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Chemical and Thermal Modification of Okaba Coal for Increased Surface and Adsorption Properties

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Abstract Activated carbon produced from Okaba coal was modified using potassium hydroxide and phosphoric acid. The effect of this chemical modification was studied using carbon tetrachloride adsorption. Characterization of the activated carbons using scanning electron microscopy and FTIR analysis showed a greater development of porosity obtained by the modified activated carbons and the FTIR spectra displayed bands confirming the presence of hydroxyl, carboxyl and carbonyl functional groups. The predicted influence of chemical modification on activated carbon surface for carbon tetrachloride uptake and adsorption isotherm study from the adsorption models agreed satisfactorily with the experimental values.

Keywords Activation, modification, nano-activated carbon, CCl_4 adsorption

Introduction

Activated carbon is the most widely used adsorbent because of its extended surface area, micro porous structure, high adsorption capacity and high degree of surface reactivity. Due to the increasing demand of activated carbon, there is a strong need for sorting out new precursors for its preparation, which should be cost effective. Although, a variety of raw materials were explored for the preparation of A.C in earlier studies, agricultural wastes such as coconut shells [1-2], wood [3-5], coal [6-7], cotton stalk [8], almond shells [9], rice husk [10-11], date pits [12] were used for the production of activated carbon. Scientists are still trying to explore new materials depending on their availability and suitability for A.C production. Activated carbon is not only used for adsorption of substances from liquid or gaseous streams; some of its other uses include corn and sugar refining, as catalysts or catalyst support, in electroplating or as electrodes in batteries [13]. However, commercially available activated carbons are very expensive [14-16]. Therefore, studies are now focusing on new natural adsorbents with low cost and local availability, such as chitosan, bentonite, zeolite, clay minerals, olive mill residue, flay ashes, coal, rice husk, waste tea leaves, peanut hull pellets and bio sorbents. This study targeted to evaluate the availability for activated carbon extraction from Okaba coal to be utilized as adsorbent material for carbon tetrachloride adsorption. The synthesis of high performance activated carbons is feasible using maize talks and KOH activation. Note that recent studies have showed that it is possible to use natural wastes (e.g., egg shell residues) to produce alternative and low cost activating agents for improving the adsorption properties of activated carbons for heavy metal removal [17]. Analysis of coal rank parameters indicated that the Okaba coal can be classified as medium volatile bituminous coal [18]. The specific adsorption characteristics of an activated carbon is however strongly de- pendent on the composition of the surface functional groups which are incorporated into the activated carbon either by physical or chemical treatment. Attempts have been made by many researchers to modify the surface structures of activated carbons with substances having oxygen-containing functional groups such as acids and/or bases e.g. nitric acid [19],

tannic acid [20], citric acid [21], sodium hydroxide [22], ammonia [21]. Other modifying techniques include using ozone, CO_2, NO_2, and plasma treatment [23-24]. The objectives of all these treatments were to modify the pore size, control the pore size distribution and modify the activated carbon's polarity in order to enhance its selective chelating ability. Carbon tetrachloride is a volatile, clear, colourless, heavy liquid and also an ozone-depleting substance. Though, not flammable and not easily soluble in water [25]. It is however used in the production of refrigeration fluid, propellant for aerosol can, as a pesticide, a dry-cleaning fluidand etc. [26]; but because of its harmful effects, these uses are now banned. However, Carbon tetra- chloride is used as a test chemical to measure the capacity of an activated carbon to adsorb chemical compounds either in liquid phase and or in gaseous phase and according to their pore dimensions, carbon tetrachloride is adsorbed in mesopores or large micropores [27].

The aim of this research was to utilize Okaba coal that is low cost and locally available for the preparation of activated carbon and to also study the influence of chemical and thermal modification of the prepared activated carbon for enhanced carbon tetrachloride adsorption.

Experimental

Chemical and Thermal Modification of Okaba Coal

Okaba coal was used as the starting raw material for nano-activated carbon production. The proximate analyses of the raw coal are shown in table 1.

