

Comparative Adsorption Capacity of Modified Activated Carbon from *Pennisetum Glaucum* and *Sorghum Bicolor*.

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Abstract: *The influence of surface modification of activated carbons prepared from straws of *Pennisetum glaucum* (millet) and *Sorghum bicolor* (sorghum) with nitric acid and sodium hydroxide showed excellent improvement in their surface characteristics. The effects of the oxidizing treatments on the surface area pore dimension and surface chemical characteristics were analyzed by means of iodine adsorption, Fourier Transform Infrared and Scanning Electron Microscopy analyses. Results obtained showed that modification with nitric acid increased the adsorptive capacity of the activated carbon samples to a greater extent compared to sodium hydroxide.*

Keywords: *Pennisetum glaucum*, *Sorghum bicolor*, surface chemical modification, adsorptive capacity

1. Introduction

The modification of the surface chemistry of activated carbon is considered an important and relevant technique used to alter the surface polarity and create functional groups on the carbon's surface in order to enhance its adsorptive capacity. The presence of functional groups such as the carboxyl, carbonyl, phenols, lactones, quinines e.t.c. are usually considered to be responsible for the uptake of substances from gaseous streams or aqueous solutions [5]. These oxygen surface complexes are formed on activated carbons when they are treated with oxidizing agents in solution [13; 15] such as nitric acid, tannic acid, citric acid, ammonia [18] or by micro wave, ozone and plasma treatment. The treatments usually produce three types of oxides, acidic, basic and neutral [15]. Fixation of the acidic groups on the surface of the activated carbons makes it more hydrophilic, removes mineral elements present on the carbon's surface and also affects the surface area and pore texture of the activated carbons [16]. Base treatment of activated carbon produces positive surface charge which in turn is helpful towards adsorption of negatively charged species in higher amounts [5]. Production of

activated carbon from low-cost agricultural by-products and wastes such as straws offers an alternative source for activated carbon. [20] prepared activated carbons from Sorghum and Millet straws by chemical activation; the carbons were used for adsorption of methylene blue and iodine from aqueous solutions. The results obtained from their study showed that the activated carbons had high adsorptive capacities. The utilization of these straws for production of activated carbons to be used for adsorption of substances in gaseous streams can also be investigated to ascertain their suitability for gaseous and liquid phase adsorption. Iodine is usually used as test chemical to measure the capacity of an activated carbon to adsorb chemical compounds in liquid phase [12]. Iodine number (milligram iodine adsorbed per gram of activated carbon) is usually used to measure the porosity of the activated carbon [10]. Each 1.0mg of iodine adsorbed is ideally considered to represent 1.0m² of the activated carbon's internal surface area [10].

The focus of this paper was to study the influence of surface chemical modification of activated carbons prepared from two different precursors for adsorption of I₂ from aqueous

solution.

2. Experimental

2.1. Materials

Millet and sorghum straws were obtained from Maguzawa Farm in Rigasa Kaduna and were identified at the Herbarium section of the Herbarium Section of Biological Sciences Department of Ahmadu Bello University Zaria Iodine (99.5 %), Potassium iodide (99.9 %), Sodium thiosulphate (99.5 %), Potassium dichromate (99.5 %), Phosphoric acid (85 %) Nitric acid (69 %), Acetic acid (99.7 %) Ascorbic acid (94.5 %), Hydrochloric acid (35.4 %), Sodium hydroxide (99.0 %) Formic acid (90 %) and potassium hydroxide (90 %) were all of analytical grade.

2.2. Methods

2.2.1. Carbonization and Activation Process

Prior to carbonization, the millet and sorghum straws were washed, dried, cut into pieces of approximately 3cm and then pulverized to obtain particle sizes of about 1180 μ m [14]. The activated carbon was then prepared by the two-step chemical activation process. The first step involves carbonization with 60 % phosphoric acid solution and the second step involves activation using muffle furnace model SXL using and 1.0 M KOH at 600 °C for 1 hr [19]. The prepared activated carbon was first washed with water containing 0.15 % formic acid and then washed severally with distilled water. They were filtered through a Buchner funnel dried at 120 °C and then weighed to determine the activated carbon yield. It was then stored in plastic sample bottles to prevent adsorption of dust and other particles from the atmosphere.

The activated carbon yield was calculated using Eq. 1

$$\text{Yield \%} = \frac{W_a}{W_p} \times 100 \quad (1)$$

Where W_a is the weight of activated carbon and W_p is the weight of precursor.

2.2.2. Modification of Activated Carbon

(a) Modification with Nitric Acid

To 10 g of the activated carbon sample, 100 cm³ of 2.0 M nitric acid was added and soaked for 24 hrs. The residual nitric acid was removed by soaking it in distilled water for 2 hrs and then washed several times with distilled water. The sample was then dried at 120 °C, cooled in a desiccator and stored in plastic sample bottles.

