Separation Science and Technology
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713708471

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V. Strelko Jr.[a]; D. J. Malik[a]; M. Streat[a]
[a] Department of Chemical Engineering, Loughborough University, Loughborough, UK

To cite this Article Strelko Jr., V. , Malik, D. J. and Streat, M.(2001) 'THE INFLUENCE OF ACTIVE CARBON OXIDATION ON THE PREFERENTIAL REMOVAL OF HEAVY METALS', Separation Science and Technology, 36: 15, 3367 — 3383
To link to this Article: DOI: 10.1081/SS-100107908
URL: http://dx.doi.org/10.1081/SS-100107908

SEPARATION SCIENCE AND TECHNOLOGY, 36(15), 3367–3383 (2001)

THE INFLUENCE OF ACTIVE CARBON OXIDATION ON THE PREFERENTIAL REMOVAL OF HEAVY METALS

V. Strelko, Jr., D. J. Malik, and M. Streat*

Department of Chemical Engineering, Loughborough
University, Loughborough, UK

ABSTRACT

Oxidized active carbons were prepared by employing air- and acid-oxidation methods. Weakly acidic surface-functional groups were incorporated on the carbon surface. The distribution of functional groups varied with the oxidation techniques used. Metal sorption characteristics of oxidized active carbons were measured in both batch and minicolumn experiments. The materials preferentially adsorbed lead and copper over nickel and cadmium. Furthermore, a variable selectivity of oxidized carbons toward copper and lead was found to be based on the means by which the carbon was oxidized. Through alteration of oxidation treatment conditions and employment of different oxidizing agents, the selectivity behavior of the materials was controlled. Possible mechanisms of metal sorption are discussed.

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*Corresponding author. Fax: +44 0 1509 222596; E-mail: M.Streat@Lboro.ac.uk

INTRODUCTION

Water intended for human consumption in the United Kingdom must comply with requirements outlined in the European Council Directive 80/778/EEC (1). Typical values for maximum metal concentrations adopted by European Union legislation are Cu = 100–3000 μg/L; Cd = 5 μg/L; Pb = 50 μg/L; and Ni = 50 μg/L. The concentration of any individual heavy metal in drinking water must be in the low μg/L range. The low limits for heavy metals set by the current legislation presents a serious challenge for water supply companies and acts as the inducement for research into novel sorption materials.

Active carbons have not been utilized on an industrial scale for the removal of heavy metals from water although their use in the removal of organic contaminants is widespread. A considerable amount of relevant bench-scale research has been carried out with active carbons. Sigworth and Smith (2) were probably the first to review previous research on the utilization of active carbons for the removal of trace heavy metals from water. Their review highlighted the potential for the removal of antimony, arsenic, bismuth, chromium, tin, silver, mercury, cobalt, zinc, lead, nickel, titanium, vanadium, and iron by carbon materials. Nevertheless, a systematic investigation was not carried out to determine the underlying metal sorption mechanisms. Their work indicated that sorption of heavy metals by active carbons was inversely proportional to the solubility of metal complexes in aqueous solutions. The researchers concluded that sorption of heavy metals was enhanced when water conditions rendered the heavy metals less soluble. House and Shergold (3) investigated the sorption of multivalent metal species such as aluminum, calcium, cobalt, copper, iron, lead, and zinc by active carbon and graphite. They reported that sorption strongly depended on pH and occurred at 1 or 2 pH-units below the value required for precipitation of the bulk metal hydroxide. The researchers argued that the structure of water molecules near a charged sorbent surface leads to a reduction in the dielectric constant, reducing metal ion solubility in the proximity of the surface and thus producing conditions that are favorable for metal hydroxide precipitation in the sorbent pores. Netzer and Hughes (4) extensively studied the adsorption of lead and other heavy metals on ten different kinds of active carbon. The investigation revealed that one carbon (Barney Cheney NL 1266) was superior for lead removal at low pH. The rest of the carbons demonstrated a large variation in lead sorption from aqueous solutions. The investigation showed that the adsorption capacity of active carbons for lead was 2 times as high as for copper and 10 times higher than for cobalt. The researchers concluded that a large number of different factors affect the adsorption of heavy metals, e.g., the surface chemistry of carbon and the medium in which the metal ion is dissolved. The surface chemistry of carbons, i.e., the kind of functional groups thought to be present in oxidized activated carbons, has been investigated by various researchers (5–9). Reed et al. studied the use of granular active carbon columns for lead and cadmium removal (10,11). Synthetic wastewaters containing the target metals, organic contaminants, and chelating agents were used in this study. In the absence of organic contaminants and chelating agents, a significant volume, up to 325 bed volumes (BV), of feed solution were treated prior to metal breakthrough. Metal uptake values of 30 mg/g were achieved.

