PRODUCTION AND CHARACTERIZATION OF ACTIVATED CARBON FROM BITUMINOUS NASARAWA COAL

E. Bala*, O. R. Momoh and B. Y. El-Yakubu

Department of Chemical Engineering, Ahmadu Bello University Zaria, Nigeria
*Corresponding Author's Email: balazibya@yahoo.com

ABSTRACT

Some varieties of coals, lignocellulosic materials like wood, coconut husk and various agricultural wastes can be used for production of activated carbon (AC). This study looks into the production of an AC from bituminous Lafia-Obi Nasarawa coal by chemical activation with phosphoric acid. The effects of activation temperature and time on the textural characteristics were investigated. A preliminary proximate analysis put the fixed carbon content of the raw coal sample at 63.6%, thereby effectively putting the coal within the rank of bituminous coal. The coal sample was activated with phosphoric acid in a coal to acid mass ratio of 1:4. As carbonization temperatures were varied between 550 and 700°C, and carbonization times of 2 and 3 hours, the effects of these two process variables on BET surface area, DR micropore volume and HK pore size were investigated. The AC sample produced at 550°C and 2 hours residence time was found to possess a BET surface area of 331.3.2 m^2/g, DR micropore volume of 0.125 cm^3/g and HK pore size of 9.237 Å, while AC sample produced at 700°C and 3 hours residence time was found to possess a BET surface area of 596.2 m^2/g, DR micropore volume of 0.173 cm^3/g and HK pore size of 9.435 Å. When using the water adsorption technique, the Langmuir and BET surface areas were 3855 m^2/g and 748.3 m^2/g respectively. These values are all within the ranges of most commercial activated carbon.
Keywords: Proximate analysis, Carbonization, Langmuir, BET, Coal.

INTRODUCTION

An Activated Carbon (AC) is a porous material which possesses a relatively large surface area, large pore volume and high adsorption capacity. It has numerous industrial applications such as in the separation/purification of liquids and gases, removal of toxic substances, catalysts and catalyst support, super capacitors, electrode and gas storage amongst others (Wu *et al.,* 2015). A variety of raw materials may be used for the production of AC. Some of the major raw materials used in its production are coal, wood, resin, coconut husk, olive stone, various agricultural wastes and nutshells (Erdogan and Kopac, 2018). Bituminous coal, due to its microstructure and surface composition has been proposed as a precursor for microporous and mesoporous AC by many researchers like Alcaniz-Monge *et al.* (2005) and Jibril *et al.* (2007). The two most widely used methods in the preparation of AC are the physical and chemical activation methods. In the physical activation method, the raw material is first carbonized and then subsequently activated using agents such as carbon dioxide, steam or air in a two-step process. The chemical activation method on the other hand is a one-step process in which the raw material is treated with chemical agents, such as metal chlorides ($AlCl_3$, $ZnCl_2$), alkali bases (NaOH, KOH), carbonates (K_2CO_3, Na_2CO_3) and acids (H_2SO_4, H3PO4) (Guo and Lua 1999; Hayashi *et al.,* 2000; Hussaro, 2014; Liou, 2010; Aravindhan*, et al.,* 2009; Toprak and Kopac 2017; Jibril *et al.*, 2007) before carbonization in an inert environment. An important advantage the chemical activation method has over the physical activation one is the relatively lower temperatures and shorter activation times in which the process is accomplished (Montoya and Petriciolet, 2012). Also, the global yield of the chemical activation method tends to be greater since the chemical agents reduce the production of tars and other volatile products such as acetic acid and methanol (Linares-Solano *et al.,* 1996; Lamine *et al.,* 2014). In general, the addition of a chemical

agent to the precursor leads to dehydration, dehydrogenation, formation of cross-links and hence polymerized, rigid matrix. The chemicals may also act as oxidation retardants, thereby leading to less release of volatiles and lower carbon burnt-off (Jibril *et al.,* 2007).