(b) Modification with Sodium hydroxide

To 10 g of the activated carbon sample, 100 cm³ of 2.0 M sodium hydroxide was added and soaked for 24 hrs. The residual sodium hydroxide was removed by soaking it in distilled water for 2 hrs and then washed several times with distilled water. The sample was then dried at 120 °C, cooled in a desiccator and stored in plastic sample bottles.

2.2.3. Characterization of Activated carbon

The surface physical morphology of the unmodified and modified activated carbons was observed using Phenom scanning electron microscope model proX and surface functional groups were identified using FTIR spectroscope (FTIR – 8400s, shimadzu) and the spectra recorded from 4000 to 500cm⁻¹.

2.2.4. Iodine Number Test

The iodine number was determined according to the ASTM D4607-94 method [4] is based upon a three-point isotherm. A 0.1 M standard iodine solution was added to three different weights of activated carbon samples in three 250 cm³ conical flasks. The experiment involved treating the activated carbon sample with 10.0 cm³ of 5 % HCl. This mixture was boiled for 30 seconds and then cooled soon afterwards, 100 cm³ of 0.1 M iodine solution was added to the mixture and stirred for 30 seconds. The resulting solution was filtered and 50.0 cm³ of the filtrate was titrated with 0.1 M sodium thiosulphate using starch solution as indicator. The amount of iodine adsorbed per gram of carbon (iodine number) and the residual iodine concentration in the filtrate were calculated using Eq 2.

$$I_N = \frac{VB - VS}{VB} \times \frac{V1}{WM1} \quad (2)$$

Where I_N is the iodine number, VB is the volume of $\text{Na}_2\text{S}_2\text{O}_3$ used for blank titration, VS is the volume of $\text{Na}_2\text{S}_2\text{O}_3$ used for test titration, M1 is molarity of iodine solution, V1 is volume of iodine solution used and W is weight of activated carbon.

2.2.5. Batch Adsorption Experiment and Adsorption Isotherm of I_2

Batch Adsorption experiments were carried out to determine the optimum contact time and adsorption isotherms of I_2 onto the activated carbon in a series of 250 mL conical flasks. The procedure involved filling each flask with 100 cm^3 of 0.1 M iodine solution. Equal weights of activated carbon were added into the different flasks and the flasks were shaken using the Griffin flask shaker to achieve equilibrium. The adsorption isotherm for I_2 were studied by varying the activated carbon weights between 0.4 to 2.4 g at a concentration of 0.1 M iodine solution and for an optimal period of 1 hr, while the effect of contact time was studied at different time periods of 10, 20, 30, 60, 90 and 120 minutes.

2.2.6. Adsorption Isotherm Models

The Langmuir and Freundlich isotherms models were employed to determine the relationship between the amount of I_2 uptake (q_e) and its concentration at equilibrium (C_e)

The amount of I_2 adsorbed per gram of carbon was calculated using Eq 3

$$q_e = \frac{(C_i - C_e)V}{m} \quad (3)$$

Where C_i and C_e are the initial and equilibrium concentration (mg/L), M is the mass of activated carbon (g) and V is the volume of the solution (mL). Percent I_2 removal was calculated using Eq. 4

$$\% \text{I} = \frac{(C_i - C_e)}{C_i} \quad (4)$$

The Langmuir model which assumes monolayer adsorption onto the activated carbon is given by Eq. 5

$$q_e = \frac{Q^\circ \cdot K \cdot C_e}{1 + K \cdot C_e} \quad (5)$$

This when manipulated to the linear form gives Eq. 6

$$\frac{1}{q_e} = \frac{1}{K \cdot Q^\circ} \times \frac{1}{C_e} + \frac{1}{Q^\circ} \quad (6)$$

The Freundlich Isotherm model represented by Eq. 7 describes the heterogeneous surface energies by multilayer adsorption [7].

$$q_e = K_F C_e^{1/n} \quad (7)$$

Freundlich Isotherm when expressed in the logarithmic form; the empirical equation becomes a straight line and the constants K_F and $\frac{1}{n}$ are found by linear regression.

$$\text{Log } q_e = \text{log } K_F + \frac{1}{n} \text{ log } C_e \quad (8)$$

3. Results and Discussion

3.1. Characterization of Unmodified and Modified Activated Carbons

The FTIR spectra of the unmodified activated carbons present broad and intense peak of O-H stretching vibrating of hydroxyl groups of alcohols, phenols or absorbed water at 3414.12 & 3444.98 cm^{-1} for the millet and sorghum straws respectively. The bands were found to be slightly shifted in the modified samples at 3472.95 and 3390.97 cm^{-1} respectively.

