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Electrochemically modified viscose-rayon-based activated carbon cloth for competitive and noncompetitive sorption of trace cobalt and lead ions from aqueous solution

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Abstract: A viscose-rayon-based activated carbon cloth (ACC) was electrochemically oxidised. As-received and electrochemically modified ACCs were characterised by sodium capacity, pH titration, elemental analysis and Fourier transform infra red (FTIR) spectroscopy analysis. Cobalt and lead noncompetitive sorption capacities for electrochemically oxidised ACC (EO) are 4.3 and 3.9 times, respectively higher than those for unoxidised ACC (UO). Cobalt and lead competitive sorption capacities for EO are 4.1 and 5.1 times, respectively higher than those for UO. Sorption of cobalt and lead onto EO was by ion exchange, while that onto UO was by surface complex formation. Affinity order of metals sorbed by EO and UO is $Pb^{2+} > Co^{2+}$. Metal uptake onto EO increased with an increase in solution pH.

Keywords: Viscose-rayon-based activated carbon cloth; Characterisation; Lead; Cobalt; Sorption isotherms; Electrochemical oxidation; Competitive and noncompetitive sorption.

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1. INTRODUCTION

Tremendous increases in the use of heavy metals in the past few decades resulted in an increased flux of metals in the environment. European Communities Council Directive has set maximum permissible concentration in drinking water for lead at 0.01 mg/L (1). United State Environmental Protection Agency has set maximum permissible concentration in drinking water for lead and cobalt at 0.015 and 0.107 mg/L, respectively (2). The effects of acute lead poisoning are nausea, abdominal pains, anorexia, insomnia, irritability, and coordination loss. In severe situations restlessness, hyperactivity, impairment of memory, coma and death can occur (3). Cobalt is essential for human health; it is part of vitamin B-12 that is essential for human nutrition (4, 5). However, ingestion of high quantities of cobalt causes neurotoxicological disorders, genotoxicity, carcinogenicity, cardiomyopathy and bruchial asthma (6, 7).

Chemical precipitation, ultrafiltration, electro dialysis, adsorption and reverse osmosis are currently used to remove heavy metal pollutants from water. Due to wide range of applications and low cost compared with possible competitive adsorbents, adsorption onto activated carbon is widely applied. Activated carbons exist in granular (GAC), powder (PAC) and fibre forms. Carbon fibres are in the form of cloth (ACC) and felt (ACF). ACC has some advantages over GAC and PAC. The intraparticle diffusion in GAC is very slow therefore, the overall rate of sorption in GAC is very low (8). The overall sorption rate in PAC is very high, but PAC presents complicated handling. The overall sorption rate in ACC is as high as PAC but it does not have the handling problems existing in PAC.

Metal sorption onto activated carbon are enhanced by introduction of acidic functional groups such as carboxylic, carbonylic, phenolic and lactonic through electrochemical oxidation of activated carbons in different electrolytes and chemical oxidation by nitric acid and ozone (8-10). Information published in literature shows very few studies of adsorption processes from multicomponent solutions of heavy metals. However, most industrial operation systems consist of multicomponent solutions and heavy metals are frequently encountered in mixtures. Consequently, in this work a viscose-rayon-based ACC was electrochemically oxidised to enhance its cation sorption capacity. Sodium hydroxide uptake, pH titration, elemental analysis and Fourier transform infra red (FTIR) spectroscopy analysis were used to characterise the electrochemically oxidised ACC (EO) and unoxidised ACC (UO). Competitive and noncompetitive lead and cobalt sorption experiments for EO and UO were studied. Metal concentration and pH effects on the sorption isotherms were investigated.

2. MATERIALS AND METHODS

2.1. Materials

A viscose-rayon-based ACC, ZORFLEX^R FM 10 (supplied by Charcoal Cloth International) was used for this investigation. 20 g of ACC in a column was converted to hydrogen form by passing 2 L of 5% (w/w) hydrochloric acid very slowly (for 48 h) through the column. The ACC was then washed with 50 L of deionised water until the conductivity of washed water was same as that of deionised water. After washing, the ACC was dried in an oven at 383 K for 24 h. All converted samples were kept in sealed plastic bags to avoid any contamination. All chemicals used were of analytical grade and obtained from Fisher Scientific, U.K.

2.2. Electrochemical Oxidation

Studies of electrochemical oxidation in several electrolytes showed that activated carbon oxidised in potassium chloride had highest cation exchange capacity (11). The electrochemical cell with 0.5 M potassium chloride solution 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 the electrolyte for 1 h prior to electrochemical oxidation. Two cathodes (platinised titanium) used as counter electrodes were placed at equal distance from the anode to achieve uniform surface oxidation of the ACC. Several 1 g pieces of ACC were electrochemically oxidised at currents of 1.1 A and 2.2 A at different oxidation times of 2, 4 and 6 h and 1, 2 and 3 h, respectively. After oxidation, the oxidised ACC was washed with deionised water until the conductivity of washed water reached the same value as the conductivity of deionised water. The oxidised ACC was then dried in an oven at 383 K for 24 h. All oxidised ACCs were kept in sealed plastic bags to avoid any contamination.

2.3. Sodium Capacity Determination

Sodium capacity was determined in order to compare the cation exchange capacity of EO and UO in aqueous solution. Sodium sorption capacity gives an indication of the cation exchange capacity of adsorbents in aqueous solution (9, 11, 12). 0.2 g of EO or UO was placed in a 50 ml conical flask containing 25 ml of 0.1 M volumetric standard sodium hydroxide. The flasks were sealed with parafilm and were agitated in Brunswick C25 series incubator shaker at 298 K and 150 rpm for 72 h. The solutions were then filtered and 10 ml of the supernatant solutions were back titrated with 0.1 M volumetric standard hydrochloric acid using methyl orange as an indicator.

2.4. pH Titrations

The pH titration determines the acidic and basic properties of ion exchangers (9, 11, 12). 25 mg of EO or UO was weighed using Sartorius BP 210 D balance (± 0.0005 g accuracy) and placed in a 50 ml conical flask containing 20 ml of 0.1 M sodium chloride and pre-determined volume (0 - 2 ml) of 0.1 M hydrochloric acid or 0.1 M sodium hydroxide to obtain a titration curve over a pH range of 2 – 12 for each sample. The flasks were sealed with parafilm and agitated in a Brunswick C25 series incubator shaker at 298 K and 150 rpm for 48 h. Blank experiments without adsorbent were also performed under otherwise identical conditions. The pH of solutions with adsorbents and solutions of the blank experiments were measured using a Mettler-Toledo 340 digital pH meter and back titrated with volumetric standard of 0.1 M hydrochloric acid or 0.1 M sodium hydroxide using phenolphthalein as an indicator to obtain the amount of H^+ or OH^- released by the adsorbent.

2.5. Elemental Analysis

The samples were analysed in the Department of Pure and Applied Chemistry, University of Strathclyde, Glasgow, UK on a Perkin Elmer series II 2400 elemental analyser. Each sample was weighed (1 - 2 mg) and wrapped in tin foil prior to analysis. Combustion of sample was done in combustion tube at 2073 K in the presence of pure oxygen after the system was purged with helium carrier gas. The gaseous combustion products were further decomposed in the presence of a series of catalysts. A thermal conductivity detector quantified the percentages of carbon, hydrogen and nitrogen. The oxygen content was determined by difference.

2.6. Fourier Transform Infra Red (FTIR) Spectroscopy Analysis

Surface chemistry of EO and UO were analysed by FTIR spectroscopy. Each sample was finely crushed with a mortar and pestle and mixed with finely crushed spectroscopic grade potassium bromide in ratio of 1:100. Thin pellet was prepared by subjecting each mixture of sample and potassium bromide to a load of 10 tonnes. Spectra for all samples were recorded on a Mattson 3000 FTIR spectrometer at a resolution of 4 cm^{-1} at 64 scans.

