



BEST JOURNAL 8(2): 129 - 134
Date received: January, 2011
Date accepted: May, 2011
Printed in Nigeria



PYROLYSIS AND CHARACTERIZATION OF COAL AS PRECURSOR OF POROUS CARBON USED IN THE PURIFICATION OF DYE EFFLUENT

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ABSTRACT

Pyrolysis and characterization of Enugu coal as precursor for porous carbon in the purification of dye effluent was investigated. The coal sample was carbonized at four different temperatures (750, 800, 850, 900 °C) and then activated using three different activating agents (potassium hydroxide, hydrochloric acid and equimolar mixture of both activating agents). The activated carbon was characterized in terms of ash content, pore volume and iodine number. The characterized activated carbon was then used in the purification of dye effluent and properties of the dye effluent such as; pH, density, biochemical oxygen demand (BOD), turbidity and total solids were analyzed before and after treatment of the dye effluent with the activated carbon at 28 °C. From the results obtained, the iodine number of the carbon produced by KOH activation was as high as 1098.17 mg/g, at a maximum pyrolysis temperature of 900 °C, with HCl and equimolar mixture (KOH + HCl) having 976.15 mg/g and 1073.77 mg/g respectively. The biochemical oxygen demand of the dye effluent was reduced from 370 mg/dm³ before treatment by KOH activation to 47.09 mg/dm³ at 900 °C carbonization temperature, indicating 87% reduction.

Keywords: Coal, Pyrolysis, Characterization, Porous-carbon, Purification, Dye-effluent

INTRODUCTION

The importance and relevance of activated carbon to an ever growing society cannot be overemphasized considering its enormous uses. Its uses range from liquid-phase to gaseous-phase applications in domestic, commercial and industrial settings. Activated carbon is produced from various materials that are rich in carbon, particularly, coal, lignite, wood, nutshell, peat, pitches, cokes etc. The performance of activated carbon is indicated by its adsorptive characteristics, which is derived from the specific surface area, pore size and pore volume, of the product (Kirk-Othmer, 2004). These physical properties depend on the precursor used, the type of activation employed and the activation process conditions. The choice of precursor is largely dependent on its availability, cost and purity, but the manufacturing process and intended application of the product are also important considerations. Basically, the methods for preparation of porous carbons can be grouped into two types, the physical activation method and the chemical activation method (Patrick, 1995). The active agents used in chemical activation process are usually KOH, ZnCl₂ and H₃PO₄, H₂SO₄ etc., the active agents used in the chemical activation method, such as KOH, has dehydrating effect that inhibits the formation of tar (Yasumasa, 1982; Takashi *et al.*, 1994), which helps to enhance the yield of porous carbon and to decrease the activation temperature compared with the physical activation method (Kandiyoti *et al.*, 1984; Ahmadpour and Do, 1996). It is also quite easy for one to prepare high quality porous carbons with well-developed pore structure by chemical activation method. Coal is a readily combustible black or brownish-black

sedimentary rock normally occurring in rock strata in layers or veins called coal beds. The harder forms, such as anthracite coal, can be regarded as metamorphic rock because of later exposure to elevated temperature and pressure. Coal is composed primarily of carbon along with variable quantities of other elements, chiefly sulfur, hydrogen, oxygen and nitrogen (BS, 2004).

Coal based activated carbon originates from coal that has undergone physical or chemical activation process to create its activated carbon form. During activation, it creates millions of pores at the surface of the carbon thus increasing the total surface area. Activated carbon pores can be divided into three general sizes Micro-pores (diameter in the range of less than 2 nm), Meso-pores (diameter in the range of 2 – 25 nm), and Macro-pores (diameter in the range of above 25 nm). Coal based carbon has mainly meso-pores and macro-pores and due to its unique distribution of pores diameter, coal based activated carbon are very popular in the gas phase purification, portable water purification industries, wastewater purification industries and aquarium/pond water purification industries (IRWI, 2010). Wastewater is any water that has been adversely affected in quality by anthropogenic influence. It comprises liquid waste discharged by domestic residences, commercial properties, industry, and/or agriculture and can encompass a wide range of potential contaminants and concentrations. In the most common usage, it refers to the municipal wastewater that contains a broad spectrum of contaminants resulting from the mixing of wastewaters from different sources (BS, 2004).