Our objective in this study was to demonstrate the efficiency of carbonaceous adsorbents in treating heavy metal–bearing solutions. Lead and copper were chosen because of their likely presence in the water distribution system as a result of corrosion and leaching from lead pipes and lead/tin-soldered joints of copper pipes commonly used in household plumbing.

Active carbons containing surface heteroatoms (e.g., having oxygen, phosphorus, or nitrogen) display high metal-sorption capacity, possess a rigid structure, and exhibit selectivity toward a number of heavy metals (12,13). However, little information is available in the literature concerning the influence of the degree of carbon oxidation on metal sorption and its relation to competitive interactions between various metal species (lead and copper in particular). Although the majority of previous studies on metal removal by carbon have been devoted to batch equilibrium and metal sorption rate determinations, several studies on the use of active carbon–packed columns have been reported in the literature (11,14,15). In our work, a range of adsorbent materials was studied in minicolumn experiments to evaluate adsorbent selectivity toward lead, copper, nickel, and cadmium.

EXPERIMENTAL

Materials

Active carbons derived from agricultural by-products (designated as KAU and prepared from apricot stones) and a polymer-based carbon CKC were precursors for the oxidized active carbons used in this study. The carbons studied were compared with the carboxylic resin Purolite C104 and the commercially available active carbon Filtrasorb F400. Active carbons were modified by oxidation through the use of either nitric acid or hot air. Carbon oxidation methodology information can be found elsewhere (16,17,18). Table 1 presents the conditions of oxidation and some properties of the materials produced.

Boehm's Titration

Samples of sorption materials in hydrogen form were mixed with 0.1 mol/L solutions of sodium hydroxide, sodium hydrogen carbonate, and sodium carbonate. The sodium hydroxide and sodium carbonate were volumetric standards. The

Table 1. Conditions of Oxidation and Some Properties of the Oxidized Carbons

Carbon	Oxidizing Agent	Exposure Time (hours)	Temperature (°C)	Na^+ Capacity (mmol/g)
KAUini	N.A.	N.A.	N.A.	0.4
KAU-1.5	HNO_3	2	90–95	1.7
KAU-1.9	HNO_3	5	90–95	2.0
KAU-2.2	HNO_3	10	90–95	2.6
KAU-2.7	HNO_3	15	90–95	2.9
KAU-0.8	Air	2	410	0.8
KAU-1.2	Air	3	430	1.3
KAU-1.8	Air	5	450	1.8
KAU-1.6	HNO_3	20	90–95	3.3
CKC	HNO_3	15	90–95	2.2
F400(ox)	HNO_3	16	90–95	1.6

N.A. Not applicable

sodium hydrogen carbonate was prepared from an analytical grade reagent. All the chemicals were supplied by Aldrich Chemicals Ltd. Two hundred milligrams of dried adsorbents (particle size 75–100 μm) were weighed in 50-mL glass conical flasks prior to the addition of 20 mL of base. The flasks were then sealed with Parafilm and agitated with an orbital shaker for 3 days. The equilibrated solutions were filtered with 0.45-μm polytetrafluoroethylene (PTFE) syringe top filters to remove the adsorbent particles. Aliquots of 5 mL were then titrated with a 0.1 mol/L volumetric HCl standard with a water-ethanol solution of methyl red as the indicator. Point-of-zero charge values (PZC) were calculated with a Zeta master (Malvern Instruments, UK). The procedure has been reported elsewhere (12).

Batch Sorption Experiments

Adsorbent particles (sized under 45 μm) were accurately weighed into 250-mL conical flasks. Five samples of carbon, with weights of between 0.01 and 0.1 g, were used. Two hundred milliliters of metal solution (of known starting concentration) was then added to each carbon sample. This solution also contained 0.5 mol/L of sodium ions as sodium nitrate to maintain constant ionic strength of the feed solution. The mouths of the flasks were sealed with Parafilm and kept in an orbital shaker at a constant temperature of 22°C ± 2°C.

Sorption isotherms were measured at a controlled solution of pH 4.8. The solution pH was held constant by the addition through a micropipette of known amounts of sodium hydroxide or nitric acid to the batch flasks. The pH of each sample was measured every 24 hours and adjusted to pH 4.8 by addition of several drops of alkali (NaOH, 1 mol/L/0.1 mol/L). The samples were assumed to have attained equilibrium when no significant change in solution pH (±0.2 pH units) was observed over a 48-hour period. The equilibrium metal concentration in each sample, as well as the blank, was measured after filtering the sample through a 0.45-μm Whatman (PTFE) disposable filter with a Varian SpectrAA-200 atomic absorption spectrophotometer (AAS) in flame mode that employed an air-acetylene flame. The wavelengths used for metal detection were lead at 283.0 nm, copper at 324.7 nm, cadmium at 228.8 nm, and nickel at 232.0 nm.

