

## Structural and Adsorption Characteristics of Carbon Adsorbent Synthesized from Polyfurfuryl Alcohol with Kaolinite Template

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**Abstract:** The main aim of this study is to synthesize porous carbon adsorbent from chemical precursor in order to prevent metal impurities that are commonly associated with porous carbon adsorbents derived from agricultural residues. Deferrated kaolinite was used as a template material for the synthesis of porous carbon adsorbent from polyfurfuryl alcohol (PFA). The structural and adsorption characteristics of the adsorbent were investigated using Fourier transform infrared (FT-IR) spectroscopy and methylene blue adsorption. FT-IR spectra showed that calcination of the kaolinite impregnated with polyfurfuryl alcohol, at 500°C ensured carbonization of the polymer (between kaolinite layers) but did not collapse the mineral layer structure which is required for the creation of pores in the templated carbon. Results from the adsorption studies showed that for all the different initial concentrations of the methylene blue, the templated carbon had higher adsorptive capacity than non templated carbon from carbonized free polyfurfuryl alcohol.

**Key words:** Carbonization, ft-ir, kaolinite, methylene blue, Polyfurfuryl alcohol, templated carbon

### INTRODUCTION

Renewed efforts in adsorption research have been witnessed in recent years. The reasons for this development include: (a) increasing emphasis on environment, health and safety; (b) emerging technologies; and (c) escalating energy costs (Putyera *et al.*, 1994). It is therefore desirable to prepare new adsorbent materials with high adsorption capacity to meet these demands. Of particular interest are the sub microporous carbons such as Carbon Molecular Sieves (CMS), prepared by the calcination of organic precursors between the layers of clay minerals. The organic material creates a thin film in the interlayer space of the inorganic matrice such that the size of pores is limited by the interlayer distance of the precursor mineral (Putyera *et al.*, 1994).

A nanoporous carbon (NPC) inherently microporous with a very narrow pore size distribution is obtained from pyrolysis of the thermosetting polymer, polyfurfuryl alcohol (PFA) (Mariwala and Foley, 1994; Burket *et al.*, 2006). The micropores act as molecular sieves and make NPC appealing for a number of applications including catalysis, gas separation (Shiflett and Foley, 1999; Eckert *et al.*, 1988; Burket *et al.*, 2006) and aqueous phase adsorption studies (Barata-Rodriguez *et al.*, 2003).

Detailed examinations of pyrolysis of PFA using Infra Red (IR) spectroscopy have been reported by Fitzer *et al.* (1969), Fitzer and Schafer (1970) and

Burket *et al.* (2006). According to these studies the furan ring was found to be stable up to 275°C but ruptured between 300°C and 400°C to release CO, CO<sub>2</sub> and H<sub>2</sub>O. At about 400°C, aromatic units appeared as the fragments began to coalesce, and at temperatures greater than 450°C a reaction of the remaining methylene bridges with water to form keto groups was suggested. Within the same temperature range, a significant amount of hydrogen was released due to the oxidation of the methylene bridges which stopped the formation of methane. The authors reasoned that in the intermediate between polymer and the final carbon, open pores with diameters smaller than 100 Å must be present and this allowed the transport of gaseous products formed during pyrolysis.

The mechanism of polymerization of furfuryl alcohol is cationic and cross-linking occurs readily (Burket *et al.*, 2006). Mariwala and Foley (1994) noted cross-linking in PFA leads to micropore formation and to the resistance to graphitization that is well known in NPC. Choura *et al.* (1996) and Burket *et al.* (2006) extensively studied the cross-linking reaction in PFA with the aid of model compounds. They suggested that cross-linking requires that mobile hydrogen atoms, present on the polymer backbone as CH<sub>2</sub> groups, undergo series of hydride ion abstraction and proton expulsion reactions that leaves the polymer highly conjugated. The conjugated structure then reacts to form a cross-link, either by condensing with the propagating center on another chain or with a furan ring (diene) in a Diels-Alder reaction.

