INFLUENCE OF OXIDATION TREATMENTS IN THE PREPARATION OF NOVEL SELECTIVE ACTIVATED CARBONS

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Introduction

The surface chemistry of carbons is determined to a large extent by the number and the nature of the surface functional groups or complexes. Carbon-oxygen surface compounds are by far the most important in influencing surface reactions, surface behaviour, hydrophilicity,and electrical and catalytic properties of carbons. The surface charge and zeta potential of carbon particles in aqueous suspensions is also conditioned by the nature of surface functional groups in a given environment [1,2]. Cationic or anionic exchange capacity has been observed for carbons depending on surface functionality [3]. The adsorptive properties of active carbons can be controlled by modification of their surface groups.

Numerous investigations have shown that carbons containing functional groups formed by oxygen chemisorbed at room temperature (i.e. conventional active carbons) are significantly different (physicochemically) from carbons which chemisorbed oxygen at high temperatures (oxidised carbons). It is now well accepted that the Brönsted acidic or basic character of carbons in solution may be attributed to surface oxidation. A good introduction to the properties of active carbons may be found elsewhere [4,5].

This paper explores the influence of alternative oxidation treatments such as air, acid and electrochemical methods to carefully control the amount and distribution of acidic surface groups. It is intended that some quantitative and qualitative hold on the presence of various oxygen containing acidic groups and their role in selective sorption of metal cations may be obtained.

Experimental

Active carbon derived from apricot stones (designated as KAU-ini) was the precursor for oxidised active carbons prepared for this study. KAU-ini was prepared as follows: 1) treatment of crushed stones with a hot solution of strong alkali; 2) washing with water to bring pH of solution down to 10; 3) treatment of crushed stones with hot hydrochloric acid; 4) washing with water to bring solution pH to 4; 5) carbonisation at 350-700°C; 6) Activation with steam at 800°C. A series of air, acid and electrochemically oxidsed carbons were prepared. Details of oxidation methodologies for air, acid and electrochemical oxidation techniques have been provided elsewhere [6]. Table 1 presents the conditions of oxidation and some properties of the prepared materials.

Surface area and pore size distribution of the adsorbents were determined from nitrogen sorption isotherms at 77 K measured by means of a Micromeritics ASAP2010. The data was modelled using the DFT method [7]. Electrophoretic mobility measurements were carried out using a Zetamaster (Malvern Instruments). Potentiometric titration data for the adsorbents was obtained using a method described by Helfferich [8]. The relative concentrations of different surface functional groups in oxidised carbons were determined by differential titration with sodium hydrogen carbonate, sodium carbonate, sodium hydroxide and sodium ethoxide [9]. Equilibrium sorption and binary metal breakthrough experiments were carried out as detailed in a previous publication [10].

Results

The pore-size distribution data clearly shows that the KAU carbons are predominantly microporous (see Table 1 and Fig. 1). The mean micropore diameter of the KAU carbons is around 20 Å The carbons possess high surface area (greater than 1000 m^2 g^{-1}; see Table 1). The apparent bi-modal distribution of pores in the microporous region (between 8-10 Å) is caused by deficiencies of the DFT model [7].

The air oxidised carbons show slightly enhanced surface area and pore volume values with respect to the starting compared with between 15-30 % of such groups in air oxidised samples.

Table 1. Conditions of oxidation and some properties of the oxidised carbons.

Carbon	Oxidising agent	Exposure time, h	Temperature (^{o}C)	BET Surface Area, $m^2 g^{-1}$	Na^+capacity mmol g^{-1}
KAU-ini	n.a.*	n.a.*	n.a.*	1823	0.4
KAU$_A$-0.8	Air	2	410	1865	0.8
KAU$_A$-1.3	Air	3	430	1815	1.3
KAU$_A$-1.8	Air	5	450	1870	1.8
KAU$_N$-1.7	HNO$_3$	2	90-95	1732	1.7
KAU$_N$-2.0	HNO$_3$	5	90-95	1694	2.0
KAU$_N$-2.6	HNO$_3$	10	90-95	1553	2.6
KAU$_N$-2.9	HNO$_3$	15	90-95	1369	2.9
KAU$_E$-1.3	Electrochem.	1	25	1587	1.3
KAU$_E$-2.4	Electrochem.	3	25	1430	2.4
KAU$_E$-3.1	Electrochem.	5	25	1280	3.1

n.a.* $\equiv$ not applicable.

