UPTAKE OF COPPER BY ACTIVATED CARBONS IN THE PRESENCE OF DISSOLVED ORGANIC MATTER

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INTRODUCTION

Natural organic matter (NOM) is nearly always present in natural waters and the amount depends on the origin and the source [1]. Surface water usually contains greater amounts of NOM than ground water. NOM is made up of complex dissolved organic matter and humic type substances are of greatest interest in adsorption processes applied to water treatment [2]. Humic type substances comprise low molecular weight compounds, e.g. fulvic acid which is soluble in acidic as well as alkaline condition and relatively high molecular weight compounds, e.g. humic acid which is only soluble under alkaline conditions. These substances will adsorb strongly onto activated carbons and affect their performance. Humic and fulvic acid also contain weakly acidic functional groups within their structure which can react with and bind metal cations in solution.

In this study, sorption of copper ions on to three activated carbons has been investigated in the presence of fulvic acid in solution or adsorbed onto the activated carbon surface.

EXPERIMENTAL

Three activated carbons used in the present study were Chemivron F400, Westvaco A1100 and Sutcliffe Speakman 207C. These were selected on the basis of the precursor material and activation step. Details of these materials are given in Table 1. The size fraction of carbon used was 106-212 μm and the concentration of fulvic acid was 20 mg.l^{-1} in order to simulate natural waters.

The fulvic acid fraction was separated from humic acid by dissolving the sodium salt of the humic acid in distilled water and collecting the permeate from a micro-filtration unit. The sodium salt of the humic acid was supplied by Aldrich Chemicals. An Amicon 0.12 mm membrane was used as filter media. The pH of the permeate was then adjusted to 1. The humic acid fraction precipitated out and was separated from the rest of the solution. The pH was then adjusted to 7 and the solution was concentrated using a rotary evaporation unit. The final fulvic acid solid fraction was obtained by freeze drying.

<u>Sorption Experiments</u> Ion exchange breakthrough studies were carried out in mini-column experiments. Packed beds of each material were prepared by placing 1 g of each carbon in between two plastic 20 μm frits. Three series of tests were carried out. Initially, 60 mg.l^{-1} copper chloride was passed through the column to generate the breakthrough curves for a feed solution containing only copper. The feed flow rate was 7 BV.h^{-1} at pH 4.7. Subsequently, fresh samples of activated carbons were tested against a solution containing a mixed feed containing 60 mg.l^{-1} copper chloride and 20 mg.l^{-1} of fulvic acid. The experimental procedure and conditions were identical to the previous tests. Finally, a set of experiments was performed by contacting carbons that had been pre-loaded with fulvic acid with 60 mg.l^{-1} copper chloride solution. Pre-loading was carried out by passing 1l of 20 mg.l^{-1} solution of fulvic acid through a 1g bed of each material.

<u>Analysis</u> The determination of copper were carried out using a Varian SpectrAA 200 atomic absorption spectrophotometer. The pH of these solutions was measured using a Mettler Toledo 340 pH meter.

RESULTS & DISCUSSION

The results of the experiments can be seen in Figures 1-3. These show the breakthrough curves of packed columns of activated carbons used in the investigations.

Table 1: Details of activated carbon used

Material	Activation	Supplier	Precursor	BET surface area [m^2.g^{-1}]	Sodium Capacity [mmol.g^{-1}]
F400	Steam	Chemviron, Bel	Coal	1210	0.5
A1100	Phosphoric acid	Westvaco, US	Wood	1768	0.9
207C	Steam	Sutcliffe Speakman, UK	Coconut shells	1035	0.8

Column Experiments Figure 1 shows the results of breakthrough experiments carried out using F400 activated carbon. The results indicate that the sorption performance of the material is unaffected by prior loading of fulvic acid. However, F400 shows improved performance when removing copper from a mixed solution containing copper and fulvic acid (breakthrough occurs after about 40 BV of solution has been treated). This may be attributed to the metal binding capacity of fulvic acid. The large organic molecule binds copper readily and then adsorbs on the surface of the carbon thus increasing the overall copper uptake capacity. Note that the fulvic acid pre-loaded sample did not show any such enhancement. This indicates that NOM does not suppress metal with this adsorbent, on the contrary, we have found that it may actually enhance sorption due to secondary binding.

