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PRODUCTION, CHARACTERIZATION AND IMPLEMENTATION IN REACTIVE BLUE DYE REMOVAL OF ACTIVATED CARBON FROM GUINEA CORN HUSK

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ABSTRACT

Production of activated carbon from guinea corn husk by chemical activation, treated with phosphoric acid (H_3PO_4) was characterized using Fourier Transform Infrared (FTIR) spectroscopy and Scanning Electron Microscope (SEM). Phytochemical analysis: pH, moisture content, volatile matter, ash content, carbon content, bulk density, electrical conductivity and surface area were also carried out. Activated carbon at 400 ºC carbonization temperature, and 45 % activating agent were observed to have a better result: surface area, 586.01 g/m^2, absorbance 0.0431, concentration of dye 8.80 mg/L, efficiency of dye removal 91.3 % and amount of dye absorbed 12.03 mg/g respectively, than at the other temperatures and 50 % activating agent along its various temperatures.

Keywords: Activated carbon, activating agents, methylene blue dye and temperature

INTRODUCTION

Activated carbon (AC) is a well-known adsorbent material, which finds its use mainly in chemical, mining, food industries and also other important applications in purification and deodoration process, treatment, medicine, etc. [1].

Activated carbon is one of the most popular adsorbents used in numerous industries for the removal and recovery of organic and inorganic compounds from gaseous and liquid streams. It has high adsorption capability due to its high internal surface area and porosity formed during carbonization process. The presence of activating agents and carbonization conditions influenced the development of pore structures [2]. The great importance of the activated carbon is as an absorbent in the separation and purification processes to reduce environmental pollution in the air, water and soil. Activated carbon capacity of absorption does not depend on the AC surface area only, but also on (i) the internal structure of the pores, (ii) characteristic of the surface, and (iii) functional groups provide on the surface of the adsorbent. These criteria depend on the method used in the preparation and the precursor used also. Therefore, an appropriate adsorbent characterization is decisive to the separation and adsorption processes [3]. It prefers to use cheap local raw materials which contain a small amount of ash and high amount of carbon in the preparation of activated carbon process to reduce the cost of the massive production [4].

The aim of the research work is to convert agricultural waste into useful product of activated carbon that can be used in degradation of methylene blue as methylene. Methylene blue is widely used in textile industry and can be found as textile effluents

MATERIALS AND METHODS

Guinea corn husks (Figure 1) was collected from Samaru, Zaria, Kaduna State, Nigeria. Prior to use, the precursor was washed gently with tap water to remove dirt, followed by distilled water to remove impurities present on the surface and then sundried.

Plate 1: Guinea Corn Husks

Sample preparation

The dried sample guinea corn husk was cleaned, washed with tap water, followed by distilled water and then dried in an oven at a temperature of 11^{o}C for 12 hours so as to dehydrate the residual water content. The dried sample was ground and sieved to desired particle size using sieve. The sample was kept in clean container for further carbonization/activation

Chemicals and impregnating agent

All the chemicals used were of analytical grade. The impregnating agent for the chemical activation of Guinea corn husk was phosphorous acid (H_3P0_4)

Chemical Activation and carbonization

The sample materials were carbonized in the absence of air in a muffle furnace at a temperature 500 – 100 ^{o}C for 60 minutes and 200 g of carbonized sample was mixed with an aqueous solution of phosphoric acid (activating agent). The mixture was then subjected to heat at a temperature of 120 ^{o}C for 3 hours to vapourize the water. The dried mixture was subjected to heat at a temperature of 650 ^{o}C in a muffle furnace to enable activation of the pores of the carbon sample [5].

Characterization of the Activated Carbon

Activated carbon from guinea corn husk obtained from Samaru, Kaduna state was prepared and various properties: moisture content, percentage of volatile matter, ash content, were characterized by following the standard procedures: oven-drying test method using (ASTM D2867 – 09) manual. Electrical conductivity was measured using procedure provided in HACH conductivity/TDS/temperature meter (model 44600.00) manual while the pH and Bulk density were determined as described by Ahmed, et al. [6]. The morphological characteristics of the prepared sample were determined using SEM analysis. The functional group of the prepared sample was analyzed using FTIR Spectroscopy. The specific surface area of the activated carbon was estimated using Sear method [7].

