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EFFECT OF ELECTROCHEMICAL OXIDATION OF A VISCOSE RAYON BASED ACTIVATED CARBON CLOTH ON SORPTION OF TOXIC ARSENIC IONS FROM AQUEOUS SOLUTION

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ABSTRACT

A viscose rayon based activated carbon cloth (ACC) was electrochemically oxidised to enhance its cation sorption capacity for comparison with as-received ACC. ACCs were characterised by sodium capacity measurement, pH titration, zeta potential measurement, elemental analysis, Brunauer-Emmet-Teller surface area measurement, Fourier transform infra red spectroscopy analysis and Scanning electron microscopy. Batch sorption experiments showed that Arsenic sorption capacity for electrochemically oxidised ACC increased 11.35 times at pH 8. Arsenic sorption increased with an increase in solution pH for electrochemically oxidised ACC. Arsenic ions were sorbed onto as-received ACC and electrochemically oxidised ACC by ion exchange.

KEYWORDS: Viscose rayon based activated carbon cloth; Sorption isotherms; Electrochemical oxidation; Arsenic (VI), Sorption; Characterisation.

INTRODUCTION

Arsenic exists in aqueous solutions mainly in two states: trivalent, (Arsenic(III)) and hexavalent, (Arsenic(VI). Arsenic(VI) is primarily present in the form of Arsenate (AsO_4^{2-}) and diarsenate (AsO_7^{2-}) ions [1-2]. Arsenic (VI) is toxic, carcinogenic, mutagenic and tetratogenic [2]. The European Community Council Directive 98/78/EC [3] has highlighted Arsenic as one of the most toxic heavy metals in residual waters and the limit of concentrations in drinking water for Arsenic is 10 μg/L. The major source of water contamination with Arsenic ions is industrial wastewaters from industrial processes [2]. There are various methods for removing heavy metals, including chemical precipitation, membrane filtration, electrodialysis, biological processes, reverse osmosis and adsorption [2]. Among these methods, adsorption onto activated carbon is a widely applied method and is economically favourable and technically easier [2]. Activated carbon now exists in granular (GAC), powder (PAC) and fibre forms. The carbon fibres are produced in the form of cloth (ACC) and felt (ACF). The porous structure of ACC is composed mainly of micropores, while GAC and PAC contain a complex porous network of macropores, mesopores and micropores. In the ACC the access to the micropores is directly from the external surface, however, in the GAC and PAC, the macropores are open to the particle external surface and they branch into mesopores and finally into micropores. Most of the sorption in all the activated carbon forms take place in the micropores, thus sorption area in ACC can be accessed more easily than in other forms [4]. ACC has some advantages over the traditional forms. Generally, the intraparticle diffusion in GAC is very slow and this makes the overall rate of sorption very slow [5]. For PAC processes, the overall rate of sorption is very fast, but PAC presents the disadvantage of complicated handling. The overall rate of sorption in ACC is as fast as PAC but it does not have the handling problems existing in PAC.To meet the above stringent regulation standards, it is necessary to modify the ACC to improve its sorption capacity for Arsenic (VI). Consequently, in this work a viscose rayon based ACC was modified by electrochemical oxidation to enhance its sorption capacity for Arsenic (VI). The efficiencies of the

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as-received ACC and electrochemically oxidised ACC for the sorption capacities for Arsenic (VI) were compared.

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. Before use the ACC was converted to hydrogen form by passing 2 L of 5 % (w/w) hydrochloric acid very slowly (for 48 h) through a column containing 20 g of the ACC. After conversion, the ACC was washed with 50 L of deionised water and the conductivity of the washed water was measured. Washing was continued until the conductivity of the washed water was the same as that of deionised water. After washing, the ACC was dried in an oven at 383 K for 24 h. It was then put in a desiccator overnight and weighed. All converted samples were kept in sealed plastic bags to avoid any contamination. All chemicals were of analytical grade and obtained from Fisher Scientific, U.K.

2.2. Electrochemical oxidation

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. 1 gm of ACC was wrapped round the anode (platinised titanium) and immersed in 0.5 M potassium chloride solution for 1 h prior to the electrochemical oxidation process. The schematic of the electrochemical cell used for oxidation is Figure 1, 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 of 1.1 A and 2.2 A at different oxidation times of 2 h, 4 h, 6 h and 1 h, 2 h, 3 h, respectively. 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 then kept in a desiccator overnight and then weighed.

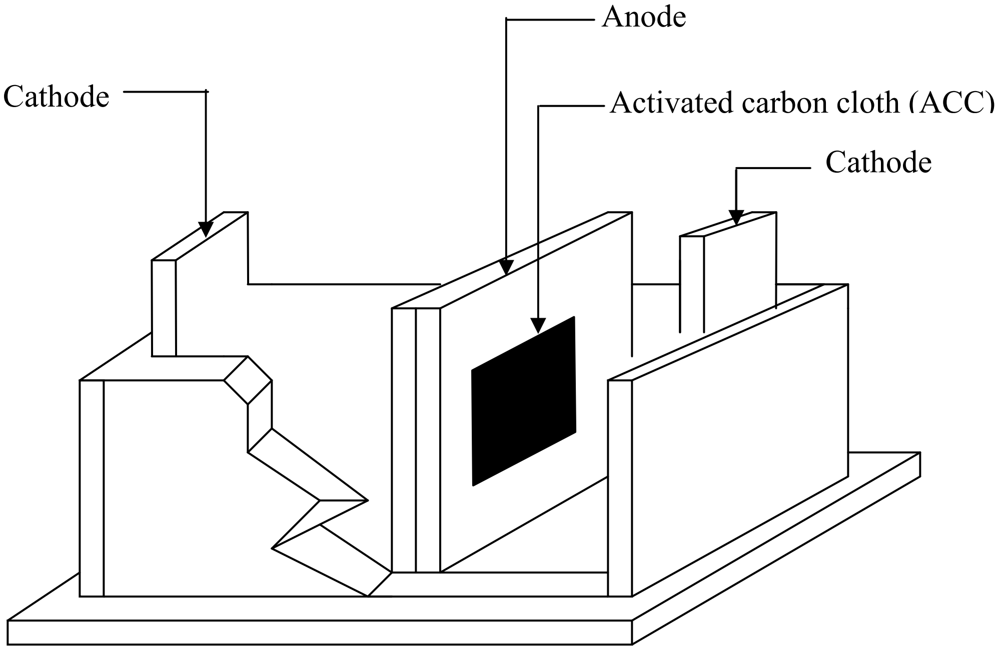


Figure 1 Schematic of electrochemical cell used for electrochemical oxidation.