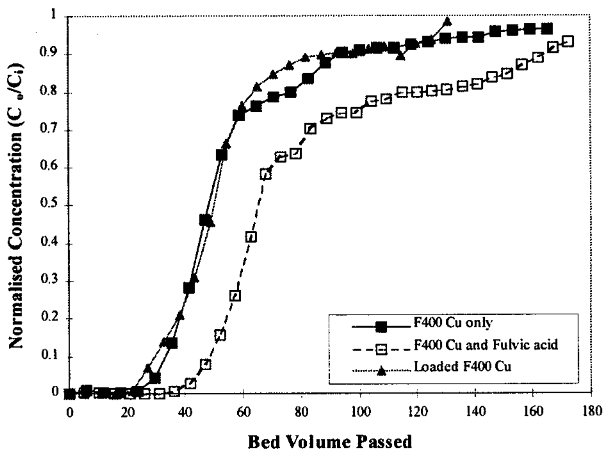

Figure 1: Breakthrough curves generated using Chemviron F400

Figure 2 shows the ion exchange performance of A1100 sample. The breakthrough curves are shallow indicating poor kinetics of the ion exchange reaction. The results also show that presence of fulvic acid in solution improves copper removal. However, the fulvic acid pre-loaded A1100 sample has much lower uptake capacity for copper. This may be due to blockage of pores by adsorbed material or interaction of the surface sites with fulvic acid molecules.

Similar results were obtained with activated carbon 207C. The presence of fulvic acid in solution increased metal uptake capacity of this material. Sorption of the fulvic acid on the carbon reduced the metal binding ability of 207C carbon. The results also show that the kinetics of sorption was largely unaffected by pre-loading but was slightly slower when the carbon was tested against a combined feed of copper and fulvic acid. This suggests that the removal of copper is enhanced in the presence of fulvic acid although fulvic acid complexes would have a low diffusion rate because of the large molecular size.

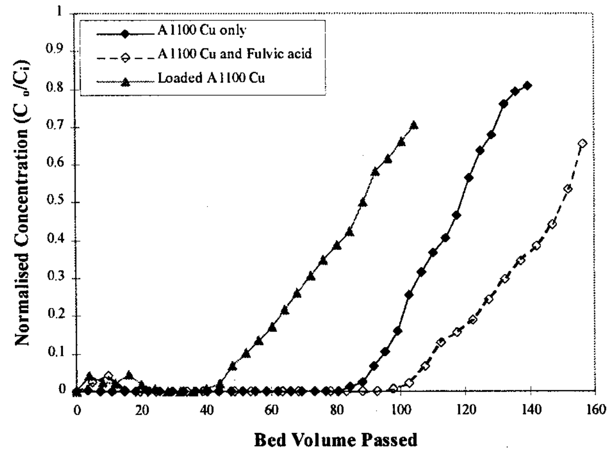

Figure 2 Breakthrough curves generated using Westvaco A1100

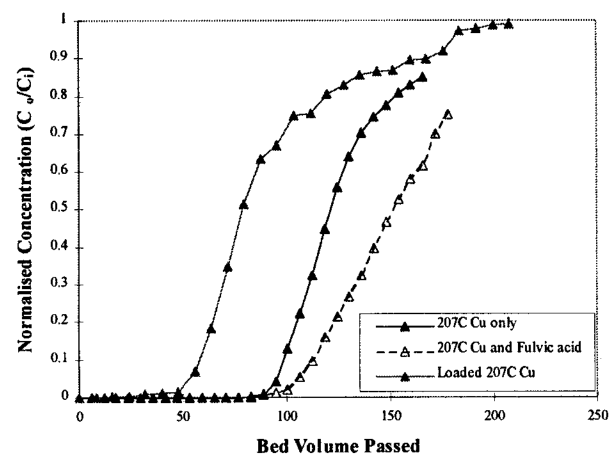

Figure 3: Breakthrough curves generated using Sutcliffe Speakman 207C

Conclusions

Copper uptake capacity is enhanced in the presence of trace fulvic acid in solution due to secondary metal binding. The uptake of copper is hindered by pre-loading with fulvic acid for Westvaco A1100 and Sutcliffe-Speakman 207C. Chemviron F400 is not significantly affected by the presence of pre-loaded fulvic acid.

References

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2. Starek, J, Zukal, A, Rathousky, J, Carbon, 1994, 32, 2, 207-211