Adsorption studies

Exactly 100 mg of reactive blue dye was dissolved in 1 liter of distilled water to prepare stock solution of dye. About 0.4 gram of synthesized AC was added to the 50 mL of dye stock solution then adjusted pH to 2.5 and magnetically stirred for 30 min. The sample was filtered after that using UV-Visible spectrophotometer (Model UH4150) to analyze dye absorbance and using calibration curve to get dye concentration. The amount of adsorbed dye (mg/gm) and the efficiency of removal dye (%) were calculated using the following equations:

Adsorbed dye (mg/g)= $\frac{(Ci-Cf)V}{Ms}$ 2.1 [8]

Efficiency of removal dye = $\frac{Ci-Cf}{Ci} \times 100$ 2.2 [9]

Where V = solution volume (L), Ci = initial concentration of dye (mg/L), Cf = final concentration of dye (mg/L), and ms = adsorbent mass (gm).

Adsorption Isotherms

Adsorption isotherms at a certain condition were used to represent the equilibrium relationship between the adsorbent in liquid phase and on the adsorbent surface to describe the absorptivity of the adsorbent. Langmuir and Freundlich isotherms were used for this study

Langmuir Isotherms

Langmuir isotherms model [10] was used to observe the biosorption phenomena of the activated carbon from Guinea corn husks. The Langmuir isotherms are based on an assumption that electron exist on the surface of the adsorbent which are capable of adsorbing molecules and at equal absorption affinity at all adsorbing site without interference. The Langmuir equation is commonly written as

$$q_e = \frac{Qmax\alpha Ce}{1+\alpha Ce} \qquad 2.3$$

where:

q_e= amount adsorbed (mg/g)

Ce = equilibrium concentration of adsorbate (mg/L)

Qmax = Langmuir constant

The linear form of Langmuir is express as:

$$1/q_e = 1/Qmax + 1/QmaxCe \qquad 2.4$$

The Qmax can be determined from the linear plot of $1/q_e$versus 1/Ce

Freundlich isotherms

The Freundlich isotherm model [11] is:

$$q_e = K_f C\ 1/n \qquad 2.5$$

where:

q_e= amount of metal ions adsorbed per unit weight of adsorbent (mg/L)

c = equilibrium concentration of adsorbate (Mg/L)

$K_f$and n = Freundlich constants: $K_f$is an indicator of adsorption capacity and n is the adsorption intensity

The linear form of Freundlich isotherms is express as:

$$\text{Log } q_e = \text{Log } K_f + 1/n \text{ Log Ce} \qquad 2.6$$

RESULTS AND DISCUSSION

Table 1: Particle Size Distribution of Guinea Corn Husk Activated Carbon

S/N	Mesh size (mm)	Particle size distribution (mm)
1	2	0.06
2	1	2.00
3	900	2.15
4	850	2.20
5	700	2.30
6	500	2.90
7	410	2.34
8	300	0.90
9	200	0.85
10	150	0.17
11	60	0.00
12	Pam	0.00

Table 1 shows the mesh size, the particle size distribution of the guinea corn husk activated carbon in millimeter (mm)

Physicochemical properties of Activated carbon from Guinea corn husk

Table 2: Physicochemical Parameters Activated Carbon at 45% Activating Agent Concentration

Carbonization Temperature (^{O}C)	pH	Moisture Content (%)	Volatile Matter (%)	Ash content (%)	Carbon content (%)	Bulk density (g/L)	Electrical Conductivity (μS/cm)	Surface Area(g/m^2)	
400		6.40	2.00	15	4.0	55	500	770	586.01
450		6.80	1.90	11	5.0	60	430	790	607.55
500		6.73	1.62	8	5.5	62	420	810	647.69
550		6.52	1.27	6	5.9	65	415	850	690.60

Table 3: Physicochemical Parameters of Activated carbon at 50 % Activating Agent Concentration