KAU-ini carbon. Air oxidation at temperatures above 400°C result in phase oxidation of the carbon backbone yielding increased burn-off and lower yields of the final carbonised material. The resulting material does display enhanced microporosity and high surface area values. The acid and electrochemically oxidised materials show reduced surface area values in comparison with the starting KAU-ini carbon. The pore size distribution shows reduction in pore volume attributed to micro- and mesopores. This reduction is widely known to be attributed to enhancement in size of certain micropores to large macropores. These macropores are not detected by nitrogen sorption measurements.

The differential titration results (Table 2) suggest that all the carbonaceous adsorbents possess oxygen functionalities in the form of non-carbonyl (i.e. carboxylic, lactonic and phenolic groups) and carbonyl surface functional groups. The concentration of acidic groups substantially increases after oxidation. The distribution of weakly acidic functional groups depends on the type and extent of treatment. The proportion of phenolic groups is higher at low degrees of surface oxidation (compare KAU$_A$-0.8 with KAU$_A$-1.8; KAU$_N$-1.7 with KAU$_N$-2.9; and KAU$_E$-1.3 with KAU$_E$-3.1 in Table 2). Sodium hydroxide titration data (represented as "total non-carbonyl") shows that surface acidity increased by a factor of four for air oxidised samples and between six and seven for the acid and electrochemically oxidised samples in comparison with the starting material KAU-ini. Progressive oxidation of KAU carbons by either air, acid or electrochemical treatment methods result in an overall increase in concentration of both carboxyl and phenolic type groups. Acid and electrochemical oxidation treatments produce between 45-55 % of carboxyl groups

The pH titration curves measured for all carbons are smooth and do not have very distinctive inflection points (see Fig. 2.). However, there is a distinguishing difference between the carbon samples oxidised in hot air and those oxidised electrochemically or in nitric acid. The titration curves for the former set of samples display less alkali neutralisation capability between the crossover point and a pH around 6. Carboxyl groups are primarily responsible for Na$^+$ uptake at these pH values. The lower Na$^+$ uptake value displayed by air oxidised carbons may be attributed to low concentration of such groups present in the carbons. This may be due to the decomposition of carboxyl groups during the high temperature oxidation process. The gradient of the proton binding curves shows a shallow decay over the pH range 3-6. The curves for acid and electrochemically oxidised samples are steeper in this pH range as a result of their greater carboxyl group concentration and hence ion exchange capacity in this pH range. It should be noted that the electrochemically oxidised samples have a greater proportion of carboxyl groups in comparison with the acid oxidised samples (see Table 2). Mironov and Taushkanov [11] suggested that carboxylic groups in carbons dissociate in the pH interval 3-6 and phenolic groups dissociate above this pH range. This is in agreement with our pH titration results.

The crossover point i.e. the point on the pH axis where the sum of anion and cation exchange are in equilibrium is called the point of zero charge (pH$_{PZC}$). As the degree of oxidation increases, the crossover point occurs at lower pH values (see Table 3). Thus, the crossover point for KAU-ini is located at a pH around 10 whereas for KAU$_E$-3.1 it occurs at pH 2.

Table 2. Concentration and distribution of surface functional groups in carbons.

