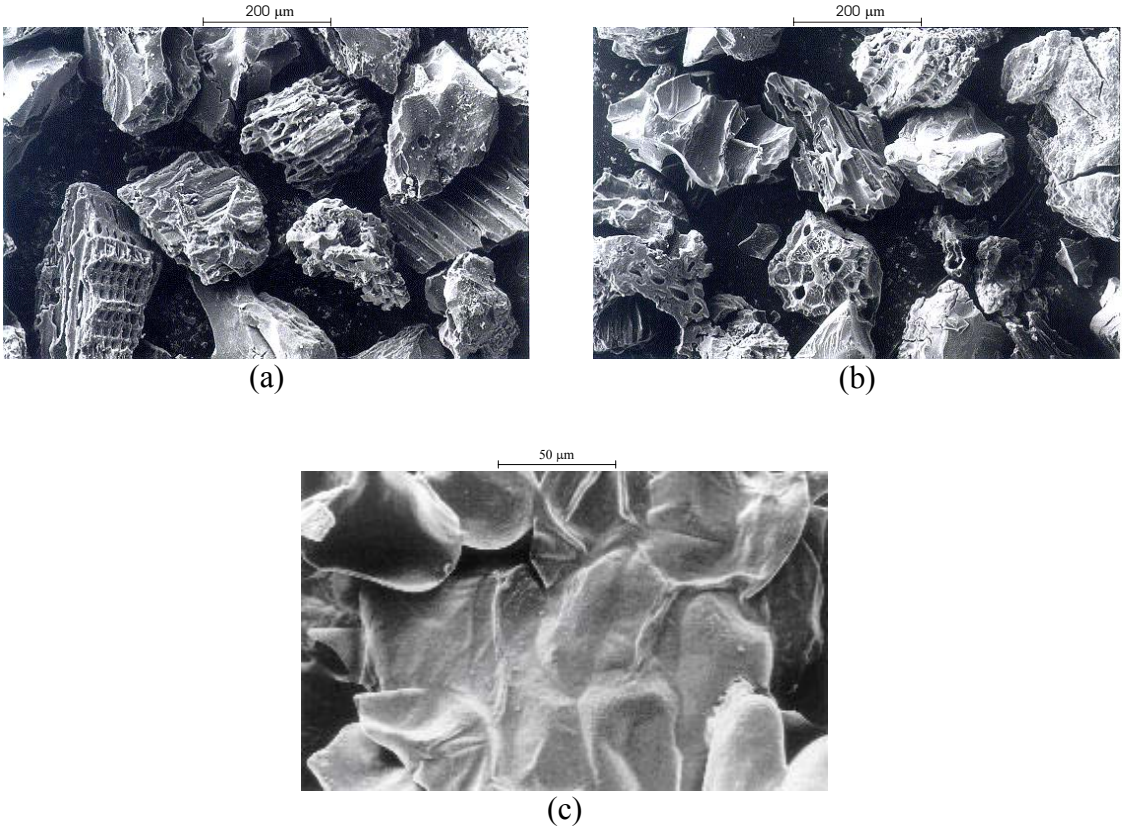


Fig. 5 Electrophoretic mobility measurements using granular carbon WHK and *A. filiculoides*



(a) (b)

(c)

