

SURFACE PROPERTIES OF ELECTROCHEMICALLY REDUCED VISCOSE RAYON BASED CARBON FIBRE

*I. D. HARRY

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ABSTRACT

A viscose rayon based activated carbon cloth (ACC) was electrochemically reduced under a wide variety of current conditions to modify the surface properties. The change in the surface properties was physically and chemically characterised. The anion exchange capacity of ACC increased with an increase in the extent of reduction. Electrochemical reduction resulted in a loss of 28% BET surface area due to formation of ether groups but its anion exchange capacity increased by 292%. The optimum constant current at which a combination of applied current and reduction time at any extent of reduction to produce ACC of maximum anion exchange capacity was found to be 5.5 A, with voltage of 9.8 V and current density of 6.4 mA/m².

INTRODUCTION

Elements in small amounts are called trace elements and are essential for effective catalytic activities of various enzymes [1]. Chromium exists in aqueous solutions mainly in two states: trivalent, (chromium(III)) and hexavalent, (chromium(VI)). chromium(VI) is primarily present in the form of chromate (CrO₄²⁻) and dichromate (CrO₇²⁻) ions [1 – 3]. Therefore chromium exists as toxic anions. Chromium(III) is required for normal carbohydrate metabolism in mammals. Chromium(III) deficiency in humans and other mammals result in symptoms like diabetes and cardiovascular disease: decreased glucose tolerance, increased concentrations of circulating insulin, elevated cholesterol and triglyceride levels [4]. In contrast chromium(VI) is toxic, carcinogenic, mutagenic and tetratogenic [2 – 5]. The major source of water contamination with chromium ions is industrial wastewaters from industrial processes such as leather tanning, electroplating, manufacturing of dye, paint and paper, glass making and automobile parts manufacturing [5 – 9]. Unlike organic pollutants in water, which are often biodegraded, metal ions are nondegradable and can accumulate in living tissues [6].

There are various methods for removing heavy metals, including chemical precipitation, membrane filtration, electro dialysis, biological processes, reverse osmosis and adsorption [3, 6]. Among these methods, adsorption onto activated carbon is a widely applied method and is economically favourable and technically easier [2, 6, 7, 9 – 12]. 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, therefore, sorption area in ACC can be accessed more easily than in other forms [13]. Generally, intraparticle diffusion in GAC is very slow and this makes the overall rate of sorption very slow [14]. For PAC processes, the overall rate of sorption is very fast, but PAC presents the disadvantage of complicated handling. The overall rate of sorption

*corresponding author Email: ibharry2001@yahoo.com. Tel: +22348064494108; (I. D. Harry)

I. D. Harry, Department of Chemical/Petrochemical Engineering, Rivers State University of Science and Technology, Nkpolu-Oroworukwo, P.M.B. 5080, Port Harcourt, Nigeria.

in ACC is as fast as PAC but it does not have the handling problems existing in PAC. Information published in literature showed no study of adsorption of toxic anions from solutions onto electrochemically reduced adsorbent. Therefore, in the present investigation, a viscose rayon based ACC was electrochemically reduced at different extent of reduction. To achieve the optimum constant current, three series of experiments were performed at different extents of electrochemical reduction, 15,840 c/g, 23,760 c/g and 47,520 c/g. (coulomb/g). The amount and nature of the surface functional groups were characterised by chloride ions uptake, pH titration, zeta potential measurements, elemental analysis, Fourier transform infrared (FTIR) spectroscopy, Brunauer-Emmett-Teller (BET) surface area, pore size distribution (PSD) and scanning electron microscopy (SEM).

Materials and Methods

2.1. Materials

A viscose rayon based activated carbon cloth (ACC), ZORFLEX[®] 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 Reduction

Viscose rayon based activated carbon cloth; ZORFLEX[®] FM 10 in hydrogen form was reduced 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 gm of ACC was wrapped round the cathode (platinised titanium) and immersed in 0.5 M potassium chloride for 1 h prior to the electrochemical reduction process. The schematic of the electrochemical cell used for reduction is shown in Figure 1. Two anodes (platinised titanium) were used as counter electrodes. As shown in