There abounds in literature various research works for the production of AC by chemical activation using different types of activation agents and coals. In 1998 Teng *et al.* prepared an AC from an Australian bituminous coal using phosphjoric acid as an activation agent. Some of their findings include the effect the acid to coal impregnation ratio had on the porosity of the starting material. Cuhadaroglu and Uygu (2008) prepared an AC from bituminous coal using different activating agents in order to establish the influence these reagents have on the surface characteristics of the AC. Varila *et al.* (2017) studied the effects of process parameters such as activation temerature and acid to coal impregnation ratio on surface area and adsorption capacity on the resulting AC. More recently, Erdogan and Kopac (2018) reported the production of a highly effective AC from a Turkish bituminous coal using KOH as an activating agent for sorption studies on organic vapours. In the chemical process industry today, demand for AC is on the rise. According to a report by Market Insider (2017), global demand for AC was about 1.65 million tons in 2016, up 6.7% from 2010, and recorded an increase of 6.3% during the period of 2012-2016. Owing to this rising demand, it becomes imperative for more detailed research into AC production form different sources. Bituminous Lafia-Obi Nasarawa coal could serve as a suitable precursur for the production of AC, but despite it's abundance in excess of 33 million metric tons in Nigeria, it's exploitation has not yet been fully undertaken (Wuyep and Obaje, 2012). This study looks into the feasability of an AC produced from Lafia-Obi Nasarawa coal by studing the

influence of some chosen process parametrs on the development of its porosity.

EXPERIMENTAL
Sample Collection Preparation
The coal samples used in the course of this study were obtained from Lafia-Obi Nasarawa state, Nigeria. The coal sample was first crushed with the aid of a jaw crusher and sieved to 2 mm aperture using an Impact test UK sieve. A preliminary proximate and elemental analysis was carried out on the coal sample prior to chemical activation. 100 g of coal sample was weighed and impregnated with 400 g of phosphoric acid, and heated at 80°C continuously on a constant temperature magnetic stirrer at 60 rpm for 3 hours to ensure maximum mixing between acid and sample. The resultant slurry was oven dried at 105°C for a period of 24 hours in accordance with a procedure described by Montoya and Petriciolet (2012).

Production of AC
50 g of phosphoric acid impregnated coal slurry was packed into a stainless steel tubular reactor (30 cm, i.d 5 cm) and placed in a tubular furnace manufactured by Hoskins Mfg. Co. USA. The furnace was heated in flowing nitrogen gas (flowrate of 5 L/min) at a rate of $13^{o}C/min$ up to a final temperature of $550^{o}C$ and then held at this temperature for 2 hours after which the furnace was switched off and allowed to cool in the nitrogen flow to room temperature. The cooled coal sample was then thoroughly washed in distilled water while constantly monitoring the pH level of the solution until a neutral solution was obtained, after which it was oven dried at 105°C for 12 hours to eliminate all moisture. This resultant AC sample is labeled AC1 in the text. Another AC sample designated AC2 was prepared using the same procedure, the only difference being in process conditions. AC2 was heated at a rate of 6.5°C/min up to a temperature of 700°C and held under these conditions for 3 hours.

Characterization of Produced AC
The samples prepared as described in section 2.2 were analyzed by a Nova 2010 series Automated Gas Sorption System manufactured by Qunantachrome Instruments for surface area, micropore volume and average pore size. The surface area of the samples was measured based on the Brunauer–Emmet–Teller (BET) method. The Dubinin–Radushkevich (DR) method was applied to calculate the micropore volume, and the average pore size was calculated based on the Horvath–Kawazoe (HK) method. The water technique surface area determination for both samples involved preparing saturated salt solutions of $CaSO_4$, $CaCl_2$, LiCl and NaCl salts by dissolving each of the salts in 10 ml of deionized water untill saturation was reached. According to Wexler and Hasegawa (1954), all saturated salt solutions have a standard relative humidity (Saturated relative vapor pressure ($\frac{P}{P_0}$)) at specific temperatures. 10 ml of a saturated solution of $CaSO_4$ was placed in an air tight desiccator alongside 1 g of AC1 sample and left to stand at room temperature (31°C) for 24 hours. Thereafter the sample was weighed with an analytical weighing balance with the water adsorbed taken by it as the increase in weight of the sample.. The values obtained were used to plot the water adsorption isotherm. This proceedure was repeated for $CaCl_2$, LiCl and NaCl salts and resultant values used to plot similar isotherms. AC2 was subjected to exactly the same proceedure too. The surface areas for both adsorbents were subsequently determined from the water adsorption isotherms using the Langmuir and BET equations as adopted by Adefila *et al.* (2003) and Diya'udeen *et al.* (2013).

RESULTS AND DISCUSSION
The results of a proximate/elemental analysis, BET characterization and water adsorption technique surface area are presented and discussed in the sections below.