2.3. Sodium Capacity Determination

Sodium capacity was determined in order to compare the cation exchange capacity of unoxidised ACC (UO) and electrochemically oxidised ACC (EO) in aqueous solution. Sodium sorption capacity gives an indication of the cation exchange capacity of adsorbents in aqueous solution. 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 (10 - 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. To verify that there was no precipitation of metal species in the experimental pH range, aqueous speciation of Arsenic as a function of solution pH was studied using JCHESS version 2.0 and CHESS version 3.0 software, written by van Der Lee [6] at concentrations of 0.01 M Arsenic(VI) in Sodium Arsenate solution. The information about the CHESS home page can be seen at URL http://chess.ensmp.fr.

2.8. Batch Sorption Experiments

Sorption of arsenic (VI) from sodium arsenate solutions was studied in batch experiments to obtain isotherms at pH of 4, 6 and 8. Equilibrium arsenic (VI) ion sorption isotherms were obtained as follows: 20 ml of arsenic (VI) ions of several initial concentrations, (0.19-9.62 mM) were added to 50 ml conical flasks with 0.025 g of electrochemically oxidised cloth (EO ACC) or as-received ACC in each flask. Initial pH of the solutions was measured using a Mettler-Toledo 340 digital pH meter and 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 measured volumes of 0.1 M sodium hydroxide or 0.1 M nitric acid to the solutions. This was continued until equilibrium was achieved i.e., when there was no significant change in solution pH for 48 h, this took about 10 days. To investigate the effect of pH on the sorption capacity of ACC, a series of batch sorption experiments were conducted at original pH values of 4, 6 and 8. It is well known that arsenic (VI) can easily be reduced to arsenic (III) when in contact with adsorbents with hydroxyl functional groups even in alkaline solutions [1, 2, 7]. The standard reduction potentials for several alcohols (-4.86 to -0.13 V) are much lower than the standard reduction potential of arsenate ion (0.36 V) [2, 7]. Therefore, alcohol groups are stronger reductants than sodium arsenate and can readily reduce arsenic(VI) to arsenic(III). The equilibrated solutions were filtered to remove ACC particles and the residual concentrations of total arsenic(VI) were determined by oxidising arsenic(III) in the filtrate with excess of potassium permanganate to arsenic(VI). The choice of Potassium permanganate is based on the fact that standard reduction potential for manganate ion (1.51 V) is higher than the standard reduction potential of arsenate ion (0.36 V) [7].Therefore, potassium permanganate is a stronger oxidant than sodium arsenate and can readily oxidise arsenic(III) to arsenic(VI), especially at high temperature. After the oxidation of arsenic(III) to arsenic(VI), the residual arsenic(VI) concentrations were determined using a Varian AA 200 atomic absorption spectrophotometer (AAS) in acetylene-air flame emission mode.

2.9. Quality Assurance / Quality Control

To establish the accuracy, reliability and reproducibility of the collected data, all experiments, except SEM were conducted in duplicate. The relative error for the analytical procedures except the batch sorption experiments was less than 2%. For batch sorption experiments, the AAS was operated at wavelengths of 240 and 320 nm, providing the optimum sensitivity for arsenic. Standard arsenic solutions from Fisher Scientific, U.K. were used for instrument calibration and standard verification. The highest relative error for the determination of arsenic (VI) concentrations using AAS was less than 5% for all batch sorption experiments. The highest relative error was less than 3% when the standard arsenic solutions were analysed.

Results and discussion.

3.1. Sodium Capacity

Sodium sorption capacity was determined in order to compare the cation exchange capacity of electrochemically oxidised ACC and as-received ACC in aqueous solution. The sodium sorption capacity gives an indication of the cation exchange capacity of adsorbents in aqueous solution which is related to the quantity of acidic functional groups generated upon electrochemical oxidation. In order to achieve the optimum constant current, three series of experiments were performed at different extents of electrochemical oxidation, 7,920 c/g, 15,840 c/g and 23,760 c/g. 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 2. The three sets of results followed the same trend. The sodium capacity for ACCs oxidised below 1 A were low. This is attributed to the fact that applied currents below 1 A do not produce sufficiently vigorous oxidising conditions. The sodium capacity for ACCs oxidised below 1 A were low. This is attributed to the fact that applied currents below 1 A do not produce sufficiently vigorous oxidising conditions. Sodium capacity for ACCs oxidised above 1.47 A decreased continuously with an increase in applied current. The lowest sodium capacity was observed for ACC electrochemically oxidised at 8.8 A. This is attributed to the fact that though 8.8 A is the highest 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. It is to be noted that above 31,680 c/g extent of oxidation, the ACCs become fragile and are not suitable for

