

ADSORPTION OF ZINC ON NITRIC ACID AND OZONE OXIDIZED ACTIVATED CARBON FIBERS

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Introduction

Activated carbon fibres are a new breed of high strength materials. They are also used as adsorbents for removing a wide range of pollutants. This application arises from the properties they possess such as high surface area, wide range of porosity and the presence of various forms of functional groups on their surface [1]. The introduction of the above properties on the surface of activated carbons is a consequence of activation, which nowadays has been reported to take place by using different substances both in liquid and gaseous forms [2-5].

In the present work, nitric acid and ozone oxidations have been employed for modifying a conventional activated polyacrylonitrile (PAN) carbon fibre, AW1501. These surface modifications have been carried out in order to introduce various acidic functional groups capable of heavy metal binding. The heavy metal of interest in this study has been zinc since it is amongst the most important pollutants in source and treated water [6,7].

Scanning electron microscopy (SEM), sodium capacity determination, point of zero charge measurement and X-ray photoelectron spectroscopy (XPS) techniques were employed for investigating the physical morphology as well as the chemical properties of the modified and as-received samples. The effect of different oxidation time and subsequent treatment was also assessed.

Experimental

Nitric Acid Oxidation

Nitric acid oxidation was performed by using 70% concentrated nitric acid. Figure 1 shows the apparatus used for this purpose. The preparation of the sample before oxidation involved drying in an oven at 105°C for 24 hrs. The sample (1g) was then placed in the reactor (See Figure 1) and oxidised at a temperature of 80-85°C with 500 ml of nitric acid. The different times employed for oxidations were 1, 1.5, 2 and 3 hours. After oxidation, the samples were placed in a column and washed with distilled water until the pH of the water in the inlet and the outlet reached the same value. The washing of the fibres with distilled water was essential in order to ensure that all the excess of nitric acid is removed from the fibre surface and therefore the oxidation is terminated. After washing, the samples

were dried and the dried samples were placed in properly sealed plastic bags prior to characterisation.

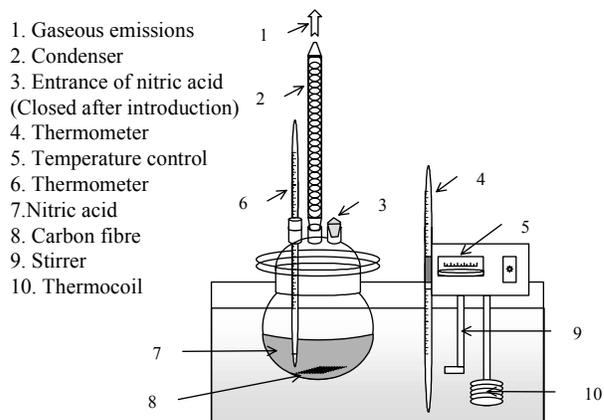


Figure 1. Apparatus for nitric acid (HNO₃) oxidation.

Ozone Oxidation

Activation of the carbon fibres also resulted by oxidation in a dry environment. Ozone (O₃) was used for this purpose and the apparatus set-up can be seen in Figure 2. Before ozone oxidation 1g of fibre was placed in an oven at 105°C for 24 hours.

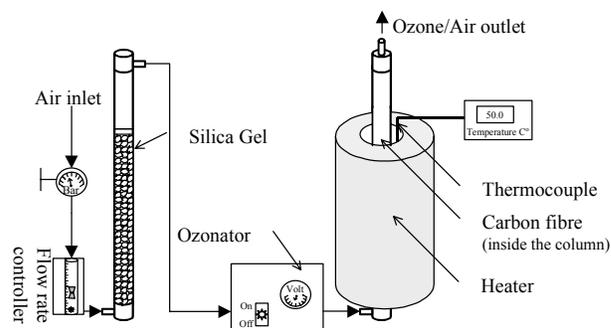


Figure 2. Apparatus for ozone (O₃) oxidation.

The flow rate of air was controlled by a flow meter at 1800 cm³.min⁻¹ and was always kept constant. The air was allowed to enter the bottom of a cylindrical column filled with silica gel in order for the moisture to be absorbed. The top of the column was connected to the inlet of the ozonator. The exit of the ozonator was connected to a

second column containing the carbon fibre sample. The oxidation of the sample commenced as soon as ozone was produced. It is to be noted that the second column was heated up by a heater and the temperature was kept constant at 50 ± 5 °C throughout the experiment. The samples were oxidised for 0.5, 0.75, 1 and 2 hrs, respectively. After treatment the samples were cooled down and then they were removed from the column and stored in plastic bags ready for further use.