Carbon	Carboxylic groups meq/g	Lactones meq/g	Phenolic groups meq/g	Total (non-carbonyl) meq/g	Carbonyl groups meq/g	Total capacity meq/g
KAUini	0.078	0.000	0.370	0.448	0.628	1.076
%[c]	17.41	0	82.59	100		
KAU$_A$-0.8	0.130	0.320	0.362	0.811	1.030	1.841
%[c]	16.03	39.46	44.64	100		
KAU$_A$-1.3	0.370	0.479	0.457	1.306	1.138	2.443
%[c]	28.33	36.68	34.99	100		
KAU$_A$-1.8	0.540	0.560	0.680	1.779	0.664	2.443
%[c]	30.35	31.48	38.22	100		
KAU$_N$-1.7	0.842	0.196	0.664	1.701	2.232	3.933
%[c]	49.5	11.52	39.04	100		
KAU$_N$-2.0	0.959	0.393	0.702	2.054	2.376	4.430
%[c]	46.69	19.13	34.18	100		
KAU$_N$-2.6	1.275	0.548	0.781	2.604	2.765	5.369
%[c]	48.96	21.04	29.99	100		
KAU$_N$-2.9	1.430	0.650	0.795	2.875	2.531	5.405
%[c]	49.74	22.61	27.65	100		
KAU$_E$-1.3	0.580	0.320	0.380	1.280	1.170	2.450
%[c]	45.30	25.00	29.70	100		
KAU$_E$-2.4	1.330	0.58	0.485	2.395	1.030	3.425
%[c]	55.50	24.20	20.30	100		
KAU$_E$-3.1	1.580	0.665	0.830	3.075	1.390	4.465
%[c]	51.40	21.60	27.00	100		

[c] % in comparison to the total non-carbonyl capacity.

Table 3. Electrochemical properties and dissociation constants of the adsorbents.

Sorbent	PZC	IEP	PZC – IEP	pK$_a$ 1	pK$_a$ 2	pK$_a$ 3
KAUini	9.9	2.5	7.4	-	-	9.9
KAU$_A$-0.8	6.2	2.3	3.9	-	9	10.7
KAU$_A$-1.3	3.7	1.8	1.9	6	8.5	10.9
KAU$_A$-1.8	3	1.7	1.3	4.7	7.0	9.8
KAU$_N$-1.7	3.1	1.5	1.6	3.6	6.5	9.7
KAU$_N$-2.0	2.8	1.4	1.4	4	6.9	10.2
KAU$_N$-2.6	2.5	1.3*	1.2	3	6.75	9.5
KAU$_N$-2.9	2.1	1.1*	1	4.1	6.5	10
KAU$_E$-1.3	2.6	1.5*	1.1	3.8	6.6	7.7
KAU$_E$ -2.3	2.2	1.5*	0.7	3.0	5.6	7.9
KAU$_E$ –3.1	2.0	1.3*	0.7	2.6	5.5	7.2

* IEP values were obtained by extrapolation

vs. pH plots for representative oxidised carbons. An important parameter used to chracterise the electrokinetic behaviour of a solid-liquid interface is the point of zero zeta potential.The pH value at this point is often called the isoelectric point (pH_{IEP}) of the interface. A shift in the pH_{IEP} of KAU-ini (pH_{IEP} 2.5) to lower values is observed as the degree of surface oxidation increases (refer to Table 3). The isoelectric point for the electrochemically oxidised carbon KAU_E-3.1 and the acid oxidised carbon KAU_N-2.9 were found to be as low as 1.3 and 1.1 respectively. The zeta potential curves for the acid and electrochemically oxidised carbons fall steeply with increasing pH until pH 5 and then start to level off. Dissociation of relatively strong carboxyl surface groups may be responsible for this effect. The dissociation of carboxyl groups is known to occur at pH values between 2 and 6, thereby imparting a negative surface potential to the carbon surface. In air oxidised carbons, phenolic groups are predominant as discussed earlier. Their dissociation begins at higher pH values (above 6). The zeta-potential curve for the air oxidised carbon KAU_A-1.8 shows a more gradual decline in comparison to those of the acid and electrochemically oxidised carbons.

