

# SORPTION PERFORMANCE OF ACTIVATED CARBON AFTER OXIDATION AND SUBSEQUENT TREATMENTS

M.H. Tai, B. Saha and M. Streat

Department of Chemical Engineering, Loughborough University  
Loughborough, Leics. LE11 3TU, UK

## INTRODUCTION

Ion exchange, precipitation, evaporation and membrane processes are widely applied for the removal of trace metals from water, wastewater and effluents. In most cases, treatment of wastewater leads to secondary effluents although metal values can sometimes be recovered in a useful form. The removal of metal contaminants from effluent streams has the advantage of reducing the cost of waste disposal and reducing water consumption by recycling of the treated water. Polymeric ion exchange resins and activated carbons are commonly used as sorbents for the treatment of metal bearing effluents.

Activated carbons are prepared from a wide range carbonaceous precursors and may be used for removal of variety of contaminants from wastewater. Metal sorption performance of these materials is significantly improved by oxidation. This is readily achieved by air oxidation or treatment with nitric acid solution [1]. Complex organic by-products are formed as a result of acid oxidation within the matrix of the modified carbon [2]. Acid oxidised samples have to be alkali washed or heat treated in order to increase the pH application range and reduce the risk of leaching.

## EXPERIMENTAL

Modified samples of activated carbon, Chemviron F400, were prepared by acid or air oxidation. Details of the samples are given in Table 1. The acid oxidised samples were washed and treated to remove organic by-products. The sorption performance of these materials was studied

for removal of copper, nickel and zinc from aqueous solution and compared with unoxidised material. The size fraction used in the present study was 106-210  $\mu\text{m}$ .

**Modification** Acid oxidation was carried out by initially adding distilled water to a F400 sample and heating the mixture to 363 K. Concentrated nitric acid was then added to reaction mixture. In the first stage, the reaction was carried out for six hours after which the solution was decanted and the remaining carbon was thoroughly rinsed with water. The same sample was then dried and re-oxidised for a further three hours at 363 K. The procedure was repeated for a further 15 hours to produce material that had been oxidised for a total of 24 hours. Samples of acid oxidised carbon were then washed with 0.1M sodium hydroxide or heat treated under vacuum. The heat treatment was done at 593 K for 12 h. The carbons were washed with 0.1M nitric acid and then finally rinsed with copious amounts of distilled water. For air oxidation, samples were placed in a quartz reactor and heated to 693 K whilst passing air over the bed of activated carbon. The reaction was allowed to continue for 24 hours. All samples were dried for 24 hours at 378 K prior to use.

A total of 6 carbons were used for this study. Ox denotes samples oxidised by nitric acid and the length of the reaction is given in hours as 9h or 24 h. HT refers to the heat-treated samples and alkali-washed samples are referred to by AW. Air oxidised sample is denoted by AOx.

**Mini-column Experiments** Packed bed mini-columns containing 1 g of each carbon were used. Breakthrough curves were generated by passing a 1 mM solution of each

Table 1: Details of the F400 samples

Sample	Oxidant	Time (h)	Treatment	Yield (%)	Sodium Capacity [mmol.g <sup>-1</sup> ]
F400 Unoxidised	na	na	na	Na	0.5
F400 Ox9h WW	Nitric Acid	9	Water Washed	92	2.5
F400 Ox9h AW	Nitric Acid	9	Alkali Washed	86	2.4
F400 Ox9h HT	Nitric Acid	9	Heat Treated	89	2.1
F400 Ox24h	Nitric Acid	24	Water Washed	77	3.1
F400 AOx	Air	24	Water Washed	39	2.1

Ox9h, Acid oxidised for 9 hours; Ox24h, Acid oxidised for 24 hours; AOx, Air oxidised

WW; Water Washed; AW, Alkali Washed; HT, Heat treated

metal chloride salt separately through the bed. The flow rate was  $10 \text{ BV}\cdot\text{h}^{-1}$  and the feed pH was 4.7.

**Analysis** Copper, nickel and zinc concentrations were analysed using a Varian SpectrAA 200 atomic absorption spectrophotometer. The pH of these solutions was measured using a Mettler Toledo 340 pH meter.

## RESULTS & DISCUSSION

Table 1 lists the samples evaluated in relation to the oxidant used, reaction time and treatments given. The yields of the samples are given on a weight basis and indicate the amount of material remaining after oxidation. This shows that the yield was reduced by alkali washing and air oxidation. The lowest yield was obtained for air oxidised sample. The results also indicate that F400 Ox24h sample has the highest sodium capacity and that F400 unoxidised the lowest. The ion exchange capacity was reduced after alkali washing and heat treatment of F400 Ox9h WW sample. The sodium capacity of the heat treated sample decreased to  $2.1 \text{ mmol}\cdot\text{g}^{-1}$  compared with  $2.5 \text{ mmol}\cdot\text{g}^{-1}$  for F400 Ox9h WW sample.