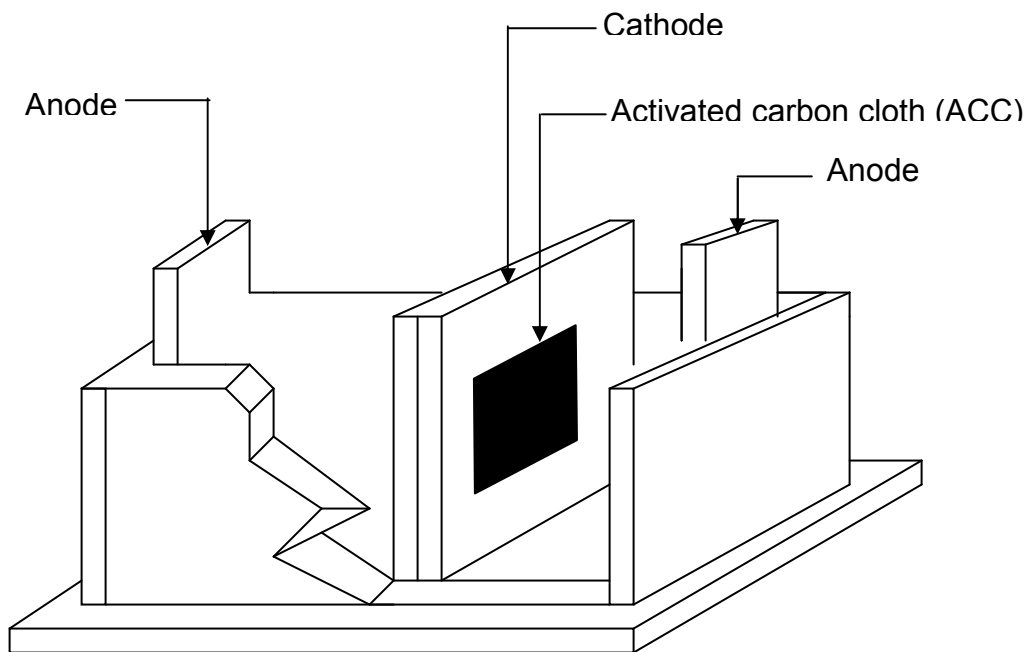


Figure 1. Schematic of the electrochemical cell used for electrochemical reduction.

Figure 1, the anodes were placed at equal distance from the cathode to achieve uniform surface electrochemical reduction of the ACC. To obtain an optimum condition for electrochemical

reduction, the process was carried out at constant currents ranging from 1.1 to 8.8 A at different reduction times (e.g. 0.5-12 h). For each reduction the chosen current was kept constant

by adjusting the voltage throughout the chosen reduction time and using fresh electrolyte each time. After reduction, the reduced ACC was washed with deionised water until the conductivity of the washed water reached the same value as the conductivity of deionised water. The reduced ACC was dried in an oven at 383 K for 24 h, put in a desiccator overnight and then weighed.

2.3. Chloride Capacity Determination

Chloride sorption capacity was determined in order to compare the anion exchange capacity of electrochemically reduced ACC and as-received ACC in aqueous solution. The chloride sorption capacity gives an indication of the anion exchange capacity of adsorbents in aqueous solution which is related to the quantity of basic functional groups generated upon electrochemical reduction. A series of experiments were conducted to determine the total chloride capacity of electrochemically reduced and as-received ACCs as follows: 0.2 g of electrochemically reduced or as-received ACC was placed in a 50 ml conical flask containing 25 ml of 0.1 M volumetric standard hydrochloric acid. The flasks were sealed with parafilm to avoid spillage and were agitated in a 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 sodium hydroxide using phenolphthalein as an indicator.

2.4 pH Titration

This technique determines the acidic and basic properties of ion exchangers and the nature of the functional surface groups. 0.025 g of electrochemically reduced or as-received ACC was weighed using Sartorius BP 210 D balance (± 0.0005 g accuracy) and placed in a 50 ml conical flask. 20 ml of 0.1 M sodium chloride was added to each flask. A pre-determined volume of 0-2 ml of 0.1 M hydrochloric acid or 0.1 M sodium hydroxide was added to each flask to obtain a shape of curve over a pH range of 2-12. The pH of the solution in each flask, prior to the addition of the adsorbent was measured using a Mettler-Toledo 340 digital pH meter. The flasks were sealed with parafilm and were 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 the solutions with adsorbent and the solutions of the blank experiments were measured after 48 h. The

solutions with the adsorbent were then filtered. The supernatant solutions and the solutions of the blank experiments were then 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. The total H^+ or OH^- ions released by the ACC at a particular pH value was calculated from the difference between the volume of sodium hydroxide or hydrochloric acid used to back titrate the supernatant solutions for the solutions with the ACC and the blank solutions using the following equation:

$$IR = \frac{C(V_b - V_a)}{ACC_m} \quad (1)$$

where C is the titrant concentration (0.1 M), IR is the ion released in mmol/g, V_b is the volume of titrant used to back titrate the blank solution at a given pH, V_a is the volume of titrant used to back titrate the supernatant solution with adsorbent at a given solution pH and ACC_m is the mass of ACC (0.025 g).