The bands at 1644.37 & 1640.51 cm^{-1} due to C=C stretching vibration in alkenes observed in the unmodified samples, were found to occur at 1642.44 & 1643.41 cm^{-1} for the modified samples. The bands in the region of 1378.18 & 1385.90 cm^{-1} that are due to the stretching vibration of the nitro group (C-NO₂) [8], were only detected in the modified samples. Other bands detected are 1138.04 & 1146.72 cm^{-1} in the unmodified samples due to C-O stretching vibration in alcohols or ether but were found at 1160.22 & 1146.01 cm^{-1} in the modified samples.

The SEM micrographs of the activated carbons are shown in Figures 1 a-f more open structures are exhibited in the modified activated carbon samples than the unmodified activated carbons, caused by the collapse of the micropores and creation of macropores which may be due to the introduction of oxy-

gen containing functional groups from the modifying agents.

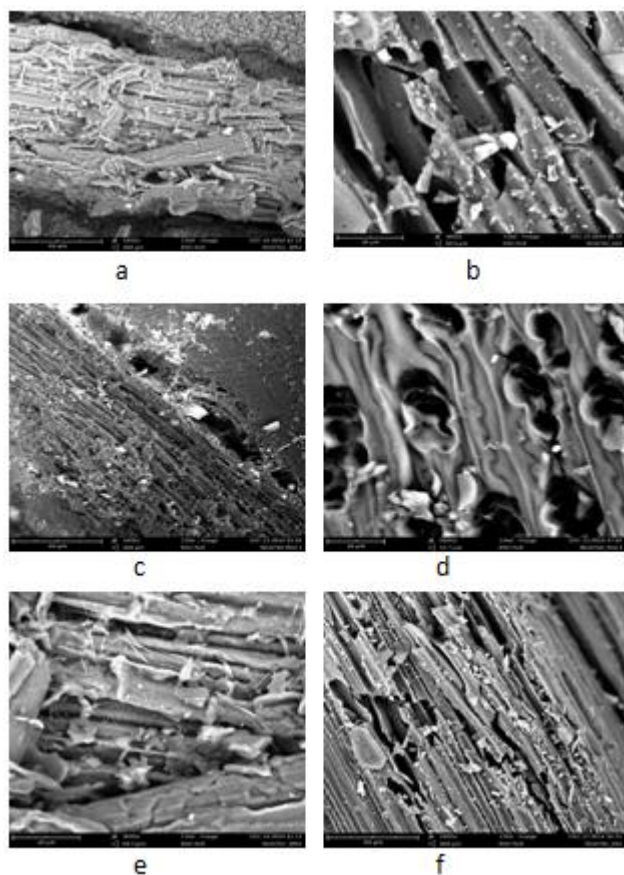


Figure 1: SEM images of (a) unmodified millet straw activated carbon, (b) unmodified sorghum straw activated carbon, (c) nitric acid modified millet straw activated carbon, (d) nitric acid modified sorghum straw activated carbon, (e) sodium hydroxide modified millet straw activated carbon and (f) sodium hydroxide modified sorghum straw activated carbon

3.2. Iodine number

Table 1 showed that the iodine numbers of the unmodified activated carbons (UMS and USS) were 689.3mg/g and 565.4mg/g, and after modification with nitric acid and sodium hydroxide higher iodine number values were obtained as presented in Table 1. Between the two modifying agents used nitric acid improves the pore structure and surface area of the activated carbons more there by leading to enhanced adsorptive capacity. Similar results were obtained by other researchers; [1] observed that the adsorption of Cr (III) was increased on oxidation of granular activated carbons with nitric acid, hydrogen peroxide and ammonium persulphate in aqueous solution. Another report [11] showed that the incorporation of acidic oxygen functional groups into activated carbon by HNO₃ oxidation dramatically enhanced the ad-

sorption of cadmium ions from aqueous solution. The adsorption of Perchlorate (ClO₄⁻) from aqueous solution was examined with ammonia treated activated carbon by [6]; the researchers noted that higher adsorption capacity for perchlorate was achieved without undermining the pore structure.

3.3. Effect of Contact Time

The effect of contact time on I₂ adsorption efficiency using the modified activated carbons showed that about 80 % of I₂ was absorbed by millet straw activated carbon while 72 % of I₂ was absorbed by sorghum straw activated carbon within 1 hr, while about 89 % of I₂ was absorbed by millet straw and 77 % of I₂ was observed by sorghum straw after 2 hrs.