Considerable attention has been given to clays especially for their potential as adsorbents for environmental application. Although deposits of clay are widely distributed in Africa, especially, Nigeria (Borode *et al.*, 2000; Fasuba *et al.*, 2001; Omowunmi, 2001; Irabor, 2002; Gbadebo, 2002; Igbokwe and Ogbuagu, 2003; Odo and Nwajagu, 2003; Lori *et al.*, 2007), presence of impurities, especially iron-associated materials mar the characteristics of clay and affects its potential use as adsorbents. Lori *et al.* (2007) characterized the Kankara clay (in Kankara Local Government Area of Katsina State, Nigeria) and confirmed its dominant mineral to be kaolinite which is suitable for production of aluminosilicate nanocomposite that is not characterized by many unwanted atoms. The authors reported optimized conditions for 99% deferration as 7 h shearing time and 1.8 mol/dm<sup>3</sup> oxalic acid concentration as the leaching agent at a temperature of 75°C.

The use of PFA as carbon source minimizes metal impurities commonly associated with agricultural wastes that are used as carbon precursors. PFA can be generated from the monomer liquid furfuryl alcohol through acid-catalyzed polymerization (Zarbin *et al.*, 2002; de Almeida-Filho and Zarbin, 2006). The use of a wide range of materials such as zeolites, layered clays, bentonite, etc. as templates for the synthesis of ordered carbons have also been reported. Badosz *et al.* (1994) reported the carbonization of PFA using the two-dimensional interlamellar opening of a sodium form of Wyoming smectite and the lithium form of taeniolite intercalated with hydroxylaluminium-zirconium cations. The carbon produced had high content of micropores. Barata-Rodriguez *et al.* (2003) prepared porous carbon using PFA as a carbon precursor and bentonite (commercial cationic clay) as a template and reported that the templated carbon appeared more ordered than the non-templated carbon, and had a specific surface area of 446 m<sup>2</sup>/g.

The present study examines the deferrated kaolinite as a template material for the synthesis of porous carbon adsorbent from PFA. The structural and adsorption characteristics of this adsorbent were studied.

## MATERIALS AND METHODS

This study was conducted at Ahmadu Bello University, Zaria, Nigeria in 2010.

**Synthesis of polyfurfuryl alcohol (PFA):** 20 cm<sup>3</sup> of furfuryl alcohol (Acros Organics, 99%) was transferred to a 250 cm<sup>3</sup> conical flask using a graduated pipette. 40 mg of oxalic acid was weighed and added to the flask. The mixture was heated to 80°C with constant stirring for 7.25 h. The product was heated in the oven at 105°C for 1 h.

**Preparation of deferrated kaolinite-polyfurfuryl alcohol composite:** Clay sample was obtained from Kankara deposit in Katsina (Nigeria) and treated as described by Lori *et al.* (2007) to obtain deferrated kaolinite. 1 g of deferrated kaolinite was weighed into a 250 cm<sup>3</sup> conical flask. 20 cm<sup>3</sup> of the furfuryl alcohol was transferred to the conical flask using a graduated pipette. 40 mg of oxalic acid was weighed and added to the flask. The mixture was maintained under magnetic stirring for 1.75 h. The composite obtained was heated in the oven at 105°C for 1 hr and cooled in a desiccator containing silica gel as the desiccant.

**Carbonization:** 2.25g each of the PFA and PFA-kaolinite composite weighed into porcelain crucibles were separately heated in the Muffle Furnace at 500°C for 2 h. The crucibles with the resulting carbon materials were cooled to room temperature of 29°C and transferred to a desiccator with silica gel as the desiccant. The kaolinite-carbon composite sample was washed with hydrofluoric acid (HF) to remove the kaolinite.

**Removal of kaolinite template by HF treatment:** The kaolinite-carbon composite produced was transferred to a 250 cm<sup>3</sup> Teflon flask. 80 cm<sup>3</sup> of 60% HF (BDH) was transferred with 100 cm<sup>3</sup> Teflon measuring cylinder to the flask. The flask was shaken vigorously and allowed to stand for 72 h in a fume chamber. The content of the flask was transferred to a 500 cm<sup>3</sup> Teflon beaker containing 400 cm<sup>3</sup> of de-ionized water. The insoluble fraction was washed with 2000 cm<sup>3</sup> of de-ionized water in portions of 200 cm<sup>3</sup> and the final content of the beaker was filtered using Teflon funnel. The residue (template carbon) was dried in the oven at 105°C for 1 h and kept in the desiccators prior to characterization.

