Development and Studies on Deferrated-Kaolinite-Template Porous Carbons from Furfuryl alcohol.

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Abstract: This study reports the preparation of porous carbon via the template synthesis technique using kaolinite clay from Kankara, Katsina State, Nigeria as template material and poly(furfuryl alcohol) as carbon precursor. Characterization of the prepared carbon was via determination of adsorptive capacities of the prepared carbons for methylene blue (indicating mesoporosity) and iodine (indicating microporosity). The adsorptive capacity of the free PFA and templated carbons for methylene blue are 256.14mg/g and 594.61mg/g respectively. The iodine number for the free PFA and template carbons are 984.30mg/g and 602.88mg/g respectively. These results reveal a higher degree of mesoporosity in the template carbons as compared to the free PFA carbon which had a higher degree of microporosity.

Introduction

Nanostructured porous carbons are potentially of great technological interests because they are excellent adsorbents, electrodes and catalyst supports for the conversion and storage of energy. They have been actively used in fuel cells, hydrogen storage carriers, electrochemical capacitors and lithium ion batteries (Liu and Cheng, 2005; Fabing *et al*., 2007).

The chemical functional groups on the surface, specific area and pore structure determines its applications (Wenzhong *et al*., 2008). The pore structure of porous carbons could be controlled via various routes such as activation conditions (activation agent, time and temperature), templates, precursor etc.

Many novel ways to precisely control the pore size and structure of different types of porous carbons have been proposed. They include the arc discharge, laser ablation, chemical vapour deposition and template synthesis techniques (Kyotani *et al*., 2000, Zhang *et al*., 2002). The properties of these nanoporous carbons are determined both by the nature and thermal history of the precursor. The template synthesis method can be used to produce novel forms of carbon with unusual properties (Goncalves *et al*., 2000; Sakintuna and Yurum, 2005). For example, polyfurfuryl alcohol (PFA) (a precursor to carbons that are not convertible into graphite even when heated at temperatures above 3000°C), when carbonized between the lamellae of montmorillonite clay, yielded template carbon that was easily graphitized. This shows that the confined environment (of carbonization) can control the process of carbonization at molecular level. The structure of the resulting carbons is also dependent upon the properties of the inorganic matrix.

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For example, carbon produced using PFA as precursor between lamellae of clays differs from that produced using same precursor, but this time, in zeolite channels (Zarbin *et al*., 2002).

The synthesis of ordered rigid arrays of nanoporous carbons using templates that leaves an ordered graphitic framework is a new trend in carbon research (Kim *et al*., 2003; Cott *et al*., 2006; Ren *et al*., 2007; Su *et al*., 2007; Zheng *et al*., 2007;). It is one of the most important techniques and has been of interest to many researchers because it has proven to be a feasible method for the preparation of well-structured porous carbons with pore sizes that span from micropores (Kyotani .T., 2000; Kyotani *et al*., 2003), to mesopores (Ryoo *et al*., 2001; Lee *et al*., 2004), and macropores (Zakhidov *et al*., 1998). The template synthesis method also has the unique advantage of being easy, inexpensive and can be suitably adapted for large-scale production.

The template synthesis technique is based on the carbonization of an organic polymer such as sucrose, poly(propylene glycol) or phenol resin in an inorganic material which serves as a host. In the resulting nanostructured carbons, the pores behave as individual nanoscale reactors. As a result, chemical reactions are confined to take place inside the pores, with only limited diffusion between them. This phenomenon clearly indicates a method of

synthesizing nanoscale materials (Kageyama *et al*., 1999). After the removal of the template, observation of the resultant carbons by means of X-ray diffraction (XRD), reveals lines which are only characteristic of a well-ordered pore arrangement. Characterization of the resultant carbon can be carried-out by observing its patterns using a diffractometer (XRD), Fourier Transform-Infrared (FT-IR) spectrophotometer, Raman spectroscope and/or Transmission electron microscope (TEM) (Darmstadt *et al*., 2000; Jun *et al*., 2000; Kruk *et al*., 2000; Cláudio and Zarbin, 2006; Zarbin *et al*., 2002).