Carbonization Temperature (^{O}C)	pH	Moisture Content (%)	Volatile Matter (%)	Ash content (%)	Carbon content (%)	Bulk density (g/L)	Electrical Conductivity (µS/cm)	Surface Area (g/m^2)
400	6.48	2.40	16	3	57	490	772	586.99
450	6.52	2.10	13	4	62	427	795	616.34
500	6.59	1.80	10	5	66	418	812	670.14
550	6.66	1.20	8	5.7	68	410	859	714.17

Efficiency of Methylene Blue Dye Removal

Table 4: Efficiency of Removal Dye (%) and the Amount of Dye Adsorbed (mg/g) for Methylene Blue Dye at Different Temperature, Constant Activating Agent 45 %

Carbonization temperature (^{0}C)	Absorbance	Concentration of dye (mg/L)	Efficiency of dye removal (%)	Amount of dye absorbed (mg/g)
400	0.0431	8.80	91.3	12.03
450	0.2084	39.56	60.6	7.00
500	0.2210	40.08	60.3	6.91
550	0.3108	42.31	56.7	5.40

Table 5: Efficiency of Removal Dye (%) and the Amount of Dye Adsorbed (mg/g) for Methylene Blue Dye at Different Temperature, Constant Activating Agent 45 %

Carbonization temperature (^{0}C)	Absorbance	Concentration of dye (mg/L)	Efficiency of dye removal (%)	Amount of dye absorbed (mg/g)
400	0.0431	8.80	89.9	11.89
450	0.382	44.50	46.81	6.67
500	0.391	50.91	46.20	4.32
550	0.498	69.74	28.37	3.40

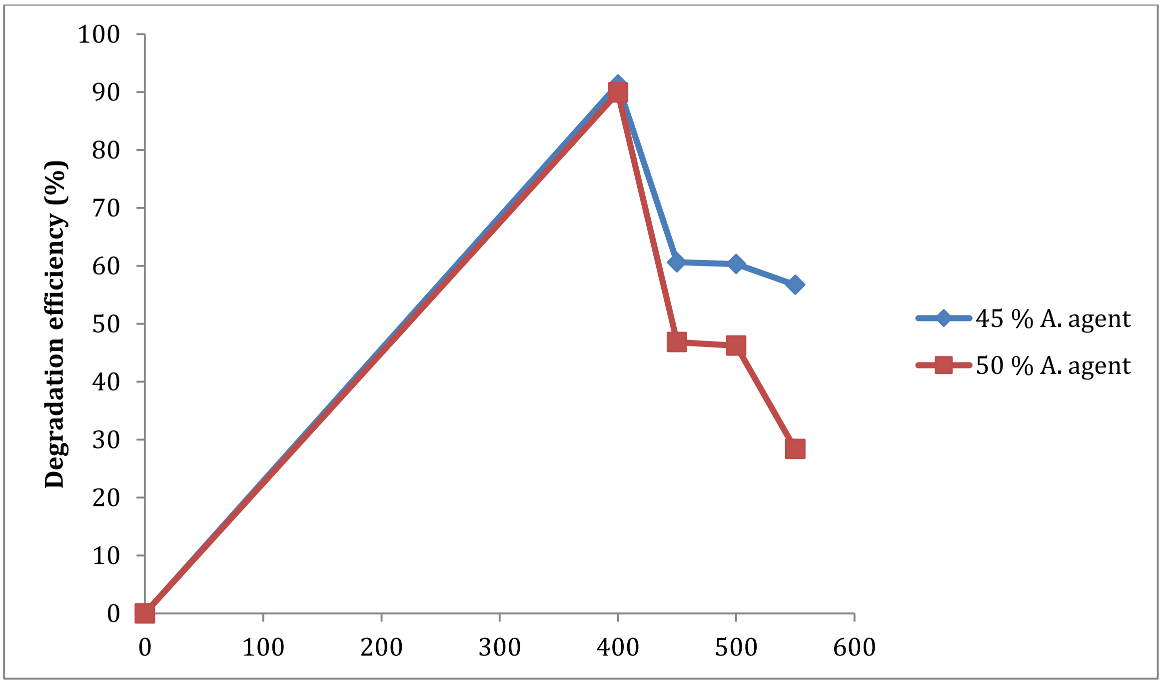

Figure 1: Degradation Efficiency of MB using Guinea Corn Husk Activated at 45 % and 50 % Activating Agent