**Characterization of free polyfurfuryl alcohol (PFA), PFA-Kaolinite composite (PFA-KC), free PFA carbon (PFAC), PFA-Kaolinite carbon (carbon composite (CC)) and HF washed carbon composite (templated carbon (TC)):** The PFA, PFA-Kaolinite composite (PFA-KC), free PFA carbon (PFAC), PFA-Kaolinite carbon (carbon composite (CC)) and washed carbon composite (Templated Carbon (TC)) were characterized using Shimadzu 8400S FT-IR spectrometer. After mixing 10 mg of the samples with 300 mg FT-IR grade KBr, the mixture was filled into a hollow steel holder. The samples were scanned within 4000 and 450 per cm. The band positions were determined by fitting the Kubelka-Munk function.

**Methylene blue adsorption:** 100 mg each of the free PFA carbon and templated PFA carbon was dispersed into a 250 cm<sup>3</sup> Erlenmeyer flask. 50 cm<sup>3</sup> of methylene blue solutions of varying amounts of methylene blue (1.0, 1.5, 2.0, 2.5 and 3.0 mg of methylene blue) was added and

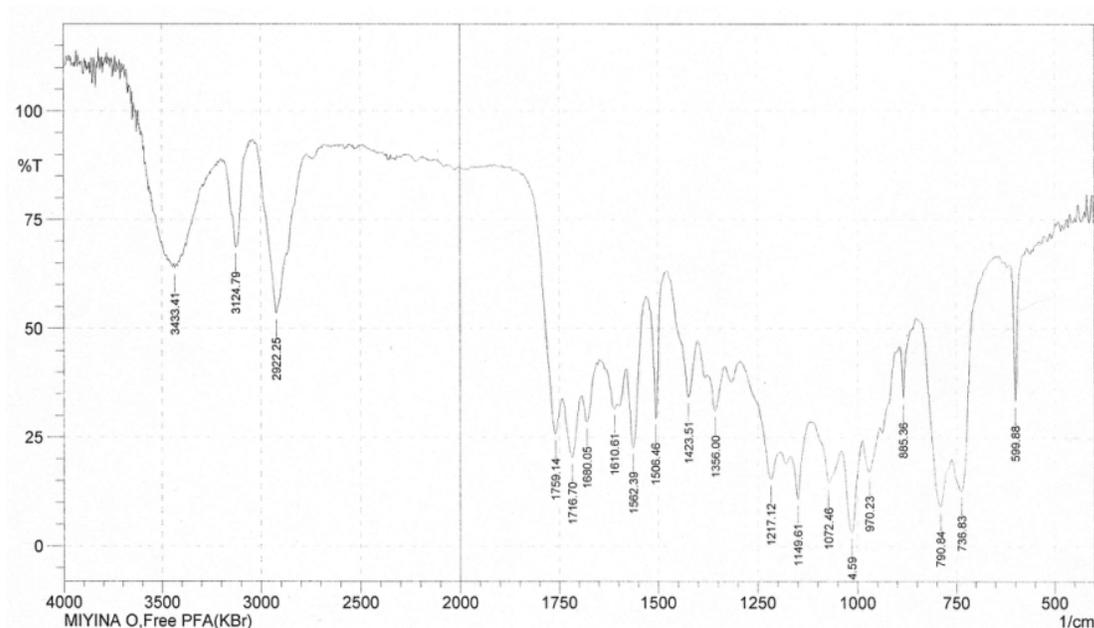


Fig. 1: FT-IR Spectrum for Free polyfurfuryl alcohol (PFA)

stopped. The flask was shaken on a Griffin flask shaker at room temperature of 29°C for varying contact times of 5, 10, 15, 25, 35 and 60 min, respectively. The mixture in each flask was centrifuged for 5 min and analyzed using Cole 7506 UV-VIS spectrophotometer at 665nm wavelength. Standard solutions of methylene blue were used for calibration.