The use of poly(furfuryl alcohol) (PFA) as carbon source has been investigated and reported by many research groups (Domingo-Garc´ıa *et al*., 2000; Cláudio and Zarbin, 2006; Wang and Yao, 2006). PFA can be generated from the monomer liquid, furfuryl alcohol (FA) to which an acid has been added to catalyse the polymerization reaction.
The use of a wide range of materials such as TiO_2, mesoporous silicas, aluminium oxides and aluminosilicates templates for the synthesis of ordered carbons have been reported (Ma *et al*., 2001; Sang *et al*., 2001; Cláudio and Zarbin, 2006; Fabing *et al*., 2007). The synthesis of mesoporous carbon from PFA/silica nanocomposites has been reported (Kawashima *et al*., 2000; Zarbin *et al*., 2002; Zimer *et al*., 2003). The use of various kinds of surfactant-templated mesoporous silica materials as templates for the synthesis of many mesoporous carbon materials has also been reported (Joo *et al*., 2001; Lee *et al*., 2002).

However, inspite of the extensive research carried-out on the production of templated carbon, no work has been reported on the suitability of deferrated kaolinite from Kankara (Nigeria), as a possible template material. Kankara clay was selected for investigation because of its bulk availability (Lori *et al*., 2007).

This work therefore investigates Kankara kaolinite clay as a suitable template for the synthesis of ordered carbons from FA as carbon source. A novel approach for the characterization of the pore structure of the resulting carbons using iodine and methylene blue adsorption was also investigated.

MATERIALS AND METHODS

Materials
All reagents used were of analytical grade. Furfuryl alcohol was distilled and all other chemicals were used as purchased. All solutions were prepared using

water that was distilled and deionized. Kankara clay was obtained from underground local mines at mining sites in kankara. Defferated Kaolinite clay was prepared using the procedure reported by Lori *et al*., 2007.

Clay Intercalated polymer carbon and porous carbon prepared by pyrolysis of poly furfuryl alcohol were investigated for use as adsorbents for environmental use.
5 cm^3 of FA was stirred with 25mg of oxalic acid and stirred for 72h at 70°C. The product was kept in a sealed flask under inert atmosphere in a sealed flask for 20 days. The product was transferred into another flask containing $CHCl_3$ and was continuously stirred by means of a magnetic stirrer for 4hrs, to ensure complete dissolution of the residual monomers and low molecular weight oligomers. The resulting mixture was filtered and the residue was washed with 10 cm^3 of $CHCl_3$ and dried at 50 ^{o}C for 1hr. The resulting product is a brown free PFA resin.

Preparation of Deferrated-Kaolinite /PFA nanocomposites (**D-KAO /PFA**)
The method for the preparation of (D-KAO /PFA nanocomposites is similar to the method described by Zarbin *et al.*, 2002, but with slight modification. The D-KAO was dried at 200°C in a vacuum for 4hrs. 5g of it was added to 2 cm^3 of furfuryl alcohol (FA) contained in a flask. The mixture was maintained under magnetic stirring for 3hrs at 80°C. Water and solvent was removed by heating at 40°C under vacuum.
The remaining furfuryl alcohol without polymerization in the core of the template pores was polymerized by heating under vacuum at 80°C.

Preparation of templated porous carbon
About 0.2g of the D-KAO/PFA sample was pyrolysed under vacuum. The temperature was ramped from room temperature to 900°C at a rate 10°C/min, and the temperature maintained at 900°C for 2hrs and then cooled to room temperature (28°C) in a dessicator. The resulting black material is the Clay templated Carbon nanocomposite (D-KAO/C). To remove the D-KAO template, the nanocomposite was boiled with vigorous stirring in 30 cm^3 of 1M NaOH solution dissolved in 50:50 mixture of water and ethanol for 1 hr. (Kim *et al*., 2004).
The resulting insoluble carbon material was retrieved by centrifugation, washed exhaustively with deionised water and dried at 50°C for 24hr.

To prepare the free polymer porous carbon (FPC) the free PFA was also subjected to the heat treatment

described above excluding the treatment with NaOH solution.