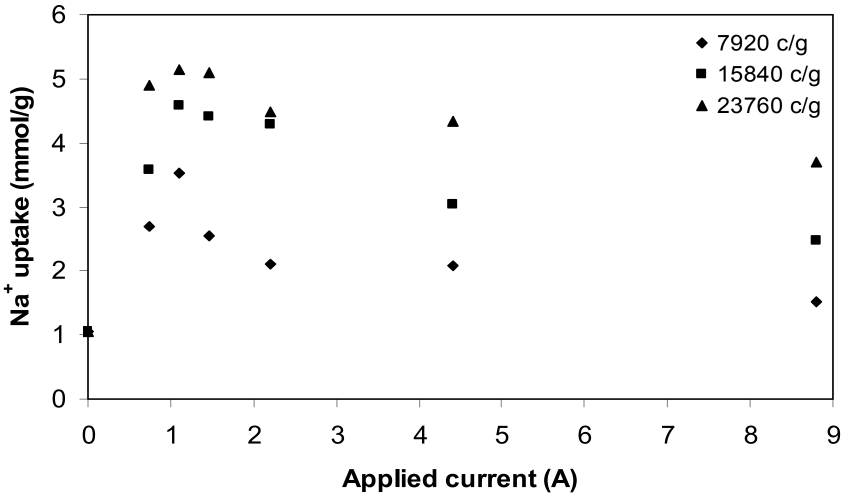


Figure 2. Sodium capacity versus applied current for different extents of electrochemical oxidation

adsorption studies. The maximum sodium capacity for electrochemically oxidised ACC was obtained at 1.1 A for 6 h (i.e. 23,760 c/g), which is 5.14 mmol/g and 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. The highest sodium capacity without breakage of fibre was observed on electrochemically oxidised ACC at 1.1 A for 6 h. For this reason electrochemical oxidation of ACC at 1.1 A for 6 h was used for the remaining oxidation experiments.

3.2. pH Titrations

This technique determines the acidic and basic properties of ion exchangers and the nature of their surface functional groups [8-10]. The pH titration curves are usually plotted as equilibrium solution pH *versus* acid/alkali added or the amount of H^+ or OH^- ion released by the adsorbent *versus* equilibrium solution pH. The proton binding curve, that is the plot of ion released *versus* equilibrium solution pH, for as-received ACC and electrochemically oxidised ACC (EO ACC) are shown in Figure 3. The point where the proton binding curve crosses the pH axis has crucial significance. It is called the point of zero charge (PZC). This has been defined as the pH value at which the surface charge is zero at a particular ambient temperature, applied pressure and aqueous solution composition [10-13]. The PZC will be shifted to lower pH values with oxidation of the ACC due to the introduction of acidic functional groups such as carboxylic, carbonyl and lactonic groups onto the surface of ACC [10]. As shown in Figure 3, PZC for as-received ACC is at pH 6.8 whereas it shifted to pH 2.8 for EO ACC. The adsorbent surface is positively charged at pH values below the PZC because the oxygen containing groups are undissociated and highly 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 remove cations in solution. The curve for EO ACC shows the highest concentration of hydrogen ions released; hence cation exchange capacity is expected to be higher than that of as-received ACC as shown by the sodium capacity results. From the pH titration curves it can be seen that the dissociation of the acidic functional groups on the as-received ACC and EO ACC to produce H^+ ions starts at equilibrium solution pH of approximately 7 and 3, respectively. Therefore, one of the types of acidic functional groups on the surface of EO ACC is likely to be carboxylic groups while that on the surfaces of as-received ACC is likely to be hydroxyl groups and ether groups, respectively.

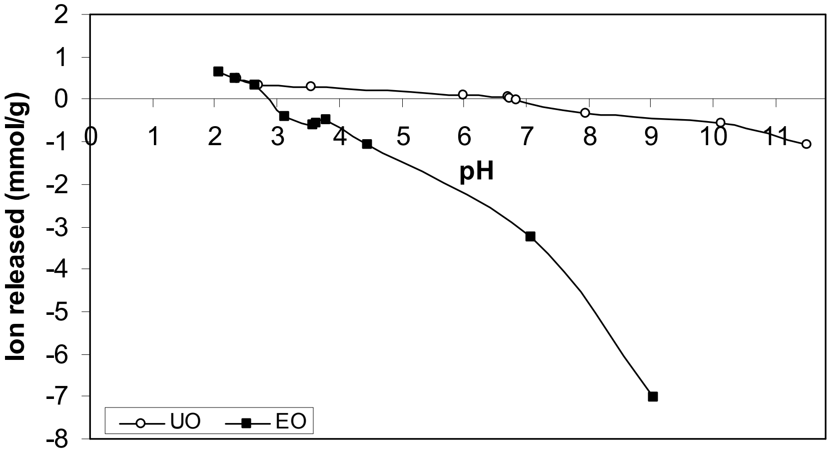


Figure 3. Ion Released versus equilibrium solution pH for as-received ACC and EO ACC.

3.3. Elemental Analysis

Elemental analysis results for as-received ACC and EO ACC are shown in Table 1. As-received ACC has 20.03% oxygen content indicating the presence of some oxygen containing groups on the surface. This is attributed to the presence of oxygen atoms in the aldehyde and hydroxyl groups of the cellulose molecules of the viscose rayon based ACC [1].The oxygen content in EO ACC increased by

Table 1. Elemental analysis of as-received ACC and EO ACC

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

120.8%. This follows the same trend as the sodium capacity results which showed the cation exchange capacity of 1.06 mmol/g for as-received ACC and 5.14 mmol/g for EO ACC. The increase in oxygen content in the EO ACC is attributed to the introduction of acidic oxygen containing functional groups.

3.4. Brunauer-Emmet-Teller (BET) Surface Area

Surface areas of as-received ACC and EO ACC were measured by nitrogen adsorption/desorption method. The BET surface area specifications of as-received ACC and EO ACC are shown in Table 2. All the ACCs analysed in this study have extensive BET surface areas that are ideal in the treatment of drinking and wastewater. However, the BET surface area decreased for EO ACC. The results showed that EO ACC lost 61.35% of the original BET surface area. This is attributed to the blockage of pores by acidic functional groups and formation of humic substances during electrochemical oxidation.

Table 2. Surface area specifications of as-received ACC and EO ACC

Adsorbents	Single point surface area (m^2/g) at P/P^0 0.205	BET surface area (m^2/g)	Average pore diameter (nm) (4V/A by BET)
As-received ACC	1395.293	1378.058	20.492
EO ACC	532.083	532.652	18.731

3.5. Fourier Transform Infra Red (FTIR) Spectroscopy Analysis

It is well known that the study of the 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/noise ratio is often not sufficiently high even if the sample is scanned many times. Also the diameter of the fibre falls in the analytical wavelength range of infrared light, which may lead to strong interference at low wavenumbers. For these reasons the intensities of FTIR spectra of ACCs are not very high. FTIR spectra for as-received ACC, and EO ACC are shown in Figures 4 and 5, respectively. The band assignments are shown in Table 3.