This work reports the pyrolysis and characterization of coal as precursor for porous carbon in the purification of dye effluent. This was performed via the use of raw coal sample obtained from Enugu coal mines, Enugu state, Nigeria. The coal sample was carbonized and there after activated using chemical activation with potassium hydroxide (KOH), hydrochloric acid (HCl) and equimolar mixture of KOH and HCl as the activation agents. The work is aimed at producing Granulated Activated Carbon (GAC) with highly developed pore structure, which is one of the best commercial proven methods for removing toxic organic chemicals, such as phenol, from wastewater (Ferguson, 1977).

MATERIALS AND METHODS

The materials and equipment employed in this work include among others, hydrochloric acid, sodium thiosulphate, potassium hydroxide, tetroxosulphate (vi) acid, dye effluent, dessicator, hotspot furnace, electric oven, heating mantle and turbidimeter. All the chemicals used are of analytical grade. In this study, the coal sample was obtained from Enugu Coal Mines, Nigeria. The proximate analysis of raw coal sample was determined as described by Adeleke *et al* (2007).

Carbonization

The 600 g pretreated sample was then divided into twelve different parts each having a mass of 50 g. Three of the 50 g sample well dried were taken and placed in three different porcelain crucible then transferred to the furnace for carbonization at an increment of 15 °C/min until a final temperature of 750 °C was reached; this was then allowed to carbonize for 2 hours. The carbonized samples were then removed and allowed to cool in the desiccator to room temperature. The procedure was repeated for the remaining nine samples which were divided into three 50 g samples each but at different carbonization temperature of 800 °C, 850 °C and 900 °C (Alenka *et al*, 2003).

Chemical Activation

Three different activating agents were used and these include; potassium hydroxide (KOH), hydrochloric acid (HCl) and equimolar mixture of both activating agents.

The carbonized coal samples at 750 °C were carefully weighed and put into three different beakers containing 1 M KOH, 1 M HCl and an equimolar mixture of KOH and HCl. The impregnating ratio of activated carbon to activating agent used was 2:1. The content of the beaker was thoroughly mixed using a stirrer until there was uniform mixture. The mixture was then transferred to a crucible and the crucible was placed in the furnace. The temperature of the furnace was raised at an increment of 15 °C/min until a final activation temperature of 600 °C was reached and the sample was left for one hour in the furnace. The activated coal sample was then cooled at room temperature in the desiccator, and washed with hydrochloric acid and thereafter with distilled water to a pH of 6 - 7, and then dried in an oven at 110 °C for three hours (Adeleke *et al*, 2007). The above procedure was repeated at different carbonization temperatures of 800 °C, 850 °C and 900 °C. The final products (activated coal sample) were kept in different air tight polyethylene bags and labeled A, B, C and D according to the carbonization temperature 750 °C, 800 °C, 850 °C and 900 °C respectively. Finally characteristic properties of produced activated carbon such as ash content, pore volume, iodine number were determined. The activated carbon was used to treat effluent using standard procedures as described by (Adeleke *et al*, 2007; Dunn and Benson, 2003; Samwel, 2005). The dye effluent was characterized before and after treatment with the produced activated carbon sample.

RESULTS

The proximate analysis results of moisture content, ash content, volatile content and fixed carbon are presented in Table 1.0 respectively. And Table 2.0 shows the properties of activated carbon at different activating agents and temperatures. The characteristics properties of dye effluent before and after treatment are shown in Tables 3.0 and 4.0. While Table 5.0 showed the results of biochemical oxygen demand after treatment. Figures 1.0 and 2.0 represent the effect of carbonization temperature on iodine number and biochemical oxygen demand.