RESULTS AND DISCUSSION

Synthesis of Furfuryl alcohol

It is well known that furfuryl alcohol can be derivatised from furfural. Upon dropwise addition of NaOH from the separatory funnel into furfural with stirring, a reddish-yellow precipitate was formed. Dissolution of the precipitate with distilled water and extraction with diethylether gave a yellow solution. Removal of the diethylether and re-distillation at 80 °C under reduced pressure (40 mmHg) gave a golden-yellow solution. About $15cm^3$ of furfuryl alcohol was obtained, which is small compared to the $86cm^3$ of starting material, furfural.

Synthesis of DKAO/PFA Composite

Poly(furfuryl alcohol) can be formed from furfuryl alcohol monomer via acid catalysis and thermal treatment (Zarbin *et al.,* 2002; de Almeida-Filho and Zarbin, 2006).

Addition of oxalic acid to the deferrated kaolinite and furfuryl alcohol monomer and heat treatment at 80°C for 3 hours with stirring brings about polymerization of the monomer. Subjecting the powdered composite obtained to further heating at 100°C for 1 hour ensures solvent removal and complete polymerization of the monomer. The dark brown composite obtained is in agreement with reports in literature (Zarbin *et al.,* 2002; de Almeida-Filho and Zarbin, 2006).

Preparation of Templated Carbon by Pyrolysis and HF Treatment of DKAO/PFA Composite.

During DKAO/PFA pyrolysis, the organic components of the composite are converted into carbon which is dispersed in the interlamellar structure of the DKAO template.

The formation of carbon is evidenced by the black colour of the DKAO/Carbon composite obtained.

Thermal treatment of the DKAO/PFA composite was carried-out at 500 °C as kaolinite remains stable at that temperature. Treatment of the DKAO/C composite with HF solution dissolves the clay fraction leaving the templated carbon as the insoluble fraction. However, results from gravimetric analysis reveal that about 95% of the clay was removed through the HF treatment.

Adsorption Characteristics

Pyrolysis of the free poly(furfuryl alcohol) resin and DKAO/poly(furfuryl alcohol) composite produced carbon which was characterized by aqueous phase adsorption of methylene blue and iodine.
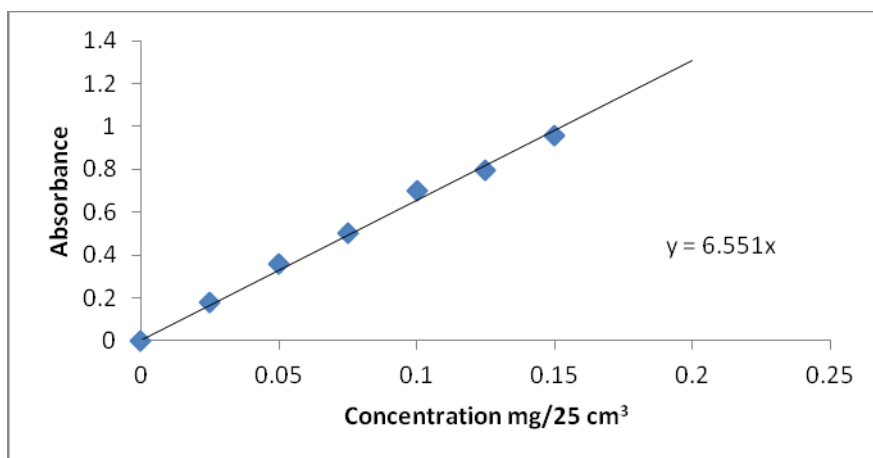

Figure 1; Calibration curve for methylene blue.