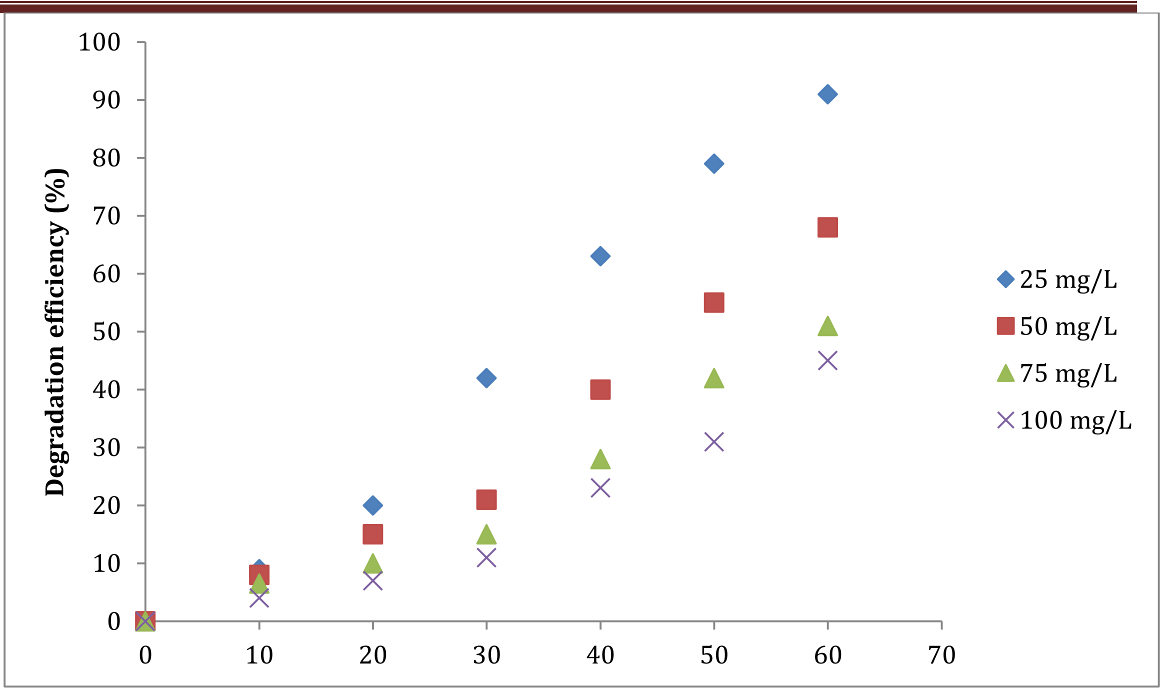

Figure 2: Effect of Concentration of the Reactive dye on its Degradation efficiency using the Acted Carbon at 400 ºC, 45 % Activating Agent.