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

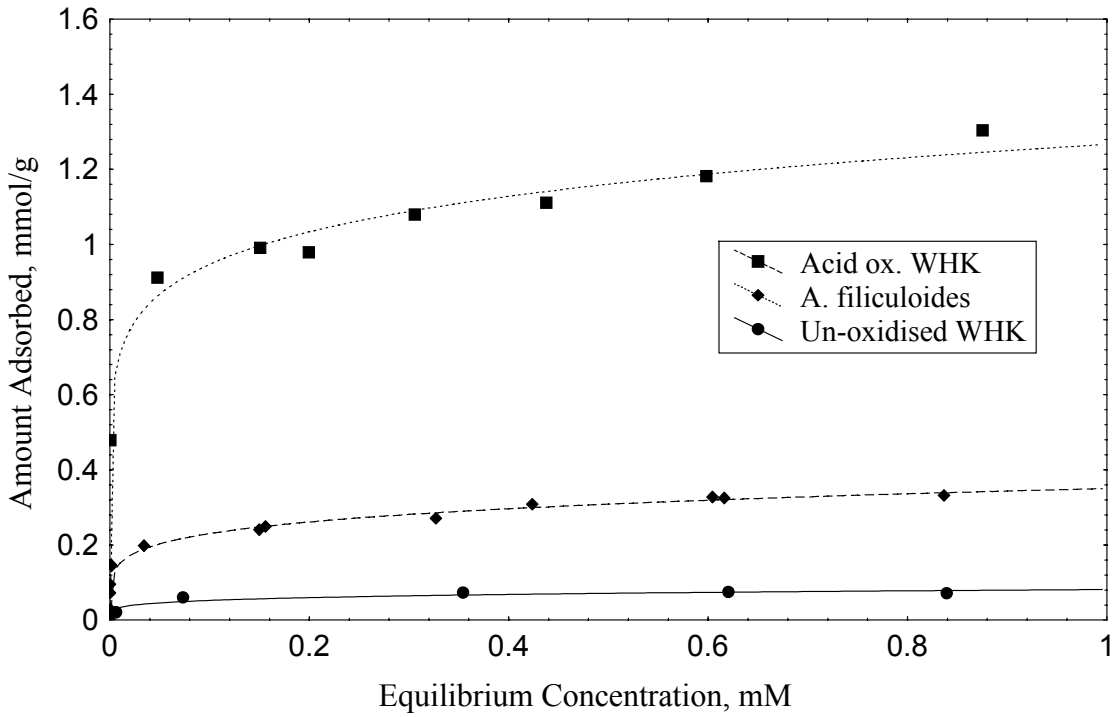


Fig. 7 Equilibrium cadmium sorption isotherms for granular carbon and *A. filiculoides* at pH 6 and room temperature.

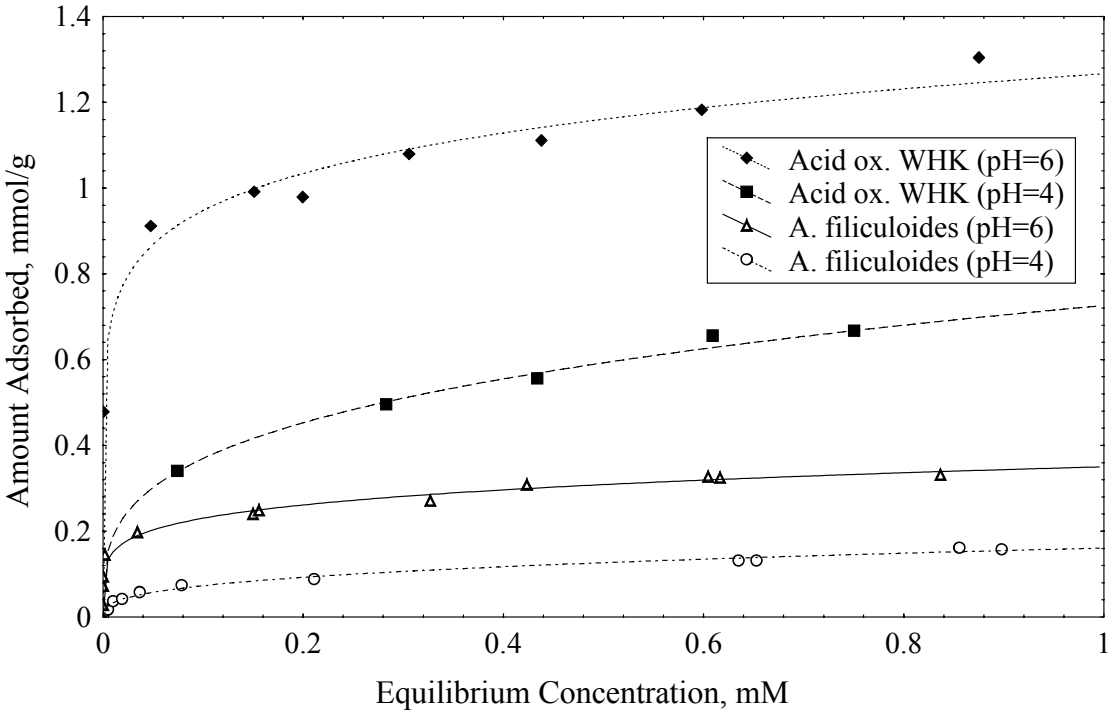


Fig. 8 Equilibrium cadmium sorption isotherms for oxidised granular carbon and *A. filiculoides* at pH 4 and 6, and room temperature.