2.5. Zeta potential measurement

Zeta potential measurements were performed on a Malvern Zetamaster 3000HS_A. The electrochemically reduced or as-received ACC was cut to small pieces, finely ground and sieved to obtain particle size $< 45 \mu\text{m}$. 0.025 g of finely ground electrochemically reduced or as-received ACC was weighed using a Sartorius BP 210 D balance (± 0.0005 g accuracy) and placed in a 50 ml conical flask. 20 ml of 0.1 M sodium chloride was added to each flask. The volume (0-20 ml) of 0.1 M hydrochloric acid or 0.1 M sodium hydroxide was added to each flask to obtain a shape of curve over a pH range of 1-12. The flasks were sealed with parafilm and were agitated in a Brunswick C25 series incubator shaker at 298 K and at 150 rpm for 48 h. The equilibrium pH of the solution in each flask was measured using a Mettler-Toledo 340 digital pH meter after which the zeta potential was measured. 5 ml aliquots of adsorbent suspensions were injected directly into the electrophoretic quartz cell with a plastic Luer syringe. Each sample was measured three times to provide an average reading. The cell was rinsed after each measurement with 40 ml of deionised water.

2.6. Elemental analysis

The ACC 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 accurately weighed (1-2 mg) and wrapped in tin foil prior to analysis. The combustion of the sample was done in the combustion tube at 2073 K in a controlled environment in the presence of pure oxygen after purging the system 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 percentage of carbon, hydrogen and nitrogen. The oxygen content was determined by difference.

2.7. Fourier transform infra red (FTIR) spectroscopy analysis

The surface chemistry of the ACCs was analysed by FTIR spectroscopy. The samples were dried at 383 K for 24 h and stored in a desiccator before use. All the samples were cut to small pieces and then finely crushed with a mortar and pestle. The samples were mixed with finely crushed spectroscopic grade potassium bromide in the ratio of 1:100. Thin pellets were prepared by subjecting the mixture of the samples and potassium bromide to a load of 10 tonnes. The Spectra were recorded on a Mattson 3000 FTIR spectrometer at a resolution of 4 cm^{-1} at 64 scans.

2.8. Surface area and pore size distribution

Brunauer-Emmet-Teller (BET) Surface area and pore size distribution measurements of ACCs were done by nitrogen adsorption and desorption method using a Micromeritics ASAP (Accelerated Surface Area and Porosimetry) 2000 surface analyser. The samples were weighed and then out-gassed at 393 K under a vacuum of less than 10 mm Hg on degas ports of the analyser for a minimum period of 24 h. The adsorption isotherms were generated by dosing 99.99% pure nitrogen onto the samples within a bath of liquid nitrogen at a temperature of 77 K. The mass of the degassed sample was determined by subtracting the weight of the

degassed empty tube from the nitrogen back-filled sample containing tube. The Density Functional Theory (DFT) model was used to determine the pore size distribution.

2.9. Scanning electron microscopy (SEM)

The surface morphology of each ACC was observed using SEM. The SEM of the ACCs were taken on Carl Zeiss 1530 field emission microscopy at room temperature. The bath normal secondary electron mode was used at an accelerating voltage of 5 kV. Prior to observation, the samples were dried in an oven at 383 K for 24 h and stored in a desiccator overnight. The samples were then attached onto aluminium platforms using PVA glue and coated with gold.

Results and discussion

3.1. Chloride Capacity

In order to achieve the optimum constant current, three series of experiments were performed at different extents of electrochemical reduction, 15,840 c/g, 23,760 c/g and 47,520 c/g. The extent of electrochemical reduction is defined as the product of current and electrochemical reduction time in coulomb per gram (c/g) of ACC. For each series of experiment, the ACCs were electrochemically reduced at different currents of 1.1, 2.2, 3.3, 4.4, 5.5, 6.6, 7.7 and 8.8 A. Plots of the chloride 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 results show that chloride capacity for ACCs reduced below 5.5 A were lower than that at 5.5 A. This is attributed to the fact that applied currents below 5.5 A do not produce sufficiently vigorous reducing conditions. The chloride capacity for reduced ACCs reached a maximum at 5.5 A and then decreased continuously with increasing applied current. The lowest chloride capacity was observed for ACCs electrochemically reduced at 8.8 A. This is attributed to the

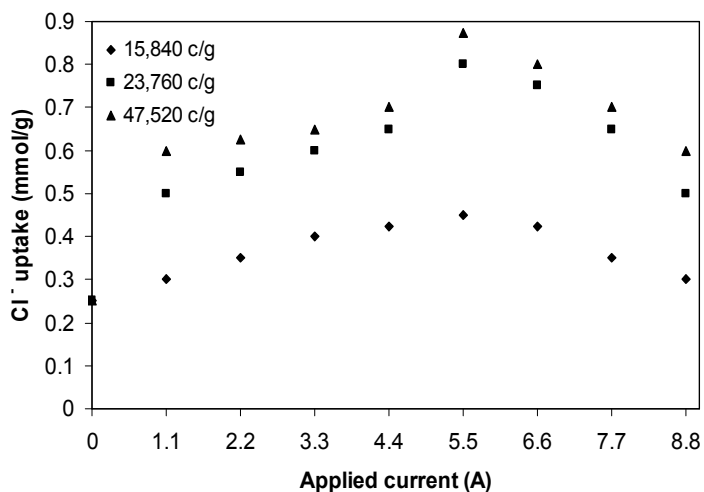


Figure 2. Chloride capacity versus applied current for different extents of electrochemical reduction.