The copper and lead sorption values increase as the degree of surface oxidation increases (see Fig. 4). This result is valid for all three series of carbons, i.e. air, acid and electrochemically oxidised carbons. In general, the air oxidised carbons show higher copper sorption values compared with lead. In the case of acid and electrochemically oxidised carbons, the less oxidised samples generally show higher copper sorption values compared to lead, however, as the extent of oxidation increases, lead sorption values overtake those of copper; see data for KAU_N-2.9 vs. KAU_N-2.6 and KAU_E-3.1 vs. KAU_E-2.4. Air oxidised carbons display a linear correlation between the amount of copper removed and the concentration of phenolic groups present in the carbons.

The breakthrough curves for the series of electrochemically oxidised carbons depict a change in preference for copper and lead depending on the degree of oxidation. The less oxidised sample KAU_E-1.3 shows preference for copper. Thus, when a mixed solution containing equimolar concentrations of copper and lead were passed through a bed of KAU_E-1.3 lead ions were detected in the effluent stream before copper ions (see Fig. 5). On the other hand, the situation is reversed in the case of KAU_E-3.1 and this time copper ions were detected in the effluent stream before lead ions. In fact, frontal elution was observed; previously bound copper was eluted by lead ions thereby leading to an increase in the copper effluent concentration such that it exceeds the feed concentration (see Fig. 5).

Discussion

The chemical properties of a carbon surface in contact with an aqueous environment are complex. Electrochemical techniques have been widely used to characterise carbon solids in aqueous solutions [12,13]. It has been suggested that the isoelectric point (pH_{IEP}) values are only representative of the external surface charges of carbon particles in aqueous solutions whereas the point of zero charge (pH_{PZC}) varies in response to the net total (external and internal) surface charge of the particles [1,2]. Therefore, the difference between pH_{PZC} and pH_{IEP} can be interpreted as a measure of surface charge distribution of porous carbon solids [1]. Greater differential values indicate a more negatively charged external than internal particle surface. Lower values correspond to a more homogeneous distribution of the surface charges.

In general, air oxidation yields carbons possessing a less acidic surface and consequently, more easily distinguishable amphoteric properties than those of carbons oxidised either electrochemically or using nitric acid as the oxidising agent. This is confirmed by zeta potential measurements and pH-titration studies. The pH values corresponding to the isoelectric point and the point of zero charge of these materials typically fall within a higher pH range than those of the nitric acid and electrochemically oxidised samples. The greater difference between pH_{IEP} and pH_{PZC} also indicates that the surface of air oxidised carbons is generally more heterogeneous than that of the most severely nitric acid-oxidised materials with respect to their surface acidity distribution. It appears that oxidation occurs preferentially on the outer surface of the air-oxidised and the less severely acid oxidized carbons. Electrochemical oxidation seems to result in a more uniform distribution of oxygenated functional groups. Thus, KAU_E-1.3 shows a lower pH_{PZC} (2.6) compared with KAU_N-2.0 (pH_{PZC} 2.8) even though it contains a lower concentration of carboxyl groups; 0.58 mmol g^{-1} vs. 0.96 mmol g^{-1} respectively. The (pH_{PZC} - pH_{IEP}) difference decreases with an increase in the severity of the carbon oxidation treatment. This suggests that oxidation is a diffusion-dependent process. The KAU-ini carbon was not stored under nitrogen, or in conditions where air was excluded, hence, an ageing effect may lead to its low pH_{IEP} value. Active carbons in general are known to pick up oxygen slowly from ambient air. Puri *et al* [14] studied this effect for various charcoals and found that in pure oxygen this process is rapid and is essentially complete in 12 hours, whereas in air it took nearly three months to complete. On the other hand, it is well known that essentially all oxygen-containing groups are removed during high temperature treatment in a nitrogen atmosphere [15]. The resultant surface is very reactive and

both elemental analysis and microcalorimetric studies have shown significant oxygen adsorption upon its re-exposure to air (oxygen) at room temperature [13].