2.7. Speciation of Metal Ions in Aqueous Solution

Adsorbent surface chemistry and metal speciation helps to explain sorption mechanisms (11, 13). To verify that there was no precipitation of metal species in the experimental pH range, aqueous speciation of lead and cobalt as a function of solution pH was studied using JCHESS version 2.0 and CHESS version 3.0 software, written by van Der Lee (14) at concentrations of 0.0193 M and 0.016 M for lead(II) nitrate and cobalt(II) nitrate solutions, respectively. The information about the CHESS home page can be seen at URL <http://chess.enscm.fr>.

2.8. Batch Sorption Experiments

For noncompetitive sorption experiments, 20 ml of cobalt(II) or lead(II) from nitrate solutions at several initial concentrations (0.34 - 8.48 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 equimolar cobalt-lead from nitrate solutions at several initial concentrations (0.34 - 8.48 mM), were added to several 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 the required value of 3, 4 or 5 by addition of 0.1 M sodium hydroxide or 0.1 M nitric acid. The flasks were then sealed with parafilm and agitated in Brunswick C25 series incubator shaker at 298 K and 150 rpm. Original pH values were maintained daily by adding 0.1 M sodium hydroxide or 0.1 M nitric acid to the solutions. Added volumes of sodium hydroxide or nitric acid were recorded. This was continued until equilibrium was achieved, i.e., when there was no significant change in solution pH for 48 h, it was 5 and 8 days for UO and EO, respectively. Equilibrated solutions were filtered and concentrations of supernatant solutions were determined using a Varian AA 200 atomic absorption spectrophotometer (AAS) in acetylene-air flame emission mode.

2.9. Quality Assurance / Quality Control

For accuracy, reliability and reproducibility of data, all experiments were conducted in duplicate. Relative error for analytical procedures except batch sorption experiments was less than 2%. For batch sorption experiments, the AAS was operated at wavelengths of 261.4 and 347.4 nm, for lead and cobalt, respectively, for optimum sensitivity. Standard lead and cobalt solutions were used to calibrate and verify AAS. Relative errors for determination of lead and cobalt concentrations for batch sorption experiments using AAS were less than 3%.

3. RESULTS AND DISCUSSIONS

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 (15). Therefore, these 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. High sodium capacity is an indication of high content of surface oxygen functional groups. The sodium capacity results for EO and UO are shown in Figure 1. The results show that sodium capacity for EO at 1.1 A for 6 h is 4.7 times higher than that of UO. This increase is attributed to

introduction of more acidic functional groups. The extent of oxidation on carbon surface depends on chemical composition of electrolyte (11). Chlorine and hypochlorous acid (HOCl) that is formed when chlorine is present

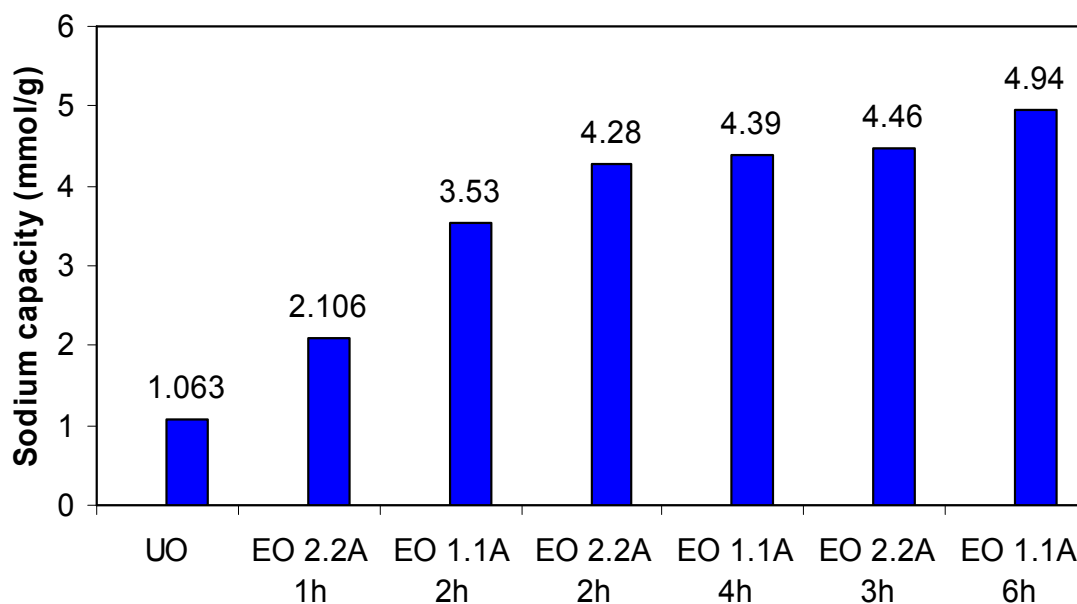


Figure 1. Sodium capacity values for UO and EO at different conditions.

in water are strong oxidants (4). Also from electrochemical series of metals (16), it is obvious that potassium is a very strong reductant. Since reduction and oxidation processes are responsible for overall reaction in an electrolytic cell, the presence of a strong oxidant and a strong reductant explains why the ACC is strongly oxidised when potassium chloride is used as an electrolyte. The highest sodium capacity (4.94 mmol/g) was observed for EO at 1.1 A for 6 h and hence all subsequent experiments were conducted with this sample.

3.2. pH Titrations

Proton binding curves, i.e., plots of ion released *versus* equilibrium solution pH, for EO and UO are shown in Figure 2. The point where the proton binding curve crosses pH axis is the point of zero charge (PZC). This has been defined as the pH value at which surface charge is zero at a particular ambient temperature applied pressure and aqueous solution composition (8). PZC will be shifted to lower pH values with oxidation of ACC due to introduction of acidic functional groups such as carboxylic, phenolic, carbonyl and lactonic groups onto the surface of ACC (17). PZC for UO is at pH 6.8 whereas it is shifted to pH 2.8 for EO. The adsorbent surface is positively charged at solution pH values below PZC because the oxygen containing groups are undissociated and ACC will remove anions from solution. At solution pH values higher than PZC, the ACC surface becomes

negatively charged due to dissociation of acidic oxygen containing functional groups and is able to attract and remove cations from solution. The slope of the EO curve increased with an increase in equilibrium pH showing

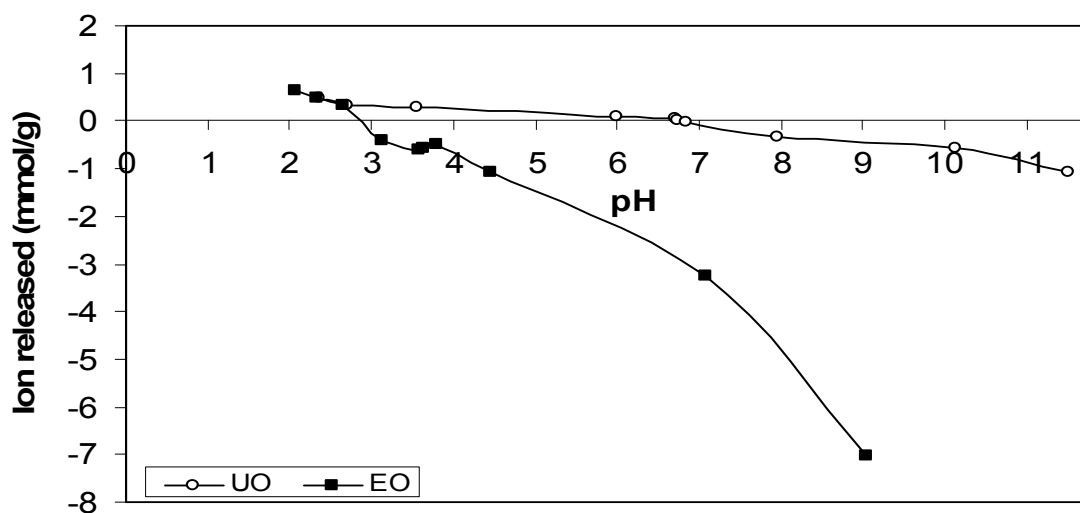


Figure 2. Ion Released versus equilibrium solution pH for UO and EO.