Minicolumn Sorption Experiments

The minicolumn experiments were carried out with Isolute solid-phase extraction columns of nominal capacity (3 mL), supplied by Jones Chromatography Ltd (Mid-Glamorgan, UK). The experimental unit had 20-μm polyethylene frits as bed supports and column adapters to seal the column and attach tubing.

A known quantity of dried sorbent sample (particle size 45–90 μm) was accurately weighed and transferred into a minicolumn. The sorbent was wet packed into the column to a bed volume of approximately 0.65 cm^3 (8.7 mm diameter and approximately 10 mm height). The column was subsequently washed with distilled water to eliminate any fines and purge any trapped air. The concentration of each metal in the feed solution was 0.15 ± 0.01 mmol/L. Feed solution was pumped at a controlled flow rate of 10 BV/h to the top of the carbon bed with a Masterflex peristaltic pump. The level of the solution above the bed was maintained by forced flow. The effluent from the column was directed either to a fraction collector or as waste using a 3-way PTFE solenoid valve (Pharmacia). The volume of fractions collected varied during the minicolumn operation but was usually between 5 and 10 mL. After saturation, the adsorbent beds were regenerated with 0.5 mol/L nitric acid. Fractions from the outlet were collected into 2-mL plastic containers. Each effluent sample was diluted 500-fold to obtain 1 L of solution. Metal concentration in the samples was analyzed through AAS.

RESULTS

Boehm's Titration

The titration results presented in Table 2 show that all the carbonaceous sorbents possessed a distribution of weakly acidic functional groups (i.e., carboxylic, lactonic and phenolic groups). The concentration of groups substantially increased after oxidation. Thus, the number of acidic groups neutralized by $NaHCO_3$ (carboxylic groups) represents only approximately 17% of the total

Table 2. Data on Surface Functional Groups, Equilibrium Metal Sorption Capacity, and Selectivity

Carbon	Carboxylate (mEq/g)	Lactones (mEq/g)	Phenolic (mEq/g)	Total Na$^+$ Capacity (mEq/g)	Carbonyl (mEq/g)	Ratio $\left(\frac{\mathrm{Cu}}{\mathrm{Cu}+\mathrm{Pb}}\right)$	Equilibrium Metal Uptake (mmol/g)	
							Lead	Copper
KAUini	0.078	0.000	0.370	0.448	0.628	–	–	–
%	17.41	0	82.59	100.0	–	–	–	–
KAU-1.5	0.842	0.196	0.664	1.702	2.232	0.65	0.18	0.22
%	49.5	11.52	39.04	100.1	–	–	–	–
KAU-1.9	0.959	0.393	0.702	2.054	2.376	0.64	0.23	0.30
%	46.69	19.13	34.18	100.0	–	–	–	–
KAU-2.2	1.275	0.548	0.781	2.604	2.765	0.59	0.44	0.47
%	48.96	21.04	29.99	100.0	–	–	–	–
KAU-2.7	1.430	0.650	0.795	2.875	2.531	0.55	0.56	0.51
%	49.74	22.61	27.65	100.0	–	–	–	–
KAU-0.8	0.130	0.320	0.362	0.812	1.03	0.96	0.05	0.11
%	16.03	39.46	44.64	100.1	–	–	–	–
KAU-1.2	0.370	0.479	0.457	1.306	1.138	0.94	0.09	0.15
%	28.33	36.68	34.99	100.0	–	–	–	–
KAU-1.8	0.540	0.560	0.680	1.780	0.664	0.87	0.15	0.26
%	30.35	31.48	38.22	100.1	–	–	–	–
KAU-1.6	1.840	0.620	0.790	3.250	2.747	0.29	1.74	2.5
%	56.62	19.08	24.31	100.1	–	–	–	–
F400ini	0.047	0.073	0.003	0.123	0.235	–	–	–
%	38.21	59.35	2.44	100.0	–	–	–	–
F400ox	0.719	0.439	0.427	1.585	1.356	0.6	0.22	0.29
%	45.33	27.68	26.92	99.9	–	–	–	–
CKC	1.149	0.585	0.462	2.196	1.056	0.54	0.54	0.47
%	52.32	26.64	21.04	100.0	–	–	–	–

Note that some percentages do not add up to 100% due to rounding errors.
–Not applicable

number of acidic groups for untreated active carbon KAUini, while after oxidation it is nearly 50% for KAU-2.7 (Table 2).