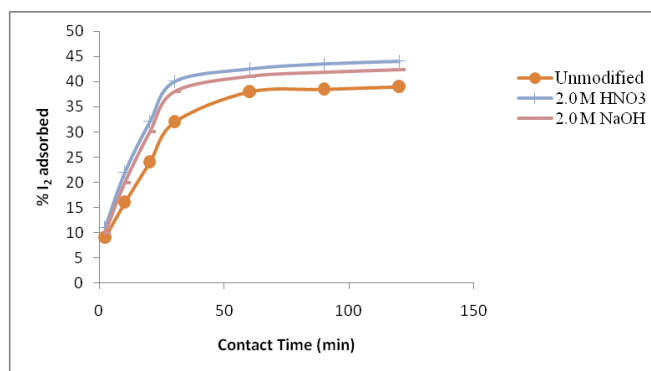


Figure 2: The percent iodine adsorbed against contact time by unmodified millet straw activated carbon and the various modified millet straw activated carbon (2.0 M HNO₃ and 2.0 M NaOH) using 1.0 M KOH at 600 °C

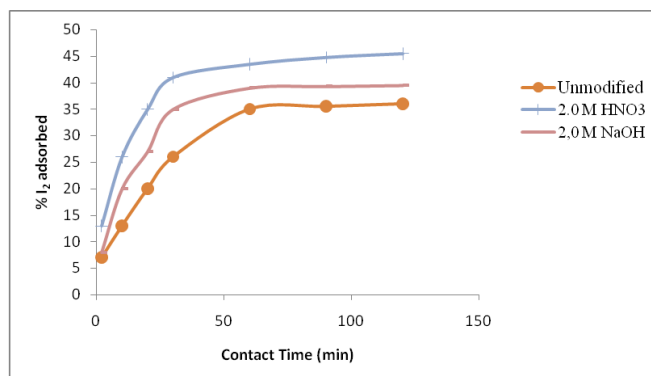


Figure 3: The percent iodine adsorbed against contact time by unmodified sorghum straw activated carbon and the various modified sorghum straw activated carbon (2.0 M HNO₃ and 2.0 M NaOH) using 1.0 M KOH at 600 °C

3.4. Adsorption Isotherms

Table 2 represents the Langmuir and Freundlich isotherm parameters for adsorption of iodine. It was found that the

equilibrium data were fitted into both isotherm models with R^2 of the modified activated carbons being higher (0.964, 0.973) than those of the unmodified activated carbons (0.759, 0.828).

K_F and $\frac{1}{n}$, indicated normal adsorption [9] and the maximum monolayer coverage (Q^0) was also found to be generally higher in the modified activated carbons (50.0 mg/g and 47.62 mg/g) compared to the unmodified activated carbons (2.976 mg/g and 3.311 mg/g). The equilibrium parameter (R_L) was found to be greater than zero but less than 1 indicating that all the adsorption processes were favourable [17].

4. Conclusion

The present study highlighted the importance and relevance of chemical modification of the surface chemistry of activated carbon produced from *Pennisetum glaucum* and *Sorghum bicolor*. SEM images and FTIR analysis showed increased pore formation and increase in the number of surface functional groups as a result of the modification treatment. A significant increase in iodine number was achieved after modification, but the best results was obtained for the nitric acid modified activated carbon samples; between the two precursors studied, nitric acid modified sorghum straw activated (MSS) apparently absorbed higher amount iodine ($I_N=911.2$ mg/g).

Table 1: Iodine Number (I_N) Values of Unmodified and Modified Activated Carbon

Unmodified Activated carbon	Iodine Number mg/g	Modified Activated carbon	Modifying Agents (2.0 M)	Iodine Number (mg/g)
UMS	689.3	MMS	HNO ₃ NaOH	898.0 835.5
USS	565.4	MSS	HNO ₃ NaOH	911.2 595.2

Key:

UMS – Unmodified Millet Straw Activated Carbon, USS- Unmodified Sorghum Straw Activated Carbon.

MMS – Modified Millet Straw Activated Carbon, MSS- Modified Sorghum Straw Activated Carbon.

Table 2: Freundlich and Langmuir Parameters for Adsorption of Iodine unto Modified and Unmodified Activated Carbon

Activated Carbon	Freundlich parameters $\frac{1}{n} K_f$	Langmuir parameters $Q^0 K R_L$	Correlation coefficients Freundlich Langmuir (R^2)
MMS	0.382 2.62 5.90	50.0 5.03 x 10 ⁻² 2.95 x 10 ⁻²	0.964 0.732
MSS	0.4 2.5 4.94	47.62 4.56 x 10 ⁻² 3.34 x 10 ⁻²	0.973 0.716
UMS	0.302 3.31 3.60	2.976 0.316 4.936 x 10 ⁻³	0.759 0.758
USS	0.312 3.21 2.838	3.311 0.239 6.515x10 ⁻³	0.828 0.829

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