Table 1: The Proximate Analysis of Okaba Coal

Parameters	Values (%)
Ash	10.25
Moisture	6.47
Volatile matter	37.59
Fixed carbon	45.69

Chemical activation of Okaba coal was performed using potassium hydroxide KOH and phosphoric acid H_3PO_4 as the reagents. The activation process was initiated in a 250 cm^3beaker. 2g of the air dried coal with a solution consisting of 50cm^3 of water and 4ml of the chemical reagent (This was carried out separately, *i.e.* in alkaline and acidic medium) were mixed in the beaker. The mixing was performed for 2 hrs in a rotary orbital shaker. After mixing, the coal slurry was subjected to drying at 110 °C for 10 hrs in an oven. The resulting chemical loaded samples were then carbonized in a muffle furnace. Carbonization was carried out by heating the samples for 30mins from room temperature to carbonization temperature in a range of 400 – 700 °C followed by holding the samples at the carbonization temperature for 90 min. The samples were allowed to cool. After cooling, the carbonized products that have been treated with KOH and H_3PO_4 was subjected to washing by stirring with 250 cm^3 of 0.5 M HCl solutions for 30 min, followed by filtration.

The acid-washed sample was then leached by mixing with 250 cm^3 of distilled water for several times until the pH value of the water-carbon mixture was 7. The leached products were then dried at 110 °C for 8 hrs to give the nano-treated samples. For the sample treated with H_3PO_4, the washed solution was alkalized with 250 cm^3 of 0.5M NaOH instead of HCl and the sample was leached with distilled water to reach a pH value of 7.

Characterization of Raw and Nano-Treated Coal Sample

i. In order to have a better understanding, the difference in the properties between the raw Okaba coal and the prepared nano-treated carbon was examined. Scanning Electron Microscope (SEM) was used to determine the surface physical morphology. Fourier Transform Infrared Spectroscope (FTIR- 8400S, Shimadzu) was used in order to determine the surface functional groups on the Okaba coal sample before and after the chemical and thermal activations.

Determination of Carbon tetrachloride (CCl_4) Adsorption

The carbon tetrachloride number test was determined according to the method described by [28] in 2007. This method involves weighing 1 g of activated carbon on a watch glass and 10 cm^3 of CCl_4 in another watch glass and both watch glasses were kept in a dessicator and the carbon tetrachloride vapour was adsorbed by the activated carbon. The adsorption process continues for 2 hrs in order to obtain the equilibrium state. The weight of the activated carbon was measured at intervals of 10, 20, 30, 60, 90 and 120 min. The percent adsorption of CCl_4 was calculated using the expression:

% CCl_4 = (Mad x 100)/Mac

Where

Mad = amount of CCl_4 adsorbed (g)

Mac = amount of activated carbon (g)

The percentage of carbon tetrachloride adsorbed was converted to amount in milligram of carbon tetrachloride adsorbed by one gram of activated carbon by using the expression below:

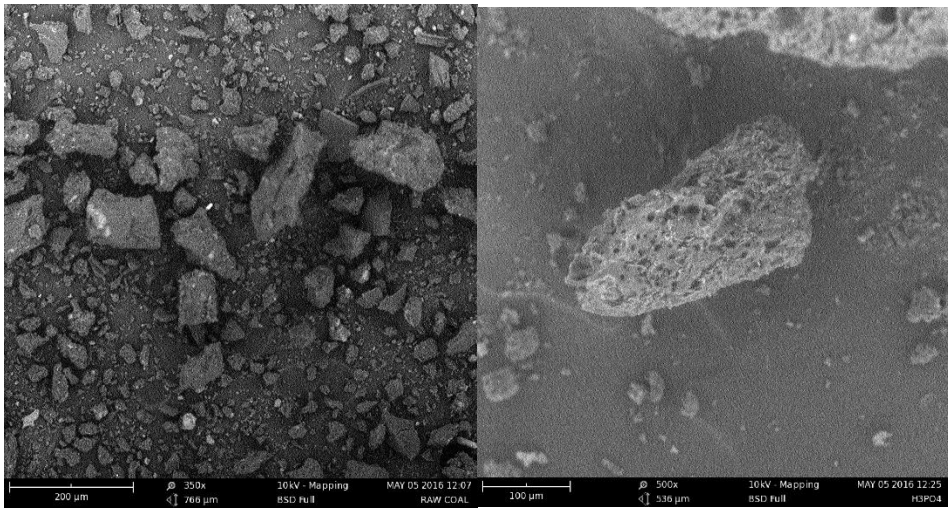
1 percent =10mg/g

Results and Discussion

The result of the proximate analysis of Okaba coal as presented in Table 1 showed moisture content to be 6.47%, ash content 10.25%, volatile matter 37.57% and fixed carbon 45.64% respectively. This result is similar to that reported by [29] for the proximate analyses of bio coal but higher than that reported by [6] who obtained 2.65%, 4.12%, 50.60% and 40.00%.

