

MERCURY AND CADMIUM ADSORPTION BY CONVENTIONAL AND MODIFIED GRANULAR ACTIVATED CARBON

J. R. Rangel-Mendez and M. Streat
Department of Chemical Engineering
Loughborough University, Leicestershire LE11 3TU, UK

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 $\text{CdCl}_2 \cdot \text{H}_2\text{O}$, 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 analyses¹. 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 elsewhere². 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 Elmer 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 method³. 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 $\pm 0.02\text{ml}$) 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, $<90\mu\text{m}$, 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 carbonyl⁴. 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 - 6⁵. 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.

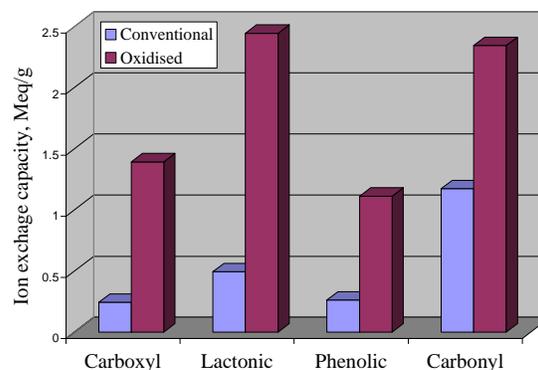


Fig 1. Oxygen containing groups on conventional and modified granular carbon WHK

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 m² g⁻¹, however an adsorbent with these characteristics is perfectly applicable in water treatment.

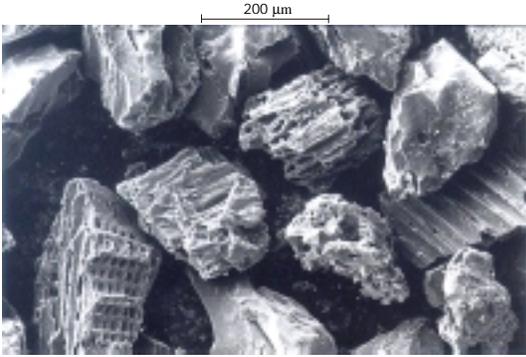


Fig 2. SEM of Un-oxidised WHK.

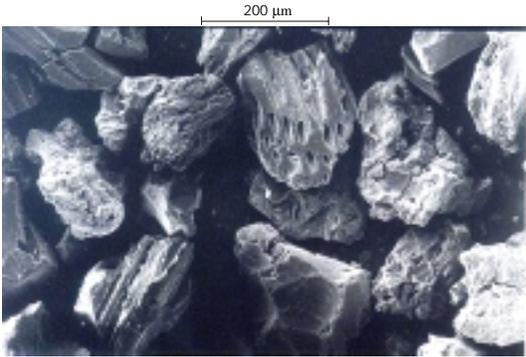


Fig 3. SEM of electrochemically oxidised WHK

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 cadmium². It must be noted that this refers to single component adsorption.

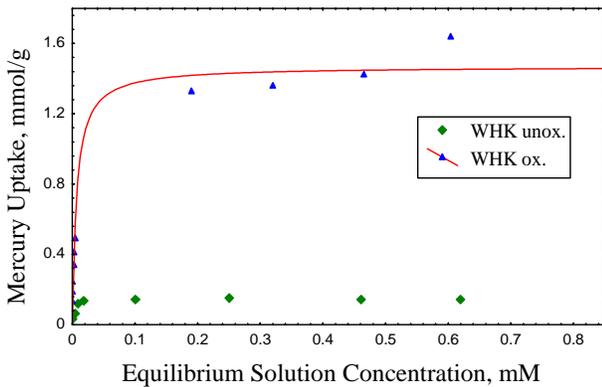


Fig 4. Sorption of mercury on conventional and modified WHK at pH 5 and room temperature