Table 1.0 Result of Proximate Analysis

Parameters (%)	Coal sample	Referenced coal sample (Adeleke <i>et al</i> , 2007).
Moisture content	8.0	8.15
Ash content	7.5	7.57
Volatile matter	43.5	43.62
Fixed carbon	41.0	40.66



Table 2.0 Properties of Activated Carbon at Different Reagents and Temperatures

Activating agent	Pyrolysis temperature (°C)	Ash content (%)	Pore volume (cm ³ /g)	Iodine number (mg/g)
KOH	750	8.0	0.65	658.90
	800	8.5	0.68	780.92
	850	9.5	0.74	902.94
	900	11.0	0.83	1098.17
HCl	750	9.5	0.57	497.84
	800	10.0	0.60	536.88
	850	11.5	0.67	732.12
	900	12.0	0.75	976.15
KOH + HCl	750	8.5	0.60	561.29
	800	9.0	0.66	732.12
	850	10.0	0.72	805.33
	900	11.5	0.81	1073.77

Table 3.0 Characteristics of Dye Effluent before Treatment

Parameters	Dye effluent
pH	12.59
Turbidity (NTU)	90.00
Temperature (°C)	28.00
Density (g/ml)	1.16
Total solids (mg/dm ⁻³)	160.00
BOD (mg/dm ⁻³)	370.00
Appearance	darkish blue
Odour	offensive

Table 4.0 Characteristics of Dye Effluent after Treatment

Activating agent	Pyrolysis temp. (°C)	pH	Density Total (g/cm ³)	Turbidity solids (mg/dm ³)	Temperature (NTU)	Temperature (°C)
KOH	750	9.78	1.13	50.23	80.57	28
	800	9.52	1.10	45.10	79.61	28
	850	9.23	1.07	42.03	78.12	28
	900	8.98	1.05	38.17	77.09	28
HCl	750	9.97	1.15	53.00	82.00	28
	800	9.91	1.12	50.09	80.04	28
	850	9.86	1.08	47.45	79.11	28
	900	9.66	1.08	46.98	78.03	28
KOH + HCl	750	10.01	1.14	51.03	83.02	28
	800	9.98	1.10	49.06	81.92	28
	850	9.95	1.10	48.91	78.88	28
	900	9.90	1.06	47.30	78.98	28

Table 5.0 Results of Biochemical Oxygen Demand after Treatment

Activating agent	Pyrolysis temp. (°C)	BOD (mg/dm ³)
KOH	750	60.54
	800	56.61
	850	50.12
	900	47.09