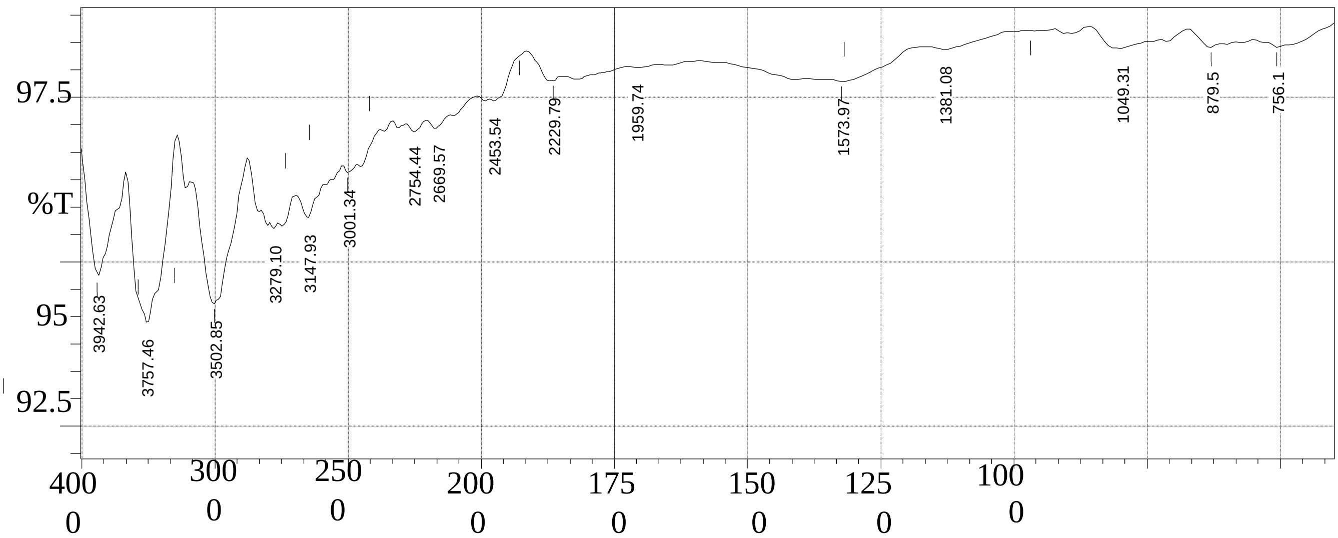

Figure 3a: FTIR Spectra of the Pure Guinea Corn Husks

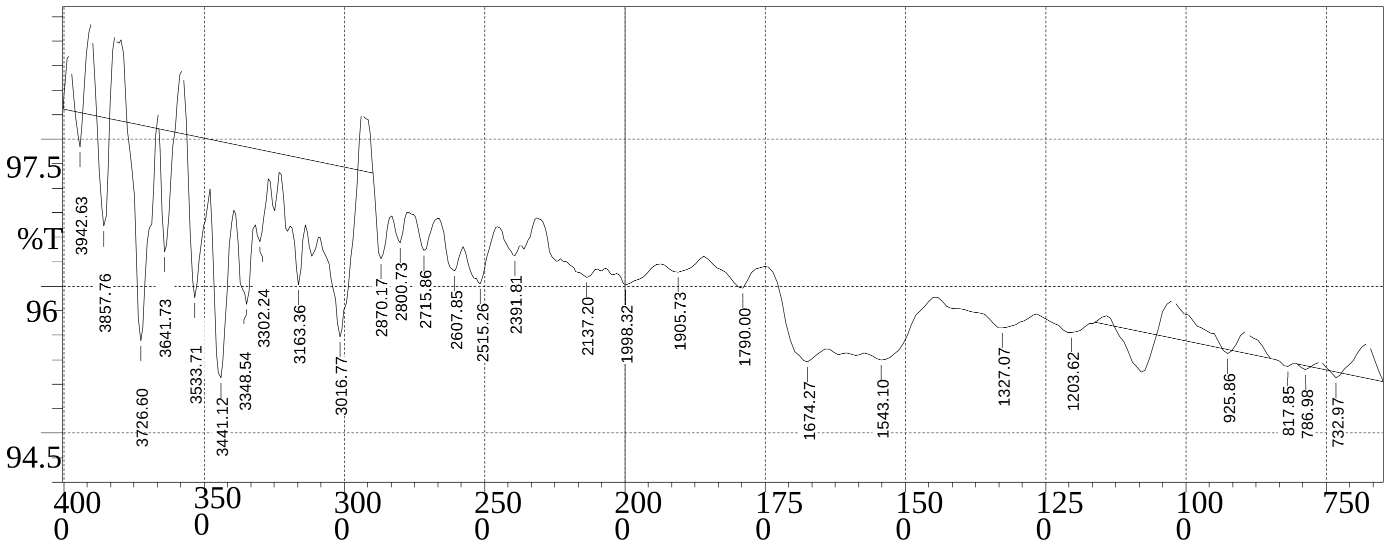

Figure 3b: FTIR Spectra of the Prepared Activated Carbon at 40 ^{0}C Carbonization, 45% Activating