## RESULTS AND DISCUSSION

**FT-IR analyses:** The FT-IR spectra for PFA, PFA-KC, PFAC, CC and TC) are presented in Fig. 1 to 5, respectively. The PFA and PFA-KC spectra (Fig. 1 and 2) show remarkable differences in the vibration modes of PFA and PFA-KC. The main characteristic bands for PFA were at 3433.41 per cm (-OH stretch), 3124.79 per cm (-CH in aromatic rings), 2922.25 per cm (aliphatic -CH stretch), 1610.61 per cm (C=C aromatic), 1562.39 per cm, 1506.46 per cm (ring vibrations), 1423.51 per cm (asymmetric CH<sub>2</sub> bending), 1355.0 per cm (-CH ring), 1140.61 per cm (C-O stretch), 790.84 per cm (2,5-disubstitution of furan ring).

In the PFA-KC spectrum, OH-stretching vibrations in kaolinite were observed at 3697 and 3620 per cm, respectively. Bands due to Si-O vibrations in kaolinite were observed at 1155 and 1014 per cm, respectively. Al-Si-O bond showed characteristic absorption at 536 per cm. The bands at 468 and 426 per cm were assigned to Si-O bonds. The band at 792.77 per cm was assigned to Si-O-Si bond. The main characteristic -OH stretch band for PFA at 3433.41 per cm became broad and was shifted to 3452.70 per cm in the composite, indicating an interaction

between the PFA and kaolinite through hydrogen bonding. This bonding scheme supports the insertion of the PFA into the kaolinite layered structure. This is consistent with the findings of Lawal *et al.* (2010) on insertion of polar molecules in kaolinite. The PFA -CH (aromatic ring) at 3124.79 per cm was shifted to 3119 per cm in the composite, while the PFA aliphatic -CH stretch at 2922.25 per cm presents at 2910.68 per cm in the composite. The C=C aromatic at 1610.61 per cm in the PFA spectra was retained at 1602.90 per cm in the composite. The PFA band at 790.84 per cm for the 2, 5-disubstitution of furan ring also presented at 792.77 per cm in the composite. These PFA bands confirmed the presence of the PFA in the PFA-kaolinite composite in its symbolic form.

Figure 3 shows the FT-IR spectrum of the carbonized PFA. The absorption bands in the spectrum show the conversion of the PFA polymer to carbon with polyatomic signatures dominating the spectrum from 1000-1687.77 per cm. This is consistent with the reports of Burket *et al.* (2006) on the genesis of porosity in polyfurfuryl alcohol derived nanoporous carbon.

Figure 4 is the FT-IR spectrum of carbon obtained from the calcination of the PFA-kaolinite composite. The characteristic bands of the kaolinite featured prominently in this spectrum and thus confirmed that the calcination temperature of 500°C ensured carbonization of the polymer between the Kaolinite layers but did not cause the collapse of the mineral layer structure which is required for the creation of pores in the intercalated carbonaceous material.