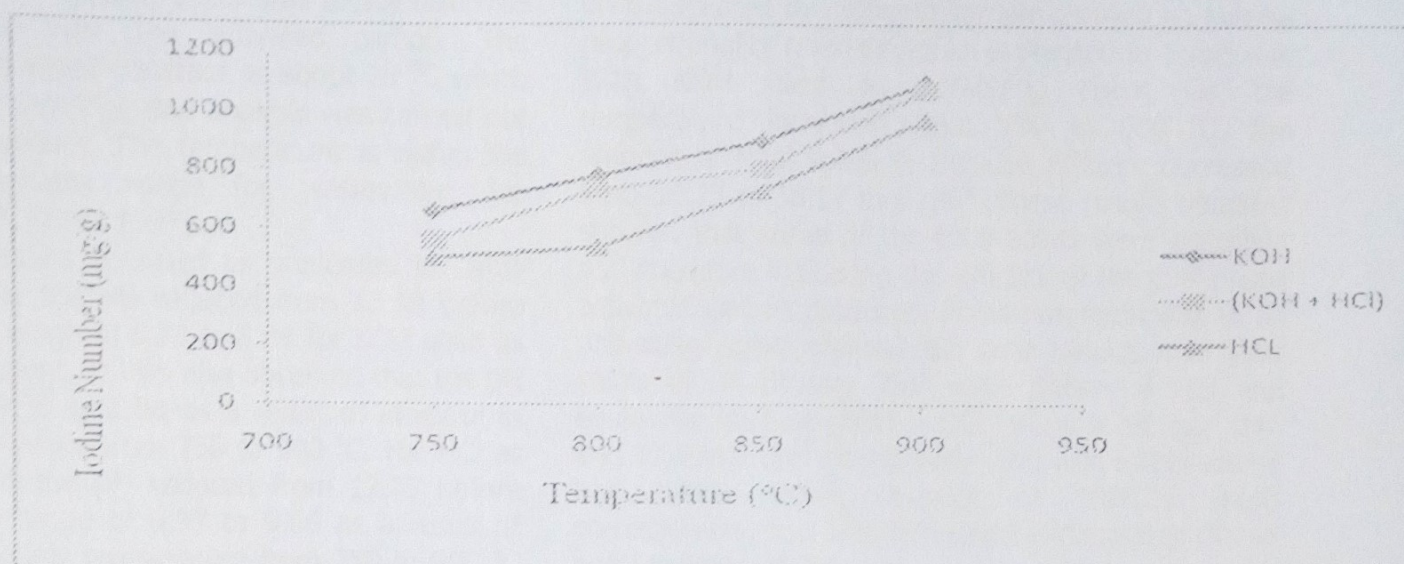


Figure 1.0 Effect of Carbonization Temperature on Iodine Number

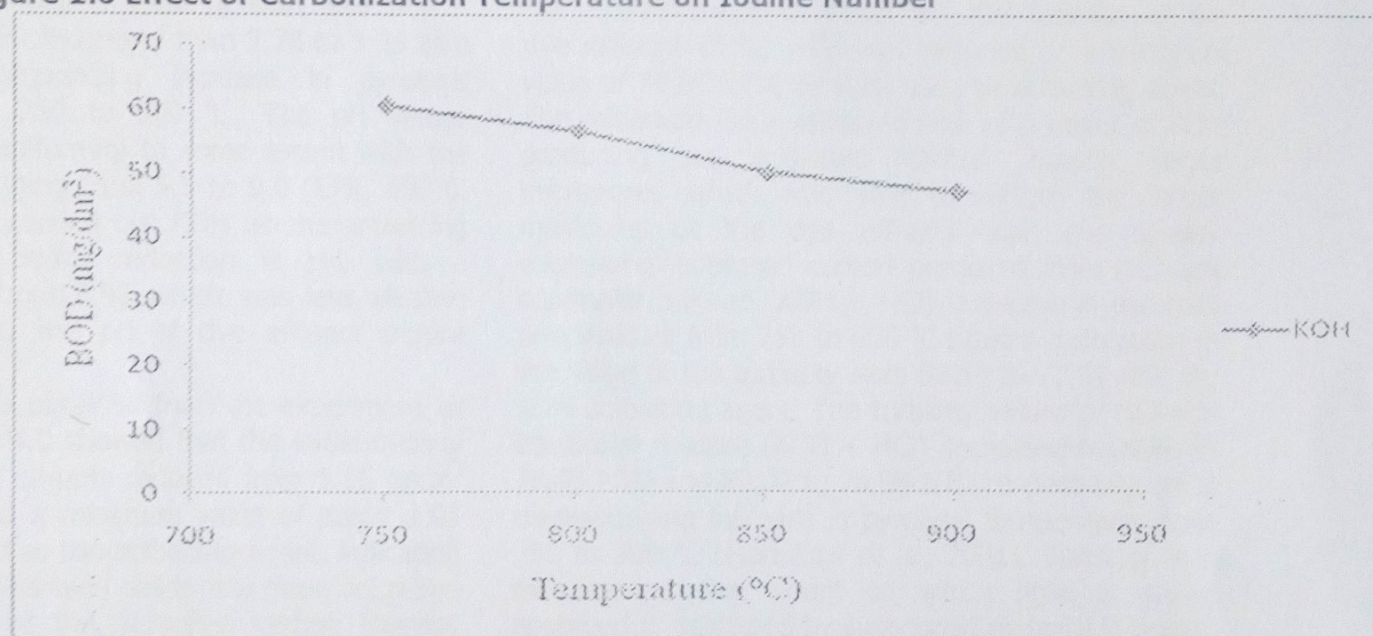


Figure 2.0 Effect of Carbonization Temperature on BOD

DISCUSSION

The results of the proximate analysis performed as shown in Table 1.0 revealed that raw coal sample is bituminous in nature (Adeleke *et al.*, 2007;). From Table 2.0 it can be seen that the ash content increased from 8 % to 11 % for a corresponding increase in pyrolysis temperature from 750 °C to 900 °C for KOH as an activating agent. While the ash content of HCl as activating agent increased from 9.5 % to 12 % for a corresponding increase in pyrolysis temperature from 750 °C to 900 °C. And the ash content of the equimolar mixture (KOH + HCl) increased from 8.5 % to 11.5 %. The referenced ash content ranges from 8-12 % (BS, 2004). For production of activated carbon, it is an advantage if the ash content is as low as possible (Alenka *et al.*, 2003). Therefore KOH with lower range of ash content (8 % to 11 %) has characteristics of the best activating agent for coal sample. While HCl with the highest ash content of 12 % is not a good activating agent for coal sample. At higher carbonization temperature more ash is formed, therefore increasing the amount of ash content. The result presented in Table 2.0 showed that KOH is a suitable activating