Proximate and Elemental Analysis of Raw Coal Sample
Tables 1 and 2 display the proximate and elemental analysis for the raw coal samples as obtained from source in accordance with a procedure described by Teng *et al.* (1998) and Adinata *et al.* (2007).

Table 1: Proximate analysis of coal sample

Parameter	Value (%)
Moisture content	9.3
Fixed Carbon	63.6
Ash	6.9
Volatile matter	20.2

Table 2: Elemental analysis of Nasarawa coal

Parameter	Value (%)
Carbon	76.2
Hydrogen	5.89
Nitrogen	2.19
Sulphur	5.9
Oxygen	9.82

The data on Tables 1 and 2 show that the raw coal samples have fixed carbon (on dry basis) of 63.6% and by way of elemental analysis a carbon content of 76.2%. Table 3 provides the values of the proximate and elemental analysis of the various coal ranks as obtained from literature (Speight, 2005). The results on Table 1 and Table 2 clearly put the coal sample used in this work within the range of bituminous coals, and so can be used as precursor raw material for the production of AC.

Influence of Temperature
The effect of temperature on the development of surface area, micropore volume and average pore size of AC1 and AC2 was investigated. The data presented on Table 4 shows that as activation temperature were increased from 550 to 700°C, a corresponding increase in surface area, DR micropore volume and HK pore size was observed. This could be attributed to the formation of new pores, widening and modification of the internal pore structure of existing ones and the increasing release of volatile matter as activation temperature is increased (Teng *et al.,* 1998; Sun *et al.,* 2006). The values obtained for the BET surface area and micropore volume are comparable to those obtained by Adinata *et al.* (2007). According to Dizbay-Onat *et al.* (2017), a linear relationship exists between the surface area, micropore volume and carbonization temperature. Rodríguez-Mirasol *et al.* (2009) studied activation conditions for H_3PO_4 activated hemp fibers and showed that BET surface areas increase as carbonization temperatures are elevated with a high acid to fiber impregnation ratio. The DR micropore volume too was observed to increase with activation temperature. With increasing temperatures, more volatile matter is released from the precursor material during carbonization, giving rise to pore development, pore widening of micropores to mesopores as well as creation of new pores (Adinata, *et al.,* 2007). The HK pore size also showed a slight increase from 9.237 Å to 9.435 Å. This increase in pore size could be as a result of the widening of pore 'mouths' by the increasingly high temperature treatment the samples were subjected to. The average pore size results obtained in this study is corroborated by the work of Dizbay-Onat *et al.* (2016), who prepared an AC from industrial waste and found the average pore size of the samples produced fall within similar range (3Å-9Å).

Table 3: Composition and property ranges for various ranks of coal (proximate and elemental analysis)

Property	Anthracite	Bituminous	Subbituminous	Lignite
Moisture content (%)	3-6	2-15	10-25	25-45
Volatile matter (%)	2-12	15-45	28-45	24-32
Fixed carbon (%)	75-85	50-70	30-57	25-30
Ash (%)	4-15	4-15	3-10	3-15
Sulphur (%)	0.5-2.5	0.5-6	0.3-1.5	0.3-2.5
Hydrogen (%)	1.5-3.5	4.5-6	5.5-6.5	6-7.5
Carbon (%)	75-85	65-80	55-70	35-45
Nitrogen (%)	0.5-1	0.5-2.5	0.8-1.5	0.6-1.0
Oxygen (%)	5.5-9	4.5-10	15-30	38-45
Calorific value (Btu/I)	12,000-13,500	12,000-14,500	7,500-10,000	6000-7,500
Density (g/ml)	1.35-1.7	1.28-1.35	1.35-1.4	1.4-1.45

Speight (2005)

Table 4: BET characterization data for AC1 and AC2

Sample	Carbonization temperature (°C)	Carbonization time (hours)	BET multi-point surface area (m^2/g)	DR micropore volume (cm^3/g)	HK pore size (Å)
AC1	550	2	331.3	0.125	9.237
AC2	700	3	596.2	0.173	9.435

Influence of activation time
An increase in surface area was observed when activation time was increased from 2 to 3 hours. This could be explained from the point of view that a prolonged residence time might be necessary for a full development of porosity. Also, a prolonged high temperature treatment could be responsible for the destruction of pore walls (conversion of micropores into mesopores). The data presented on Table 4 backs this assumption. This postulation is in agreement with the work of Teng *et al.* 1998 who studied the effect of activation time on the development of porosity in activated carbons and came to a similar conclusion. Ahmad *et al.* (2014) observed that surface area and micropore volume increased in their AC samples as holding time was increased. They attributed it to the fact that longer residence times favour the evolution of volatiles from within the material's structure giving rise to an increased surface area and micropore volume. They did not however observe a corresponding increase in average pore size.