Methylene blue Adsorption

Figure 1 is the calibration curve for methylene blue, a plot of absorbance against various concentrations, at a wavelength of maximum absorption (λ_{max})of 665nm. The equation of the line determined from the curve is given by
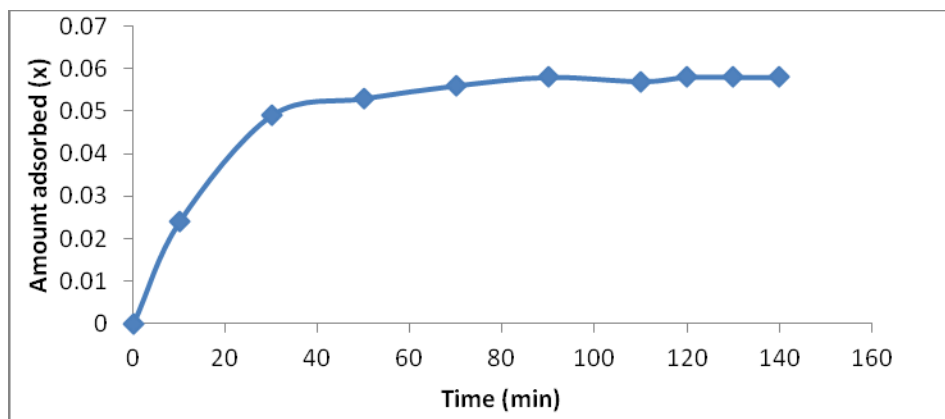
$$Y = 6.551x$$

Figure 2: Graph showing time for equilibrium adsorption

From Figure 2, the time for equilibrium adsorption of methylene blue at the wavelength of maximum absorption (λ_{max}) 665nm is 100 minutes. This is less than the stipulated contact time of 2 hours ASTM D3860-98 (2003). However, it was recommended that time for equilibrium adsorption be determined for carbon samples.
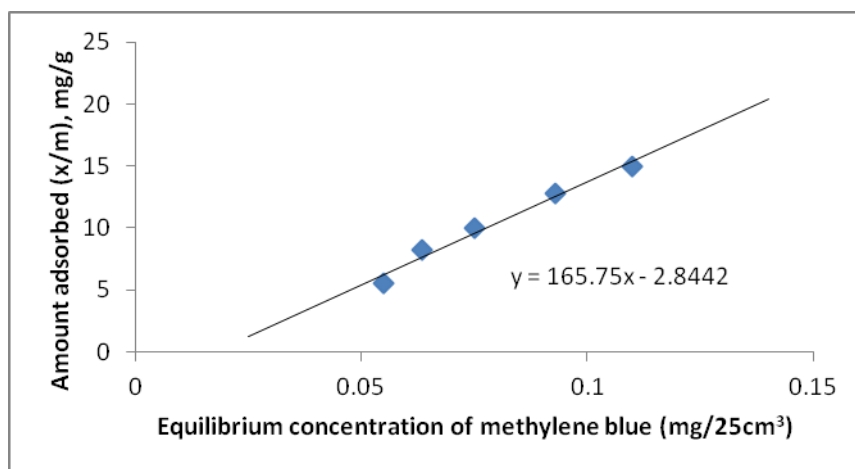

Figure 3: Adsorption isotherm of methylene blue on free PFA carbon at room temperature (28 °C).
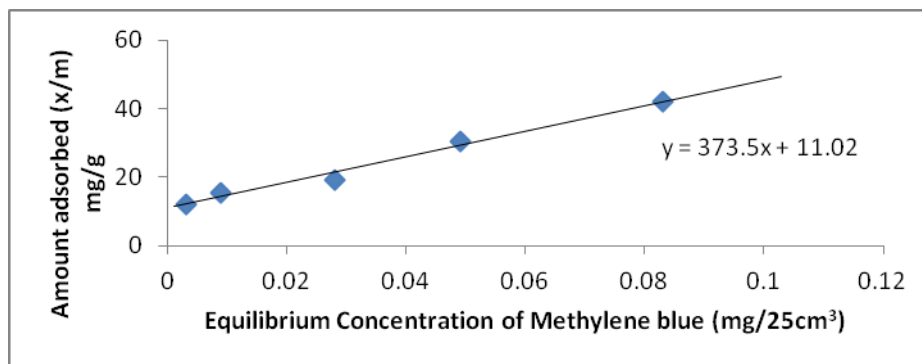.

Figure 4: Adsorption isotherm of methylene blue on templated carbon at room temperature (28 °C).

Figures 3 and 4 show the adsorption isotherms of methylene blue at room temperature (28 °C) on both free and templated carbon respectively.

The adsorptive capacity of the carbon for methylene blue is given by the value of x/m at a concentration of 0.0625 mg/cm^3.