agent for the preparation of high-porosity carbons from coals. The iodine number and the pore volume of the carbon produced by KOH activation was as high as 1098.17 mg/g and 0.83 cm³/g, respectively, at a pyrolysis temperature of 900 °C, the iodine number and the pore volume of the activated carbon produced by HCl activation was as high as 976.15 mg/g and 0.75 cm³/g, respectively and for KOH + HCl activation was as high as 1073.77 mg/g and 0.81 cm³/g (Tanzil, 2001). The table also revealed that for each activating agent, the iodine number increased appreciably with increase in carbonization temperature. This is so because the surface area of the activated carbon is improved greatly by temperature, thereby increasing the rate of adsorption of iodine into the well developed pores of the activated carbon. From the result presented in Table 3.0 above, the pH shows that the dye effluent is highly alkaline with a pH of 12.59 which conformed with literature with pH ranging from 9 to 12 (Sivaramakrishnan, 2004). The odour of the effluent was found to be offensive. Table 4.0 shows the result of the characteristics of dye effluent after treatment for the twelve samples analyzed.



The appearance of the dye effluent became a little clearer while the offensive odour was totally removed after treatment with the activated carbon. The temperature remained constant at about 28 °C which was due to the fact that, the analysis was carried out at room temperature. The temperature is within the minimum acceptable range for wastewater, for example ≤ 37 °C (EPA, 1997).

The results obtained as presented in Table 4.0 showed that the pH reduced from 12.59 before treatment to a range of 9.78 to 8.98 for KOH used as the activating agent. It was also observed that the pH reduced from 9.78 to 8.98 as a result of increase in pyrolysis temperature from 750 to 900 °C. For HCl as activating agent the pH reduced from 12.59 before treatment to a range of 9.97 to 9.66 as a result of increase in pyrolysis temperature from 750 to 900 °C while for the equimolar mixture of KOH and HCl as activating agent, pH decreased from 9.78 to 8.98 as a result of a corresponding increase in pyrolysis temperature from 750 to 900 °C. The pH values obtained showed uniformity to some extent with the standard of pH ranging from 5.5 to 9.0 (EPA, 1997). From the analysis carried out KOH as the activating agent showed a better reduction in pH, with a minimum pH of about 8.98 which was less alkaline when compared to the pH of dye effluent before treatment.

The results obtained from the experiment as presented in Table 4.0 showed that the initial density of the dye effluent sample reduced from 1.16 g/cm³ before treatment to a minimum value of about 1.05 g/cm³ for KOH used as the activating agent, indicating that some of the dissolved solids had been adsorbed onto the surface of the activated carbon thereby reducing the mass of the wastewater sample and consequently a proportional decrease in the density of the effluent. Consequently the density of HCl used as an activating agent decreased from 1.16 g/cm³ before treatment to a minimum value of about 1.08 g/cm³ while for equimolar mixture of the activating agent (KOH + HCl), the density reduced from 1.16 g/cm³ before treatment to a minimum value of about 1.06 g/cm³. Finally, it was also observed that for KOH as the activating agent, the density of treated dye effluent decreased from 1.13 to 1.05 g/cm³ with increase in pyrolysis temperature from 750 to 900 °C. While for HCl and equimolar mixture of activating agent, the density of treated dye effluent decreased from 1.15 to 1.08 g/cm³ and 1.14 to 1.06 g/cm³ respectively, for a corresponding increase in pyrolysis temperature from 750 to 900 °C. Potassium hydroxide as activating agent has a higher iodine number of about 1098 mg/g which implied a higher adsorption rate, thereby reducing the density of dye effluent better than HCl and equimolar mixture of KOH and HCl.