Water technique adsorption surface area determination of AC1 and AC2
A water technique adsorption surface determination was carried out for both AC samples. The adsorption isotherms generated are shown on Figures 1 and 2. Table 5 shows a comparison between the surface area data obtained by standard nitrogen Langmuir and BET and the corresponding Langmuir and BET surface areas obtained by the water adsorption technique.
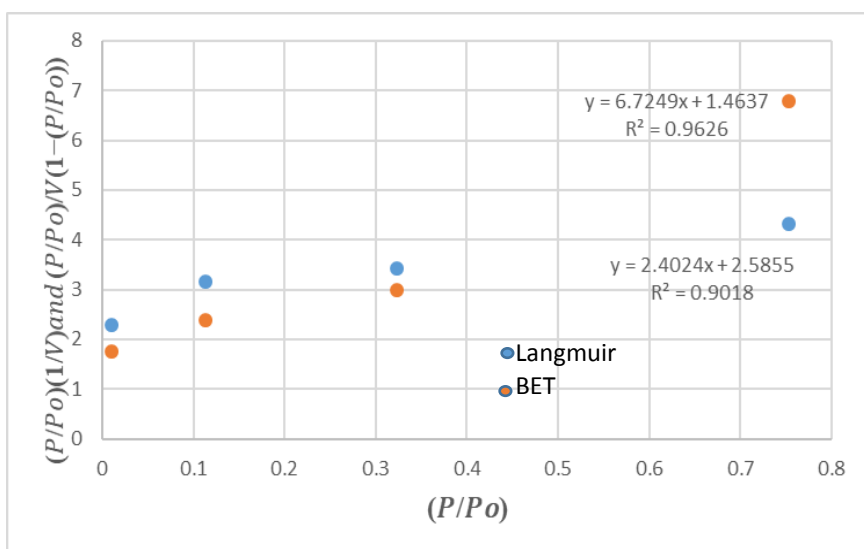
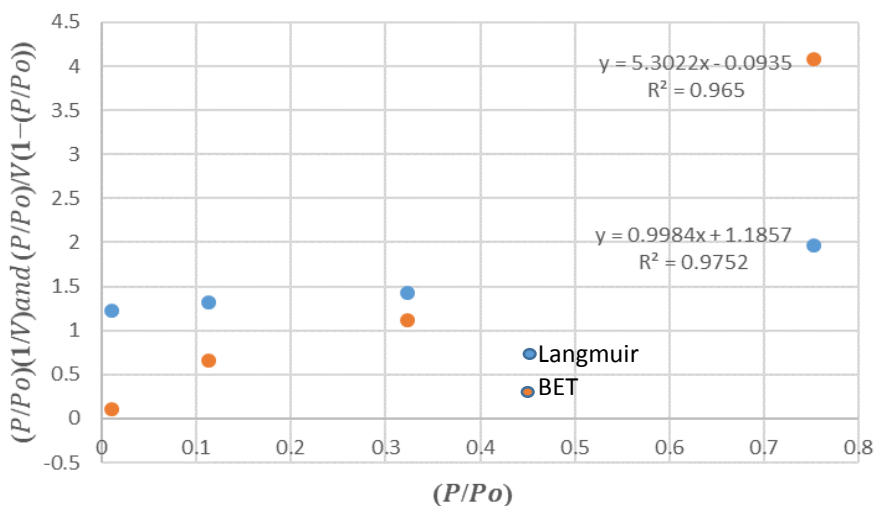Figure 1: Langmuir and BET water adsorption isotherm for AC1

Figure 2: Langmuir and BET water adsorption isotherm for AC2

Table 5: Comparative values between standard nitrogen Langmuir and BET surface areas and water adsorption technique Langmuir and BET

Sample	Standard nitrogen BET surface area (m²/g)	Water technique BET surface area (m²/g)	Standard nitrogen Langmuir surface area (m²/g)	Water technique Langmuir surface area (m²/g)
AC1	331.3	475.9	1983	2192
AC2	596.2	748.3	3567	3855

