Electrochemical oxidation of activated carbon fibre – an efficient way of enhancing toxic metal ion sorptive capacity

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Abstract

A viscose rayon based activated carbon cloth (ACC) was electrochemically oxidised under a wide variety of current conditions to modify the surface properties. The ACCs were characterised in detail. A loss of 49% BET surface area and a significant loss in microporosity were observed on the electrochemically oxidised ACC (EO) and attributed to blockage of pores through formation of carboxylic acidic groups. However, the cation exchange capacity and oxygen content increased by 365% and 121%, respectively. Increase in surface acidity shifted the point of zero charge (PZC) from pH of 6.8 to 2.8. The optimum constant current for electrochemical oxidation was found to be 1.1 A. Batch sorption experiments confirmed that EO is more effective for the removal of lead and copper ions compared to unoxidised ACC (UO) for both competitive and non-competitive sorption.

Keywords: Viscose rayon based activated carbon cloth; Lead; Copper; Electrochemical oxidation; Competitive and non-competitive sorption.

1. Introduction

There have been increasing concern and more stringent regulation standards pertaining to the discharge of heavy metals to the aquatic environment, due to their toxicity and detriment to living species, including humans. The European Community (EC) Council Directive 98/78/EC have set the maximum permissible concentrations in drinking water for lead and copper at 0.01 and 2 mg/L, respectively (Council Directive 98/78/EC). Acute lead poisoning can seriously affect the gastrointestinal track and the nervous system. In severe situations neurological effects such as restlessness, hyperactivity, confusion and impairment of memory, coma and death can occur (Fergusson, 1990). Copper is a very important trace metal that is predominantly found in the nuclei and mitochondria of the living cell. It is an essential element required for the activity of several biological enzymes (Hill *et al.,* 2000). However, ingestion of high quantities of copper may cause gastrointestinal bleeding, hypotension, convulsion and significant DNA damage (Goyal *et al.,* 2001). Many treatment processes such as chemical precipitation, ultrafiltration, biological processes, electrodialysis, adsorption and reverse osmosis are currently used to remove heavy metal pollutants from water. Among these methods, adsorption onto activated carbon is a widely applied method. The selectivity and sorption capacity of conventional activated carbons towards heavy metals is rather low. However, metal

sorption onto activated carbon can be considerably enhanced by the introduction of weakly acidic functional groups such as carboxylic, carbonyl, phenolic and lactonic through electrochemical oxidation of activated carbons in different electrolytes and chemical oxidation by reagents such as nitric acid, air, phosphoric acid, hydrogen peroxide and ozone (Rangel-Mendez and Streat, 2002; Park *et al.,* 2001).

Consequently, in this work a viscose rayon based ACC was electrochemically oxidised to enhance its cation sorption capacity. The cation sorption capacity was compared with that of the as-received ACC. In order to characterise the electrochemically oxidised and unoxidised ACCs, techniques such as sodium hydroxide uptake, pH titration, elemental analysis and Brunauer-Emmett-Teller (BET) surface area were used. Competitive and non-competitive lead and copper sorption experiments for the electrochemically oxidised ACC (EO} and unoxidised ACC (UO) were studied. Metal concentration and pH effects on the sorption isotherms were investigated.

2. Experimental

2.1. Materials

A viscose rayon based activated carbon cloth (ACC), ZORFLEX^R FM 10 (supplied by Charcoal Cloth International) was used as a starting material for this investigation. All chemicals were of analytical grade and obtained from Fisher Scientific, U.K.

2.2. Electrochemical Oxidation and Characterisation of ACC

Viscose rayon based activated carbon cloth; ZORFLEX^R FM 10 in hydrogen form was modified electrochemically using 0.5 M potassium chloride as an electrolyte. The electrochemical cell was immersed in a thermostatically controlled water bath regulated at 303 K. 1 g of ACC was wrapped round the anode (platinised titanium) and immersed in 0.5 M potassium chloride for 1 h prior to the electrochemical oxidation process. Two cathodes (platinised titanium) were used as counter electrodes. The cathodes were placed at equal distance from the anode to achieve uniform surface oxidation of the ACC. The electrochemical oxidation was carried out at currents ranging from 0.55 to 8.4 A at different oxidation times (e.g. 0.25, 0.5, 0.75, 1, 2, 3, 4 and 6 h). For each oxidation, the chosen current was kept constant by adjusting the voltage throughout the chosen oxidation time and using fresh electrolyte each time. After oxidation, the oxidised ACC was washed with deionised water until the conductivity of the washed water reached the same value as the conductivity of deionised water. The oxidised ACC was dried in an oven at 383 K for 24 h and was kept in a desiccator overnight and then weighed.