that the concentration of hydrogen ions released increased with an increase in equilibrium pH. Hence the cation exchange capacity is higher than that of UO as shown by the sodium capacity results. The carboxylic groups in adsorbents dissociate in pH values within 2 and 6 and hydroxyl groups dissociate in pH values above 6 (18, 19). From pH titration curves the dissociation of acidic functional groups on EO and UO to produce H^+ ions starts at equilibrium solution pH of approximately 3 and 7, respectively. Therefore, acidic functional group on EO is likely to be carboxylic while that on UO is likely to be hydroxyl. Viscose rayon manufacturing process involves alkalisation, shredding, preripening, xanthation, dissolving, maturing and viscose fibre spinning stages (20). At spinning stage, cellulose is regenerated from viscose for production of the viscose rayon filament. Therefore, ACC matrix is composed of cellulose molecules and so it is expected that the UO will have hydroxyl groups on its surface since the cellulose molecules contain hydroxyl groups (4, 20).

3.3. Elemental Analysis

Table 1 shows the elemental analysis results of UO and EO. UO has 20.03% oxygen content. This is attributed to the presence of oxygen atoms in aldehyde and hydroxylic groups of the cellulose molecules in it. The results

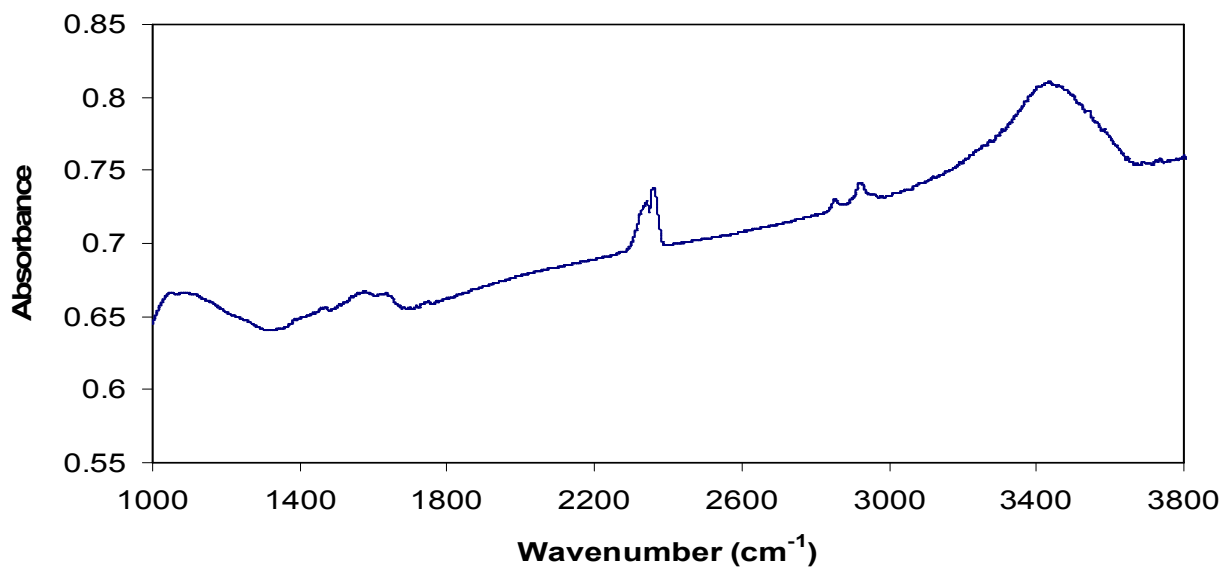
Table 1. Elemental analysis of UO ACC and EO ACC.

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

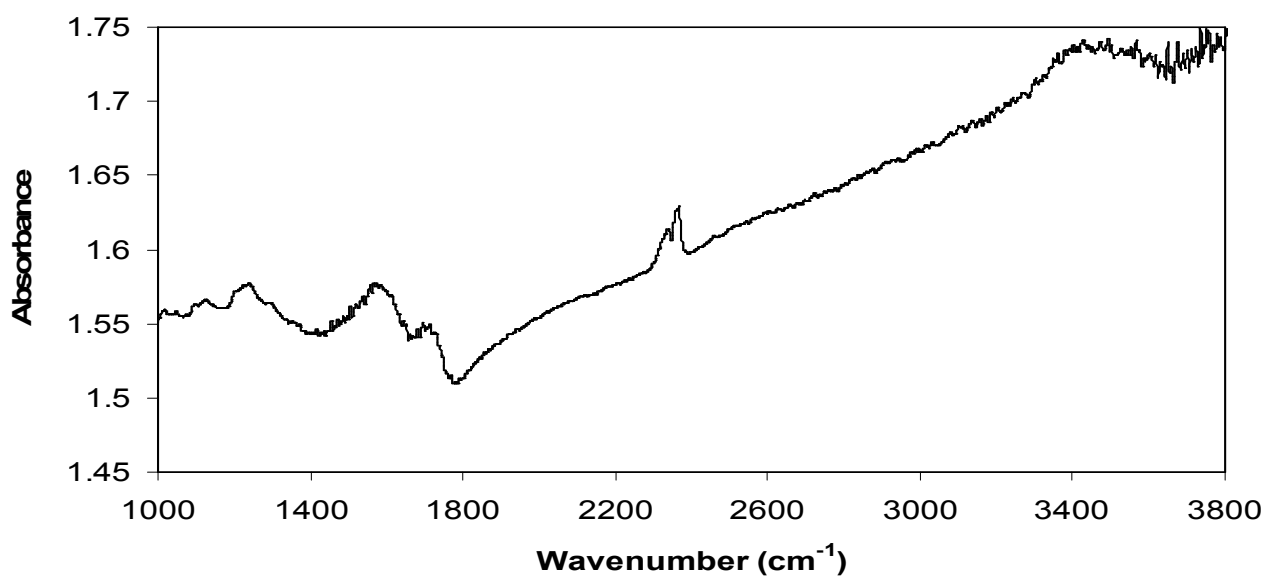
also show that the oxygen content in EO increased by 120.8%. This is attributed to the introduction of more acidic oxygen containing functional groups during electrochemical oxidation. These results follow the same trend as the sodium capacity results of UO and EO which are 1.063 mmol/g and 4.94 mmol/g, respectively.

3.4. Fourier Transform Infra Red (FTIR) Spectroscopy Analysis

The FTIR spectra for UO and EO are shown in Figures 3a and 3b, respectively. The band assignments are shown in Table 2. The study of chemical composition of carbon fibres by FTIR is difficult because the absorption of the fibre is very intense while the concentration of the different functional groups on its surface is relatively low. So the signal to noise ratio is not sufficiently high even if the sample is scanned many times (21). Therefore, the intensities of FTIR spectra of carbon fibres are not very high. The marked difference in the functional groups observed on UO and EO are the presence of aldehyde and carboxylic acid groups, respectively. Since cellulose molecule has aldehyde and hydroxyl ends, it is expected that ACCs should have aldehyde and hydroxyl functional groups. Aldehyde groups are readily oxidised to produce carboxylic acid groups while alcohol groups need to be oxidised to aldehyde groups, which are further oxidised to carboxylic acid groups (4, 20). As aldehyde groups are more readily oxidised than alcohols, they were not found on EO. The carboxylic acid groups observed on EO confirms the pH titration results that showed that the acidic functional groups on EO are likely to be carboxylic acids. This also confirms the elemental analysis results that showed that oxygen content in EO sample increased by 120.8%. This also explains why there was a high increase in the sodium capacity of the ACC after electrochemical oxidation in potassium chloride.