From the surface area values on Table 5, it can be seen that when the water technique was employed to determine the surface areas of both adsorbents, the BET isotherm generated values well over and above those obtained from the standard BET. This can be explained from the point of view of the differences in kinetic diameter of the different probe molecules used in the generation of the surface areas by both techniques. The water adsorption technique employs the water molecule to probe into the pore structure of the adsorbent, while the standard BET makes use of the nitrogen molecule. Since the average area of one adsorbed molecule of water (10.5×10^{-20} m²) is smaller than that of nitrogen (16.0×10^{-20} m²), the pore structure of both adsorbents are able to adsorb more water molecules due to polycondensation and hence generate isotherms that consequently register higher surface areas (Adefila *et al*., 2003; Diya'udeen *et al*., 2013). The plots on Figures 1 and 2 depict a Type II isotherm indicating the presence of a wide and indefinite multi-layer formation after completion of the monolayer and is found in adsorbents with a wide distribution of pore sizes, which as is reported in literature common with AC of this kind (Hussaro, 2014).

CONCLUSIONS

The present work shows that Lafia-Obi Nasarawa bituminous coal based AC with highly developed porosity can be prepared by chemical activation with H_3PO_4. The proximate analysis carried out on the raw coal sample showed it to have a fixed carbon content of 63.6%, thereby establishing it as being bituminous in coal ranking. Data are tabulated for Multi-point BET surface area, DR micropore volume, and HK pore size. The sample produced having the most suitable porosity designated as AC2 in text had a BET Multi-point surface area of 596.2 m²/g, DR micropore volume of 0.173 cm³/g and a HK pore size of 9.435 Å. A comparison of the surface areas obtained by standard BET with that obtained by the water adsorption technique was also made. Using this technique, the BET Multi-point surface area of the AC2 sample was calculated to be 748.3 m²/g, while Langmuir surface area was found to be 3855 m²/g. It is evident from the data generated that activation temperature and time play important roles in the development of porosity in ACs. The textural characterization of the AC samples produced suggests its possible application in molecular separation processes.

REFERENCES

Adefila, S. S., Aderemi, B. O., Ajayi, O. A. and Baderin, D. A. (2003). Comparative surface area determination using water adsorption method. *Nigerian Journal of Engineering, 11,* 88-95.

Adinata, D., Daud, W. M. and Aroua, M. K. (2007). Production of carbon molecular sieves from palm shell based activated carbon by pore sizes modification with benzene for methane selective separation. *Fuel Processing Technology*, 88, 599-605.

Ahmad, M. A., Herawan, S. G. and Yusof, A. A. (2014). Effect of activation time on the pinang frond based activated carbon for remazol brilliant blue R removal. *Journal of Mechanical Engineering and Sciences,* 7, 1085-1093.

Alcaniz-Monge, J., Castello, D. L., Cazorla-Amorós, D., Linares-Solano, A., Zhu, W., Kapteijn, F. and Moulijn, J. A. (2005). Adsorption properties of carbon molecular sieves prepared from an activated carbon by pitch pyrolysis. *Carbon*, 43(8), 1643–1651.

Aravindhan, R., J. R. Rao and B. U. Nair. 2009. "Preparation and Characterization of Activated Carbon from Marine Macro-Algal Biomass. *Journal of Hazardous Materials* 165: 688–694.

Diya'uddeen, B. H., Mohammed, I. A., Jibril, B. Y. and Bugaje, I. M. (2013). Comparison of BET and water adsorption techniques. *American Journal of Engineering and Applied Sciences*, 6 (30), 282-285.

Dizbay-Onat, M., Vaidya, U. K. and Lungu, C. T. (2017). Preparation of industrial sisal fiber waste derived activated carbon by chemical activation and effects of carbonization parameters on surface characteristics. Industrial Crops and Products, 9, 583 – 590.

Erdogan, F. and Kopac, T. (2018). Highly Effective Activated Carbons from Turkish–Kozlu Bituminous Coal by Physical and KOH Activation and Sorption Studies with Organic Vapors. *International Journal of Chemical Reactor Engineering*.

Guo, J. and Lua, A. C. (1999). "Textural and Chemical Characterizations of Activated Carbon Prepared from Oil-Palm Stone with H2SO4 and KOH Impregnation." *Microporous and Mesoporous Materials* 32: 111–117.

Hayashi, J., Kazehayaa, A., Muroyamaa, A. K. and Watkinso, P. (2000). Preparation of activated carbon from lignin by chemical activation. *Carbon*, 1873-1878.