Scanning Electron Microscopy (SEM)

It is very important to visualise the surface morphology of the activated carbon fibres. SEM is a technique providing valuable information regarding external and internal features of the sample. Micrographs of low magnification (10 μ m and 2 μ m) were taken using a Cambridge Stereoscan 360 Scanning Electron Microscope at an accelerating voltage of 10 kV. The preparation of the samples involved 24-hour drying in an oven at 105°C prior to analysis. The samples were glued to aluminium platforms and sputter-coated with gold dust.

Sodium Capacity Determination

In determining the maximum sodium capacity, i.e. the surface acidity of all samples, 0.1 g of each sample was weighted accurately and placed in a 50 ml conical flask containing 25 ml of 0.1 M NaOH standard solution. The flasks were then sealed with Parafilm and were placed in an orbital shaker where they were shaken for 72 hours. After the completion of this time, the flasks were removed from the shaker and their solutions were filtered through filter paper. Aliquots of 5 ml were back titrated with 0.1 M volumetric standard solution of HCl using methyl red as indicator.

Point Of Zero Charge

The procedure for determining the point of zero charge follows the method described by Babić et al. [8]. About 0.1 g of carbon fibre sample was shaken in 50 ml conical flasks for 24 hr, with 25 ml of 0.1M KNO₃ solution, in different pH values. Initial values were obtained by adding an amount of NaOH or HNO₃ solution (0.1 M), keeping the ionic strength constant. The amount of H⁺ or OH⁻ adsorbed by the activated carbon cloth was calculated from the difference between the initial and the final concentrations of H⁺ or OH⁻ ions.

X-ray Photoelectron Spectroscopy (XPS)

X-ray photoelectron spectroscopy quantification was achieved by measurement of peak areas after subtraction of a Shirley-type background. This quantification has been made accounting the appropriate corrections for photoelectron cross-sections, inelastic mean free paths, energy analyser transmission and angular asymmetry in photoemission when required. Peaks were charge-referenced to a major C-C/C-H 1s peak at 285.0 eV. The

type of instrument used was VG ESCALAB Mk 1 and the X-ray parameters are presented in Table 1. Intensive information about the technique and the instrument is given by Briggs and Seah [9].

Table 1. XPS parameters.

Type	Al k _α X-rays
Energy	1486.6eV
Anode voltage	10kV
Filament current	20mA
Power	200W

Treatment

In order to investigate the effect of treatment after oxidation, the samples were cleaned by 0.1 M of NaOH followed by distilled water. This method was adopted for removing the humic substances that were produced on the surface of the carbon fibres after oxidation.

Batch sorption experiments

Zinc uptake determination was achieved by performing batch sorption isotherms. 0.035 g of carbon fibre sample were shaken in 50 ml volumetric flasks until equilibrium was established, with 25 ml of zinc nitrate solution of different concentrations at pH 6. The flasks were sealed with parafilm and kept in an orbital shaker at a constant temperature of 25°C.

The pH of the solution in the flasks was measured and adjusted periodically by adding appropriate amount of NaOH or HNO₃ solution (0.1 M) in the flasks so that the pH of the solution in the flasks remained constant. The amounts of NaOH or HNO₃ solution added in each flask were noted carefully. The experiments were stopped when the equilibrium was achieved, i.e. when no change occurred in the solution pH over a 48-hour period.

Analysis

The equilibrium and the initial concentration of zinc were measured by using a Varian SpectraAA-200 atomic adsorption spectrophotometer (AAS) in flame mode with an air-acetylene flame.

Results and Discussion

Scanning electron micrographs were taken in order to obtain visual representation of the surface of the activated carbon fibres before and after its modification. However, the micrographs did not clearly show the difference in surface morphology for different oxidation processes. This was also reported by Pittman et al. [10] for the SEM characterisation technique.

The results of sodium capacity determination are given in Table 2 and Table 3. Table 2 clearly shows the correlation between adsorption capacity and time of oxidation. It can be seen that sodium capacity increases with time of oxidation. This can be easily justified by taking into account that oxidation with nitric acid and ozone introduces oxygen-containing functional groups on the surface of the carbon fibres. When these groups are present in alkaline environments they dissociate releasing hydrogen ions and thus creating a negatively charged fibre surface. This surface is the ideal environment for adsorbing sodium ions and therefore neutralising the oxygen containing groups.

Table 2. Na⁺ capacity results: effect of time.