From Table 4.0 the initial value of the total solids of dye effluent obtained to be 160 mg/dm³ was reduced to a minimum value of 38.17 mg/dm³, which implied that an adsorption ratio of about 76 % of the

total solids was achieved. The effect of temperature on the treated dye effluent sample showed an inverse proportionality relationship as presented in Table 4.0. With KOH used as activating agent, as the temperature increased from 750 to 900 °C, the amount of total solids in the dye effluent decreased from 50.23 to 38.17 mg/dm³. These results obtained showed that some of the total solids were adsorbed and therefore indicating the efficacy of the coal based activated carbon produced. Potassium hydroxide as an activating agent showed the best reduction of total solids of 38.17 mg/dm³ while those of HCl and equimolar mixture (KOH + HCl) were 46.98 mg/dm³ and 47.3 mg/dm³ respectively. This was so because it had better iodine number of 1098.17 mg/g corresponding to a well developed surface area (Yusuf and Sonibare, 2005).

As shown in Table 4.0 the turbidity of the dye effluent of 90 NTU was reduced to a minimum value of 77.09 NTU, by KOH used as activating agent. The minimum value obtained was as a result of KOH producing an activated carbon having larger micropores which was able to adsorb the larger molecules of the dye effluent than the smaller micropores activated carbon produced from HCl and equimolar mixture (KOH + HCl). Increase in pyrolysis temperature from 750 to 900 °C caused a decrease in the value of the turbidity from 80.57 to 77.09 NTU for KOH activating agent. The turbidity values of HCl and equimolar mixture (KOH + HCl) decreased from 82 to 78.03 NTU and 83.02 to 78.98 NTU respectively, for a corresponding increase in pyrolysis temperature from 750 to 900 °C (Madukasi *et al.*, 2001). Turbidity is a measure of the extent to which light is either absorbed or scattered by suspended material in water, but it is not a direct quantitative measurement of suspended solids. Both the size and surface characteristics of the suspended material influence absorption and scattering. Clarity of water is usually measured by its turbidity.

The results of the BOD obtained for KOH as activating agent for four different temperatures of 750, 800, 850 and 900 °C are tabulated in Table 5.0. This was used to test for the biochemical oxygen because KOH as activating agent had the best rate of adsorption with a higher iodine number of 1098.17 mg/g. The values of biochemical oxygen demand obtained were found to decrease from 60.54 to 47.09 mg/dm³ with increase in pyrolysis temperature from 750 to 900 °C. The acceptable biochemical oxygen demand values for textile effluent ranging from 30 to 100 mg/dm³ when compared with the values of biochemical oxygen demand obtained revealed that the treated dye effluent had standard biochemical oxygen demand values (BS, 2004). Biochemical oxygen demand is a sum parameter and the amount of oxygen required to oxidize organic matter present in the water biochemically. Therefore, biochemical oxygen demand is an indirect measure of the concentration of organic contamination in water (Dunn and Benson, 2003).



Figure 1.0 shows the effect of carbonization temperature and activating agent on the iodine number of coal based activated carbon. The iodine number is an important characteristic of activated carbon. Activation by KOH from Figure 1.0 showed the best plot with higher iodine number, activation by equimolar mixture of KOH and HCl showed the second best plot as against that of activation by HCl. This is due to the fact that the potassium hydroxide present in the equimolar mixture (KOH + HCl) increased its efficiency. The figure also revealed that for each activating agent, the iodine number increased appreciably with increase in carbonization temperature. This is so because the surface area of the activated carbon is improved greatly by temperature, thereby increasing the rate of adsorption of iodine into the well developed pores of the activated carbon. Figure 2.0 shows the effect of carbonization temperature on the biochemical oxygen demand (BOD). The figure shows that the biochemical oxygen demand decreased with increase in the carbonization temperature of the activated carbon, indicating that at higher carbonization temperature more of the oxygen contained in the wastewater was adsorbed by the activated carbon. Judging from the fact that activation by KOH has the best adsorption

rate, analysis of the biochemical oxygen demand was done using activated carbon samples produced by KOH activation.