Hayashi, J. T. Horikawa, I. Takeda, K. Muroyama and F. N. Ani. 2002. "Preparing Activated Carbon from Varios Nutshells by Chemical Activation with K₂CO₃." *Carbon* 40: 2381–2386.

Hussaro, K. (2014). Preparation of Activated Carbon from Palm Oil Shell by Chemical activation with Na₂CO and ZnCl₂ as impregnated agents for H₂S Adsorption. *American Journal of Environmental Sciences ,* 10 (4), 336-346.

Jibril, B. Y., Al-Maamari, R. S., Al-Mandhary, N., Hegde, G. and Houache, O. (2007). Effects of feedstock pre-drying on carbonization of KOH-mixed bituminous coal in preparation of activated carbon. *Journal of analytical and applied pyrolysis,* 80 , 277–282.

Lamine, S. M., Ridha, C., Mahfoud, H., Mouad, C., Lotfi, B and Al-Dujaili, A. H. (2014). Chemical activation of an Activated carbon Prepared from coffee residue. *Energy Procedia,* 50, 393 – 400.

Liou, T. H. 2010. "Development of Mesoporous Structure and High Adsorption Capacity of Biomass-Based Activated Carbon by Phosphoric Acid and Zinc Chloride Activation." *Chemical Engineering Journal* 158: 129–142.

Linares-Solano, A., Illa´n-Go´mez, M. J., Garcı´a-Garcı´a, A. and Salinas-Martı´nez de Lecea, C. (1996). Activated Carbons from Spanish Coals. 2. Chemical Activation. *Energy and Fuels,* 10 (5), 1108-1114

Montoya, V. H. and Petriciolet, A. B. (2012). *Thermal Treatments and Activation Procedures Used in the Preparation of Activated Carbons.* Intech publishers Rijeka, Croatia (1st ed, pp.19-36).

Market Insider (2017). *Global and China Activated Carbon Market 2017-2021 - 6 Foreign and 19 Chinese Activated Carbon Enterprises.* New York: Business Insider. Retrieved from https://markets.businessinsider.com/news/stocks/global-and-china-activated-carbon-market-2017-2021-6-foreign-and-19-chinese-activated-carbon-enterprises-1002245568.

Sun,Y., Zhang , J., Yang, G. and Li, Z. (2006). Removal of Pollutants with Activated Carbon Produced from K2CO3 Activation of Lignin From Reed Black Liquors. *Chem. Biochem. Eng Journal,* 20(4), 429-435.

Toprak, A. and Kopac, T. (2017). Carbon Dioxide Adsorption Using High Surface Area Activated Carbons from Local Coals Modified by KOH, NaOH and ZnCl2 Agents. *International journal of chemical reaction engineering,* 15(3), 1-16.

Rodríguez-Mirasol, J., Cordero, T., Rosas, J. M. and Bedia, J. (2009). HEMP-derived activated carbon fibers by chemical activation with phosphoric acid. *Fuel,* 88, 19-26.

Speight, J. G. (2005). *Handbook of Coal analysis.* John Wiley and sons Inc., Hoboken, New Jersey. Vol 166, pp 42.

Sun,Y., Zhang , J., Yang, G. and Li, Z. (2006). Removal of Pollutants with Activated Carbon Produced from K2CO3 Activation of Lignin From Reed Black Liquors. *Chem. Biochem. Eng Journal,* 20(4), 429-435.

Teng, H., Yeh, T. and Hsu, L. (1998). Preparation of activated carbon from bituminous coal with phosphoric acid activation. *Carbon,* 36*(9).* 1387-1395.

Wexler, A. and Hasegawa, S. (1954). Relative Humidity-Temperature Relationships of Some Saturated Salt Solutions in the Range 0°C to 50°C. *Journal of Research of the National Bureau of Standards, 53(1).* 2512.

Wuyep, E. O. and Obaje, N. G. (2012). *Petrographic Evaluation of the Ranks and Technological Applications of Some Coal Deposits in the Anambra Basin and Middle Benue Trough of Nigeria.* Journal of Earth Science and Engineering 2 Pg. 220-234.

Wu, Z., Xiao, X., Liu, D., Yan, X., Wu, Z. and Caravotto, G. (2015). Preparation of activated carbon from Xinjiang region coal by microwave activation and its application in naphthalene, phenanthrene, and pyrene adsorption. *Journal of the Taiwan Institute of Chemical Engineers, 000,* 1-8.