fact that though 8.8 A is the highest current, the small time of the electrochemical reduction of 30 min, 45 min and 90 min were not enough for effective reduction of most of the cellulose molecules in the ACC matrix. The optimum current was found to be 5.5 A for all electrochemical reduction times. It is to be noted that above 59,400 c/g extent of oxidation, the ACCs become fragile and are not suitable for adsorption studies. The maximum chloride capacity for electrochemically reduced ACC was obtained at 5.5 A for 2.4 h (i.e. 47,520 c/g extent of reduction), which is 0.875 mmol/g and for as-received ACC in hydrogen form (i. e. the value at 0 A), it is 0.25 mmol/g. Therefore, the chloride capacity for electrochemically reduced ACC is 3.5 times higher than that of the as-received ACC in hydrogen form. This increase is attributed to the introduction of more basic functional groups by electrochemical reduction. The highest chloride capacity without breakage of fibres was observed on electrochemically reduced ACC at 5.5 A for 3 h. For this reason electrochemical

reduction of ACC at 5.5 A for 3 h was used for the remaining reduction experiments. The total anion exchange capacity (i.e. the quantity of basic functional groups) was determined in hydrochloric acid solution. Oxygen-containing groups like carbonyl, ether, hydroxyl, phenolic and lactonic groups present on carbonaceous materials are protonated increasingly with a decrease in solution pH values. Therefore, these surface groups are completely protonated in solutions at low pH and are available for anion exchange. Under this condition the total anion exchange capacity can be determined. A high chloride capacity is an indication of a high content of basic surface oxygen functional groups. Preliminary experiments measuring chloride capacity indicated that best adsorption took place using a current of 5.5 A or 6.6 A. Chloride capacity results for as-received ACC and electrochemically reduced ACCs at 5.5 A and 6.6 A are shown in Figure 3. The results in Figure 3 show that the chloride capacity of electrochemically

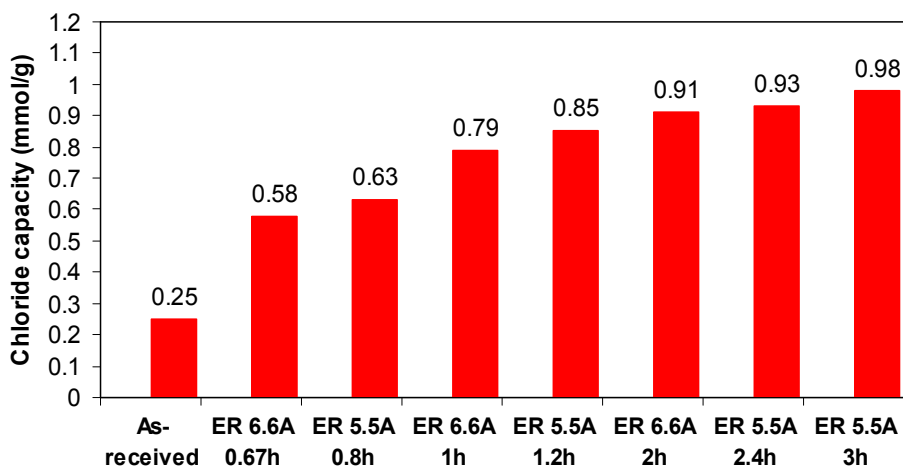


Figure 3. Chloride capacity result for as-received ACC and electrochemically reduced (ER) ACC at different conditions.

reduced ACC at 5.5 A for 3 h is 3.9 times higher than that of as-received ACC. This is attributed to the introduction of basic functional groups. The extent of reduction on the carbon surface depends on the composition of the electrolyte. It is obvious that the potassium chloride is a very strong reductant. Since the reduction and oxidation processes are responsible for the overall reaction in an electrolytic cell, the presence of strong oxidant and strong reductant explains why the ACC is strongly reduced when potassium chloride is used as an electrolyte. The chloride capacity data gives an indication of the

anion exchange capacity of the ACC in aqueous solution. So ACC, electrochemically reduced in potassium chloride has a high potential for toxic anion removal from aqueous solutions.