CONCLUSION

In this study, the use of Enugu coal for the production of activated carbons with chemical activation was investigated. The effects of process variables such as chemical reagents, and carbonization temperature were investigated. The resultant activated carbons were characterized in terms of iodine number, pore volumes and ash content. Iodine number and pore volumes were the most important characteristics of the activated carbon. This study has demonstrated that KOH is a suitable activating agent for the preparation of high-porosity carbons from coals. The iodine number and the pore volume of the activated carbon produced by KOH activation was as high as 1098.17 mg/g and 0.83 cm³/g, respectively, at a pyrolysis temperature of 900 °C. The biochemical oxygen demand of the dye effluent was reduced from 370 mg/dm³ to a minimum of 47.09 mg/dm³ showing about 87 % reduction and the offensive odour was totally removed. And hence the main objective of the study was achieved.

REFERENCES

- Adeleke, A.O.; Makan, R.S.; and Ibitoye, S.A. (2007). Gray-king Assay Characterization of Nigerian Enugu and Polish Bellview Coals for Co-carbonization. *J.Applied Sci.*,7: 455- 8
- Alenka, Z.; Christian, W.; Joerg, W.; and Franci, L. (2003). Characterization of Carbonizate Produced From Velenje Lignite in Lab-Scale Reactor. *Acta chim. Slov.* 50: 789-798.
- Ahmadpour, A. and Do, D.D. (1996). The Preparation of Active Carbons from Coal by Chemical and Physical Activation. *Carbon* 34(4): 471- 479.
- BS. (2004). Britannica software. Coal mining: ancient use of outcropping coal. 209-215
- Dunn, R. P. and Benson, J. A. (2003). Turbine Air Filtration Cogeneration and on-Site Power. Institute of Water Management Hamburg University of Technology. 5-49.
- EPA. (1997). Environmental Protection Act. Carbon Dioxide Emissions from the Generation of Electric Power in the United States, *DOE Am J Emerg Med* 7 (5): 474-80.
- Ferguson, G. (1977). Treatment of Phenolic Wastes: *Chem. Engng.* 889-896.
- IRWI. (2010). The Information Resource for the Water Industry, [http:// www.google.com/](http://www.google.com/) (Accessed June 27th 2010).
- Kandyoti, R.; Lazaridis, -J.I.; Dyrvoid, - B.; and Weerasinghe, C.R. (1984) Pyrolysis of a ZnCl₂-Impregnated Coal in Inert Atmosphere. *Fuel* 63:1583-1585.
- Kirk-Othmer, W. (2004). *Encyclopedia of Chemical Technology*, 4th ed. John Wiley and Sons, New York, pp. 1015-1036.
- Madakasi, E.; Olayinka, K.O.; and Osinowo, F.A.O. (2001). Treatment of Textile Effluents using Alum and Activated Carbon. Federal Institute of Research Oshodi, Lagos, Nigeria. *J. Chem.Soc. Nigeria* 26(2) :174-178.
- Patrick, J.W. (1995). *Porosity in Carbons: Characterization and Applications*, Halsted Press, New York,USA. Pp. 2-3.
- Samwel, M. (2005). *Alternatives for Sanitary Systems Ecological Sanitation - A chance for Rural Romanian Areas*, WECF Women in Europe for a Common Future. 118-129
- Sivaramakrishnan, C.N. (2004). *Colourage, Textile Effluent Treatment - A Solution to the Environmental Pollution LI*, 9:27-32.
- Takashi, W.; Yasuo, O.; and Yoshiyuki, N. (1994). Nitrogen Removal and Carbonization of Polyacrylonitrile with Ultrafine Metal Particles at Low Temperatures. *Carbon* 32(2):329-34.
- Tanzil, H. U. (2001). *Preparation and Characterization of Activated Carbon from Rice Husk, Acacia Arabica and Low Rank Coals*, Dept. of Applied Chemistry/ University of Karachi. Pp 99-102.
- Yasumasa, Y. (1982). Influence of Alkali on the Carbonization Process-I. Carbonization of 3, 5-dimethylphenol Formaldehyde Resin with NaOH. *Carbon* 20(1):41-45.
- Yeheskel, -A. (1978). *Activated-Carbon-manufacture and Regeneration*. Park Ridge (USA), Noyes Data Corporation. Pp 118-119.
- Yusuf, R.O. and Sonibare, J.A. (2005). Characterization of Textile Industries' Effluents in Kaduna, Nigeria and Pollution Implications. *Global Nest: the Int. J* 6(3): 212-221.