

ACIDITY OF SURFACE FUNCTIONAL GROUPS AND ELECTROPHORETIC AND ION-EXCHANGE PROPERTIES OF CARBONS OXIDISED AT DIFFERENT CONDITIONS

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Introduction

The oxidising conditions used to modify activated carbon can drastically affect the nature of the oxygen-containing surface functional groups. These groups have a strong influence on the ability of carbonaceous materials to sorb acids and bases, to remove organics from aqueous and gaseous media, to exhibit catalytic properties in electron and proton exchange reactions and, most importantly, to selectively remove heavy metals from aqueous solutions. The aim of the present research is to investigate how the degree of oxidation can influence the proportion, the concentration and the type of oxygen-containing groups on the surface of carbon. The effect of oxidation on the selectivity of activated carbon towards Cu(II) and Pb(II) is also considered.

Experimental

Activated carbon derived from apricot stones was a precursor for the oxidised material used in this work. Oxidation of activated carbon was performed in hot air (KAU-1.8) and in nitric acid (KAU-2.7). The relative concentrations of different surface functional groups after oxidation were determined by titration with sodium hydrogen carbonate, sodium carbonate and sodium hydroxide.

pH-titration of the carbons (particle size < 45µm) with 0.01M NaOH and 0.5M HCl was carried out in 0.1M NaCl solution.

Electrophoretic mobility of the sorbent in 0.1M NaCl was determined as a function of pH. The pH of the sorbent suspensions was adjusted with 0.01M NaOH or 0.01, 0.1 and 0.5M HCl. After equilibration for 24 hours the suspensions were injected directly into an electrophoretic cell. The results obtained were compared to those of a conventional polymeric carboxylic acid resin (Purolite C104). The selectivity tests were performed under dynamic conditions using packed mini-columns. Feed concentrations of Pb and Cu were 0.143mmol/l and 0.158mmol/l respectively. In all mini-column experiments, the flow-rate was 1.6ml/min and feed pH was 4.7.

Results and Discussion

Table 1 shows that acidic groups of weak character are predominantly formed on the air oxidised sample. The proportion of carboxylic groups over other weakly acidic groups is increased in the acid treated sample. Figure 1, shows that the exchange of Na⁺ for H⁺ on air oxidised carbon begins at higher pH values (pH 3 for KAU-1.8). As the degree of surface oxidation increases, ion-exchange starts at lower pH values (pH 2 for KAU-2.7). This confirms that the surface acidity strongly depends on the degree and the method of surface oxidation. Purolite C104 carboxylic resin, despite its high exchange capacity of 9.3mmol/g, appears to be less acidic than KAU carbons. The apparent pK values determined using the Henderson-Hasselbach equation¹ also revealed that the functional groups in carbons are more acidic than those of C104. Thus pK1 values for KAU carbons are between 3.3 and 3.6 whereas for C104 the pK value is 5.3.

It follows that these changes in surface acidity suggest that cation exchange on active carbons begins at lower pH values when compared to a polymeric carboxylic acid resin.

Table 1. Concentrations of surface functional groups for the carbons studied.

Groups titrated	Carbons KAU	
	1.8	2.7
Carboxylic groups, (meq/g)	0.540	1.430
% of total capacity	30	50
Lactones-lactoles, (meq/g)	0.560	0.650
% of total capacity	31	23
Phenolic groups, (meq/g)	0.680	0.795
% of total capacity	39	27
Total capacity, (meq/g)	1.779	2.875

Figure 2 gives the results of electrophoretic mobility studies. The isoelectric point for KAU-2.7 is at pH 1.1 whereas it occurs at pH 2 for Purolite C104, despite its high sorptive capacity (9.3meq/g for Na⁺) and this is similar to the value for KAU-1.8. The electrophoretic mobility curve for the resin also indicates lower surface

negativity when compared to active carbons. It is concluded that carbon based sorbents are more acidic than carboxylic resin despite the lower concentration of functional groups on their surface.

Mini-column studies (Figure 3) were conducted in order to evaluate how the degree of carbon surface oxidation and distribution of surface functional groups influences the selectivity of sorbents towards Pb and Cu in aqueous solutions. The carbons studied possess a different distribution of surface functional groups (Table 1). The air oxidised sample exhibits greater selectivity towards Cu over Pb.