Phenolic groups were dominant at low degrees of surface oxidation. This finding was true for both acid- and air-oxidized samples; compare KAU-1.5 with KAU-2.7 and KAU-0.8 with KAU-1.8 in Table 2. For carbons oxidized with nitric acid, the total acidity increased up to 7 times compared to the original, KAUini, carbon and reached a 12-fold increase for F400. In the case of air-oxidized carbons, the increase in total capacity was approximately 4 times that of the starting material. Progressive oxidation of carbon with nitric acid created a greater quantity of relatively strong carboxylic surface groups (KAUini < KAU-1.5 < KAU-1.9 < KAU-2.2 < KAU-2.7). The results in Table 2 suggest that the proportion of phenolic-type functional groups contributing toward the total amount of acidic functional groups decreased throughout the range of acid-oxidized carbons while carboxylic functionality remained relatively constant at around 50%. Thermal treatment of carbons in an oxidizing atmosphere (hot air) led to a lesser increase in the total acidity of the final material than was found with acid-oxidized samples. Phenolic groups were found to be present in greater proportions in air-oxidized samples; for example, in KAU-1.8 approximately 40% of the functional groups are phenolic compared with KAU-2.7 where they comprised less than 30% of the functional groups.

The concentration of surface functional groups in unoxidized F400ini was significantly lower than those that had been oxidized. It is also significantly lower than results presented by Mazet, Farkhani, and Baudu (19). The difference between the results may be due to the different chemical composition of the F400 titrated by Mazet; the material may have been exposed to an oxidizing atmosphere (air) for a longer period than was our carbon. This prolonged exposure would result in an increase in the amount of surface groups due to surface oxidation.

The Influence of pH on Metal Removal by Active Carbons

The surface of active carbons immersed in aqueous solutions can be either positively or negatively charged. The surface charge largely depends on the solution pH. The solution pH is important and controls the extent of metal sorption (20–22). House and Shergold (3) found that the metal sorption capacity of active carbons depends on the pH value at the PZC. These researchers observed an abrupt reduction in metal sorption as the external solution pH approached this value. The removal of cations is favored at pH values above PZC and is inhibited for anions. PZC values have been determined from potentiometric titration curves (Table 3). Acidic functional groups on the surface of carbons act as ion-exchange sites for metals. The solution pH must be above or near the p*K* values of functional groups cations to be adsorbed. The p*K* values of the acidic functional groups found on the carbon surface were calculated and are shown in Table 3.

The effect of the external solution pH on the extent of the lead sorption for various carbons is depicted in Fig. 1. The amount of lead uptake by the oxidized active carbons increased sharply between pH 2 and 5. The adsorption experiments were not conducted above pH 5 so that formation of metal precipitate would be avoided (10). Active carbons with high degrees of surface oxidation, i.e., those oxidized by nitric acid (KAU-2.7, KAU-1.6, and CKC), have discernible lead sorption capacity (>0.05 mmol/g) at low solution pH values (e.g., at approximately pH

Table 3. Electrochemical Properties and Dissociation Constants of the Adsorbents

Sorbent	PZC	IEP	PZC–IEP	p*K*a 1	p*K*a 2	p*K*a 3
KAUini	9.9	2.5	7.4	–	–	9.97
KAU 0.8	6.2	2.3	3.9	–	9	10.7
KAU 1.2	3.7	1.8	1.9	6	8.5	10.85
KAU 1.8	3	1.7	1.3	4.7	7.0	9.8
KAU 1.5	3.1	1.5	1.6	3.6	6.5	9.7
KAU 1.9	2.8	1.4	1.4	4	6.9	10.2
KAU 2.2	2.5	1.3*	1.2	3	6.75	9.5
KAU 2.7	2.1	1.1*	1	4.1	6.5	10
CKC	2.1	1.2*	1	2.8	6.9	9.8
Purolite C104	3	2	1	5.9	–	–

IEP (isoelectric point) values were obtained by extrapolation. PZC = point of zero charge.