Characterization of Raw and Nano-activated Okaba coal

In order to identify the morphological structures of the raw Okaba coal and prepared material after the chemical and thermal modification process, SEM images for both the raw coal and the nano- activated carbon were investigated in Figure 1.



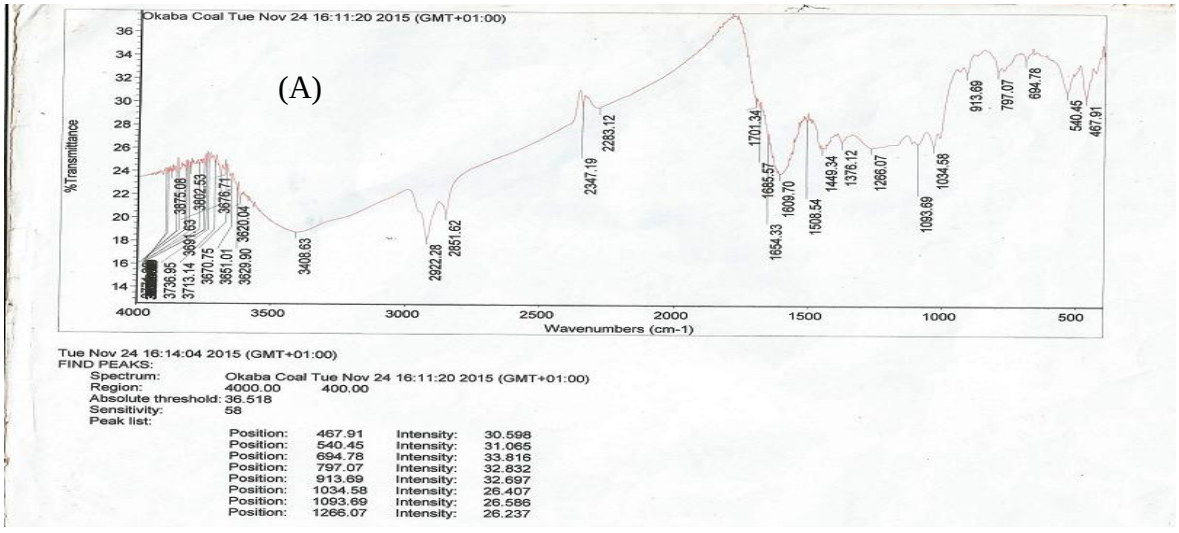
(A) (B)

Figure 1: SEM images of raw Okaba coal (A) and the prepared nano- activated carbon (B)

The surface of the raw coal was constricted, without a deeper pore structure. Conversely, the image of the produced nano- activated carbon displayed a well pronounced porosity, with series of irregular cavities distributed over the surface. Moreover, noticeable nano-size spherical particles were indicated as a light spots at the material surface that represents the morphology structure of the prepared activated carbon. Comparison of the surface morphologies verified substantial changes occasioned by both the chemical and thermal modification process [30-31].

FTIR Analysis Chemical structures of the raw coal was compared with the prepared sample using FTIR, Figure 2 (a, b) shows the FTIR spectra of the two samples. The FTIR spectra obtained were in agreement with the result

reported by [6] for the synthesis and characterization of nano-activated carbon from el-Maghara coal. It was indicated that the raw coal sample exhibited IR bands in the region of 3408 cm^{-1} are a result of an O-H stretching mode of hydroxyl group. This was found to be slightly broader in the treated sample which shifted to 3422cm^{-1}. The broad band represented at approximately 1266 cm^{-1} may due to the overlapping of C–O–C stretching, C–O stretching and O-H bending modes of alcoholic, phenolic and carboxylic groups. The band at 1600 cm^{-1} is assigned to C=C stretching conjugated with another C=C bond, an aromatic nucleus, or a C=O bond. It has been reported that the C=C stretching frequently occurs at approximately 1600 cm^{-1} for carbonaceous materials. These surface functional groups can serve as active sites where chemical transformations occur [6].