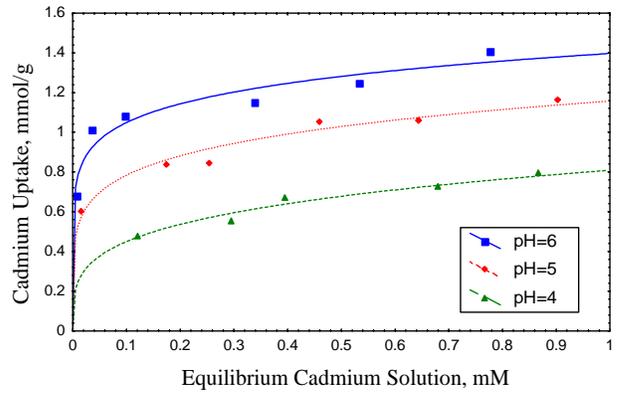


Fig 5. Sorption of cadmium on modified WHK at room temperature

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.

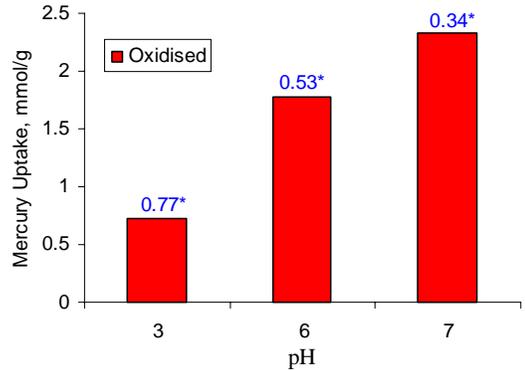


Fig 6. Sorption of mercury on oxidised WHK and room temperature. Initial concentration 0.9 mM mg L⁻¹. * Equilibrium concentration, mM.

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 medium⁶. 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 Morgan⁷. A knowledge of the relationship between the adsorbent surface chemistry and the species in solution helps to explain the metal sorption mechanisms.

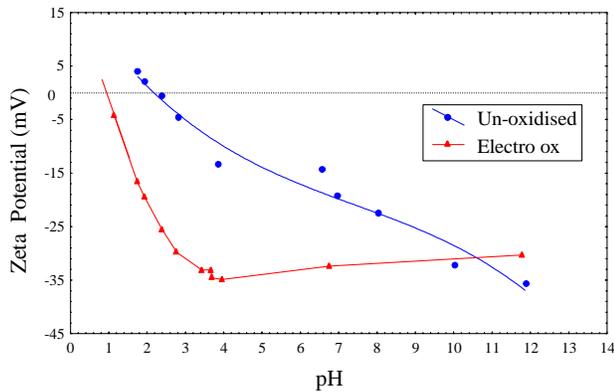


Fig 7. Electrophoretic mobility measurements using conventional and oxidised granular carbon WHK.