The details of the experimental procedures for sodium capacity determination, pH titration measurement, elemental analysis, BET surface area have been reported by Harry *et al.* (2006).

2.3. Batch sorption experiments

Competitive and non-competitive sorption of copper (II) and lead (II) from nitrate solutions were studied in batch experiments to obtain isotherms at pH 5. Equilibrium

copper and lead ion sorption isotherms were obtained as follows: for non-competitive sorption experiments, 20 ml of copper (II) nitrate or lead (II) nitrate solutions of several initial concentrations, (0.03 - 7.87 mM) were added to 50 ml conical flasks with 0.025 g of EO or UO in each flask. For competitive sorption experiments, 20 ml of equal molar copper-lead nitrate solutions of several initial concentrations, (0.03 - 7.87 mM) were added to 50 ml conical flasks with 0.025 g of EO or UO in each flask. The pH of the solutions were measured using a Mettler-Toledo 340 digital pH meter and were adjusted to particular values by the addition of 0.1 M sodium hydroxide or 0.1 M nitric acid. The flasks were then sealed with parafilm and agitated in a Brunswick C25 series incubator shaker at 298 K and 150 rpm. The original pH values were maintained daily by adding 0.1 M sodium hydroxide or 0.1 M nitric acid to the solutions. The added volume of sodium hydroxide or nitric acid was recorded each time. This was continued until equilibrium was achieved i.e. when there was no significant change in solution pH for 48 h, this was about 5 days for UO and 8 days for EO. The equilibrated solutions were filtered to remove ACC particles and the concentrations of the supernatant solutions were determined using a Varian AA 200 atomic absorption spectrophotometer (AAS) in acetylene-air flame emission mode.

3. Results and Discussion

3.1 Sodium capacity

Oxygen-containing groups like carbonyl, carboxyl, phenolic and lactonic groups present on carbonaceous materials dissociate increasingly with an increase in solution pH values (Leon y Leon and Radovic, 1994). Therefore, these surface groups are completely dissociated in solutions at high pH and are available for ion exchange. Under this condition the total cation exchange capacity can be determined. A high sodium capacity is an indication of a high content of surface oxygen functional groups. In order to achieve the optimum constant current, three series of experiments were performed at different extents of electrochemical oxidation, e.g. 7,920 c/g, 15,840 c/g and 23,760 c/g. The extent of electrochemical oxidation is defined as the product of current and electrochemical oxidation time in coulomb per gram (c/g) of ACC. For each series of experiment, the ACCs were electrochemically oxidised at different currents of 0.73, 1.1, 1.47, 2.2, 4.4 and 8.8 A. Plots of the sodium capacity *versus* applied current for the three series of experiments are presented in Figure 1. The three sets of results followed the same trend. The lowest sodium capacity was observed for ACCs electrochemically oxidised at 8.8 A. This is attributed to the fact that though 8.8 A is the highest applied current, the small time of electrochemical oxidation of 15 min, 30 min and 45 min were not enough for effective oxidation of most of the cellulose molecules in the ACC matrix. The highest sodium capacity was obtained at 1.1 A for ACCs electrochemically oxidised at 7,920, 15,840 and 23,760 c/g extents of electrochemical oxidation. Therefore, the optimum current was found to be 1.1 A for all electrochemical oxidation times. The sodium capacity for electrochemically oxidised ACC at 1.1 A for 6 h (i.e. 23,760 c/g) is 4.94 mmol/g and the sodium capacity for as-received ACC in hydrogen form (i.e. the value at 0 A) is 1.063 mmol/g. Therefore, the sodium capacity for electrochemically oxidised ACC is 4.7 times higher than that of the as-received ACC in hydrogen form. This increase is