The present study also confirmed the acidic nature of the stabilised form of carbon KAU-ini. The high pH_{PZC} value for this sample indicates that its internal surface preserves its basic character. The oxidation process through ageing preferentially occurs on its external surface, as indicated by the low pH_{IEP} value of this carbon. The difference between pH_{PZC} and pH_{IEP} decreases as the degree of oxidation increases. At low degrees of surface oxidation, functional groups are preferentially introduced onto the external surface, thus causing the difference between pH_{PZC} and pH_{IEP} to be large. As the degree of oxidation progressively increases, more oxygen-containing groups are added to the internal surface of carbon thus decreasing the pH_{PZC} - pH_{IEP} difference. The similar values of pH_{PZC} and pH_{IEP} obtained for the carbons with a high degree of surface oxidation indicate that oxidation affects the entire surface i.e. external as well as internal surface to a similar extent i.e. the concentrations of functional groups on external and internal surfaces approach one another.

The results of carbon titration experiments with bases of varying strength suggest that the distribution of acidic surface groups differ for air, acid and electrochemically oxidised samples. Apparently, air oxidation leads to the formation of a higher proportion of relatively weaker acid groups, whereas electrochemical and nitric acid oxidation results in the formation of relatively stronger acidic groups on the adsorbent surface. The concomitant heat treatment of the carbons at the temperatures employed for air oxidation (see Table 1) results in the decomposition of carboxylic groups. This may be a reason for the relative popularity of phenolic functional groups on the surface of air oxidised carbons, since they are exposed to higher treatment temperatures than acid and electrochemically oxidized carbons. During air oxidation, various types of groups begin to form on the carbon surface and it is known that carboxylic groups are less stable than phenolic groups when exposed to heat treatment [16,17]. In contrast, phenolic and carbonyl groups have been found to remain stable up to about $800^{o}C$.

The oxidation of carbonaceous materials employing liquid phase oxidation techniques are analogous to the oxidation of aromatic hydrocarbons. The aliphatic side chains of the molecules are susceptible to oxidation and in many cases the final product will be an arylcarboxylic acid. If side chains of more than one carbon atom are present, the splitting of the C-C bond may occur at the α-position of the benzylic carbon atom [18]. For example, the oxidation of 9,10-dihydrophenantrene yields the corresponding dicarboxylic acid. When one methylene group is present between two aromatic systems, the oxidation is expected to stop at the ketone stage. This process can be illustrated by the oxidation of diphenylmethane yielding diphenylketone and nitrous acid [18]. The oxidation treatments with nitric acid, as applied in this study, can be compared to the work performed by Papirer et al. [16] and Otake and Jenkins [17]. In these studies, the formation of surface carboxylic groups was observed. The formation of hydroxyl and carbonyl groups upon nitric acid oxidation was suggested by Donnet and Ehrburger [19] and by Donnet [20]. Our investigation clearly supports the presence of similar functional groups on the carbon surface.

The acid-base titration studies indicate the presence of carboxylic acids on oxidised carbons. Hydrogen carbonate and carbonate anions were used as titrants for acidic carbon surface oxides. To observe an end point, the surface acid being titrated should be at least two orders of magnitude stronger than the conjugate acid of the base employed; the pK_a values of the conjugated acids H_2CO_3 and HCO_3^- are 6.4 and 10.3, respectively [21]. The pK_a values of the surface acids titrated using Boehm's method must be in the ranges (a) $pK_a<4.4$ and (b) $4.4<pK_a<8.3$. Several aromatic carboxylic acids possess dissociation constants which fall within these ranges. The surface functional groups (i.e. carboxylic, phenolic, etc.) in oxidised carbons are analogous to those in aromatic carboxylic acids and phenols. Oxidation of the edges of the ring structures present in the carbon basal planes may result in the formation of aromatic acids similar to phthalic or salicylic acids.