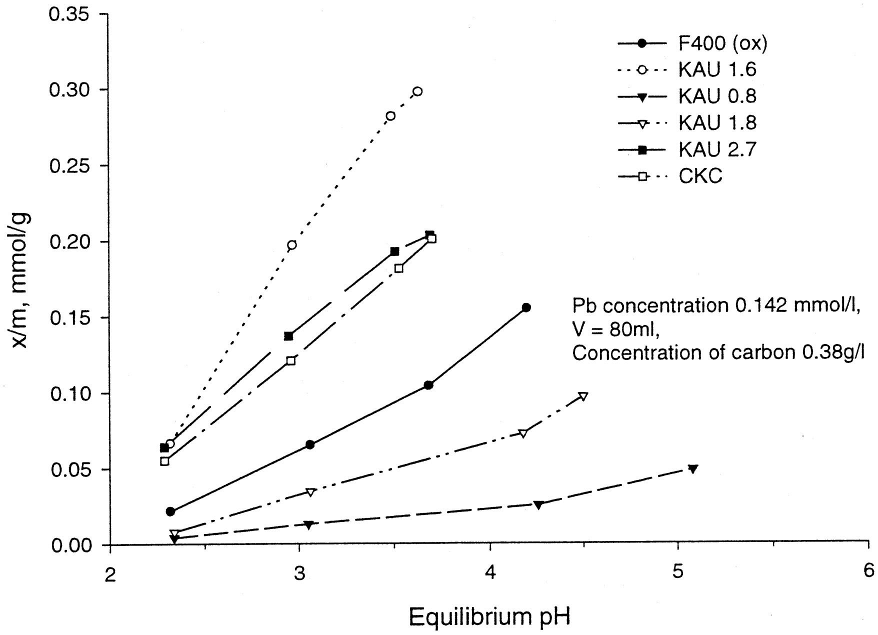

Figure 1. Effect of solution pH on the extent of metal sorption by carbons.

2). This pH dependence may be attributed to acidic surface functional groups that dissociate at relatively low pH values. (Compare the PZC values for air-oxidized and acid-oxidized carbons; see Table 3.) KAU-2.7 has a PZC value of 2.1 while the KAU-1.8 PZC value is 3.0. At pH values above 2.1, cation exchange dominates between lead ions in solution and protons on the surface of KAU-2.7. In the case of the air-oxidized carbon KAU-1.8, cation exchange dominates at pH values higher than the PZC value, i.e., at approximately pH 3. This is reflected in the lead sorption data obtained for the series of carbons at different pH values. Surface functional groups with electronegative atoms that possess a lone pair of electrons, e.g., oxygen, can form coordinated covalent bonds with metal ions in solution. Delocalized π electrons enhance the electronegative nature of these atoms, thereby facilitating complexation of metal ions to the carbon surface. This delocalized electron effect is found in addition to parallel ion-exchange reactions where protons of weakly acidic surface functional groups are exchanged for metal ions. Although groups that are stronger acids than carboxylic acids are not generally thought to exist on carbons, the experimental results published by Strazhesko and Tarkovskaya (23,24) indicate the existence of some relatively strong acidic groups on oxidized carbons that can participate in metal sorption reactions at pH 1–2 and even lower.

Metal Sorption from Aqueous Solutions

The metal sorption results show that sorption capacity strongly depends on the degree of surface oxidation (Table 2). The carbons oxidized by nitric acid possess greater metal sorption capacity than do air-oxidized carbons. Air-oxidized carbons remove more copper than lead; for example, KAU-1.8 carbon shows an equilibrium sorption capacity of 0.15 mmol/g for lead and 0.26 mmol/g for copper. As the degree of surface oxidation increases, lead sorption values approach those of copper (Table 2). KAU-1.5 carbon removes 0.18 mmol/g of lead and 0.22 mmol/g of copper; i.e., approximately 20% more copper than lead is removed. In the case of the KAU-2.7 carbon, the situation is reversed and lead uptake is 0.56 mmol/g while 0.51 mmol/g of copper is taken up; i.e., 10% more lead than copper is removed.

Minicolumn Experiments

The pH of the effluent leaving the adsorbent beds was significantly lower than the influent solution pH; this result was observed for all carbons (Fig. 2). As the F400(ox) adsorbent bed reached exhaustion, the metal concentration of the effluent approached the feed concentration values indicating that breakthrough had been achieved. The reduction of effluent pH suggests that metal sorption by active