attributed to the introduction of more acidic functional groups by electrochemical oxidation.
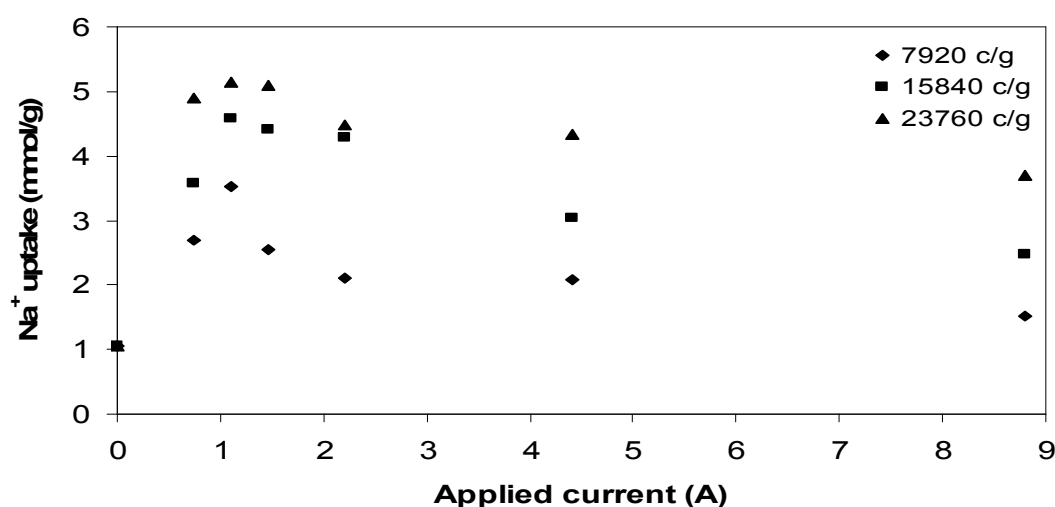

Figure 1. Sodium capacity *versus* applied current for different extents of electrochemical oxidation.

3.2 Proton binding curves

The proton binding curves, that is the plots of ion released *versus* equilibrium solution pH, for UO and EO are shown in Figure 2. The point where the proton binding curve crosses the pH axis is the point of zero charge (PZC). This is the pH value at which the surface charge is zero at a particular ambient temperature, applied pressure and aqueous solution composition. (Harry *et al.,* 2006). The PZC will change depending on the type and amount of functional groups present on the adsorbent. It will be
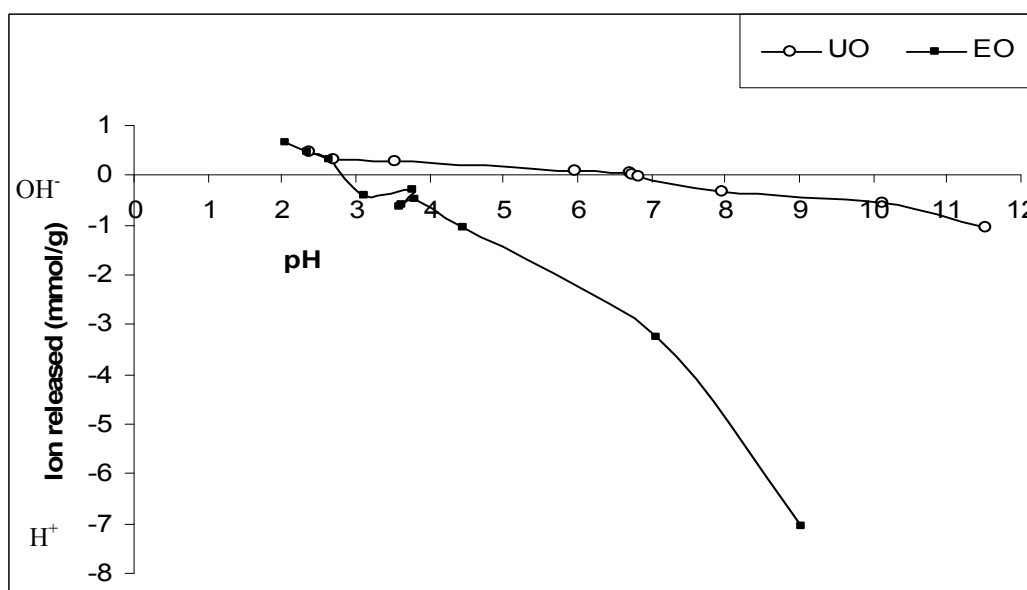