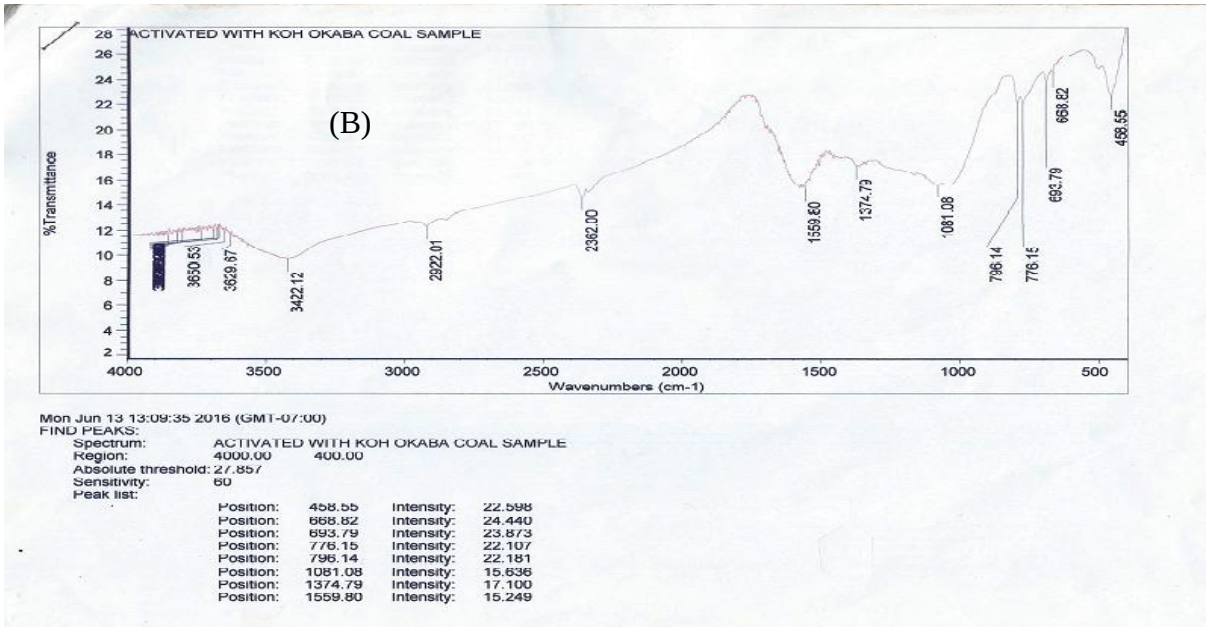


Figure 2: FTIR spectrums of raw Okaba coal (A) and the prepared nano-activated carbon (B)

Table 2: Freundlich Parameter for adsorption of CCl_4 onto nano-treated sample and raw coal sample

Nano Activated Carbon	1/n	N	K_f	Correlation coefficient (R^2)
KOH modified	0.543	2.91	0.95	0.9804
Raw coal	0.311	1.95	0.87	0.8338

Table 3: Langmuir Parameter for adsorption of CCl_4 onto nano-treated and raw coal sample

Nano Activated Carbon	Q^o	K	RL	Correlation coefficient (R^2)
KOH modified	3.10	0.285	0.11	0.888
Raw coal	1.99	0.143	0.10	0.764

Adsorption Isotherms The equilibrium data for carbon tetrachloride (Table 2) were well fitted into the Freundlich model with correlation coefficients (R^2) of the modified activated carbon being higher (0.980) than those of raw Okaba coal (0.833). In the equilibrium data for carbon tetrachloride adsorption (Table 3) was fitted into the Langmuir model (R^2=0.888, and 0.764) for modified activated carbon and raw Okaba coal. K_f and 1/n, the intercept and the slope, which are parameters de-picting the adsorption capacity and adsorption intensity also indicated normal adsorption as reputed by [32]. The maximum mono-layer coverage (Q^o) was found to be higher in the modified activated carbon (3.10 mg/g) compared to the raw Okaba coal (1.99 mg/g) with the highest value of 3.10 mg/g obtained by modified activated carbon. This result was lower than that reported by [33] for an equilibrium adsorption study using modified coconut straw activated carbon. [34], reported higher Q^o values for the removal of Ni (II) from aqueous solutions. The equilibrium parameter (RL) which indicates the nature of the adsorption process [35] were greater than zero but less than 1 thereby indicating that all the adsorption processes were favourable [36].

Conclusions

The use of Okaba coal a source of carbon mainly used as fuel when burned to provide heat energy, was successfully prepared to produce porous activated carbons which offers a cheap and viable source of adsorbents. The modification of the activated carbon using potassium hydroxide, produced activated carbons with desired physical properties and higher adsorptive capacities. Phosphoric acid modified activated carbon also possess moderate physical properties and their adsorptive capacities were good though not as high as those modified with potassium hydroxide. Two adsorption isotherms were tested (Freundlich and Langmuir models), the Freundlich isotherm gave the best fit for the adsorption of CCl_4. The adsorption processes were also found to be favourable.

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