Sample	Oxidant	Time (hr)	Na ⁺ capacity (mmol g ⁻¹)
AW1501	No oxidation	0	0.897
AW1501.2	Nitric acid	1	5.134
AW1501.3	Nitric acid	1.5	6.261
AW1501.4	Nitric acid	2	6.912
AW1501.5	Nitric acid	3	NA*
AW1501.6	Ozone	0.5	2.837
AW1501.7	Ozone	0.75	4.411
AW1501.8	Ozone	1	5.069
AW1501.9	Ozone	2	NA*

NA*: Results are not reported since the end-point of the titration was masked.

2-hr nitric acid oxidised sample showed the highest sodium capacity, which was approximately 6.9 mmol g⁻¹. When comparing the two different oxidation techniques, for the same time of oxidation, it was found that with 1 hr nitric acid oxidation the capacity of sodium is slightly higher. Thus, it is concluded that nitric acid oxidation introduces more oxygen containing functional groups on the surface of AW1501 than ozone oxidised sample under otherwise identical conditions.

It was difficult to conduct the titration when sodium capacity experiments were conducted for 2 hrs and 3 hrs ozone and nitric acid oxidised samples respectively, as the solutions in the flasks after 72 hours of stirring turned completely black. Moreover, the mechanical strength of AW1501.5 and AW1501.9 was markedly reduced during these oxidation processes.

The above phenomena can be attributed to the presence of humic substances on the surface and pores of the fibre. These substances are produced during the oxidation process. Alkaline washing was performed in order to remove these substances from the fibres. Bahl et al. [11] reported that oxidation removes many organised portions of the fibre, most of which are responsible for its

mechanical strength. Therefore, after certain period of oxidation the fibres tend to lose their mechanical strength.

As already mentioned, humic substances are formed during oxidation of fibre. These humic substances also take part in the metal binding process. During this treatment, these humic substances are removed from the pores and surface of the fibre. Table 3 shows the effect of cleaning with NaOH solution. The removal of these substances results in lower sodium capacity for both cases. Although these products enhance the capacity of the fibres but results an undesirable brown colouration when they come in contact with alkaline solutions.

Table 3. Na⁺ capacity results. Effect of cleaning.

Sample	Oxidant	Time (hr)	Na ⁺ capacity (mmol g ⁻¹)
AW1501.4	Nitric acid	2	6.912
AW1501.4 ^{a*}	Nitric acid	2	2.661
AW1501.8	Ozone	1	5.069
AW1501.8 ^{a*}	Ozone	1	2.480

a*: These samples have been washed with NaOH and then distilled water.

Once the sodium capacity of all samples was determined, the materials that possessed the highest capacity were further characterised and employed for adsorption of zinc from aqueous solutions.

X-ray Photoelectron Spectroscopy (XPS) was also employed in order to find the elements comprising the surface of the fibres and their compositions. The results can be seen in Table 4. It is to be noted that oxygen is expressed as the percentage found from the difference between hundred percent and the sum of carbon, nitrogen, sodium and any other element that might exist.

Table 4. X-ray Photoelectron Spectroscopy results.

Sample Description	Surface composition excluding H (atom %)				
	C	O	N	Na	Si
Un-treated (as received).	91.2	7.5	Traces	0	1.3
2 hr HNO ₃ oxidised, H ₂ O washed.	78.6	21.4	0	0	0
2hr HNO ₃ oxidised, NaOH & H ₂ O wash.	74.8	20.4	3.5	1.3	0
1 hr O ₃ oxidised, unwashed.	82.5	11.3	2.3	0	3.9
1 hr O ₃ oxidised, NaOH & H ₂ O wash.	85.6	10.0	4.4	Traces	0

Results showed that the commercial carbon fibre showed the smallest amount of oxygen compared to the oxidised

samples. Therefore, it can be concluded that the oxidation methods introduce oxygen containing functional groups on the carbon fibre surface. At this case, the best oxidation method was proved to be nitric acid oxidation, since it increases oxygen content of the original sample by approximately 14% and 13% for the nitric acid oxidised samples, in comparison to an increase of 3.8% and 2.5% for the ozone oxidised samples.

XPS also showed the presence of silicon (Si) in the samples, which were not washed with H₂O or NaOH prior to characterisation. It was assumed that the presence of this material was a form of contamination of the original sample probably from the packaging (plastic bags). The presence of nitrogen in the samples was also noticed. This may be due to the incomplete carbonisation of carbon fibre (PAN precursor) raw material, or may have resulted from contamination during packaging, transportation and storage of the sample cloths.