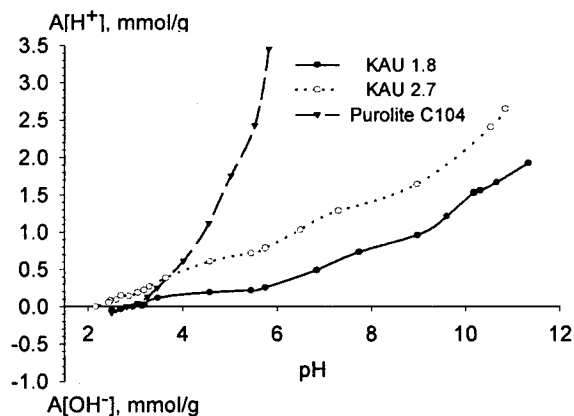


Figure 1. Proton binding curves for the sorbents investigated.

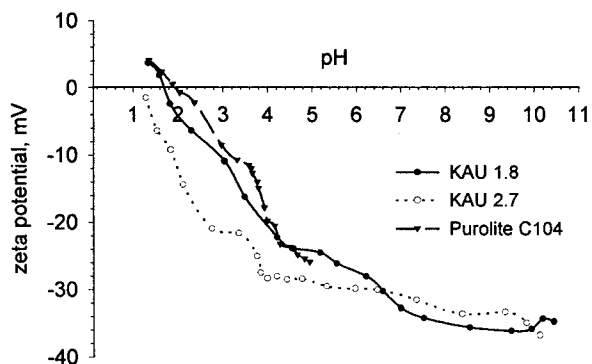


Figure 2. Electrophoretic mobility curves for the sorbents investigated.

However in the case of acid oxidised carbon, the difference in breakthrough curves for Pb and Cu is less distinct. As for C104, this material is highly selective for Pb over Cu and Pb breakthrough did not occur up to about 1,400BV of feed solution passed. It may be concluded that the selectivity towards Pb over Cu is associated with the

presence of carboxylic groups, since C104 is a monofunctional carboxylic cationite. By comparison, only 50% of KAU-2.7 functionality is associated with carboxylic groups.

Carbonaceous sorbents possess significant electrical conductivity because of the special electrophysical properties of carbon, (i.e. the presence of delocalised π -electrons easily transferable in conjugated systems of bonds). The exchange properties of functional groups attached to a carbon surface and a non-conductive polymeric matrix (ion-exchange resin) may, therefore, be quite different. The strength of protonogenic surface groups (primarily carboxylic groups) in carbons should increase because the negative charge builds up close to the surface of oxidised carbon. This is illustrated by the fact that cation-exchange on oxidised carbons begins at somewhat lower pH values than on carboxylic resin, i.e. the acidity of carboxylic groups on the oxidised carbon surface is 10 times stronger than that of carboxylic resin.

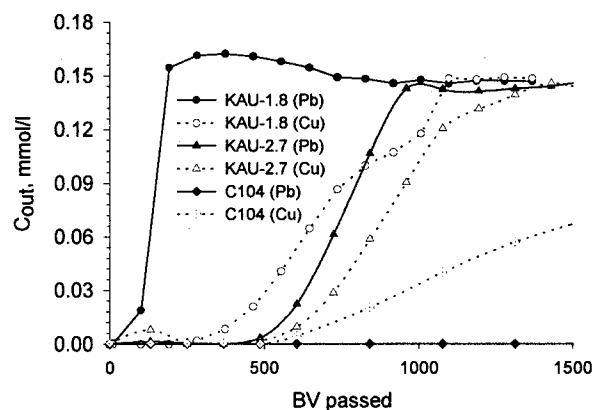


Figure 3. Breakthrough curves for the sorbents studied.

Conclusions

The distribution of functional groups in oxidised carbons depends on the degree and method of surface oxidation. pH titration and zeta potential studies have shown that the functional groups on the surface of carbonaceous sorbents are more acidic than those on carboxylic ion-exchange resin. It has also been found that the selectivity of carbons towards Pb may be dependent on the concentration of relatively strong carboxylic groups on their surface.

References

1. F.Helfferich, *Ion Exchange*, (1962), McGraw Hill, New York.