A plot of the hydrochloric acid uptake (chloride capacity) *versus* the extent of electrochemical reduction of ACC at a constant time of 4 h but at different currents of 0, 1.1, 2.2, 3.3 and 5.5 A are shown in Figure 4. The extent of electrochemical reduction is defined as the product of current and electrochemical reduction time in coulomb per gram (c/g) of ACC. Figure 4 shows that the chloride

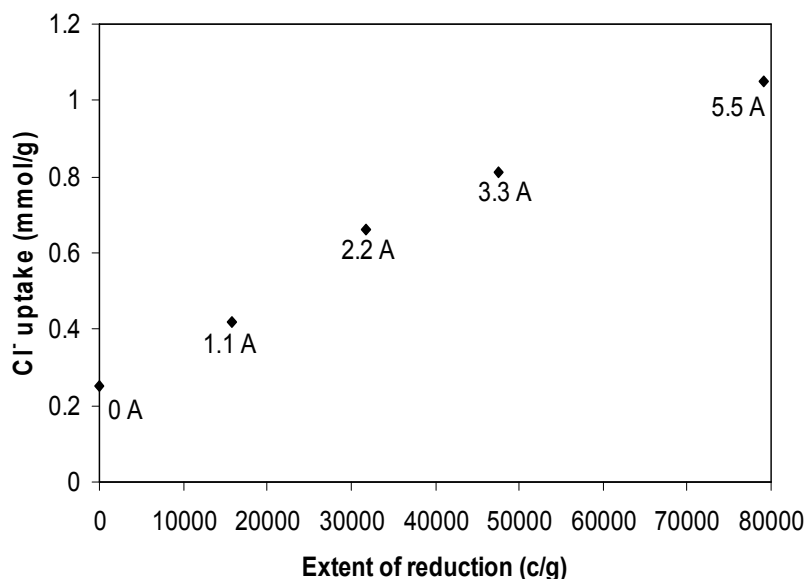


Figure 4. HCl uptake *versus* extent of electrochemical reduction for 4 h at different currents.

capacity is in direct proportion to the extent of reduction. This is attributed to an increase in the amount of basic functional groups introduced onto the surface of the ACC as the reduction process increased with an increase in current. This also suggests that it is not just the total current that passed through the electrolyte to the cathode (i.e. the ACC) that is important. The chemical conditions at the cathode are very complex. As the electrolyte was potassium chloride, chlorine, oxygen and hypochlorous acid were evolved at the anode. Hydrogen and carbon dioxide were also evolved at the cathode. The composition of these products will depend on the current used as well as the diffusion processes at

the electrodes. Therefore, the generation of exchangeable groups on the ACC depends on both current used for electrochemical reduction as well as the total coulombs (i.e. product of current and reduction time) passed through the solution. In order to observe the effect of reduction time, a series of electrochemical reductions of ACC were performed at a constant current of 5.5 A, but at different periods of reduction 0, 0.8, 1.2, 1.6, 2.4, 3 and 4 h to achieve different extents of reduction. The plot of hydrochloric acid uptake *versus* the extent of reduction at constant current is shown in Figure 5. It can be seen that

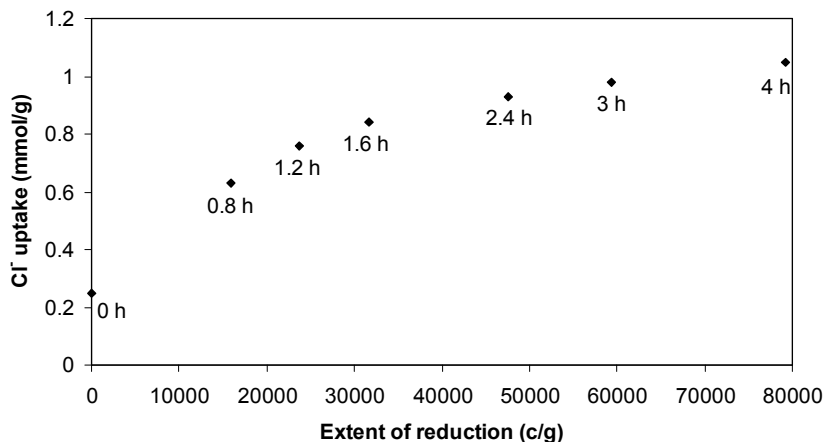


Figure 5. HCl uptake *versus* extent of electrochemical reduction at 5.5 A for different reduction times.

the chloride capacity increased rapidly for 31,680 c/g extent of reduction and then further increased at a rate directly proportional to the extent of reduction at constant current of reduction. This is attributed simply to the longer exposure of the ACC to the reducing condition allowing a greater reaction time for the introduction of basic groups on the ACC. The process of manufacturing viscose rayon consists of the following steps: alkalisation, shredding, preripening i.e. ageing, xanthation, dissolving, maturing and viscose fibre spinning [15]. At the spinning stage, the cellulose is regenerated from the viscose for the production of the viscose rayon filament. Therefore, the ACC matrix is composed of interlinking cellulose molecules. At short periods of reduction, some of the cellulose molecules in the viscose rayon based ACC matrix will not be reduced and so the amount of basic functional

groups to be introduced to the surface of the ACC will be less than the amount introduced at long periods of reduction when more of the surface molecules are reduced. The anion exchange capacity of electrochemically reduced ACC depends on both the applied current and the time of reduction, indicating that electrochemical reduction is a diffusion-dependent process.