**Column Experiments** Results of mini-column experiments can be seen in Figures 1-3. Figure 1 shows that the copper capacity increases with surface oxidation (breakthrough occurs at about 200 BV of feed solution passed for nitric acid oxidised alkali- and water washed samples of F400). The breakthrough performance of the sample oxidised for 9 hours was generally similar to the 24 hour oxidised sample. This indicated that 9 hours oxidation was sufficient to produce a material suitable for treatment of metal bearing effluents.

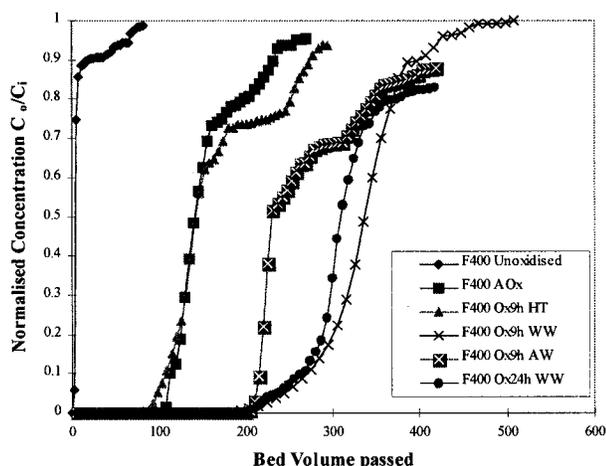


Figure 1: Copper breakthrough curves for F400 Samples

The results show that the copper uptake capacity was significantly improved by surface oxidation. Alkali washing and heat treatment produce carbons that have markedly lower copper uptake capacities. This indicates that the organic by-products of the oxidation reactions

possess metal binding ability. Figure 3 and 4 show similar results for removal of zinc and nickel.

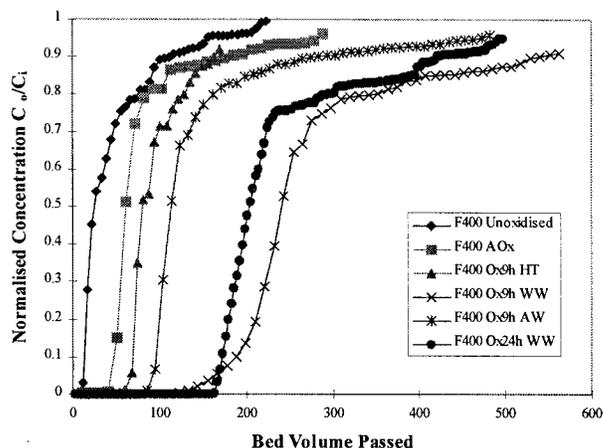


Figure 2: Nickel breakthrough curves for F400 Samples

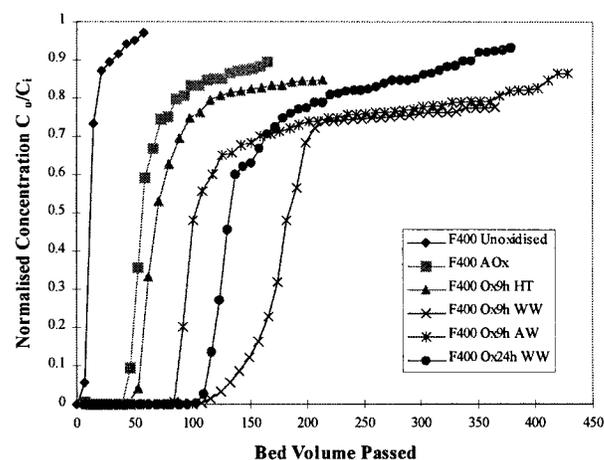


Figure 3: Zinc breakthrough curves for F400 Samples

## CONCLUSIONS

The sorption capacity of Chemviron F400 is significantly enhanced by air and acid oxidation. Chemviron F400 carbon, modified by acid oxidation has 50 times higher copper capacity than unoxidised material. Alkali washing and heat treatment reduces the metal uptake capacity of the acid oxidised sample.

## REFERENCES

1. M. H. Tai, M. Streat, Extended abstracts of *EuroCarbon 98*, 1998, Vol. I, 288-289
2. Kuzin A., Strashhko B.K., Zhurnal Prikladnoi Khimii, 1967, 40, 12, 2840-2843

## ACKNOWLEDGEMENT

This work was funded by EU under Brite-Euram Project BRPR-CT96-0158.