(a)



(b)

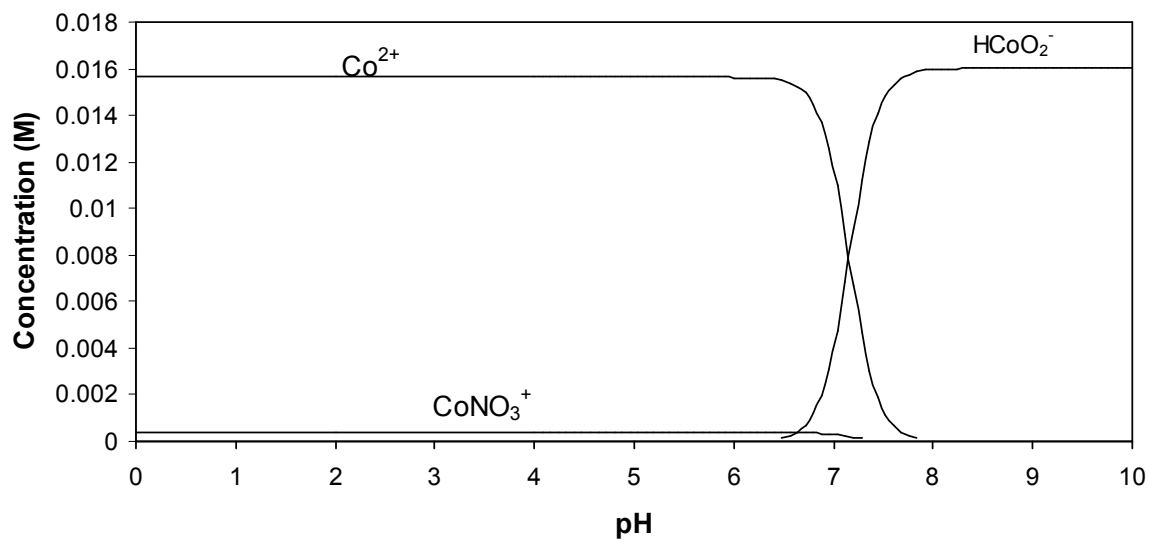
Figure 3. FTIR spectra for (a) UO ACC and (b) EO ACC at 1.1 A for 6 h.

Table 2. Band assignments for FTIR spectra of UO ACC and EO ACC.

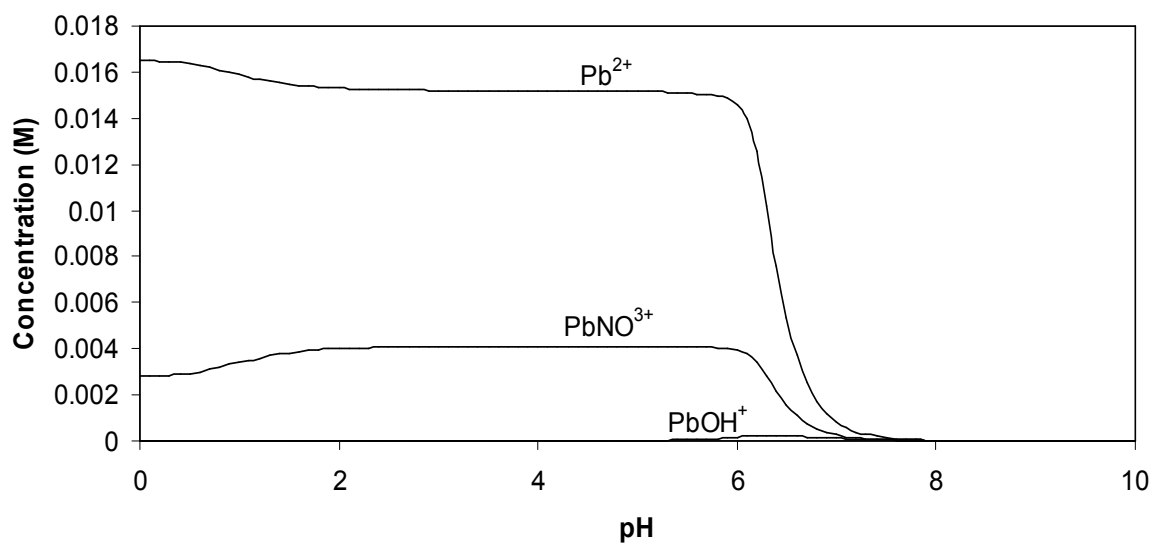
UO		EO	
Wavenumber (cm^{-1})	Band Assignment	Wavenumber (cm^{-1})	Band Assignment
3435	— O — H Hydroxyl group	3412	— O — H Hydroxyl group
2851 and 2943	— CHO Aldehyde group	2359	O = C = O Carbon dioxide
2349	O = C = O Carbon dioxide	2349	O = C = O Carbon dioxide
1742	— CHO Aldehyde group	1725-1700	— COOH saturated Carboxylic acids
1634	C = O Ketones	1600	C = O Ketones
1458	= C — H deformations	1453	= C — H deformations
1384	— CH ₃ deformations	1383	— CH ₃ deformations

3.5. Speciation of Lead and Cobalt Ions in Aqueous Solution

Speciation curves for 0.016 M cobalt and 0.0193 M lead in nitrate solutions are presented in Figures 4a and 4b, respectively. Figure 4a shows that at pH 5 (maximum pH used in this study), 97.6%, 2.3% and 0.1% of cobalt exists in aqueous solution as Co^{2+} , CoNO_3^+ and HCoO_2^- , respectively. Figure 4b shows that at pH 5, 78.6%, 21.2% and 0.2% of lead exists in aqueous solution as Pb^{2+} , PbNO_3^+ and PbOH^+ , respectively. The speciation curves obviously show that there is no precipitation of lead and cobalt species at pH 5. Maximum concentration of lead or cobalt used for batch sorption experiments is 0.00848 M which is lower than the concentrations at which aqueous speciation diagrams were prepared. This confirms that lead and cobalt removal process in all batch sorption experiments is purely due to sorption and not precipitation.



(a)



(b)

Figure 4. Speciation curves for (a) 0.016 M cobalt in nitrate solution and (b) 0.0193 M lead in nitrate solution.

3.6. Batch Sorption Experiments

Sorption isotherm models, effect of electrochemical oxidation, effect of competitive sorption, effect of pH on lead and cobalt sorption and mechanism of lead and cobalt sorption onto EO and UO are discussed in the following sections.

3.6.1. Sorption Isotherm Models

The analysis of isotherm data is important to develop an equation that represents the results. Correlation of the data using empirical or theoretical equations is required in the analysis and design of adsorption processes. Langmuir and Freundlich equations are the most widely used equations for modeling equilibrium isotherms. The Langmuir isotherm is expressed as:

$$q_e = \frac{q_{\max} b C_e}{1 + b C_e} \quad (1)$$

where q_e is the amount of adsorbate adsorbed per unit mass of adsorbent (mmol/g), C_e is the equilibrium concentration of the adsorbate (mmol/L) and q_{\max} and b are empirical constants; q_{\max} is the maximum value of q_e obtainable with an increase in C_e and b gives an indication of the strength of bonding between the adsorbate and the adsorbent. The Freundlich isotherm is expressed as:

$$q_e = K_f C_e^{1/n} \quad (2)$$

where q_e is amount of adsorbate adsorbed per unit mass of adsorbent (mmol/g), C_e is the equilibrium concentration of the adsorbate (mmol/L), K_f is an approximate indicator of adsorption capacity and $1/n$ is a function of strength of adsorption. The experimental data for competitive and noncompetitive sorption of lead and cobalt ions onto EO and UO were analysed using Langmuir and Freundlich isotherm models. The corresponding Freundlich and Langmuir parameters and correlation coefficients (R^2) are shown in Table 3. The correlation coefficients for the Langmuir isotherm model were higher than those for the Freundlich isotherm model for EO. However, correlation coefficients for Freundlich isotherm model were higher than those for UO.