3.2. pH Titrations

The pH titration curves are usually plotted as equilibrium solution pH versus the amount of H⁺ or OH⁻ ion released by the adsorbent. Proton binding curve, that is the plot of ion released versus equilibrium solution pH, for as-received ACC and ER ACC are shown in Figure 6. The point where the proton

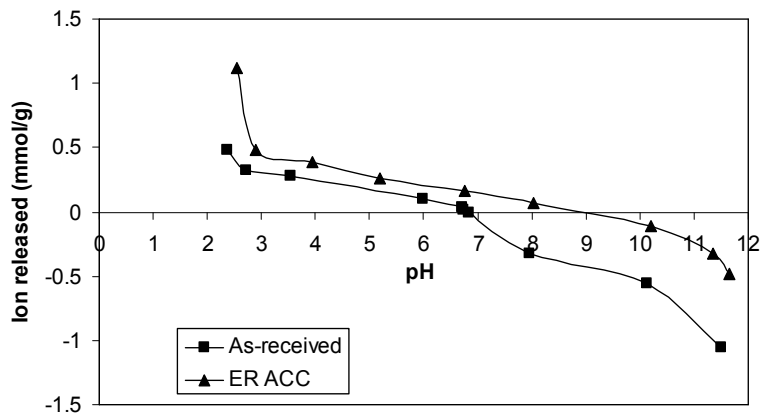


Figure 6. Ion Released *versus* equilibrium solution pH for as-received ACC and ER ACC.

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. The PZC will be shifted to higher pH values with reduction of ACC due to introduction of basic functional groups such as ether, hydroxyl and quinone groups onto the surface of the 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 adsorbent will remove anions from solution under these conditions. The curve for ER ACC shows the highest concentration of hydroxyl ions

released, hence the anion exchange capacity is expected to be higher than that of as-received ACC as shown by the chloride capacity results. It is known that carboxylic groups in activated carbons dissociate at pH values within the range of 2 and 6 and hydroxyl and ether groups dissociate at pH values above 6. From the pH titration curves it can be seen that the dissociation of the acidic functional groups on the as-received ACC, and ER ACC to produce H^+ ions starts at equilibrium solution pH of approximately 7 and 9.5, respectively. Therefore, one of the types of functional groups on the surfaces of as-received ACC and ER ACC are likely to be hydroxyl groups and ether groups, respectively.

3.3. Zeta Potential Measurements

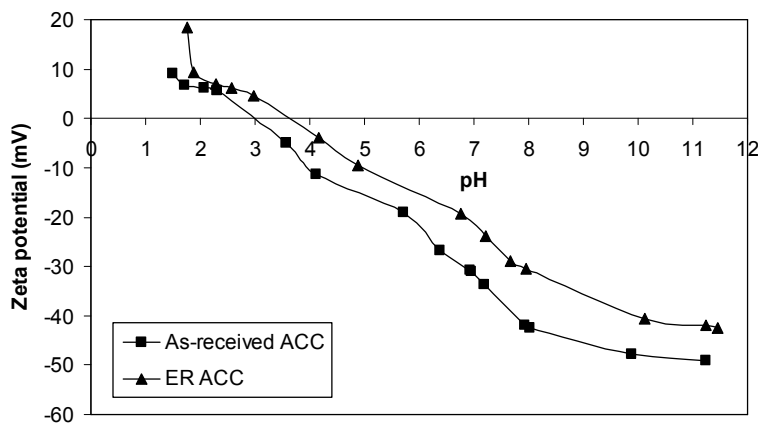


Figure 7. Zeta potential *versus* equilibrium solution pH for as-received ACC and ER ACC.

Figure 7 shows zeta potential versus equilibrium solution pH plots for as-received ACC and ER ACC.

An important parameter used to characterise the electrokinetic behaviour of a solid- liquid interface is the isoelectric point (IEP). This is the equilibrium solution pH at which the zeta potential is zero. The IEP for as-received ACC is 3 while that for ER ACC is 3.6. This shows that ER ACC is more basic than as-received ACC which confirms pH titration results. The higher IEP value for ER ACC is attributed to the presence of more basic functional groups.

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

Sample	C (%)	H (%)	N (%)	O (%)
As-received ACC	76.89	2.03	1.05	20.03
ER ACC	77.35	1.75	1.5	19.4

This result follows the same trend as the chloride capacity results which showed anion exchange capacity of 0.25 mmol/g for as-received ACC and 0.875 mmol/g for ER ACC. The hydrogen content in ER ACC decreased by 13.8%. The decrease in both hydrogen content and oxygen content indicates that the likely reaction on the ACC by electrochemical reduction is dehydration of the hydroxyl functional groups. The small decrease in oxygen content in the ER ACC is attributed to the formation of weakly basic oxygen containing functional groups. It is well known that the more basic oxygen containing functional groups have a lower oxygen content than hydroxyl functional groups and dehydration of two molecules of hydroxyl functional groups produces one

3.4. Elemental Analysis

Elemental analysis results for as-received ACC and ER 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. The oxygen content in ER ACC decreased by 3.2%.

molecule of ether [1]. Therefore one of the types of basic functional groups on the surface of ER ACC is ether groups.