The adsorptive capacity of the free PFA carbon for methylene blue is 256.14mg/g. while the adsorptive capacity of the templated carbon for methylene blue is 594.61mg/g.
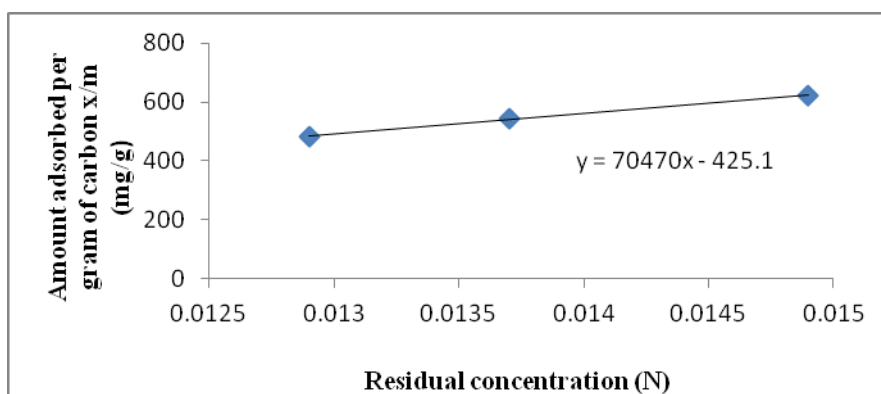

Figure 5: Adsorption isotherm of iodine on free PFA carbon at room temperature (28°C).
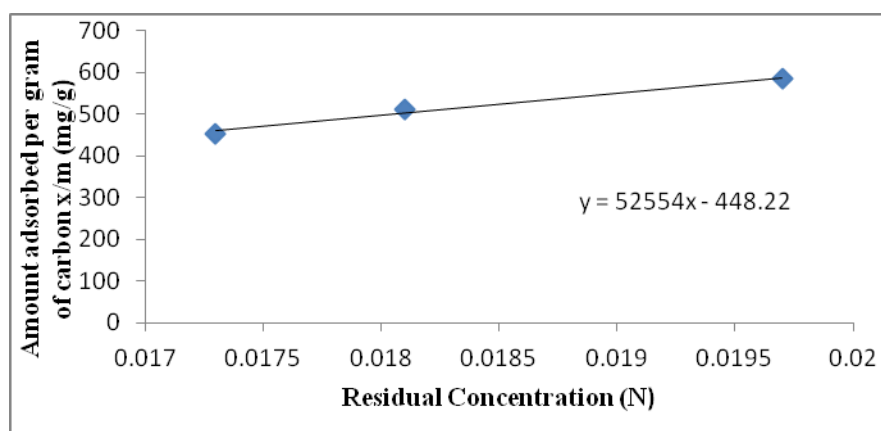

Figure 6: Adsorption isotherm of iodine on templated carbon at room temperature 28°C.

Figures 5 and 6 show the adsorption isotherms of iodine on the free PFA and templated carbon respectively, at room temperature (28°C).

The iodine number of the free PFA carbon is 984.3mg/g. Whereas, the iodine number for the template carbon is 602.88 mg/g.

These results show the extents of mesoporosity and microporosity of the synthesized carbon materials as represented by the adsorption of methylene blue and iodine respectively.

The higher value of methylene blue number for the templated carbon compared to the methylene blue number for the free PFA carbon is indicative of the presence of more of wider micropores (> 1.4nm) and mesopores. This can only be explained by the template effect during the synthesis of the templated carbon.

Whereas, the higher value of iodine number for the free PFA carbon as compared to the iodine number for the templated carbon is indicative of the presence of more of micropores (< 0.5nm). This tends to be in agreement with report by Burket *et al.,* that from 500 °C and above, free PFA carbon is almost completely microporous with pore size centered at 0.4 – 0.5nm (Burket *et al.,* 2006).

Conclusion

In this study, porous carbon was produced using deferrated-kaolinite template. The characterization data presented reveal that the carbon may not necessarily be of a uniform pore size, though, there is a higher degree of mesoporosity in the templated carbon as compared to the free PFA carbon (control). This characteristic is linked with the presence of the template. However, it is difficult to conclude that the carbon is an exact replica of the template material and that it is more ordered than the free PFA carbon as this would require further investigation with more sophisticated equipments.

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