Table 3. Langmuir and Freundlich isotherm constants for noncompetitive (N Co) and competitive (C Co) cobalt and noncompetitive (N Pb) and competitive (C Pb) lead and experimental maximum noncompetitive (N Co) and competitive (C Co) cobalt and noncompetitive (N Pb) and competitive (C Pb) lead sorbed onto EO and UO

Sample	Langmuir isotherm constants			Freundlich isotherm			Experimental maximum ion sorbed (mmol/g)
	q_{\max}	b	R^2	K_f	1/n	R^2	
N Co UO pH 5	0.211	2.841	0.91	0.14	0.24	0.99	0.227
N Co EO pH 3	0.335	4.644	0.97	0.26	0.13	0.89	0.335
N Co EO pH 4	0.622	2.461	0.99	0.42	0.23	0.89	0.622
N Co EO pH 5	0.967	9.998	0.99	0.75	0.19	0.82	0.968
C Co UO pH 5	0.122	8.352	0.76	0.10	0.10	0.97	0.129
C Co EO pH 5	0.528	2.359	0.97	0.32	0.26	0.88	0.528
N Pb UO pH 5	0.379	286.8	0.85	0.36	0.13	0.98	0.448
N Pb EO pH 3	0.884	9.608	0.99	0.72	0.16	0.83	0.884
N Pb EO pH 4	1.391	23.57	0.99	1.25	0.07	0.82	1.386
N Pb EO pH 5	1.731	25.23	0.99	1.46	0.17	0.88	1.731
C Pb UO pH 5	0.214	1.523	0.85	0.11	0.42	0.99	0.266
C Pb EO pH 5	1.359	10.14	0.99	1.04	0.23	0.79	1.359

This is confirmed by experimental and Langmuir isotherm model maximum metal ions sorbed onto EO and UO that are shown in Table 3. The maximum metal ions sorbed was approximately the same for experimental and Langmuir isotherm model prediction by EO, while they differ from experimental maximum metal sorbed by UO. Therefore, experimental data for sorption onto EO and UO were fitted with Langmuir isotherm model (solid lines) and Freundlich isotherm model (dashed lines), respectively as shown in Figures 5 - 8. Langmuir and Freundlich models have been used in modelling metal ions isotherms by several researchers (13, 22-25).

3.6.2. Effect of Electrochemical Oxidation on Lead and Cobalt Sorption Equilibrium

Figure 5 shows cobalt and lead sorption of EO and UO evaluated at pH 5 and 298 K.

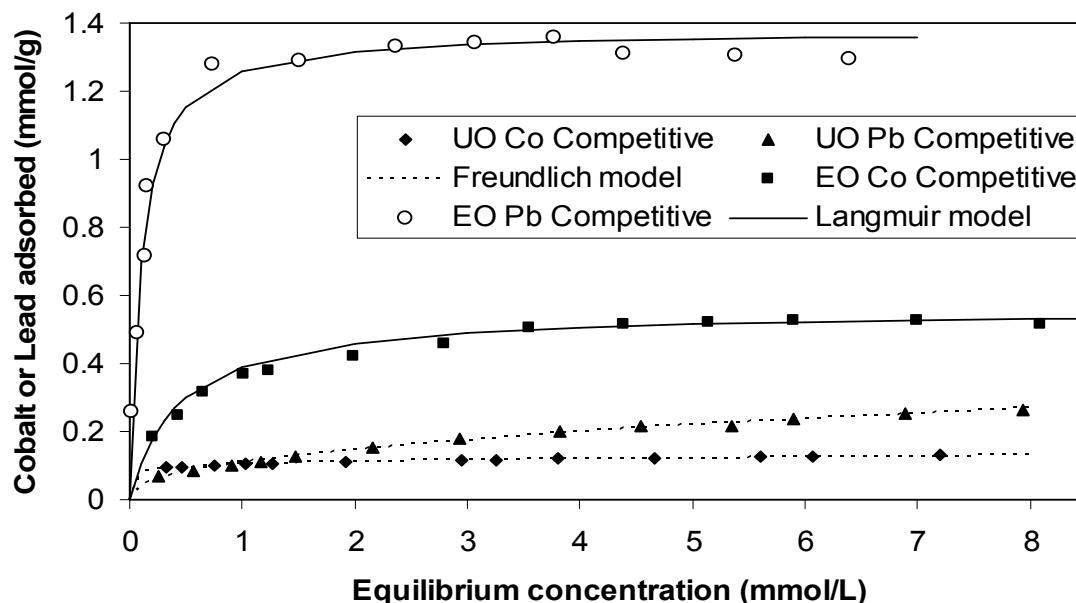


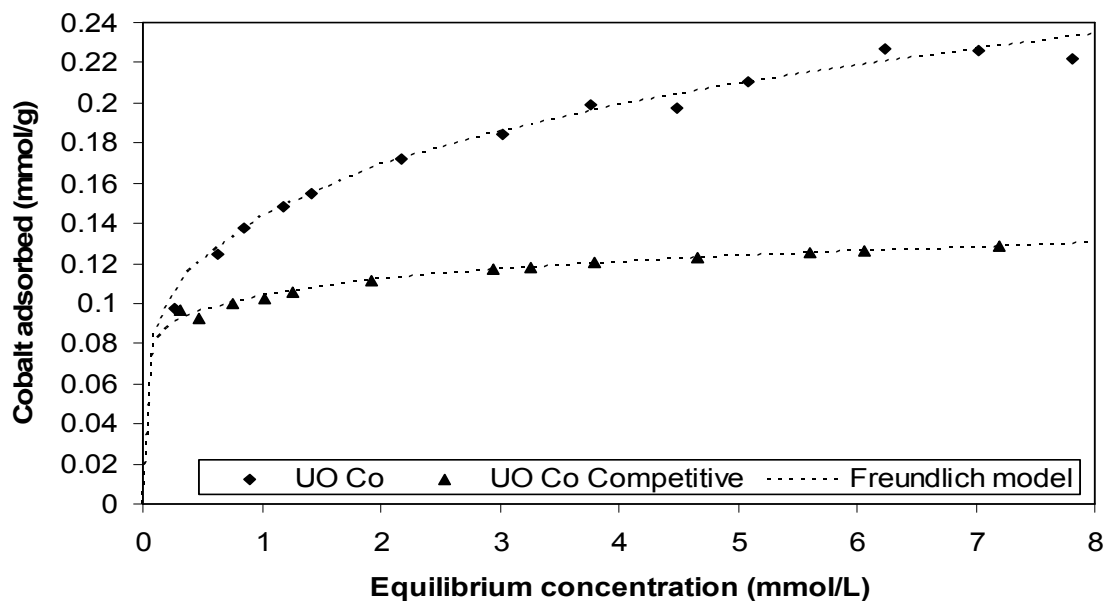
Figure 5. Isotherms of competitive sorption of cobalt and lead onto UO and EO at pH 5.

The maximum noncompetitive cobalt and lead sorption capacities for EO are 0.968 and 1.731 mmol/g, respectively, while the maximum noncompetitive cobalt and lead sorption capacities for UO are 0.227 and 0.448 mmol/g, respectively. The noncompetitive cobalt and lead sorption capacities for EO are 4.3 times and 3.9 times greater than the noncompetitive sorption capacities for UO, respectively. The maximum competitive cobalt and lead sorption capacities for EO are 0.528 and 1.359 mmol/g, respectively and the maximum competitive cobalt and lead sorption capacities for UO are 0.129 and 0.266 mmol/g, respectively. The competitive cobalt and lead sorption capacities for EO are approximately 4.1 times and 5.1 times greater than the competitive sorption capacities for UO, respectively. Therefore, electrochemical oxidation of ACC markedly increased its sorption capacity for both competitive and noncompetitive sorption of lead and cobalt ions. This is directly related to increase in more acidic oxygen containing functional groups as detected by elemental analysis and pH titration results. This is confirmed by FTIR spectroscopy analysis results that detected carboxylic acid on EO that is more acidic than the aldehyde and hydroxyl groups on UO. This is also confirmed by sodium capacity results which showed a much higher cation exchange capacity for EO than UO.

