

# 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  $\mu\text{m}$ . This was washed thoroughly with distilled water and then dried at 115  $^{\circ}\text{C}$  for 24 hours prior to use.

Cadmium solutions were prepared using  $\text{CdCl}_2 \cdot \text{H}_2\text{O}$  and distilled water. The solution pH was adjusted by addition of 0.1M  $\text{HNO}_3$  and 0.1M  $\text{NaOH}$ .

**Acid Oxidation.** Granular and fibrous activated carbons were oxidised using nitric acid. Samples of the carbon based materials and nitric acid solution were placed into a flask and the oxidation reaction was carried out for 3 hours at 90  $^{\circ}\text{C}$ . 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  $^{\circ}\text{C}$  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  $\text{h}^{-1}$ .

**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.

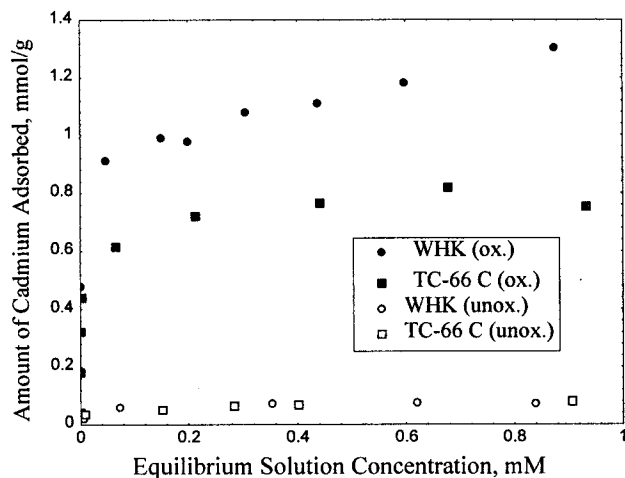
**Analysis.** The cadmium concentration was determined using a Varian SpectrAA 200 atomic absorption spectrophotometer in flame emission mode. The solution pH was measured using a Mettler Toledo 340 pH meter.

## Results and Discussion

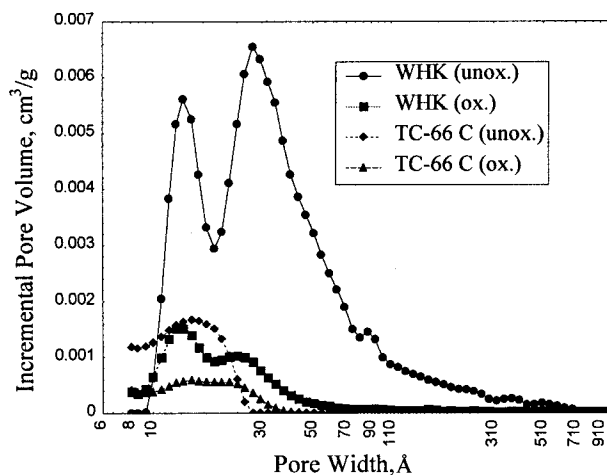
Figure 1 shows that there is a significant increase in cadmium adsorption when acid oxidised adsorbents are used. The cadmium adsorption capacity increased by a factor of 15.5 and 12 respectively when acid oxidised WHK and TC-66 C were used. This large improvement in adsorption capacity can be attributed 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.



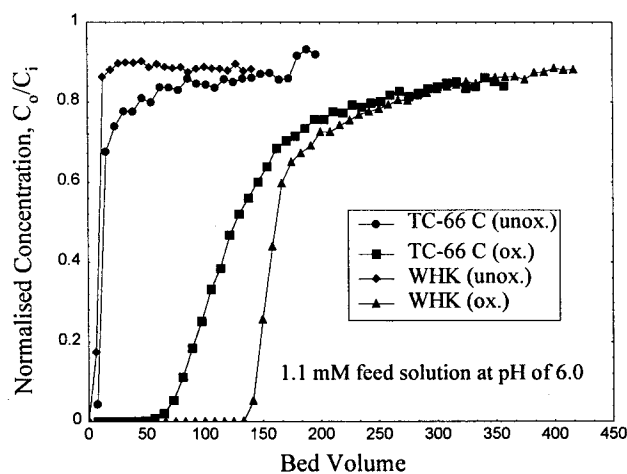
**Figure 1.** Cadmium adsorption isotherms for unoxidised and acid oxidised WHK and TC-66 C, at pH 6 and room temperature.



**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, [m <sup>2</sup> /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.

## References

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