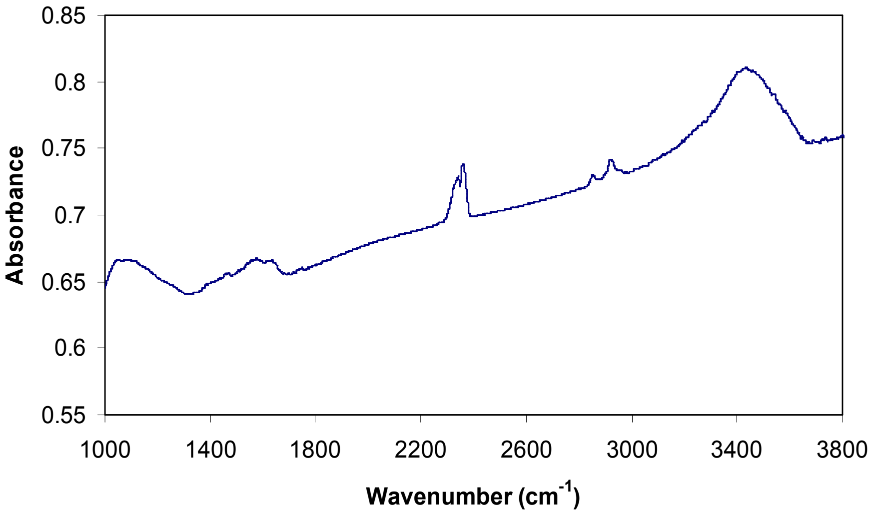


Figure 4. FTIR spectra for as-received ACC.

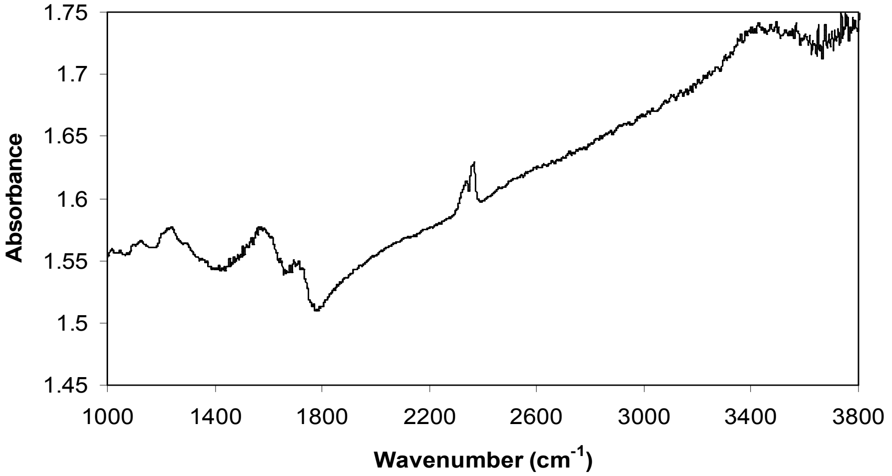


Figure 5. FTIR spectra for EO ACC.

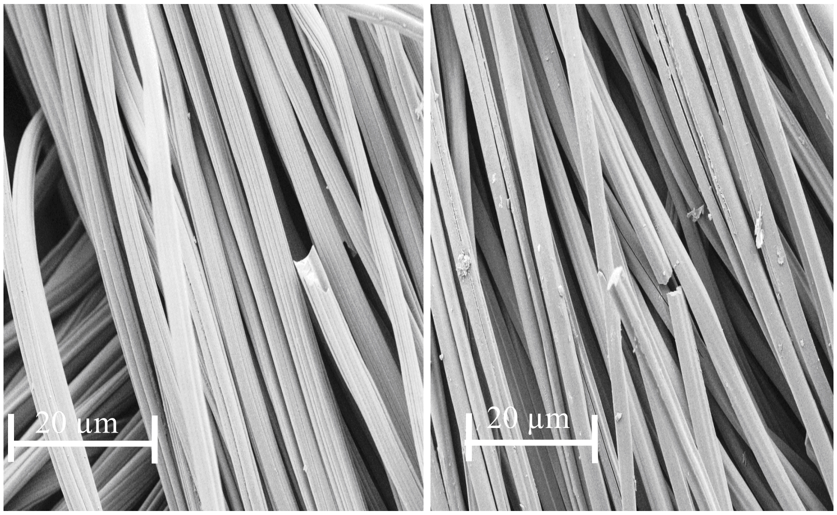
Table 3. Band assignments for FTIR spectra of as-received ACC and EO ACC.

As received ACC		EO ACC	
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	2349	— O = C = O
2349	O = C = O	2349	O = C = O
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

The distinguishing difference in the functional groups observed on the as-received ACC and EO ACC as shown in Table 4 are aldehydes and carboxylic acid, respectively. Hydroxyl groups were observed on as-received ACC and EO ACC. Since a cellulose molecule has aldehyde and hydroxyl ends it is expected that the ACCs should have aldehyde and hydroxyl functional groups on their surfaces. However, aldehyde groups were not observed on the EO ACC. It is known that aldehydes and alcohols are oxidised to produce carboxylic acid and that the alcohols need to be oxidised into aldehydes which are then readily oxidised into carboxylic acid [1]. Therefore, it is possible that the aldehydes are more readily oxidised than the alcohols and so were not found on EO ACC. The aldehydes and alcohols observed on the as-received ACC are weaker acids than carboxylic acids. Therefore, as-received ACC exhibits less acidic properties than the EO ACC as observed from the pH titration and zeta potential results. Carboxylic acid groups observed on EO ACC confirms the pH titration and zeta potential results. This also explains why there was a high increase in the sodium capacity of the ACC after electrochemical oxidation in potassium chloride.