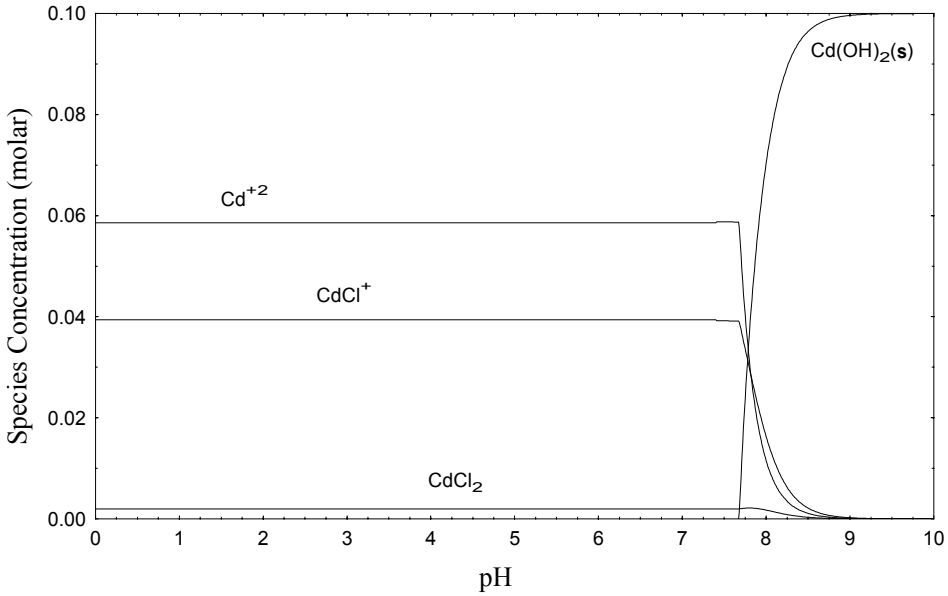


Fig. 9 Speciation diagram of 0.1 M $CdCl_2$ in aqueous solution at 298.15 K

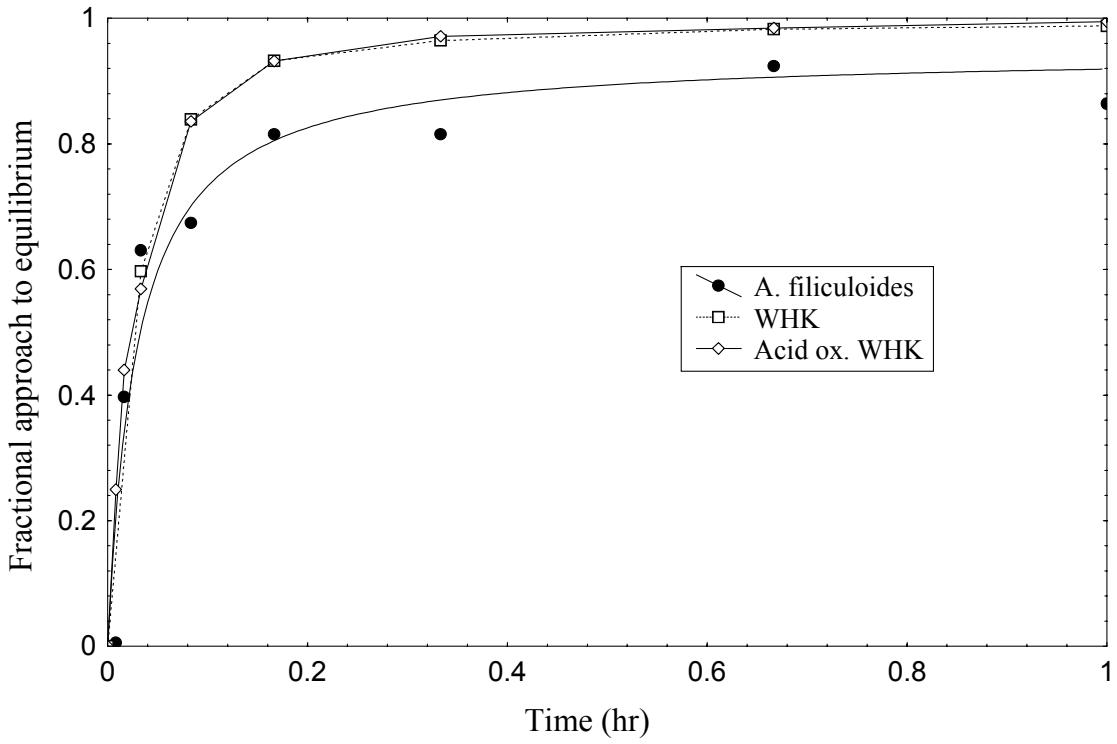


Fig. 10 Comparison of kinetics for granular carbons and the biosorbent

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