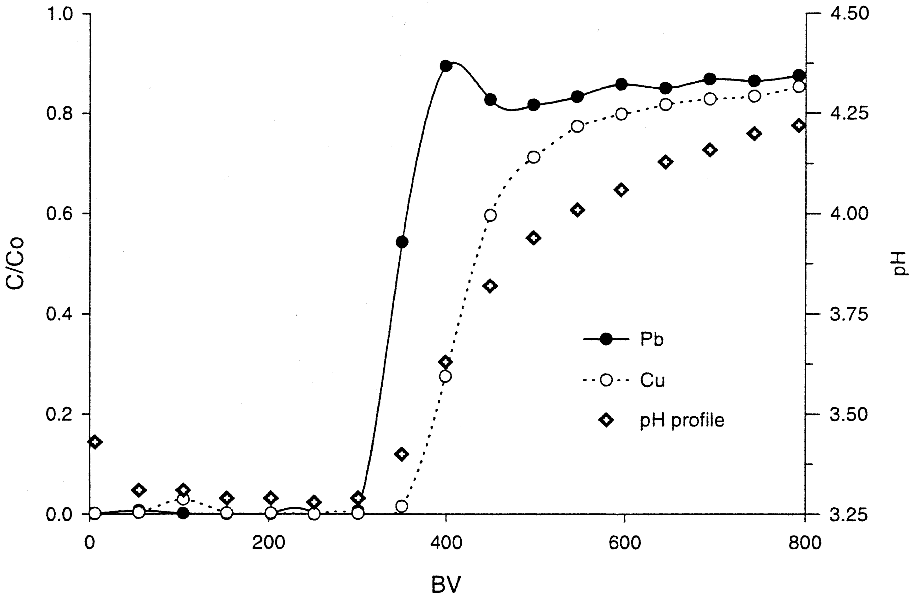

Figure 2. Lead and copper normalized breakthrough curves and effluent pH profile for F400(ox).

carbons may involve ion exchange; i.e., metal cations in solution exchange with protons present on the adsorbent surface. As the adsorbent bed approaches exhaustion, no more protons are released into solution, hence the effluent pH rises to the feed pH value (Fig. 2).

The breakthrough curves depict a carbon adsorbent preference for lead and copper over nickel and cadmium (Fig. 3). The effluent concentrations of cadmium and nickel exceeded the influent concentrations during the course of the breakthrough experiment. This phenomenon is typical of frontal elution chromatography. As the feed solution passes through the adsorbent bed, leading-edge adsorption sites saturate with all metal ions present in the feed solution. The metal ions with low sorption affinity (nickel and cadmium) are displaced by the preferred cations (lead and copper) that are competing for the same adsorption sites. The less preferred metals are eluted from the active carbons, making the effluent concentration of these metals higher than in the influent concentration.

Closer examination of breakthrough curves also reveals that the preference of oxidized carbons toward lead and copper is variable. Although both ions were removed, the adsorbents did not exhibit complete preference toward any of 2 metal cations. The comparative metal sorption data are summarized in Table 2 and Fig. 4; the percentage ratio between copper and lead removed by carbons depended on the extent of surface oxidation and the method of oxidation used.

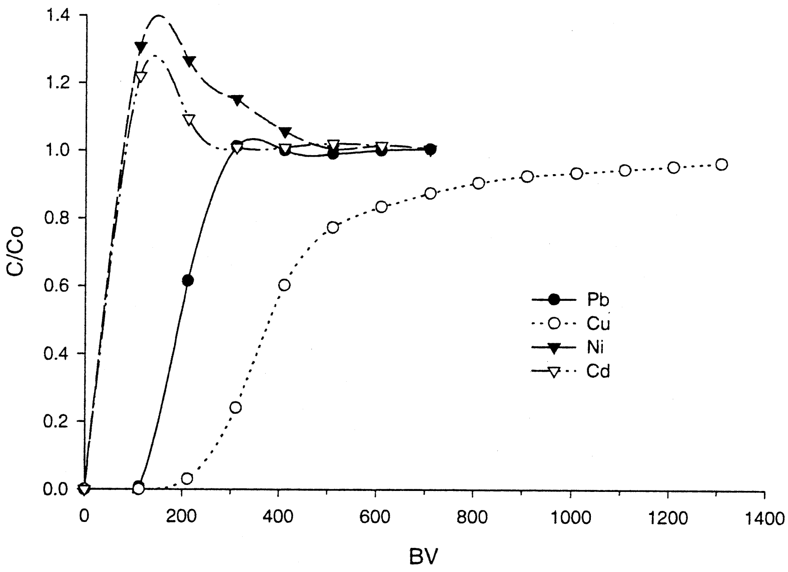

Figure 3. Lead, copper, nickel, and cadmium normalized breakthrough curves for KAU 1.5.