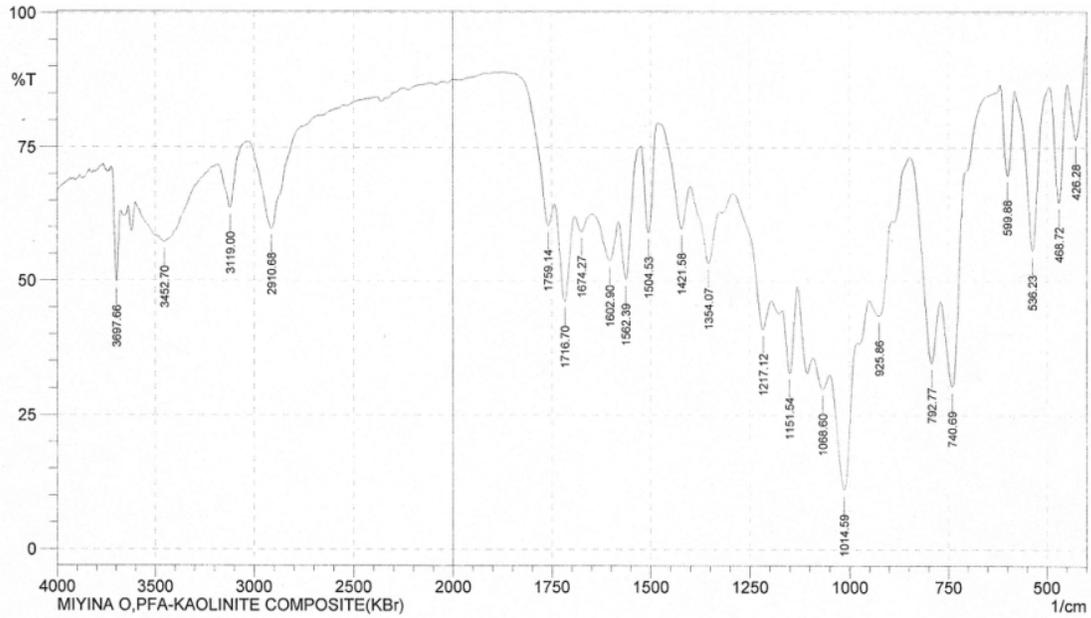


Fig. 2: FT-IR Spectrum for PFA-Kaolinite Composite (PFA-KC)

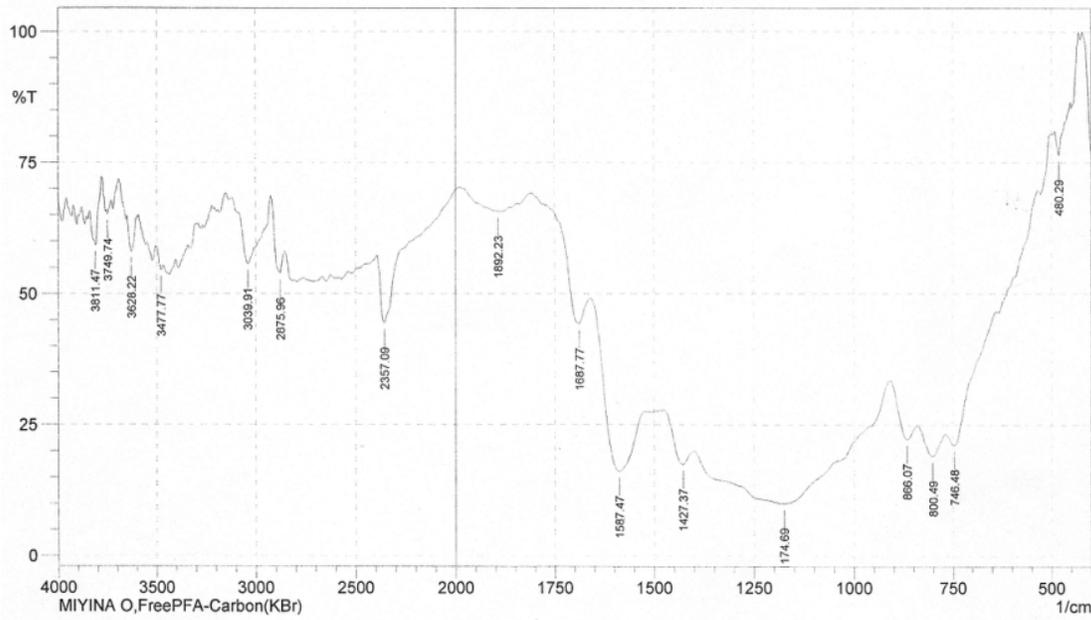


Fig. 3: FT-IR Spectrum for Free PFA Carbon (PFAC)

The TC spectra (Fig. 5) clearly showed the absence of the characteristic signature bands for the kaolinite, indicating complete removal of the kaolinite template from the carbon composite by the HF treatment.

The absorption intensities of the polyatomic signatures (1000-1687.77 per cm) in the PFAC and TC

spectra also show remarkable differences indicative of changes in the morphology of the PFA carbon due to the kaolinite template.