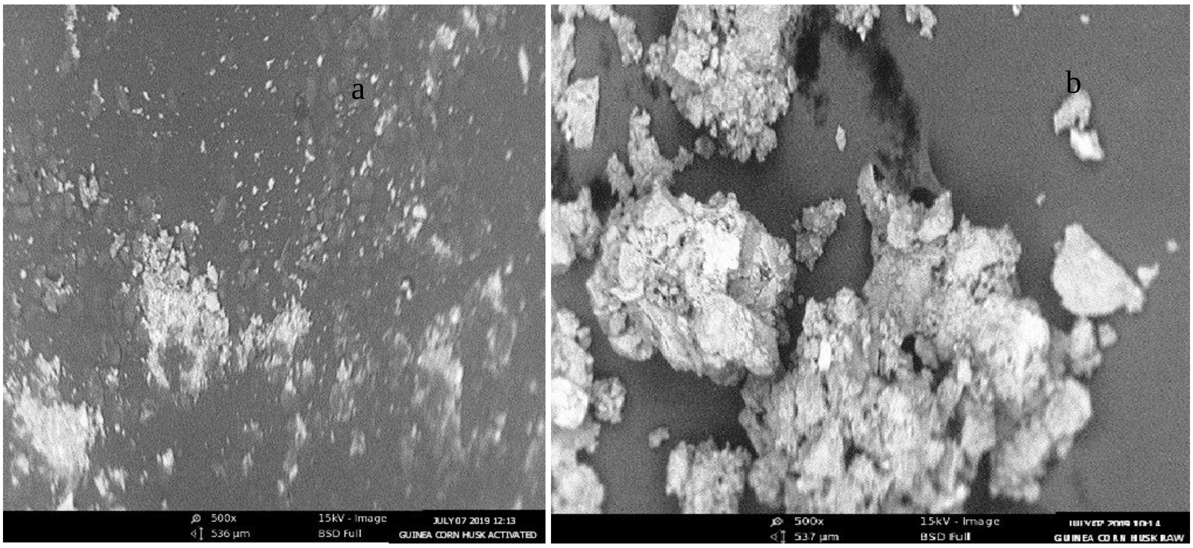

Plate 2**:** Image of Scaning Electron Microscope of (a) Pure Guinea corn husk (b) Activated Guinea corn husks

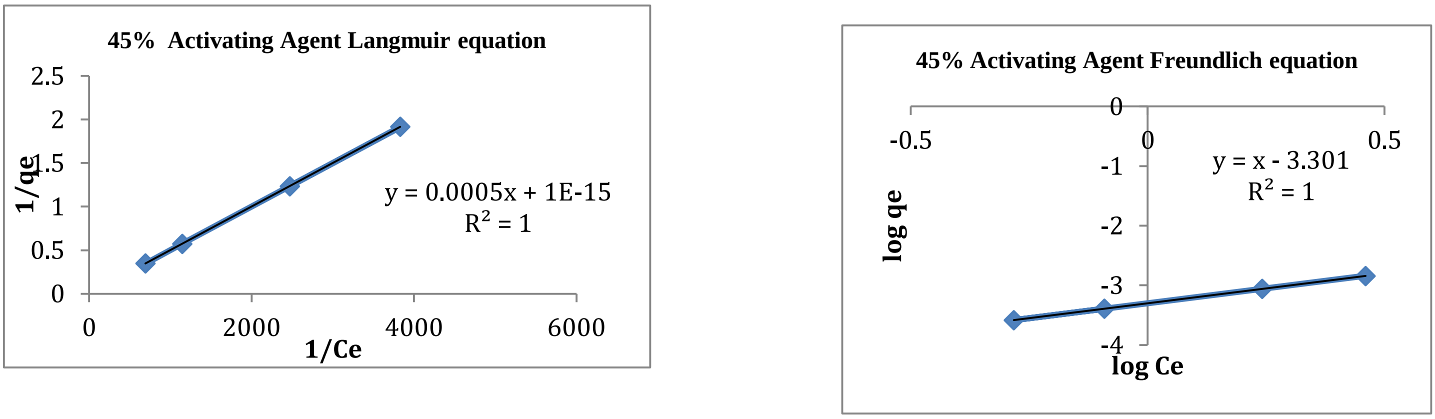

Figure 5: Application of Langmuir and Freundlich Equation for the Removal of Blue Dye at 45 % Activating Agent