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

Surface areas of as-received ACC and ER ACC were measured by nitrogen adsorption/desorption method. The BET surface area specifications for as-received ACC and ER 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 ER ACC. The results show that

Table 2. Surface area specifications of as-received ACC and ER 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
ER ACC	1024.582	997.683	19.672

ER ACC lost 27.6% of the original BET surface area. The reduction of BET surface area on ER ACC is attributed to the intermolecular reactions within the ACC matrix during electrochemical reduction.

3.6. 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 ER ACC are shown in Figures 8 and 9, respectively. The band assignments are shown in Table 3. The marked difference in the functional groups observed on

the as-received ACC and ER ACC as shown in Table 3 are the presence of aldehyde and ether groups, respectively. Since a cellulose molecule has aldehyde

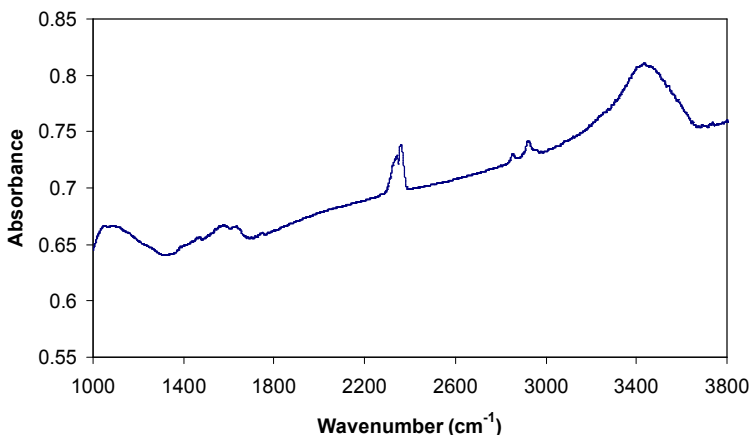


Figure 8. FTIR spectra for as-received ACC.

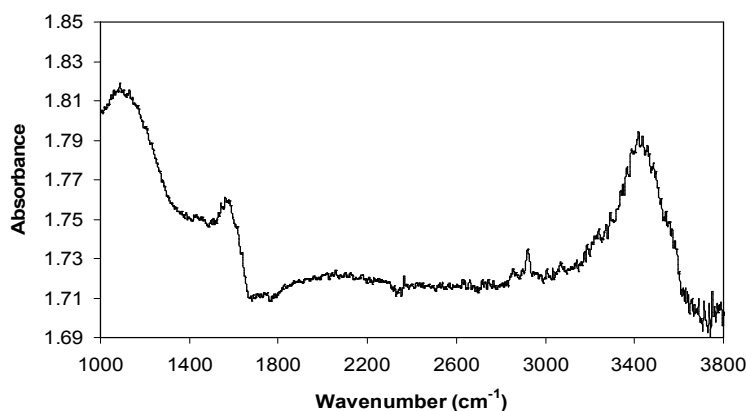


Figure 9. FTIR spectra for ER ACC.

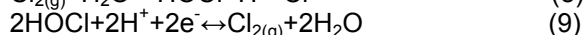
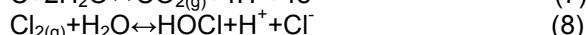
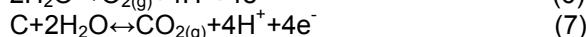
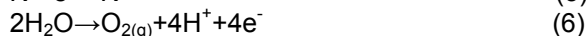
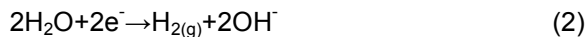
Table 3. Band assignments for FTIR spectra of as-received ACC and ER ACC.

As-received ACC		ER ACC	
Wavenumber (cm ⁻¹)	Band Assignment	Wavenumber (cm ⁻¹)	Band Assignment
3435	- O - H Hydroxyl group	3434	- O - H Hydroxyl group
2851 and 2943	- CHO Aldehyde group	2914	Saturated C - H and C - C
2349	O = C = O	2352	O = C = O
1742	- CHO Aldehyde group	1600	C = O Ketones
1634	C = O Ketones	1383	- CH ₃ deformations
1458	= C - H deformations	1255 and 1218	= C - O - C = Ether
1384	- CH ₃ deformations	1095	= C - O - C = Ether

and hydroxyl ends, it is expected that the ACCs should have aldehyde and hydroxyl functional groups on their surfaces. However, aldehyde groups were not detected on ER ACC, because aldehyde groups readily react with hydroxyl groups to produce ether groups by dehydration [1, 4]. It is also well known that dehydration of two molecules of hydroxyl functional groups produces one molecule of ether [1]. The ether groups observed on ER ACC confirms the pH titration and zeta potential results that showed that ER ACC is more basic than as-received ACC, since the negative logarithm of acidity constants (pKa) for an ether molecule produced by dehydration of two alcohol molecules is larger than the pKa value of the alcohol molecules that produced it [1]. It also confirms the Elemental analysis result that showed that the likely reaction on the ACC by electrochemical reduction is dehydration of the hydroxyl functional groups. This also explains why there was an increase in the chloride capacity of ER ACC after electrochemical reduction in potassium chloride.