Figure 2. Ion Released *versus* equilibrium solution pH for UO and EO.

shifted to lower pH values with oxidation of the ACC due to the introduction of acidic functional groups such as carboxylic, phenolic, carbonyl and lactonic groups onto the surface of the ACC. As shown in Figure 2, the PZC for UO is at pH 6.8 whereas it shifted to pH 2.8 for EO. The adsorbent surface is positively charged at pH values below the PZC because the oxygen containing groups are undissociated and protonated and the carbon will remove anions from solution under these conditions. In contrast, at solution pH values higher than the PZC, the carbon surface becomes more negatively charged due to dissociation of weakly acidic oxygen containing functional groups. Thus the carbon is able to attract and exchange cations in solution.

3.3 Elemental analysis

Table 1 shows the elemental analysis results of UO and EO. The results show a significant difference in oxygen content between the UO and EO. The oxygen content in EO increased by 120.8%. These results follow the same trend as the sodium capacity results which showed a cation exchange capacity of 1.063 mmol/g and 4.94 mmol/g for UO and EO respectively. The increase in oxygen content in the EO is attributed to the introduction of more acidic oxygen containing functional groups during electrochemical oxidation.

Table 1. Elemental analysis of UO and EO.

Sample	C (wt%)	H (wt%)	N (wt%)	O (wt%)
UO	76.89	2.03	1.05	20.03
EO	52.33	2.6	0.84	44.23

3.4 BET Surface area

The BET surface area for UO and EO are 1395.29 and 532.08 m^2/g, respectively. All the ACCs analysed in this study have extensive BET surface areas that are ideal in the treatment of drinking and waste water. However, the BET surface area decreased with electrochemical oxidation. The results show that EO lost 61.9% of the original BET surface area. This is attributed to the blockage of pores by oxygen containing functional groups and humic substances produced during electrochemical oxidation. The reduction in the surface area of carbonaceous materials by by-products from oxidation has been discussed by other researchers (Saha *et al.,* 2003)

3.5 Aqueous speciation of metals

The speciation curves for 0.0157 M copper and 0.0193 M lead in nitrate solutions are presented in Figure 3. Figure 3 shows that at pH 5 which is the pH used in this study, copper exists in aqueous solution predominantly as Cu^{2+} in approximate proportion of 98.3%. The concentration of other copper species ($CuNO_3^+$, $CuOH^+$ and $Cu_2(OH)^{3+}$)
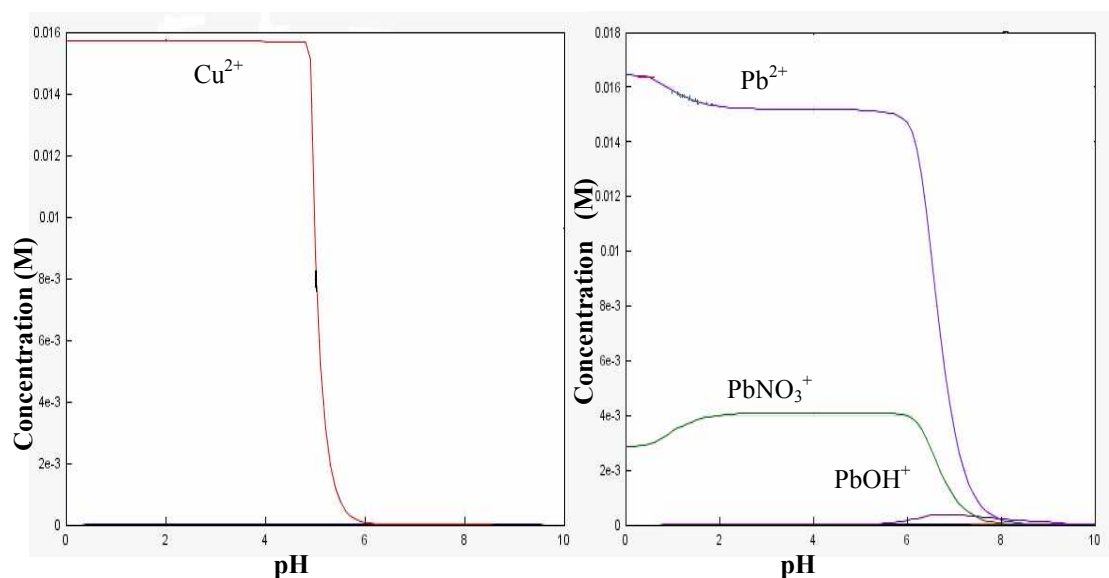
Figure 3 Speciation curve for 0.0157 M copper and 0.0193 M lead in nitrate solution.