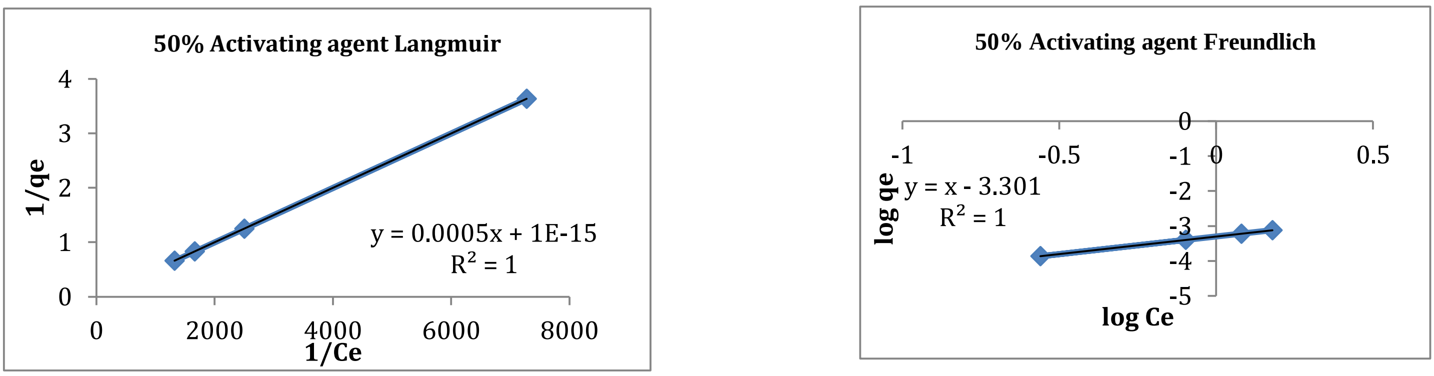

Figure 5: Application of Langmuir and Freundlich Equation for the Removal of Blue Dye at 50 % Activating Agent

Tables 2 and 3 show the results of proximate analysis (pH, moisture content (%), volatile matter (%), ash content(%), carbon content (%), bulk density (g/L), electrical conductivity (µS/cm) and surface area (mg/L). It was observed that the surface area increased with an increase in carbonization temperature. The increased surface area with an increase in carbonization temperature was also observed by Guo and Lua [12]

Due to its high degree of micro porosity, one gram of activated carbon has a surface area in excess of 3,000m^2 [13]. It was also observed that the surface area increases with an increase in activating agent concentration. This pattern of increase in activating agent concentration with increase in surface area was also observed by Guo et al. [14]. This increase in surface area may also be attributed to the formation of new micro pores and widening of the micro pore size as reported by Halim [15]. The pH of the produced activated carbon falls within the range of pH of most agricultural by products.

The synthesized activated carbon was evaluated by removal of reactive blue dye from aqueous solution using the activated carbon treated with 45 % and 50 % activating agents respectively at various temperatures ranging from 400 ^{o}C to 550 ^{o}C. Tables 4 and 5 showed the various carbonization temperatures, absorbance, concentration of dye (mg/L), the efficiency of dye removal (%) and amount of dye absorbed. Activated carbon treated with 45 % activating agent at 400 ^{o}C better dye concentration, 8.80 mg/L, efficiency of dye removal, 91.3 %, amount of dye absorbed, 12.03 mg/g were observed than at the other temperatures and treated with 50 % activating agent along its various temperatures. Figure 2 also, showed the degradation efficiency of the activated carbon at 400 ^{o}C treated with 45 % and 50 % activating agent which conformed to the Table 5 that better degradation efficiency was obtained using the activated carbon treated with 45 % activating agent at 400 ^{o}C.