3.6. Scanning Electron Microscopy (SEM)

Scanning electron micrographs (SEMs) of as-received ACC and EO ACC used in this investigation are shown in Figure 6. The micrographs of the two ACCs are very similar. Therefore, no significant breakage of fibres was observed during electrochemical oxidation of ACC at 1.1 A for 6 h. Therefore all ACCs used in this investigation are suitable for adsorption studies.



(a) As received ACC (b) EO ACC

Figure 6. SEM of ACCs: (a) as -received ACC, (b) EO ACC and (c) ER ACC.

3.7. Speciation of Arsenic(VI) Ions in Aqueous Solution

The speciation curve calculated using JCHESS and CHESS software for 0.01 M Arsenic(VI) in sodium arsenate solution is presented in Figure 7. Figure 7 shows that at pH 8 which is the maximum pH used in this study, arsenic exists in aqueous solution as AsO_4^{2-}, $As_2O_7^{2-}$, and $HAsO_4^-$ in proportions of 98.09%, 0.016%, and 1.89%, respectively. At pH 6 arsenic exists in aqueous solution as AsO_4^{2-}, $As_2O_7^{2-}$ and $HAsO_4^-$ in proportions of 29.12%, 13.67%, and 57.2%, respectively. At pH 4 arsenic exists in aqueous solution as AsO_4^{2-}, $As_2O_7^{2-}$, and $HAsO_4^-$ in proportions of 0.36%, 21.58%, and 78.05%, respectively. The concentrations of the other Arsenic specie (H_2AsO_4) in approximate proportions of 0.004 %, 0.01 % and 0.01 %, at pH 8, 6 and 4, respectively, are therefore negligible. It is clear from the speciation curves that there is no precipitation of any of the arsenic species at pH 8.

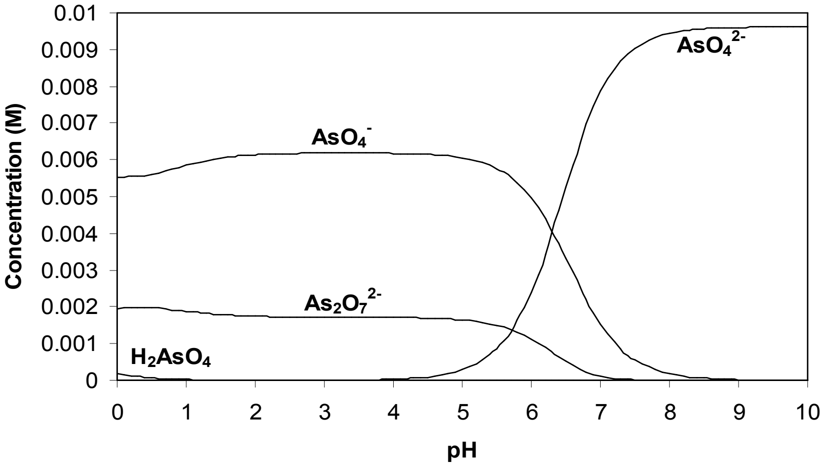


Figure 7. Speciation curves for 0.01 M Arsenic(VI) in sodium arsenate solution

Therefore, at pH 4, 6 and 8 used for the batch sorption experiments, arsenic exists predominantly in anionic species in aqueous solution. The maximum concentration of arsenic(VI) used for the batch sorption experiments is 0.00962 M which is lower than the concentrations at which the aqueous speciation was calculated; therefore the batch sorption process is purely adsorption and not precipitation.

3.8. Batch Sorption Experiments

The sorption isotherms for arsenic(VI) ions in aqueous solutions onto as-received ACC and EO ACC at pH values of 4, 6 and 8 are shown in Figures 8, 9 and 10. The sorption isotherm models, effect of electrochemical oxidation, the effect of pH on the sorption of arsenic(VI) and the likely mechanism of arsenic(VI) sorption onto as-received ACC and EO ACC samples are discussed in the following sections.

3.8.1. Sorption Isotherm Models

Sorption isotherms establish the relationship between the equilibrium concentration and the amount of adsorbate adsorbed by the unit mass of adsorbent at a constant temperature. Classical sorption models, such as Langmuir and Freundlich models have been extensively used to describe the equilibrium established between adsorbed metal ions on the adsorbent and the metal ions remaining in solution.

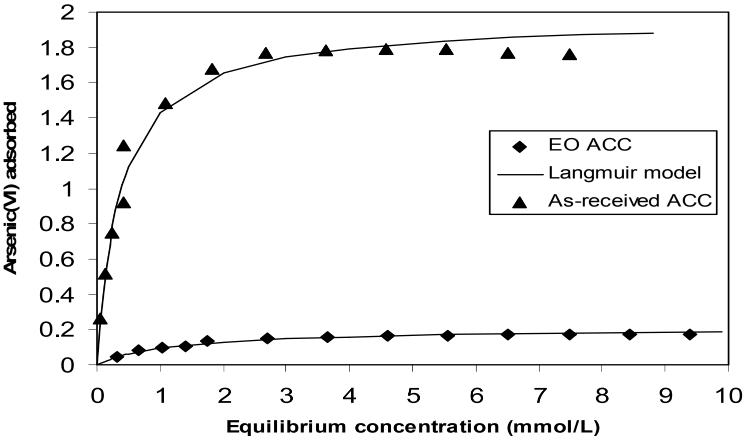


Figure 8. Sorption isotherms of Arsenic(VI) onto as-received ACC and EO ACC at pH 4.