at pH 5 in approximate proportion of 1.7% is therefore negligible. It also shows that at pH 5 lead exists in aqueous solution as Pb^{2+} and $PbNO_3^+$ in approximate proportions of 78.6% and 21.2% respectively. The concentrations of other lead species ($PbOH^+$ and $Pb(OH)^{3+}$) at pH 5 in approximate proportion of 0.2% is therefore negligible. It is obvious from the speciation curves that there is no precipitation of any of the metal species at pH 5. The maximum concentration of lead or copper used for the batch sorption experiments is 0.00787 M which is lower than the concentrations at which the aqueous speciation was produced, therefore the batch sorption process is purely adsorption and not precipitation.

3.6 Batch sorption experiments

The sorption capacities of EO and UO samples were evaluated for copper and lead ions. Figure 4 shows the copper and lead sorption of EO and UO samples evaluated at pH 5 and 298 K. A dramatic increase in the lead and copper ions uptake by EO sample for competitive and non-competitive sorption are observed and the results are shown in Figure 4. The maximum non-competitive copper and lead sorption capacities of EO sample are 1.69 mmol/g and 1.87 mmol/g, respectively while the maximum non-competitive copper and lead sorption capacities of UO sample are 0.098 mmol/g and 0.47 mmol/g, respectively. The non-competitive copper and lead sorption capacities of EO sample are approximately 17 times and 4 times greater than the non-competitive sorption capacities of UO sample, respectively. The maximum competitive copper and lead sorption capacities of EO sample are 0.75 mmol/g and 1.01 mmol/g, respectively and the maximum competitive copper and lead sorption capacities of UO sample are 0.085 mmol/g and 0.12 mmol/g, respectively. The competitive copper and lead sorption capacities of EO sample are approximately 8.8 times and 8.6 times greater than the competitive sorption capacities of UO sample, respectively. Therefore, electrochemical oxidation of ACC dramatically increased its

sorption capacity for both competitive and non-competitive sorption of lead and copper ions. This is directly related to the increase in more acidic oxygen containing functional groups as detected by the elemental analysis and pH titration results. This is also confirmed by the sodium capacity results which showed a much higher cation exchange capacity for the EO sample than the UO sample.
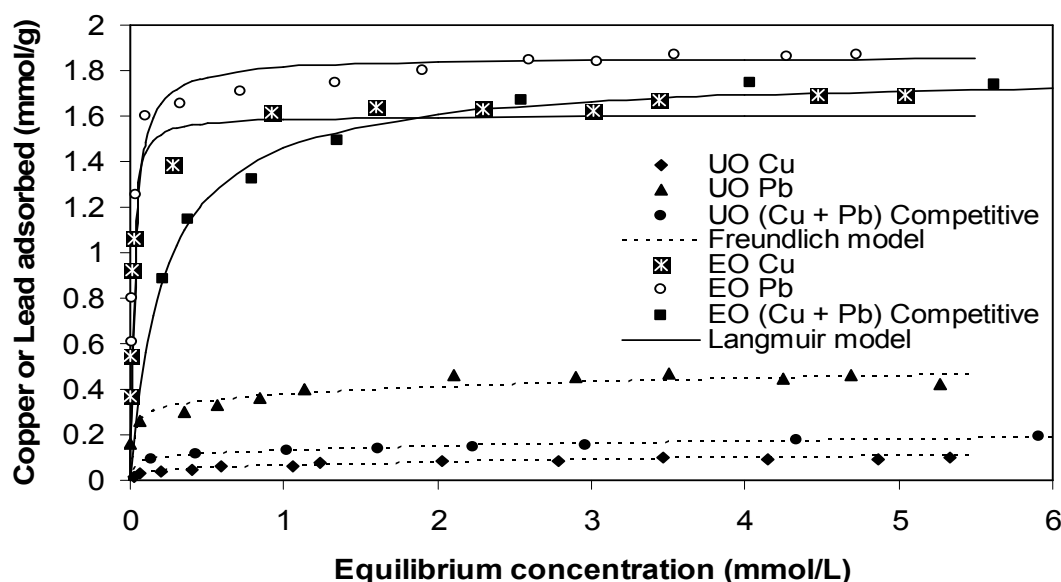

Figure 4. Non-competitive and competitive (Cu + Pb) sorption isotherms of copper and lead onto UO and EO at pH 5.