3.7. Reactions in Electrochemical Cell

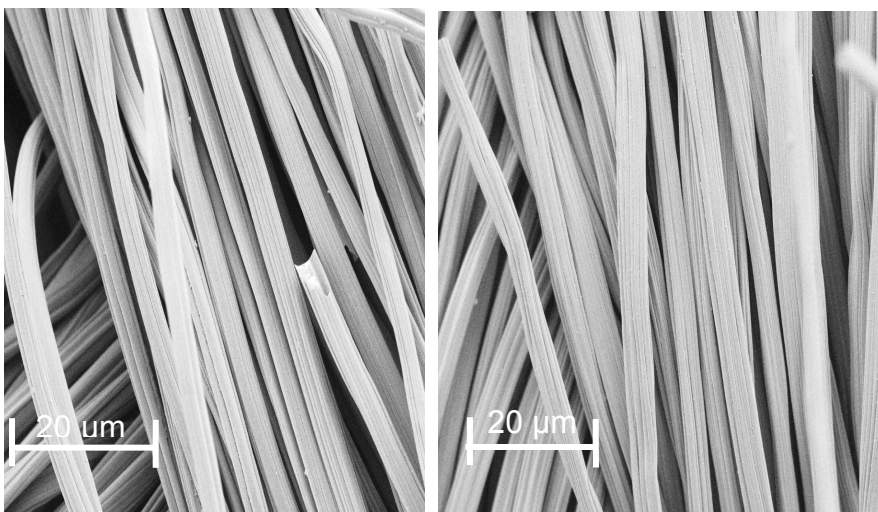
With the confirmation that ether groups are introduced onto the ACC by electrochemical reduction and since it is known that aldehydes and alcohols react to produce ethers in the presence of H^+ by dehydration in the presence of excess alcohols, it is possible to postulate the likely reactions that took place in the electrochemical cell. The reactions most likely to occur are as follows:-



The above reactions show that in reducing environment (e.g. in the presence of Cl^-), all accessible hydroxyl groups in the cellulose $(C_6H_{10}O_5)_n$ molecules of viscose rayon based ACC react with aldehyde groups to produce ether groups by dehydration. Hence from the above reactions scheme it can be concluded that the reduction of the aldehyde and hydroxyl groups within the cellulose molecules in the ACC to produce ethers are the most likely reactions that occurred during the electrochemical reduction of viscose rayon based ACC in the electrochemical cell.

3.8. Scanning Electron Microscopy (SEM)

Scanning electron micrographs (SEMs) of as-received ACC and ER ACC used in this investigation are shown in Figure 10. The micrographs of the two ACCs are very similar. Therefore, no significant breakage of fibres was observed during electrochemical reduction of ACC at 5.5 A for 3 h. Therefore all ACCs used in this investigation are suitable for adsorption studies.



(a) As received ACC (b) ER CC
Figure 10. SEM of ACCs: (a) as -received ACC and (b) ER ACC.

CONCLUSIONS

It has been shown that electrochemical reduction of a viscose rayon based ACC using potassium chloride as an electrolyte introduced weakly basic functional groups on the surface of the ACC as indicated by pH titration, chloride capacity measurements, zeta potential and elemental analyses results. This was also confirmed by the FTIR spectra that showed the presence of ether groups on the electrochemically reduced ACC. A significant increase in anion exchange capacity for ACC was obtained by electrochemical reduction and it increased with an increase in the extent of reduction. This is due to the introduction of ether groups onto the ACC. It has also been shown that the extent of electrochemical reduction depends on both the applied current and reduction time showing that electrochemical reduction is both a diffusion-dependent and current-dependent process. The optimum constant current at which a combination of applied current and reduction time at any extent of reduction used in this study to produce ACC of maximum anion exchange capacity was 5.5 A with voltage of 9.8 V and current density of 6.4 mA/m². The PZC and IEP shifted to higher pH values for the electrochemically reduced ACC due to the introduction of ether groups during electrochemical reduction. However, a small decrease in BET surface area by electrochemical reduction was observed, which was due to the cross-linking by bond formation between hydroxyl groups within the ACC matrix that reacted with other hydroxyl groups and aldehyde groups to produce ether groups during the electrochemical reduction. However, the production of ether from hydroxyl and aldehyde also involved dehydration, which produced some micropores, thereby, reducing the decrease in the BET surface area. Pore size distribution was not altered by electrochemical reduction.

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