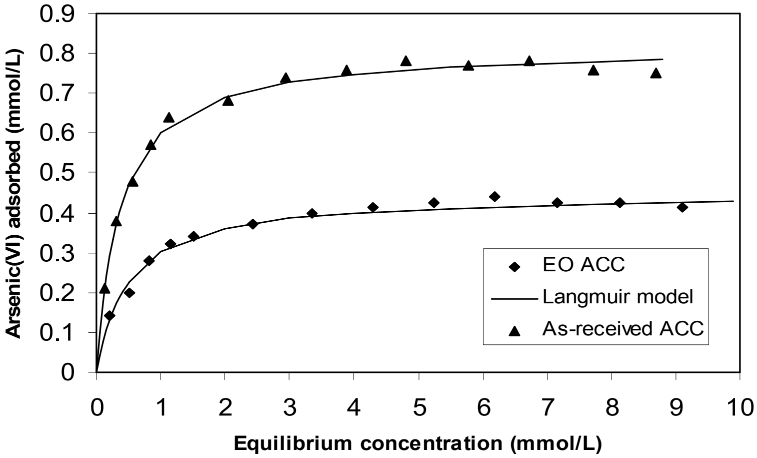


Figure 9. Sorption isotherms of Arsenic (VI) onto as-received ACC and EO ACC at pH 6.

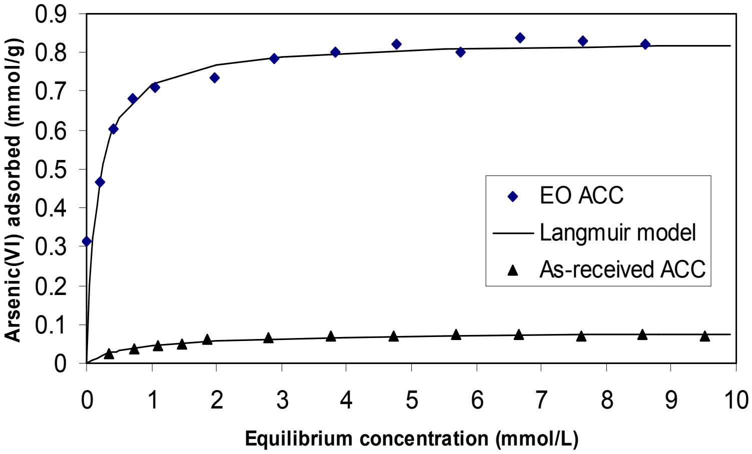


Figure 10. Sorption isotherms of Arsenic(VI) onto as-received ACC and EO ACC at pH 8.

The Langmuir isotherm is expressed as

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

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), q_{max} is the maximum value of q_e obtainable with an increase in C_e and b is the constant related to the free adsorption energy which gives an indication of the strength of bonding between the adsorbate and the adsorbent. The Langmuir model is valid for monolayer adsorption onto a surface containing a finite number of identical sites. The model assumes that there is a constant number of active sites having uniform energy on the adsorbent surface and adsorption energy is constant. The Freundlich isotherm is expressed as

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

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), k_f is a measure of the adsorption capacity of the adsorbent while 1/n is a measure of adsorption intensity. The Freundlich model assumes that the adsorbent surface energy is heterogeneous and the adsorption energy changes as a function of surface coverage by the adsorbate. The experimental data for sorption of Arsenic (VI) ions onto as-received ACC and EO ACC were analysed using the Langmuir and Freundlich isotherm models. The corresponding Freundlich and Langmuir parameters, correlation coefficients (R^2) and experimental values for maximum Arsenic(VI) ion sorbed (q_e) are shown in Table 4. Correlation coefficients for the Langmuir isotherm model were higher than those for Freundlich isotherm model for all experimental data for sorption onto all the ACCs. Therefore, the correlation coefficients demonstrate that Langmuir isotherm model fitted the experimental data for sorption onto as-received ACC and EO ACC. This is confirmed by the experimental (q_e) and the Langmuir isotherm model maximum Arsenic (VI) ions (q_{max}) adsorbed onto as-received ACC and EO ACC that are shown in Table 4. The Langmuir isotherm model maximum Arsenic(VI) ions sorbed are approximately the same as the experimental maximum Arsenic(VI) ions sorbed by as-received ACC and EO ACC. Therefore, all the experimental data for sorption onto ACCs were fitted with the Langmuir isotherm model (solid lines) as shown in Figures 8–10.

Table 4. Langmuir and Freundlich isotherm constants and experimental values for maximum Arsenic (VI) ions sorbed (q_e) for ACCs at pH values of 4, 6 and 8

Sample	pH	q_e (mmol/g)	Langmuir isotherm constants			Freundlich isotherm constants		
			q_{max} (mmol/g)	B	R^2	K_f	1/n	R^2
As-received ACC	4	1.79	1.96	2.685	0.996	1.124	0.345	0.856
As-received ACC	6	0.78	0.815	2.785	0.998	0.506	0.264	0.851
As-received ACC	8	0.074	0.0799	1.326	0.987	0.043	0.297	0.896
EO ACC	4	0.173	0.208	0.838	0.993	0.089	0.366	0.889
EO ACC	6	0.44	0.448	2.048	0.977	0.265	0.277	0.883
EO ACC	8	0.84	0.83	6.394	0.99	0.658	0.131	0.886

3.8.2. Effect of Electrochemical Oxidation on Arsenic (VI) Sorption Equilibrium

Figure 8 shows Arsenic(VI) sorption of as-received ACC and EO ACC evaluated at pH 4. Maximum Arsenic(VI) sorption capacities of as-received ACC and EO ACC are 1.79 and 0.173 mmol/g, respectively. The sorption capacity of EO ACC is 10.35 times lower than the sorption capacity of the as-received ACC.

Figure 9 shows the Arsenic (VI) sorption of as-received ACC and EO ACC evaluated at pH 6. The maximum Arsenic(VI) sorption capacities of as-received ACC and EO ACC are 0.78 and 0.44 mmol/g, respectively. The Arsenic(VI) sorption capacity EO ACC is 1.77 times lower than the sorption capacity of as-received ACC.

Figure 10 shows Arsenic(VI) sorption of as-received ACC and EO ACC evaluated at pH 8. Maximum Arsenic(VI) sorption capacities of as-received ACC and EO ACC are 0.074 and 0.84 mmol/g, respectively. The Arsenic (VI) sorption capacity of EO ACC is 11.35 times higher than the sorption capacity of as-received ACC.