## 3.7 Mechanism of lead and copper sorption onto EO and UO ACCs

The PZC for EO and UO samples are at pH 2.8 and 6.8, respectively. The pH at which the batch sorption experiments were performed was pH 5. This is below the PZC of UO, so the ACC surface was positively charged. This explains why the solution pH increased during the copper and lead sorption process indicating that hydroxyl (OH⁻) ions were released from the surface of the UO sample. The pH was adjusted by adding specific volumes of 0.1 M nitric acid to maintain the original pH. Since the ACC is viscose rayon based and the double bonds in the aldehyde ends of the cellulose molecules in the ACC matrix consist of σ bonds and π bonds (Hill and Holman, 2000), therefore, there are greater electron distributions over the more electronegative oxygen atoms. This makes it possible for lead and/or copper ions to be attached to them, therefore, complex formation between the metal ions and the UO sample surface is the likely mechanism for sorption of lead and copper onto UO sample. The pH value of 5 is above the PZC of EO sample. Hence, the surface of the EO sample was negatively charged. The EO sample therefore, behaved as a cation exchanger indicating that the sorption process was ion exchange. This explains why the solution pH decreased during the lead and copper sorption indicating that H$^+$ ions were released from the surface of the EO sample. The pH was adjusted by adding specific volumes of 0.1 M sodium hydroxide to maintain the original pH. Mass

balance to obtain the maximum H^+ ions released were performed using the volumes of 0.1 M sodium hydroxide added to adjust the solution pH. The experimentally determined non-competitive and competitive metal ions sorbed onto EO sample and H^+ ion released from EO sample are shown in Table 2. It is obvious that one Pb^{2+} or Cu^{2+} ion was sorbed for approximately every two H^+ ions released from the EO sample surface. This confirms that the sorption of lead and copper onto EO sample is mainly governed by ion exchange mechanism. FTIR analysis result in our

Table 2. Experimental maximum non-competitive (N Cu and N Pb) and competitive (C Cu and C Pb) metal ions sorbed onto EO and H^+ ion released from EO

Sample	Maximum metal ion (Cu^{2+}/Pb^{2+}) sorbed (mmol/g)	Maximum H^+ ion released (mmol/g)
N Cu EO pH 5	1.693	3.352
N Pb EO pH 5	1.867	3.68
C Cu+Pb EO pH 5	1.755	3.4

previous publication (Harry *et al.,* 2007) confirmed that carboxylic acids were introduced to EO sample by electrochemical oxidation. Therefore, the ion exchange mechanism involving the interaction of the carboxylic sites of EO sample can be represented by the following reaction scheme.

$$2(S-COOH) + M^{2+} \leftrightarrow (S-COO)_2M + 2H^+$$
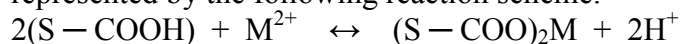
where S is the surface of the EO sample and M^{2+} is the metal ion, i.e., Pb^{2+} or Cu^{2+}.

4. Conclusions

This work demonstrates that electrochemically oxidised ACC can be used as an effective adsorbent for treating water/waste-water contaminated with copper and/or lead in both single and multi-component systems. The copper and lead ions adsorption capacities of ACC increased by factors of 17 and 4 times respectively for non-competitive adsorption when it was electrochemically oxidised. The capacities also increased by factors of 8.8 and 8.6 times for competitive adsorption of copper and lead, respectively by electrochemical oxidation. The competitive and non-competitive studies showed that the affinity order of the two metal ions adsorbed by unoxidised and electrochemically oxidised ACCs is $Pb^{2+} > Cu^{2+}$. Lead and copper ions were adsorbed onto electrochemically oxidised ACC by an ion exchange mechanism while they were adsorbed onto unoxidised ACC by complex formation with the ACC surface. Therefore, it is concluded that electrochemical oxidation of viscose rayon based ACC markedly enhances the removal of lead and copper ions from aqueous solutions.

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