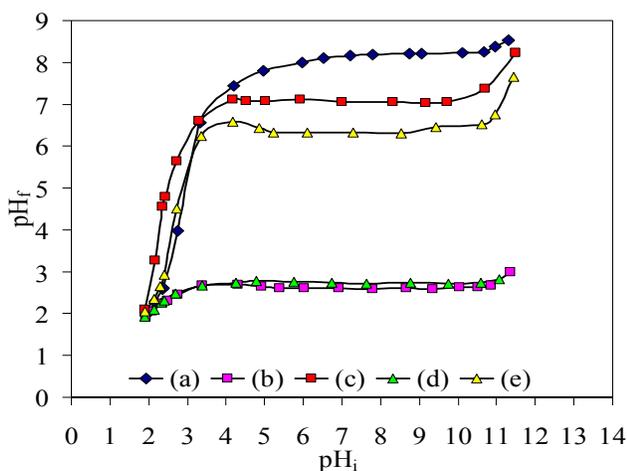


Figure 3. Point of zero charge for commercial and activated carbon fibres. (a) Un-oxidised (b) Nitric acid ox., H₂O washed (c) Nitric acid ox., NaOH & H₂O washed (d) Ozone ox., unwashed (e) Ozone ox., NaOH & H₂O washed.

The point of zero charge (PZC) is important to be determined for each sample since it is the pH value at which the surface net charge is zero. Below the pHPZC the surface is negatively charged and the oxygen containing groups of the surface of the fibres dissociate.

It was found (see Figure 3) that the pHPZC was 8.2, 7.1, 6.6, 2.8, and 2.6 for AW1501, AW1501.4, AW1501.8, AW1501.8^a and AW1501.4^a, respectively. It can be seen that washing with NaOH removed the humic substances and converted the surface of the fibres from acidic to neutral (closer to 7).

Finally, batch adsorption experiments were performed for adsorption of zinc from aqueous solutions. The isotherms at pH 6 are reported below (see Figure 4). It can be seen that 2 hr nitric acid oxidised sample washed with distilled water only showed the highest zinc capacity. This was expected since the sodium capacity was also the highest for this material. The increase in the uptake of these ions is attributed to the introduction of more oxygen containing functional groups on the surface during this process.

Zinc capacities reported at pH 6 are 1.12 and 0.95 mmol g⁻¹ for AW1501.4 and AW1501.4^a, respectively. For ozone oxidised samples, zinc uptake was found to be 0.63 and 0.59 mmol g⁻¹ for the washed and unwashed samples. The as-received sample showed the least uptake of the value 0.1495 mmol g⁻¹ that was expected considering the characterisation of the sample.

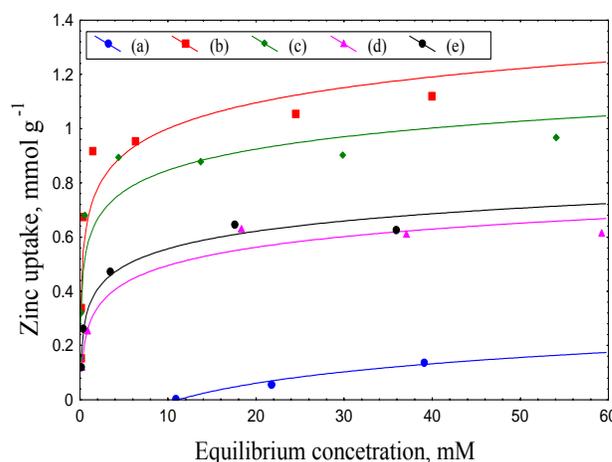


Figure 4. Isotherms for commercial and activated carbon fibres at pH=6. (a) As-received (b) Nitric acid oxidised, H₂O washed (c) Nitric acid oxidised, NaOH & H₂O washed (d) Ozone oxidised, unwashed (e) Ozone oxidised, NaOH & H₂O washed.

The effect of washing is clearly indicated. The washing with NaOH in both cases (for nitric acid and ozone oxidised sample) has decreased the zinc uptake. Thus, it can be concluded that the humic substances help in adsorbing zinc ions. However, washing with NaOH is strongly recommended since it minimises the possibility of the fibres to leach, which in turn reduces the undesirable dark brown colouration in the treated water.

Conclusions

Nitric acid and ozone oxidations were performed to modify the activated carbon fibre for trace heavy metal removal. These modifications introduce oxygen-containing groups on the surface of the fibre. The results showed that after oxidation the modified fibres were capable to adsorb

more positively charged ions like sodium and zinc from aqueous solution. 2-hr nitric acid oxidised sample was found to be the most favourable one since higher zinc uptake was observed by using this material. The zinc uptake was found to have increased by 8 times than the as-received material. The effect of different treatment was also investigated. Water-washed materials showed higher metal sorbing capacity compared to NaOH-washed materials. This study also demonstrates that humic substances take part in adsorbing zinc ions from aqueous solution.

References

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