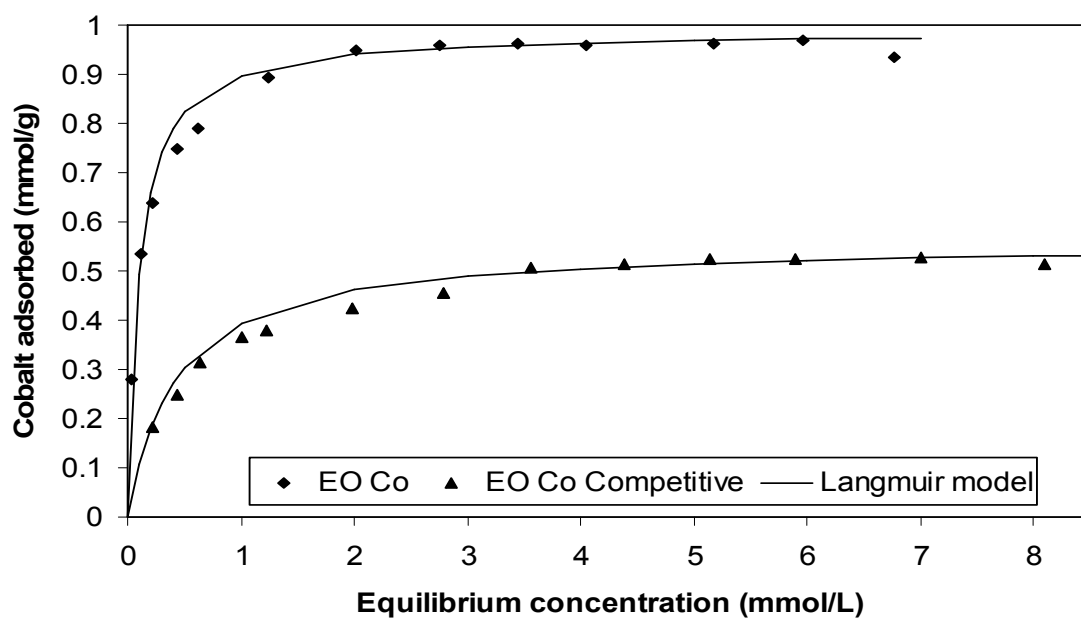
3.6.3. Competitive Lead and Cobalt Sorption Equilibria

Figures 6 and 7 show the results of competitive sorption of individual lead and cobalt ions from aqueous solutions at pH 5 and 298 K containing both ions in equimolar concentrations compared with noncompetitive sorption results from the solutions containing only one (either cobalt or lead) ion. Since the sorption studies

included the two metal ions in the same solution at the same molar concentration, the amount of a particular metal ion sorbed by the ACC indicates its ability to compete with the other ion in solution. Observed sorption preference for EO and UO is $Pb^{2+} > Co^{2+}$. The noncompetitive sorption affinity for lead is 1.8 and 2 times greater than that for cobalt for EO and UO, respectively. For EO, competitive sorption resulted in maximum sorption reduction of 22% and 46% for lead and cobalt, respectively. It also resulted in maximum sorption reduction of 41% and 43% for lead and cobalt, respectively for UO. The significant reduction in the sorption of lead in the presence of cobalt (though lead is preferred to cobalt) is due to weaker interaction of lead with EO or UO caused by higher concentration of cobalt ion in the solution after the initial sorption of lead onto EO or UO since both metal ions had initial equal molar concentrations. The sorption preference for EO and UO which is $Pb^{2+} > Co^{2+}$, is attributed to the fact that adsorbents prefer: ion with smaller hydrated ionic radius, greater polarizability and higher valence (18, 26). Crystal ionic radius for Pb^{2+} and Co^{2+} are 1.19 and 0.56 Å, respectively, (27, 28). Effective hydrated ionic radius for Pb^{2+} and Co^{2+} are 4.5 and 6 Å, respectively (28) and

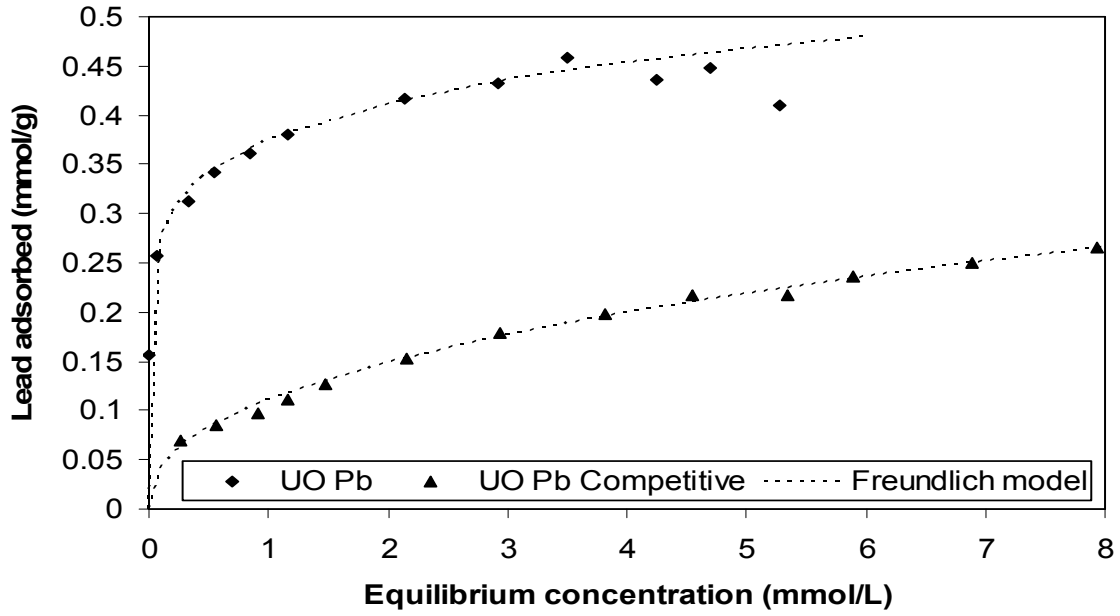


(a)

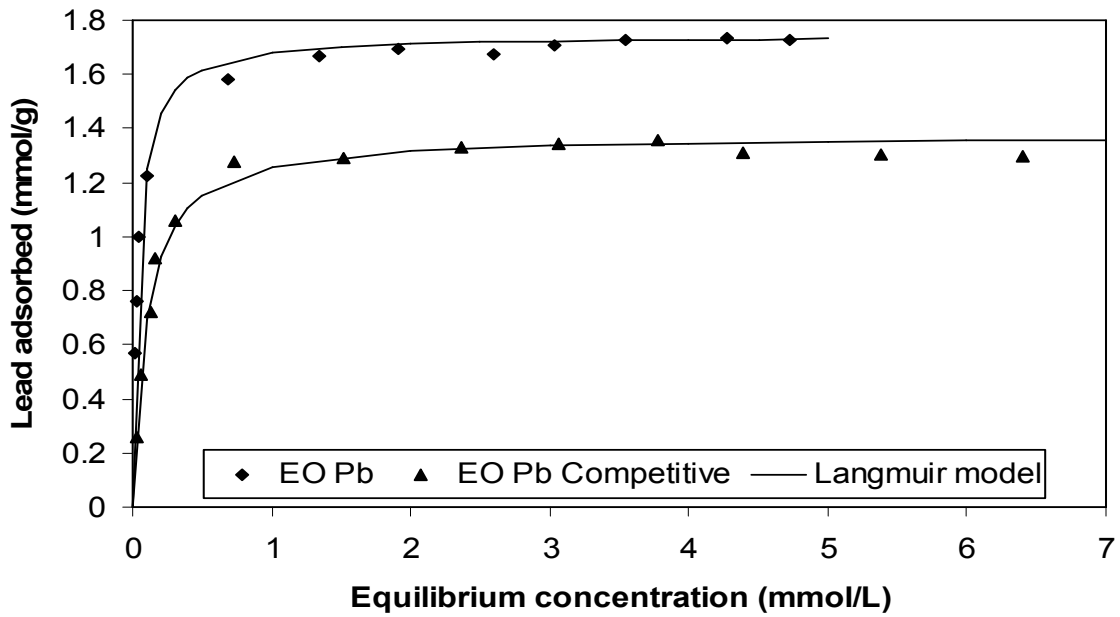


(b)