The highest Arsenic(VI) sorption capacity in all the batch sorption experiments was Arsenic(VI) sorption capacity of EO ACC at pH 8 (i.e. 0.84 mmol/g).. This is directly related to the increase in more acidic oxygen containing functional groups (carboxylic acid groups) as detected by the elemental analysis, sodium capacity and pH titration results. Therefore, adsorption of Arsenic(VI) onto EO ACC is by reduction of Arsenic(VI) to Arsenic (III) by the hydroxyl groups on EO ACC and sorption of Arsenic(III) ions onto the negatively charged surface of EO ACC due to dissociation of the carboxylic groups. This is attributed to the fact that, though all the carboxylic groups on EO ACC dissociated completely at pH 8, the quantity of hydroxyl groups on the EO ACC for reduction of Arsenic(VI) to Arsenic (III) is limited.

3.8.3. Effect of pH on Arsenic(VI) Sorption

The effect of pH on the removal of Arsenic(VI) was investigated by determining sorption isotherms of Arsenic onto as-received ACC and EO ACC at solution pH values of 4, 6 and 8. The maximum Arsenic(VI) sorption capacities of as-received ACC, at pH 4, 6 and 8 are 1.79, 0.78 and 0.074 mmol/g, respectively. The maximum Arsenic(VI) sorption capacity decreased with an increase in solution pH for as-received ACC. It decreased by a factor of 2.3 times with an increase in solution pH from 4 to 6. With a further increase in solution pH from 6 to 8 the maximum sorption capacity decreased by a factor of 10.5 times. The effect of pH on the sorption isotherms was due to interactions between Arsenic(VI) ions in solution and the surface charge on the as-received ACC. The PZC for as-received ACC is pH 6.8. Therefore at pH 4 the surface is positively charged due to protonation of hydroxyl groups which results in high Arsenic(VI) sorption capacity. As pH of the solution increased to pH 6 the as-received ACC undergoes deprotonation and the Arsenic(VI) sorption capacity decreases. As pH of the solution increased to pH 8 which is above the PZC of the as-received ACC, it becomes negatively charged due to dissociation of hydroxyl functional groups and can only adsorb the Arsenic(III) ions produced by reduction of Arsenic(VI). However, the dissociation of the hydroxyl groups is small since the difference between pH 8 and the PZC is small, therefore the Arsenic(VI) sorption capacity of as-received ACC at pH 8 is very low. The maximum Arsenic(VI) sorption capacities of EO ACC at pH 4, 6 and 8 are 0.173, 0.44 and 0.84 mmol/g, respectively. The maximum sorption capacity increased with an increase in solution pH. It increased by a factor of 2.54 times with an increase in solution pH from 4 to 6. With a further increase in solution pH from 6 to 8, the maximum sorption capacity increased by a factor of 1.91 times. The effect of pH on the sorption isotherms was due to interactions between Arsenic(VI) ions in solution and the surface charge on the EO ACC. The PZC for EO ACC is at pH 2.8. Therefore at pH 4, 6 and 8 the EO ACC was negatively charged due to dissociation of carboxylic groups and adsorbed the Arsenic(III) produced by reduction of Arsenic(VI) by the hydroxyl groups on EO ACC. It becomes more negatively charged as the pH increases due to increase in dissociation of the carboxylic functional groups. Hence, the amount of positively charged Arsenic(III) that will ion exchange with the oxygenated functional groups increased with an increase in pH. The reduction in the increase of the maximum sorption capacity with an increase in pH from 6 to 8 as compared to that with an increase in pH from 4 to 6 is attributed to the fact that the number of hydroxyl groups on EO ACC for reduction of Arsenic(VI) to Arsenic (III) is limited. It is also noticeable from Figure 16 that the maximum sorption capacity is low for the sorption isotherm for pH 4. This is due to the fact that at pH 4, the dissociation of carboxylic functional groups is low. Also the concentration of H^+ ions is high and will react with the few anionic functional groups on the surface of the EO ACC thereby restricting the number of binding sites for Arsenic (III) ions.

3.8.4. Mechanism of Arsenic (VI) Sorption onto as-received ACC and EO ACC

To elucidate the sorption mechanism of Arsenic(VI) onto as-received ACC and EO ACC, it is necessary to understand the interactions among the metal ions in aqueous solution with the surface functional groups of the ACCs. The PZC for as-received ACC and EO ACC are at pH 6.8 and 2.8, respectively. At pH 4 and 6, which are below the PZC for as-received ACC, the surface of the as-received ACC was positively charged due to protonation of hydroxyl groups, therefore, it behaved as an anion exchanger indicating that the sorption process was ion exchange. During the Arsenic(VI) sorption process, cleavage occurs on the protonated surface of as-received ACC to release OH^- ions into the solution. This explains why the solution pH increased during the sorption process and so was adjusted by adding specific volumes of 0.1 M nitric acid to maintain solution pH at 4 and 6. However at pH 8, which is above the PZC, the surface of the as-received ACC surface was positively charged due to the dissociation of hydroxyl groups, therefore, it behaved as a cation exchanger and could only adsorb Arsenic(III) that is in cationic form indicating that the sorption process was ion exchange. This explains why the solution pH decreased during the sorption process indicating that H^+ ions were released from the surface of the as-received ACC. The pH was adjusted by adding specific volumes of 0.1 M sodium hydroxide to maintain the pH 8. Mass balances to obtain the maximum H^+ or OH^- ions released were

Table 5. Experimental values for maximum As(VI) ions sorbed onto ACCs and H^+ or OH^- ion released from ACCs