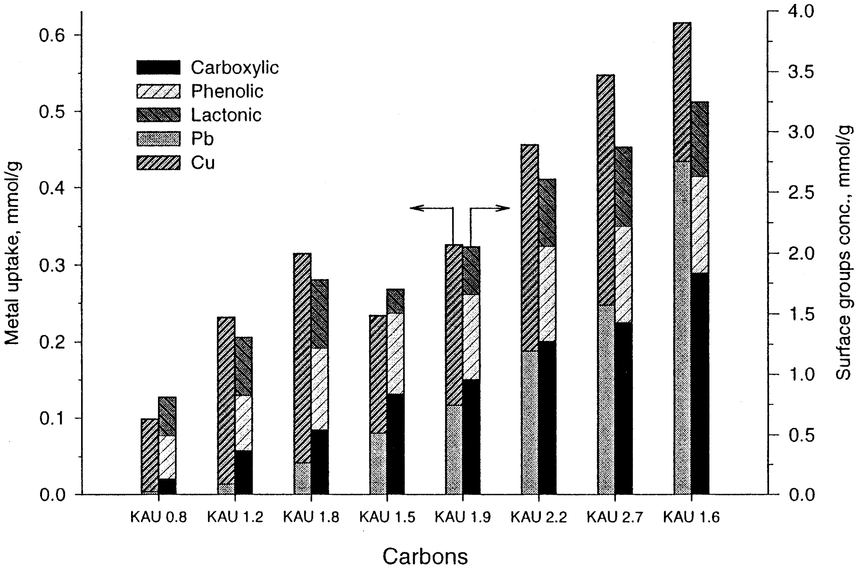

Figure 4. Correlation of metal uptake and surface functional group development for the oxidized carbons.

Air-oxidized active carbons exhibited greater preference for copper than did acid-oxidized carbons (Fig. 4). The KAU-1.8 (air-oxidized, Na^+ capacity 1.8 mmol/g) copper-lead removal ratio was 0.87, indicating predominant copper removal from a mixed solution of copper and lead. (The ratio was calculated as the amount of copper uptake compared with the sum total; i.e., copper and lead uptake.) In comparison, the KAU-1.9 (acid-oxidized, Na^+ capacity 2 mmol/g) removal ratio value was 0.64, suggesting higher affinity for copper but not to the same extent as that displayed by KAU-1.8. The copper-lead uptake ratio changed with an increase in the extent of carbon oxidation; e.g., compare values for KAU-1.5 (0.65) with KAU-1.6 (0.29). A preference reversal such that lead is preferred by the activated carbon occurred as the degree of surface oxidation increased from KAU-2.7 to KAU-1.6 (Fig. 4).

DISCUSSION

Introduction of acidic functional groups onto the surface of active carbons radically changes the ability to bind metal ions from aqueous solutions. Thus, the metal sorption capacity of active carbons can be substantially enhanced by either heat treatment in an oxidizing atmosphere or by interaction with hot nitric acid.

The degree of carbon surface oxidation strongly affects the metal uptake capacity of oxidized carbons. Longer exposure of the active carbon to the oxidizing agent results in formation of a greater amount of weakly acidic surface groups that are capable of binding metal ions. The oxidized active carbons show selectivity toward copper and lead over nickel and cadmium. The latter two metal ions are not taken up in the presence of copper and lead.

Metal sorption from binary solutions revealed that copper-lead distribution on the oxidized active carbons is different for the adsorbents modified by hot air and those treated with nitric acid. Air-oxidized samples tend to show preference for copper over lead. Acid-oxidized materials with a low degree of surface oxidation show a similar trend. The amount of lead removed by oxidized active carbons gradually increases as the degree of surface oxidation increases. Highly oxidized active carbon samples, e.g., KAU-2.7 and KAU-1.6, display a reverse selectivity pattern that show a preference toward lead over copper. Purolite C104 carboxylic resin shows a similar preference for lead from a binary solution of lead and copper (17,25).

The use of different oxidation techniques results in oxidized active carbons that possess different surface functional group distributions (18). Oxidation with nitric acid generates a higher concentration of carboxylic groups on the surface. Other weakly acidic functional groups (phenolic type) represent a lower proportion of the overall sorption sites in nitric acid–modified carbons. In contrast, hot air oxidation produces oxidized active carbons with dominant weaker types of acidic functional groups, e.g., phenolic acids. Examination of Boehm's titration data and metal sorption results suggest that the selectivity of the oxidized carbons is related to the quantity and proportion of various acidic functional groups. An increase in the amount of lead removed from a binary solution of lead and copper coincides with the gradual increase in carboxylic groups on the surface of oxidized active carbons. Correlations between lead-copper sorption as a function of carboxyl, lactonic, phenolic, or carbonyl group concentrations were obtained (data not shown). A linear correlation was found between copper sorption and the concentration of phenolic groups present in both air- and acid-oxidized KAU carbons. R^2 values greater than 0.999 were obtained for both air- and acid-oxidized carbons. In the case of air-oxidized carbons, the linear regression pattern passed through the origin. This was not the case for the acid-oxidized carbons and a negative y-intercept value was obtained for this series of carbons. The linear dependence of copper on the concentration of phenolic groups has not been validated over an extended concentration range; for acid-oxidized carbons, the concentration range was between 0.65 and 0.8 mmol/g, whereas for air-oxidized carbons, the range was between 0.35 and 0.7 mmol/g. We would be interested in the results of experiments in which carbons with phenolic group concentrations outside of the concentration range studied here were used to verify the extent to which copper sorption by oxidized activated carbons is linearly dependent upon the phenolic functional-group concentration.