Figure 6. (a) Isotherms of noncompetitive (UO Co) and competitive (UO Co competitive) sorption of cobalt onto UO at pH 5 and (b) isotherms of noncompetitive (EO Co) and competitive (EO Co competitive) sorption of cobalt onto EO at pH 5.



(a)



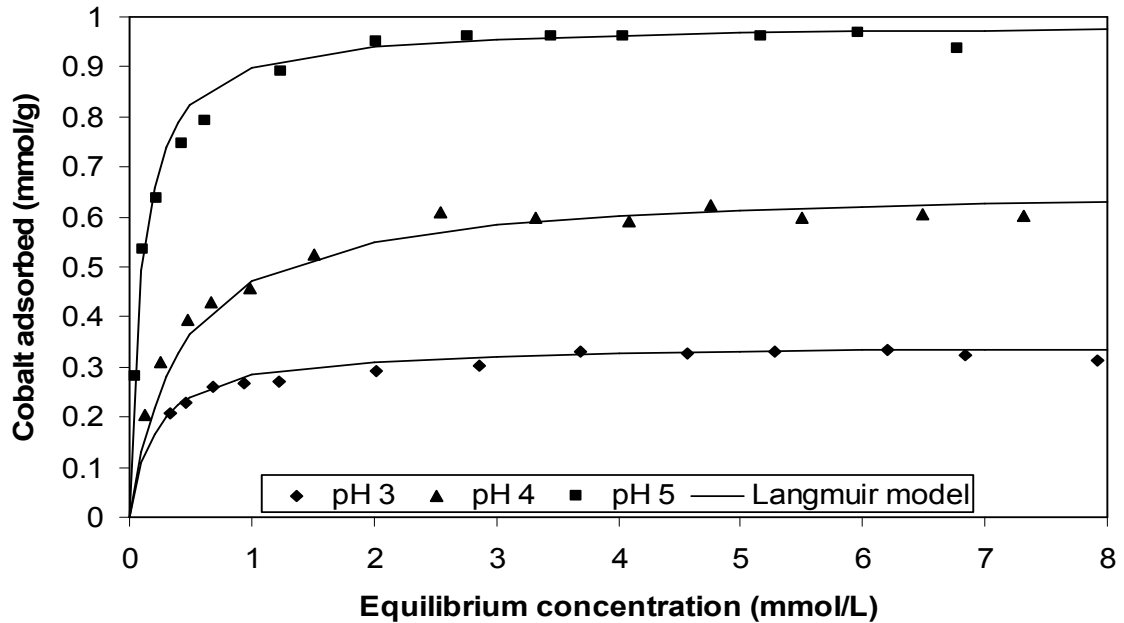
(b)

Figure 7. (a) Isotherms of noncompetitive (UO Pb) and competitive (UO Pb competitive) sorption of lead onto UO at pH 5 and (b) isotherms of noncompetitive (EO Pb) and competitive (EO Pb competitive) sorption of lead onto EO at pH 5.

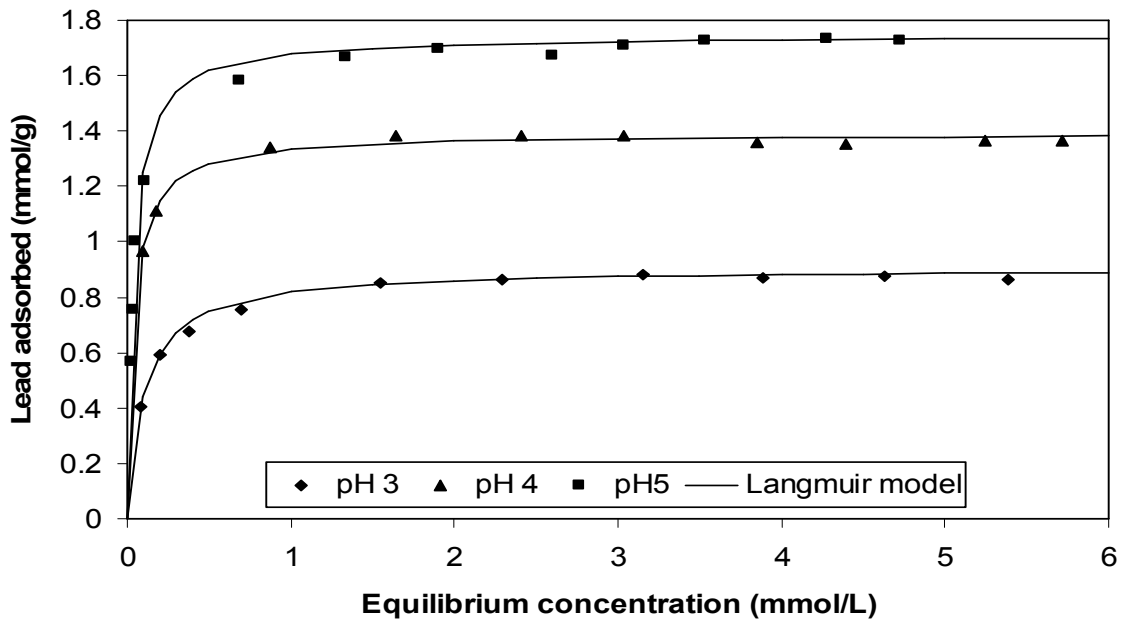
the polarizability for lead and cobalt atoms are 6.8×10^{-24} and $7.5 \times 10^{-24} \text{ cm}^3$, respectively (27). Both ions have the same valency and the difference in the polarizabilities (i.e., $7 \times 10^{-25} \text{ cm}^3$) is very small, therefore, lead ions with smaller effective hydrated radii are able to diffuse into parts of the porous structure that are not easily accessible by the larger hydrated cobalt ions, thereby resulting in increased sorption of lead ions.

3.6.4. Effect of pH on Lead and Cobalt Sorption

Effect of pH on lead and cobalt sorption was investigated by determining sorption isotherms of noncompetitive lead and cobalt onto EO at solution pH of 3, 4 and 5. The results are shown in Figures 8a and 8b. In order to avoid precipitation of metal species, no sorption experiments were performed at solution pH higher than 5.



(a)



(b)

Figure 8. (a) Isotherms of noncompetitive sorption of cobalt onto EO at pH 3, 4 and 5 and (b) isotherms of noncompetitive sorption of lead onto EO at pH 3, 4 and 5.