**Methylene blue adsorption:** In order to further investigate the characteristics of the carbon-matrix,

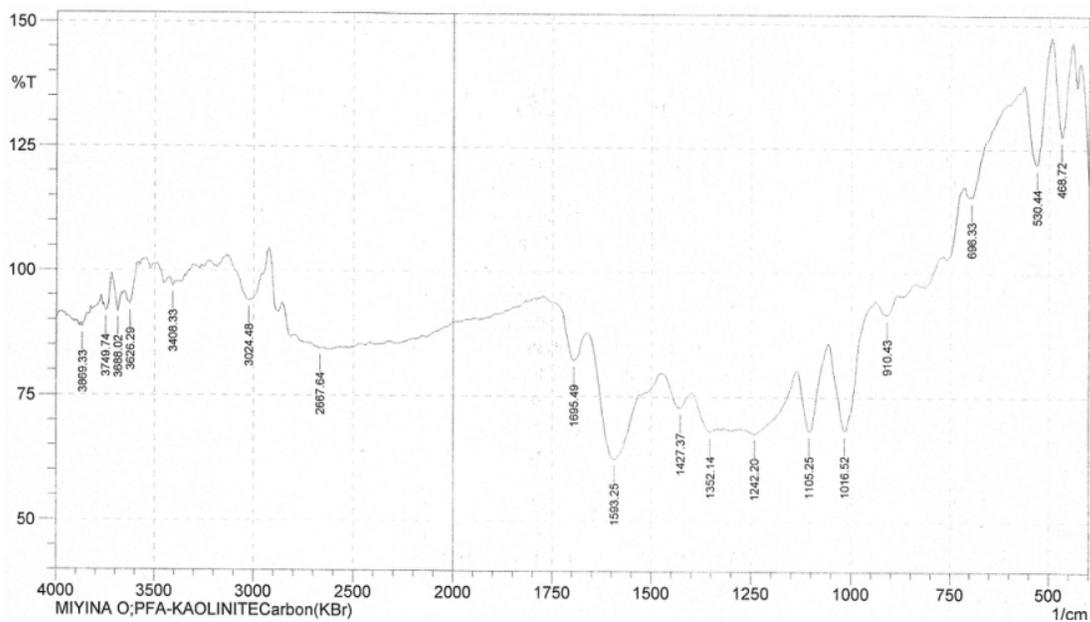


Fig. 4: FT-IR Spectrum for PFA-Kaolinite Carbon (CC)

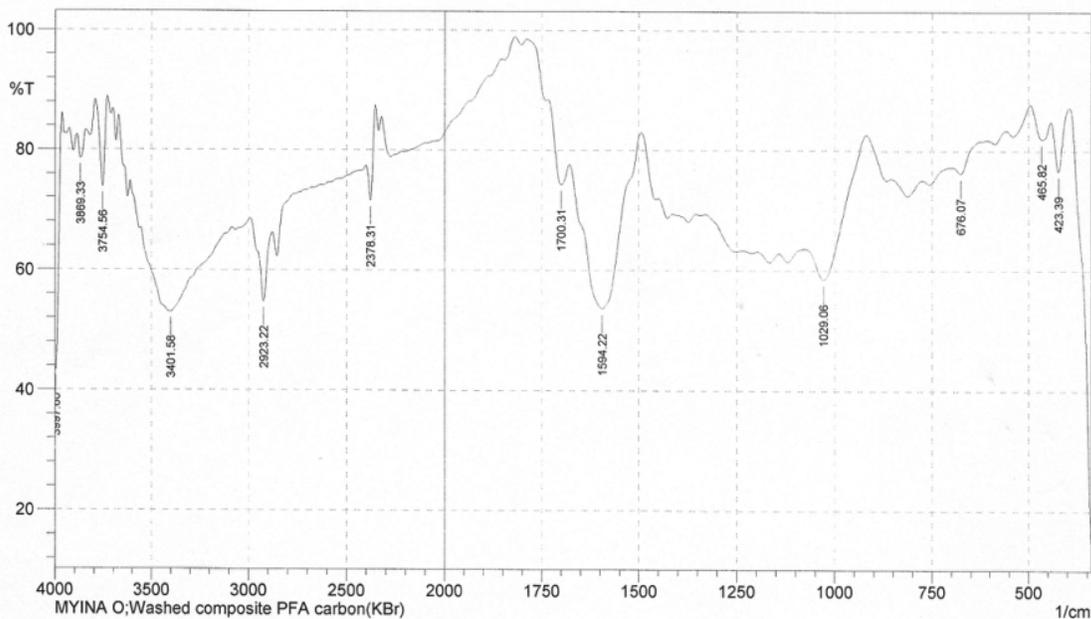


Fig. 5: FT-IR Spectrum for Washed Composite PFA Carbon (TC)

systematic adsorption studies were carried out using methylene blue. The adsorption pattern of the free PFA carbon and templated carbon were as presented in Fig. 6.