Earlier studies support the suggestion that the sorption properties of oxidized carbons strongly depend on the degree of surface oxidation. Kovyrshin, Ponomarev, and Kozmin (26) 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 oxidized carbons and found that selective sorption was due to phenolic, surface, functional groups. Strashko, Kuzin, and Semushin (27) carried out a series of experiments to determine the influence of the degree of carbon oxidation on the separation of potassium and cesium. 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. A comparison of the stability constants for the complexes between metal ions and organic ligands derived from aromatic compounds indicates that lead and copper usually form more stable complexes than do nickel and cadmium (e.g., the stability constants with benzoic acid (28) for $Pb^{2+} = 2.0$; $Cu^{2+} = 1.6$; $Cd^{2+} = 1.4$; and $Ni^{2+} = 0.9$). The stability constants of these complexes coincide with the selectivity series for oxidized carbons. The formation of stronger surface complexes between surface functional groups and copper and lead ions than between nickel and cadmium ions and functional groups may result in better retention of the former ions.

Modification of carbons through different oxidizing techniques generates some undesirable by-products such as humic compounds (12). This is particularly pronounced for nitric acid–modified carbon samples with a high degree of surface oxidations. Humic acids are readily soluble in alkaline solutions and may leach from carbons if sorption experiments are carried out at high solution pH. Exhaustive alkaline washing may be necessary to eliminate these undesired substances after preparation. However, if the sorption operations are performed under neutral or slightly acidic conditions, humic substances do not leach out from the carbon. The exact nature of the humic substances is ill-defined. However, Kuzin and Strashko (29) showed that functional groups of humic compounds are very similar to those of oxidized carbons and are capable of binding heavy metals strongly and selectively. They found that the humic compounds extracted from the carbon surface were similar to those obtained from other sources, i.e., naturally occurring humic substances. The authors also suggested that structural similarity exists between the carbon surface and the humic acid molecules.

Large, complex, humic acid macromolecules are present within the oxidized active carbon granules. The flexibility of these macromolecules may allow rotation of surface functional groups, facilitating the interaction of several neighboring functional groups with a heavy metal ion and thereby resulting in formation of chelates (relatively stronger complexes). This is in sharp contrast to the rigid structure of the active carbon matrix in which the possibility of metal ion interaction with multiple functional groups is restricted. As a consequence of their flexibility, humic acids may contribute to the overall metal sorption capacity and selectivity of oxidized carbons.

The electron cloud of copper is held strongly to the nucleus, and copper is categorized as a harder metal than is lead. Low concentrations of dissociated carboxylic groups may show preference for the harder copper ions. As the degree of carbon oxidation (i.e., the concentration of carboxylic groups) progressively increases, the preference for copper is diminished and breakthrough curves for lead and copper begin to coincide. Purolite C 104 resin is a monofunctional cationite that contains only carboxylic groups. The high concentration of these groups in Purolite C 104 may result in a larger amount of undissociated groups under similar sorption conditions (e.g., solution pH). Electrostatic interactions between the carbonyl-oxygen atom and the metal cations may be responsible for the carboxylic resin displaying selectivity for lead over copper.

CONCLUSIONS

The results of this study show that modified active carbons can be prepared for the selective removal of heavy metals from aqueous solutions. Various surface functional groups containing heteroatoms (e.g., oxygen) are responsible for the improved selectivity toward lead and copper over nickel and cadmium. Furthermore, the selectivity of carbons toward copper and lead can be controlled by varying the extent of the oxidation treatment as well as employing different oxidizing agents. Oxidized carbons are capable of removing metal ions from relatively acidic solutions. This property is related to the relatively low pK values of carboxylic groups present on the surface. The electron-donating carbon matrix enhances the negative charge residing on the functional group oxygen. These negative charges promote more dissociation of acidic groups at reduced pH values than does conventional carboxylate ion exchange resin, e.g., Purolite C104.

The active carbons display variable selectivity toward copper and lead. The selectivity is dependent on the distribution of weakly acidic, surface, functional groups. The oxidized active carbons prefer copper ions at low degrees of surface acidity. This selectivity is reversed as the degree of surface acidity increases. Lead ions are preferred over copper ions as the concentration of carboxylate groups increases. Varying the distribution of acidic functional groups in active carbons may be used to produce adsorbents that show selective sorption properties for specific metal cations.

ACKNOWLEDGMENTS

The authors would like to acknowledge the financial support of Brite-Euram Contract BRPR-CT96-0158 grant, Severn-Trent Water Ltd, and 2 ORS awards from the British Government.

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Received August 2000
Revised February 2001

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