Sample	pH	Maximum Arsenic(VI) ion sorbed (mmol/g)	Maximum H^+ ion released (mmol/g)	Maximum OH^- ion released (mmol/g)	Ratio of maximum H^+ or OH^- ion released to maximum Arsenic(VI) ion sorbed
As received ACC	4	1.79	0	1.826	1.02
As received ACC	6	0.78	0	1.178	1.51
As received ACC	8	0.074	0.237	0	3.2
EO ACC	4	0.173	0.529	0	3.06
EO ACC	6	0.44	1.352	0	3.07
EO ACC	8	0.84	2.425	0	2.89

performed using the volumes of 0.1 M sodium hydroxide or nitric acid added to adjust the solution pH. The experimentally determined Arsenic ions sorbed onto as-received ACC and H^+ or OH^- ions released from its surface are shown in Table 5. At pH 4 one Arsenic(VI) ion was sorbed for approximately every one OH^- ion released from as-received ACC surface. This confirms that sorption of Arsenic(VI) onto the as-received ACC is mainly governed by ion exchange mechanism, since the speciation curves show that at pH 4 Arsenic exists as AsO_4^- in proportion of 78.05%. Therefore, it is expected that for every Arsenic ion sorbed, one OH^- ion will be released from the as-received ACC. At pH 6, two Arsenic(VI) ions were sorbed for approximately every three OH^- ions released from the as-received ACC surface. This confirms that the sorption of Arsenic(VI) onto as-received ACC is mainly governed by ion exchange mechanism, since the speciation curves show that at pH 6, Arsenic exists as AsO_4^- in proportion of 57.2% and as AsO_4^{2-} and $As_2O_7^{2-}$ in proportion of 43%. Therefore, it is expected that for two arsenic ions sorbed, three OH^- ions will be released from the as-received ACC. At pH 8, one As^{3+} ion was sorbed for approximately every three H^+ ions released from the as-received ACC surface. This confirms that the sorption of Arsenic(III) onto as-received ACC is mainly governed by ion exchange mechanism. The sorption sites on all the as-received ACC are mainly hydroxyl functional groups. Therefore, the ion exchange mechanism involving the interaction of the hydroxyl sites of as-received ACC can be represented by the following reaction schemes:

At pH 4 the reactions are:

$S\text{-}OH+H_2O \rightarrow S\text{-}O^+(H_2)+OH^-$ (3)

$S\text{-}O^+(H_2)+HAsO_4^- \rightarrow SHAsO_4+H_2O$ (4)

Where S is the surface of the as-received ACC. Combining equations (3) and (4) gives:

$S\text{-}OH+HAsO_4^- \rightarrow SHAsO_4+OH^-$ (5)

At pH 6 the reactions are: equation (5) and

$2S\text{-}OH+2H_2O \rightarrow 2S\text{-}O^+(H_2)+2OH^-$ (6)

$2S\text{-}O^+(H_2)+As_2O_7^{2-} \rightarrow SAs_2O_7S+2H_2O$ (7)

Combining equations (6) and (7) gives:

$2S\text{-}OH+As_2O_7^{2-} \rightarrow SAs_2O_7S+2OH^-$ (8)

At pH 8 the reactions are:

Reduction of Arsenic(VI) by hydroxyl groups:

$ACC+AsO_4^{2-} \rightarrow As^{3+}+H_2O+ACC(oxidised)$ (9)

Adsorption of As^{3+}:

$3S\text{-}OH+As^{3+} \rightarrow (S\text{-}O)_3As+3H^+$ (10)

The pH at which the batch sorption experiments were performed i.e. pH 4, 6 and 8 are above the PZC of EO ACC. Hence, the surface of the EO ACC was negatively charged due to dissociation of carboxylic groups. Therefore, EO ACC behaved as a cation exchanger in all the batch sorption experiments and could only adsorb Arsenic(III) that is in cationic form indicating that the sorption process was ion exchange. This explains why the solution pH decreased during the sorption process indicating that H^+ ions were released from the surface of the EO ACC. The pH was adjusted by adding specific volumes of 0.1 M sodium hydroxide to maintain the initial pH. Mass balances 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 Arsenic ions sorbed onto EO ACC and H^+ ion released from EO ACC are shown in Table 5. At pH 4, 6 and 8, one As^{3+} ion was sorbed for approximately every three H^+ ions released from the EO ACC surface. This confirms that the sorption of Arsenic (III) onto EO ACC is mainly governed by ion exchange mechanism. The sorption sites on the EO ACC are mainly carboxylic functional groups. Therefore, the ion exchange mechanism involving the interaction of the carboxylic sites of EO ACC can be represented by the following reaction schemes:

Reduction of Arsenic (VI) by hydroxyl groups takes place as shown in equation (9).

Adsorption of As^{3+}:

$3(S''\text{—}COOH)+As^{3+} \leftrightarrow (S''\text{—}COO)_3As+3H^+$ (11)

Where S'' is the surface of EO ACC.

CONCLUSIONS

This work demonstrates that electrochemically oxidised ACC can be used as an effective sorbent for treating basic or neutral aqueous solutions contaminated with Arsenic(VI). Arsenic(VI) sorption capacity of ACC increased by a factor of 11.35 times at pH 8 for electrochemically oxidised ACC. The highest Arsenic(VI) sorption capacity in all the batch sorption experiments was found to be for electrochemically oxidised ACC at solution pH 8 (i.e. 0.84 mmol/g). It was 11.35 times higher than the Arsenic(VI) sorption capacity of as-received ACC at solution pH 8 (i.e. 0.074 mmol/g). The solution pH plays a very important role on the sorption of Arsenic(VI) ions onto as-received ACC and electrochemically oxidised ACC. The uptake of Arsenic(VI) ions increased with an increase in solution pH for electrochemically oxidised ACC. It is confirmed that Arsenic(VI) ions were sorbed onto all the ACCs mainly by ion exchange mechanisms. However, Arsenic was adsorbed onto electrochemically oxidised ACC in cationic form due to reduction of Arsenic (VI) ions to Arsenic (III) ions by hydroxyl functional groups on the ACCs. The present study concludes that electrochemical oxidation of viscose rayon based

ACC markedly enhanced the removal of Arsenic(VI) ions from aqueous solutions.

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