Surface oxidation generates a distribution of surface functional groups. The positioning of these groups in close proximity to one another may influence their acidity. For example, the acidity increases by more than an order of magnitude from benzoic to m-phthalic and salicylic acids. The surface carboxyl groups of oxidised carbons exhibit even lower dissociation constants. This may be related to the fact that the surface groups are connected to a π-conjugated condensed system of graphite-like planes. The number of the conjugated benzene rings and the positioning of the groups will also influence their acidity. For example, carboxylic acids derived from naphthalene and anthracene possess different dissociation constants depending on the location of the carboxylic functional group on the aromatic ring.

Owing to the special electrophysical properties of carbons (namely the presence of delocalised π-electrons that are relatively easily transferable in a conjugated system of aromatic bonds) the carbonaceous sorbents possess significant electrical conductivity. The properties of functional groups attached to a carbon surface should diverge considerably in comparison to those of groups attached to a non-conductive polymeric matrix (ion-exchange resins). The strengths of real protonogenic

surface functional groups (primarily carboxylic groups) in carbons should be higher than in resins, since the negative charge usually builds up close to the surface of the oxidised carbons. This is demonstrated by the fact that cation-exchange on many oxidised carbons, as opposed to typical carboxylic resins, begins at pH values around 1 [22] i.e. the acidity of carboxylic groups on the oxidised carbon surface is 10 times stronger than that of the carboxylic resin. Delocalisation of the $2p$ electrons of functional group-oxygen into the π-conjugated system results in a decrease in the effective negative charge present on the surface oxygen. This will result in an increased mobility of the associated protons thereby resulting in lower pK_a values.

Introduction of acidic functional groups onto the surface of active carbons radically changes their ability to bind metal ions from aqueous solution. The degree of carbon surface oxidation strongly affects the metal uptake capacity of oxidised carbons. Longer exposure of the active carbon to the oxidising agent results in formation of a greater amount of weakly acidic surface groups that are capable of binding metal ions. Kovyrshin *et al* [23] showed that selective removal of a particular metal is related to the distribution of surface functional groups. These researchers studied the removal of thallium by oxidised carbons and found that selective sorption was due to phenolic surface functional groups. Strashko et al [24] carried out a series of experiments to determine the influence of the degree of carbon oxidation on the separation of potassium and caesium. The chromatographic separation of these metals was found to be related to the extent of carbon oxidation.

Weakly acidic surface functional groups may be loosely considered as derivatives of aromatic compounds. None of the oxygen-containing groups present on the carbon surface is capable of forming strong complexes with metal ions. However in some micropores (since carbons are mostly microporous materials) favourable sterical conditions may be achieved where polydentate complexes may form between metals and oxygenated groups. Ideal case would be when two protonogenic and two non-protonogenic groups participate in metal complex formation. A high density of phenolic groups may lead to formation of stable complexes with copper ions whereas in the presence of a high carboxyl group concentration, lead complexes might be more prevalent.

Conclusions

The results of this study have shown that modified active carbons may be prepared for the selective removal of heavy metals from aqueous solutions. Introduction of oxygen containing surface functional groups result in variation in the metal sorption behaviour towards specific metal ions. The selectivity of carbons towards copper and