The efficiency of dye removal were observed to decrease with increasing carbonization temperature (400 ^{o}C – 550 ^{o}C) this is expected since volatile matter decreases with an increase in activating temperature. Haimour and Emeish [16] suggested that the percentage of volatile matter decrease with an increase of carbonization temperature and the variation of this parameter is high between 200 ^{o}C and 800 ^{o}C due to rapid carbonization occurring in this region.

The desired removal of dye efficiency and amount of dye absorbed from tables 4 and 5 are 91.3 % and 12.03 mg/g respectively at 400 ^{o}C carbonization temperatures, and 45 % chemical activating agent.

The reactive blue dye concentrations were varied ranging from 25 mg/L to 100 mg/L to investigate its on effect on the degradation using the synthesized (Guinea corn husk) activated carbon. Figure 2 shows that the degradation efficiency decreased with increases in the concentration of the reactive blue dye. For instance, when the concentration of the reactive blue dye varied from 25 mg/L to 100 mg/L, the degradation efficiency decreased from 91 % to 45 %

The functional groups present in the pure and activated carbon produced was identified using Fourier Transform Infrared Spectroscopy (Figure 3a and b). The wave numbers of each peak in the spectrum of the FTIR were assigned to their respective functional groups as shown in Figure 4. The peaks of the FTIR spectrum at the wavelength observed at 3942.63–3016.77 cm^{-1}, 2870.17 – 2391.81 cm^{-1}, 2137.20 -1203.57 cm^{-1} and 925.86 – 732.97 cm^{-1}respectively can be assigned to phenols, carboxyl and carbonyl functional groups. According to Zheng et al. [17] the adsorption behavior and its mechanisms of an adsorbent are function of the adsorbent functional groups. The essence of the chemical nature of those functional groups presented on the adsorbent surface is important in understanding the adsorption process and capacity of the adsorbent [18].

Scanning Electron Microscopy was employed to study the effect of the activation on porosity to observe the surface physical morphology of the guinea corn husks shell-driven activated carbon. Plate 2 shows the scanning electron microgram of the pure guinea corn husks (untreated) or before chemical activation and after chemical activation. The microgram of the guinea corn husks before activation shows presences of flaky, smooth with small pores which is not rich in porous cavity while the chemically activated guinea corn husks shows deep cavity pores which are partly broken and canals like structure due to the corrosive and dehydrating nature of the chemical activating agent

The absorption isotherms of the reactive blue dye were represented by both the Freundlich and Langmuir isotherm equations. The data were analyzed using isotherm: Langmuir and Freundlich adsorption equations (Figure 4 and 5) for the removal of dye at 45 % and 50 % activating agent. The results show that the adsorption process could be fitted and described with the kinetic isotherms of the Langmuir and Freundlich. The correlation coefficient value greater than 0.9 were well fitted in to Langmuir equations equilibrium. Both the isotherms perfectly described the adsorption process but the Langmuir isotherm fitted better for sample of each adsorbate, although recorded the same correlation coefficient with the Freundlich isotherm. This is also observed in the work ofKehinde et al. [19]. The Langmuir was also found to give better adsorption equilibrium in the removal of iron (Fe) and manganese (Mn) [20].

The Langmuir equation is valid when the valence on the surface of the absorbent are homogenously distributed [21]. The shape of the graph plot using Langmuir equation can predict the favorability of the sorption system in the under batch adsorption process. The essential characteristics of Langmuir isotherms can be described by a separation factor [22].

Freundlich isotherms is used for non-ideal adsorption on heterogeneous surface energy systems [23]

CONCLUSION

Guinea corn husk was activated at various temperatures ranging from 400 ^{0}C to 550 ^{0}C using 45 % and 50 % activating agent. Activated carbon at 400^{0}C, 45 % activating agent produced better result in the implementation of reactive blue dye such as absorbance, concentration of dye, efficiency of the dye removal and the dye adsorbed than at the other temperatures and 50 % activating agent along with its various temperature. It was characterized by Fourier Transform Infrared and Scanning Electron Microscope. Phytochemical analysis: pH, moisture content, volatile matter, ash content, carbon content, bulk density, electrical conductivity and surface area were also carried out.

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