The methylene blue uptake within the first 10 min of contact time was generally slow for both PFAC and TC at lower concentrations of the methylene blue. However, as the methylene blue concentration increases, the uptake

increased as indicated by the sharp gradient of the respective isotherms.

In the range of methylene blue concentrations considered, the templated carbon showed higher adsorptive capacity than the free PFA carbon. This is consistent with the morphological differences indicated by PFAC and TC which suggests enhanced porosity in the

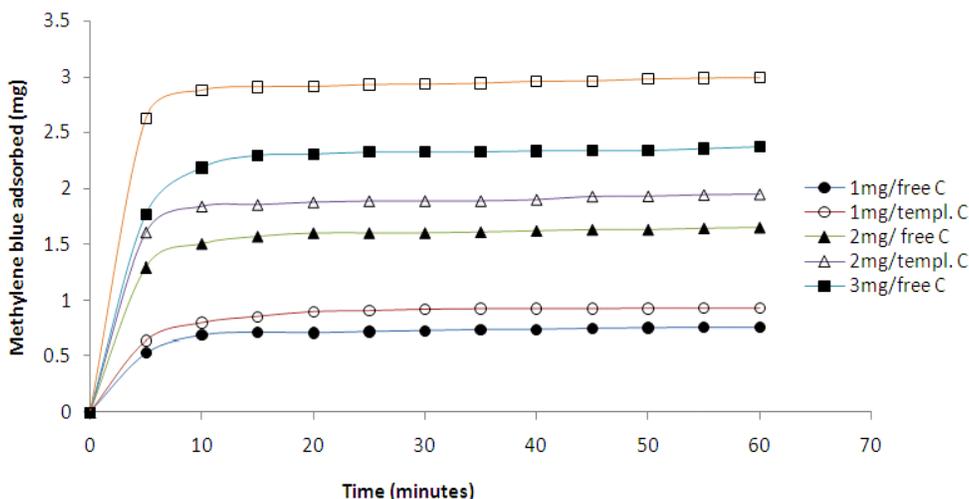


Fig.6: Effect of contact time on adsorption of different initial concentration of methylene blue [ $C_x$  (mg/50cm<sup>3</sup>)] on templated carbon and free carbon from carbonised poly furfuryl alcohol

templated carbon. These observations are consistent with previous reports on the adsorption capacity of carbon with tailored morphological characteristics (Barata-Rodriguez *et al.*, 2003; Sonobe *et al.*, 1988; Kyotani *et al.*, 1994; Bandosz *et al.*, 1996; Kyotani *et al.*, 2000).

### CONCLUSION

Kaolinite impregnated with polyfurfuryl alcohol was used to obtain a structured carbon adsorbent that carried the morphological features of the clay template. The presence of the template and its interaction with the synthesis conditions, introduces controllable features into the resulting carbon adsorbent, which cannot be achieved by activated carbon preparation methods. The templating effort results in higher surface area microporous carbon.

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### REFERENCES

Bandosz, T.J., J. Jagiello, K. Putyera and J.A. Schwarz, 1996. Pore structure of carbon-mineral composites and derived carbons obtained by template carbonization. *Chem. Mater*; 8(8): 2023-2029.

Bandosz, T.J., K. Putyera, J. Jagiello and J.A. Schwarz, 1994. Study of carbon-smectite composites and carbons obtained by insitu carbonization of polyfurfuryl alcohol. *Carbon*, 32(4): 659-664.

Barata-Rodriguez, P.M., T.J. Mays and G.D. Moggridge, 2003. Structured carbon adsorbents from clay, zeolite and mesoporous aluminosilicate templates. *Carbon*, 41: 2231-2246.

Borode, J. O., O.O. Onyemaobi, J.A. Omotoyinbo, 2000. Suitability of some Nigerian clay as refractory raw materials. *Nig. J. Eng. Manag.* 1: 14-18.

Burket, C.L., R. Rajagopalan, A. Marencic, K. Dronvajjala and H.C. Foley, (2006). Genesis of porosity in polyfurfuryl alcohol derived nanoporous carbon. *Carbon*, 44: 2957-2963.

Choura, M., M.N. Belgaeem and A. Gandini, 1996. Acid catalyzed polycondensation of furfuryl alcohol: mechanisms of chromophore formation and crosslinking. *Macromolecules*, 17: 1087-90.