lead ions may be controlled by varying the extent of the oxidation treatment as well as employing different oxidation treatments.
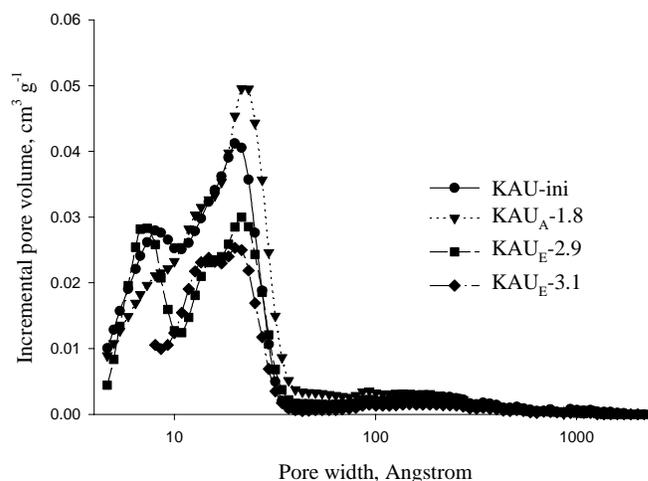
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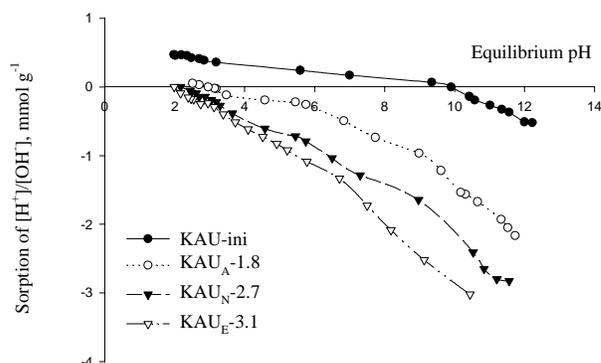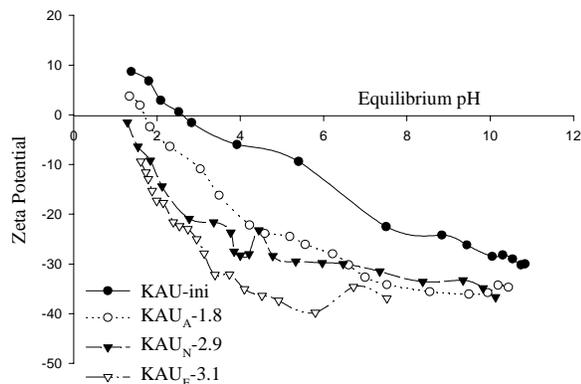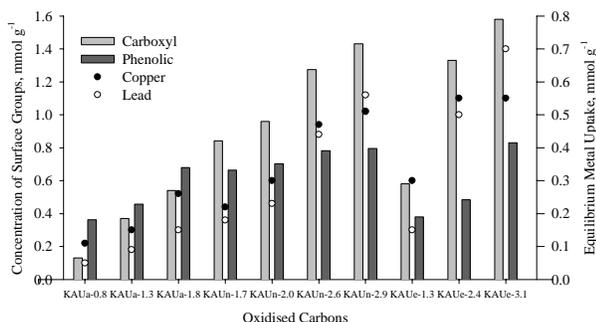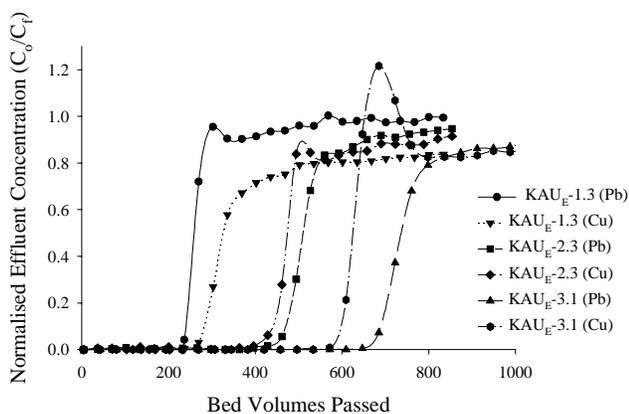**Figure 1.** Pore size distributions for KAU carbons.

Figure 2. Proton-binding curves for KAU carbons.

Figure 3. Electrophoretic mobility curves for KAU carbons.

Figure 4. Correlation of metal uptake and surface functional groups in oxidised carbons.

Figure 5. Selectivity reversal between copper and lead ions.

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