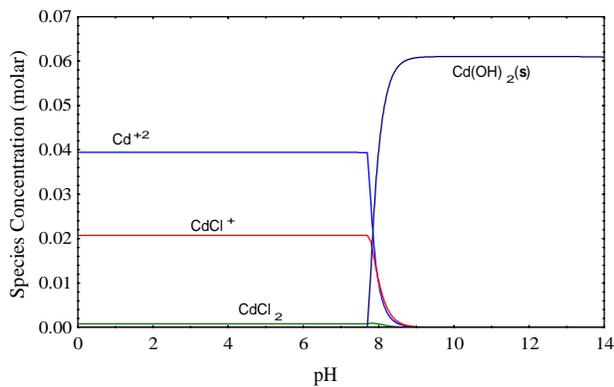


Fig 8. Speciation diagram of CdCl_2 0.1 M in aqueous solution

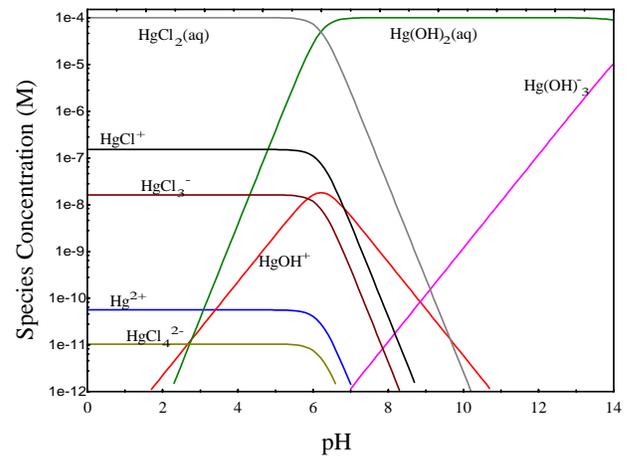


Fig 9. Speciation diagram for $1e-4$ M HgCl_2 in aqueous solution

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.

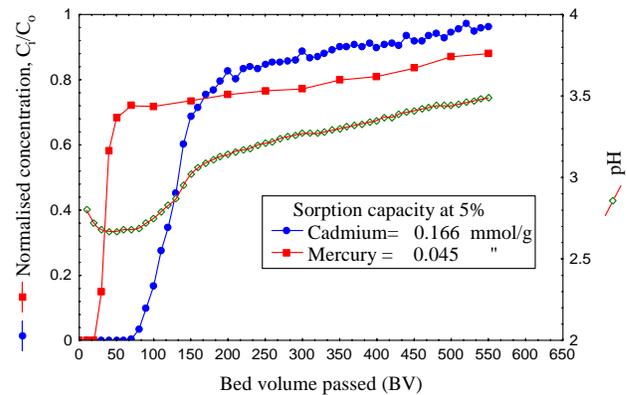


Fig 10. Breakthrough curves for mercury and cadmium using electrochemically oxidised WHK. 1 mM initial concentration at pH 6.

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 $\text{HgCl}_2(\text{aq})$ to $\text{Hg}_2\text{Cl}_2(\text{s})$. It has been reported that the phenolic and hydroquinonic groups on the surface of activated carbon are capable of reducing $\text{Hg}(\text{II})$ to $\text{Hg}(\text{I})$, according to the following reaction⁸

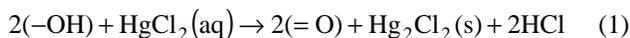


Figure 9 shows that $\text{HgCl}_2(\text{aq})$ occurs to the extent of 99% in a solution containing 10^{-4} M HgCl_2 up to pH 5. Thus reduction of $\text{Hg}(\text{II})$ to $\text{Hg}(\text{I})$ forming $\text{Hg}_2\text{Cl}_2(\text{s})$ as a colloidal precipitate might contribute to the removal of Hg 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. $\text{Hg}_2\text{Cl}_2(\text{s})$ is insoluble and therefore mercury uptake by chemical reduction is only partially reversible.

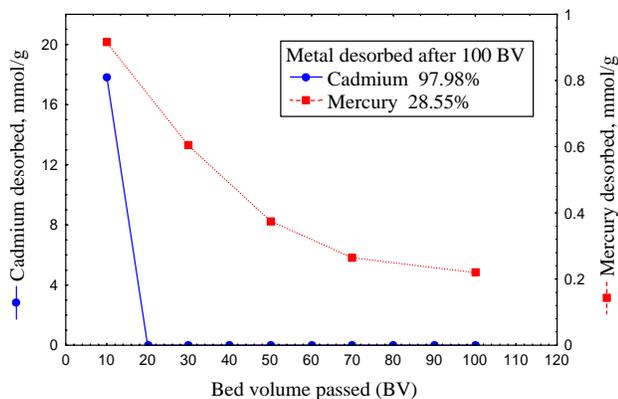


Fig 11. Desorption of mercury and cadmium with 0.2M HCl

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

J. R. Rangel-Mendez appreciates the scholarship (Ref. 70767/125253) from CONACyT, Mexico, and the support for the project by Severn Trent Water Limited.

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