De Almeida-Filho, C. and A.J.G. Zarbin, 2006. Porous Carbon obtained by the Adsorption of reactive dyes from aqueous solution. *J. Braz. Chem. Soc.*, 17(6): 1151-1157

Eckert, H., Y.A. Levendis and R.C. Flagan, 1988. Glassy carbons from poly(furfuryl alcohol) copolymers: Structural studies by high-resolution solid state NMR techniques. *J. Phys. Chem.*, 92: 5011-5019.

Fasuba, O. A., O. Egunlae, B. Jimoh, 2001. Metallurgical analysis of Orin-Ekiti alumina clay deposit for use as a refractory. *J. Eng. Tech. and Ind. Appl.* 1(4): 67-71.

Fitzer, E. and W. Schafer, 1970. The effect of crosslinking on the formation of glasslike carbons from thermosetting resins. *Carbon*; 8; 353-64.

- Fitzer, E., W. Schafer and S. Yamada, 1969. The formation of glasslike carbon by pyrolysis of polyfurfuryl alcohol and phenolic resin. *Carbon*; 7: 643-648.
- Gbadebo, A.M., 2002. Evaluation of Engineering and Industrial Potentials of Tidal Flat clays in parts of Niger Delta, Nigeria. *Nig. J. Eng. Res. Dev.*, 1(3): 20-27.
- Igbokwe, P.K. and J.O. Ogbuagu, 2003. Effects of process parameters on the extraction of alumina from indigenous kaolinite clay deposit. *Nig. J. Eng. Res. Dev.*, 2(2): 23-26.
- Irabor, P.S.A., 2002. Physical and chemical investigation on some Nigerian kaolinite clays for use in the ceramics and allied industries. *Nig. J. Eng. Res. Dev.*, 1(1): 54-59.
- Kyotani, T., 2000. Control of pore structure in carbon. *Carbon*, 38(2): 269-286.
- Kyotani, T., H. Yamada, N. Sonobe and A. Tomita, 1994. Heat-treatment of polyfurfuryl alcohol prepared between taeniolite lamellae. *Carbon*, 32(4): 627-635.
- Lawal, A.O., J.A. Lori and E.J. Ekanem, 2010. Production of biomass carbon-aluminosilicate hybrid sorbent via urea intercalation into deferrated kaolinite. *J. Appl. Sci. Res.*, 6(11): 1662-1668.
- Lori, J.A., A.O. Lawal and E.J. Ekanem, 2007. Characterization and optimization of deferration of Kankara clay. *J. Eng. Appl. Sci.*, 2(5): 60-74.
- Mariwala, R. K. and H.C. Foley, 1994. Evolution of ultramicroporous adsorptive structure in poly(furfuryl alcohol)-derived carbogenic molecular sieves. *Ind. Eng. Chem. Eng.*, 33: 607-615.
- Odo, J.U. and C.O. Nwajagu, 2003. Possible Application of Eha-Alumona clay deposit in the production of refractories and ceramic wares. Proceedings of the Nigerian Materials Congress and Meeting of the Nigerian Materials Research Society at Conference Hall, Engineering Materials Development Institute, Akure. Nov. 12-14, pp: 109-111.
- Omowunmi, O.J., 2001. Characterization of some Nigerian clays as refractory materials for furnace lining. *Nig. J. Eng. Manag.*, 2(3): 1-4.
- Putyera, K., T.J. Badosz, J. Jagiello and J.A. Schwarz, 1994. Sorption properties of carbon composite materials formed from layered clay minerals. *Clays Clay Mine.*, 42(1): 1-6.
- Shiflett, M.B. and H.C. Foley, 1999. Ultrasonic deposition of high-selectivity nanoporous carbon membrane. *Science*, 285: 1902-1905.
- Sonobe, N., T. Kyotani and A. Tomita, 1988. Carbonization of polyacrylonitrile in a two-dimensional space between montmorillonite lamellae. *Carbon*, 26(4): 573-578.
- Zarbin, A.J.G., R. Bertholdo and M.A.F.C. Oliveira, 2002. Preparation, characterization and pyrolysis of polyfurfuryl alcohol/porous silica glass nanocomposite: A novel route to carbon template. *Carbon*, 40: 2413.