The maximum sorption capacity increased with an increase in solution pH. It increased by a factor of 1.9 and 1.6 times for cobalt and lead, respectively, with an increase in solution pH from 3 to 4. With a further increase in solution pH from 4 to 5, the maximum sorption capacity increased by a factor of 1.6 and 1.3 times for cobalt and lead, respectively. The effect of pH on sorption isotherms was due to interactions between lead and cobalt ions in solution and the surface charge on EO. It has already been pointed out that the adsorbent surface is negatively charged at pH values higher than PZC which is pH 2.8 for EO. It becomes more negatively charged as the pH increases due to dissociation of carboxylic acid functional groups. Hence, the amount of Pb^{2+} and Co^{2+} ions that will ion exchange with H^+ ions from the carboxylic acid functional groups will increase with an increase in pH. The reduction in the increase of the maximum sorption capacity with an increase in pH from 4 to 5 as compared to that with an increase in pH from 3 to 4 is attributed to the fact that the number of sorptive sites per gram of EO is limited. It is also noticeable from Figures 9a and 9b that the maximum sorption capacity is low for the sorption isotherm for pH 3. This is due to the fact that at low solution pH, the dissociation of the carboxylic acid functional groups is low. Also the concentration of H^+ ions is high at low solution pH, which will react with the few anionic functional groups on the surface of EO thereby restricting the number of binding sites for metal ions.

3.6.5. Mechanism of Lead and Cobalt Sorption onto EO and UO ACC

PZC for EO and UO are 2.8 and 6.8, respectively. Batch sorption experiments were performed at a maximum solution pH of 5. This is below the PZC of UO, so the UO surface was positively charged. This explains why the solution pH increased during the cobalt and lead sorption process and so was adjusted by adding specific volumes of 0.1 M nitric acid to maintain the original solution pH. It is well known that the double bond in the aldehyde ends of the cellulose molecules in ACC matrix consist of a σ bond and a π bond (4, 20). Unlike the $C=C$ group the aldehyde group does not have an electron distribution between the two atoms. There is a greater electron density over the more electronegative oxygen: $^+C=O^-$ (4). It is well known that electrophiles are attracted to groups that donate electrons (4). This makes it possible for Pb^{2+} and Co^{2+} ions that are electrophiles to be attached to them and hence complex formation between the metal ions and UO surface is the mechanism for sorption of lead and cobalt onto UO. Therefore, complex formation between the metal ions and UO involving interaction of aldehyde sites on UO is:



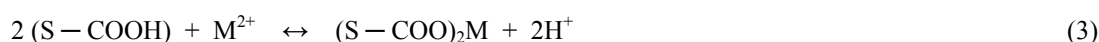
where S is the surface of the UO and M^{2+} is the metal ion, i.e., Pb^{2+} or Co^{2+} .

Batch sorption experiments were performed at solution pH values of 3, 4 and 5, which are above the PZC of EO, so the EO surface was negatively charged. This explains why solution pH decreased during lead and cobalt sorption indicating that H⁺ ions were released from EO. The pH was adjusted with specific volumes of 0.1 M sodium hydroxide to maintain the original solution pH. Mass balance (to obtain the maximum H⁺ ions released) was performed with the volume of 0.1 M sodium hydroxide added to adjust the solution pH. The experimentally determined noncompetitive and competitive metal ions sorbed onto EO and H⁺ ion released from EO are shown

Table 4. Experimental maximum noncompetitive cobalt (N Co), noncompetitive lead (N Pb) and competitive (C Co + C Pb) ions sorbed onto EO and H⁺ ion released from EO.

Sample	Maximum metal ion (Co ²⁺ /Pb ²⁺) sorbed (mmol/g)	Maximum H ⁺ ion released (mmol/g)	Ratio of maximum H ⁺ ion released to maximum metal ion (Co ²⁺ /Pb ²⁺) sorbed
N Co EO pH 3	0.335	0.68	2.03
N Co EO pH 4	0.622	1.24	1.994
N Co EO pH 5	0.968	1.96	2.03
N Pb EO pH 3	0.884	1.80	2.04
N Pb EO pH 4	1.386	2.82	2.04
N Pb EO pH 5	1.731	3.48	2.01
C Co+Pb EO pH 5	1.887	3.76	1.993

in Table 4. It is obvious that one Pb²⁺ or Co²⁺ ion was sorbed for approximately two H⁺ ions released from EO. This confirms that the sorption of lead and cobalt onto EO was by ion exchange mechanism. FTIR spectroscopy analysis and pH titration results confirmed that carboxylic acids were introduced to EO by electrochemical oxidation. Therefore, ion exchange mechanism involving interaction of carboxylic sites on EO is:



where S is the surface of the EO and M²⁺ is the metal ion, i.e., Pb²⁺ or Co²⁺.

3.6.6. Comparative Study for Maximum Noncompetitive Cobalt, Lead and Sodium Ions Adsorption Capacity

Smiciklas *et al* (5) used synthetic hydroxyapatite for adsorption of cobalt from aqueous solution. The maximum cobalt adsorbed by synthetic hydroxyapatite was 0.35 mmol/g. Krishnan *et al* (6) used sulphurised activated carbon for adsorption of cobalt from aqueous solution and they reported the maximum cobalt adsorption capacity as 0.69 mmol/g. Arakaki *et al* (29) used ethyleneimine anchored on thiol-modified silica gel for adsorption of cobalt from aqueous solution and the maximum cobalt adsorption capacity is 0.54 mmol/g. Sales

et al (30) reported the highest cobalt adsorption capacity as 0.85 mmol/g using mesoporous silica as an adsorbent. However, the maximum cobalt adsorption capacity in the present study is 0.968 mmol/g by EO.

Pimental *et al* (31) used retorted shale for adsorption of lead from aqueous solution and the maximum lead adsorbed was 0.178 mmol/g. King *et al* (32) used *syzygium cumini* L for adsorption of lead from aqueous solution and the maximum lead adsorption capacity was 0.178 mmol/g. Girgis *et al* (33) used activated carbon produced by H_3PO_4 under flowing gasses for adsorption of lead from aqueous solution and the maximum lead adsorption capacity was reported as 0.985 mmol/g. Gercel *et al* (34) reported maximum lead adsorption capacity as 1.16 mmol/g using activated carbon prepared from biomass plant material of *euphorbia rigida*. However, the maximum lead in this study was found to be 1.731 mmol/g by EO. From this comparison, it is obvious that electrochemical oxidation of ACC is an efficient method for enhancing the lead and cobalt sorptive capacity for water treatment. However, no information is published in the literature for multicomponent adsorption of cobalt and lead from aqueous solution. Saha *et al* (9) used nitric acid oxidised wood-based granular activated carbon and air oxidised wood-based granular activated carbon samples for adsorption of copper from aqueous solution and the reported maximum copper adsorption capacity values are 0.47 mmol/g and 0.34 mmol/g, respectively. Saha *et al* (12) also oxidised coal-based granular activated carbon with nitric acid and air. The sodium capacity values were 3.1 mmol/g and 2.1 mmol/g for the nitric acid oxidised coal-based granular activated carbon and air oxidised coal-based granular activated carbon, respectively. However, the maximum sodium capacity in this study was found to be 4.94 mmol/g by EO. From this comparison, it is obvious that electrochemical oxidation of ACC produces adsorbents with higher cation exchange capacity than acid oxidized granular adsorbents (11).

4. CONCLUSIONS

This work confirms that for noncompetitive sorption cobalt and lead ions sorption capacities for EO increased 4.3 and 3.9 times, respectively. The capacities also increased 4.1 and 5.1 times for competitive sorption of cobalt and lead, respectively for EO. Affinity order of metal ions sorbed by UO and EO is $Pb^{2+} > Co^{2+}$. Solution pH plays a very important role for sorption of lead and cobalt ions by EO. The uptake of lead and cobalt ions increased with an increase in solution pH. It is confirmed that lead and cobalt ions were sorbed onto EO by ion exchange mechanism. However, lead and cobalt ions were sorbed onto UO by complex formation with the UO surface. The present study concludes that electrochemical oxidation of a viscose rayon based ACC markedly enhanced the removal of lead and cobalt ions from aqueous solutions.

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