PRODUCTION AND CHARACTERIZATION OF ACTIVATED CARBON (AC) FROM CORNCOB FOR METHYLENE BLUE AND CHROMIUM (VI) ADSORPTION

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ABSTRACT

Corn cob activated carbon (AC) was produced via chemical activation with H_3PO_4 for the hydrolysis step and KOH for the impregnation step. The optimal conditions for the preparation of AC using central composite design (CCD) software were 358.15 ℃, 116.90 minutes, 0.29 mg/l H_3PO_4, 0.09 mg/l KOH. This set of conditions gave hydrolysate yield of 76.9339 %, while activated carbon yield and methylene blue (MB) adsorption capacity were 21.84 % and 1.98 mg/g respectively. The ash content value for the best activated carbon sample was 12.3 wt % and the specific surface area of the AC using Sear's method was 314.2 m^2/g. Isotherm study on chromium (VI) was predicted by Langmuir and Freundlich model with R^2 value of 0.9974 and 0.7691 respectively. The parameters for the two models are indicated in the paper.

Key words: Activated Carbon, adsorption capacity, ash content, CCD, corn cob, specific surface area.

INTRODUCTION

Activated carbon is a versatile derivative of biomass. It is a crystalline solid that has high surface area. The structure of AC gives rise to its application ranges from liquid to gas phase adsorption. Industrial ACs can be produced from agricultural cellulosic materials, with high carbon component such as wood, coconut shell, corn cob, almond shells, peach stones, grape seeds, apricot stones, cherry stones, olive stones, peanut hull, nut shells, rice husk, oil palm shells, sugar cane bagasse [1,2], palm shell, rattan, mango stem peel, and corn cob [3], canarium schewein furthii nutshell [4,5,6], groundnut shells, palm kernel shells, bamboo, wood chips [7], waste tea [8] and saw dusts [9].

AC has been widely used in the treatment of liquid and gas throughout the world [10]. Charcoal being the pioneer of AC has been recognized as the oldest adsorbent known in waste water treatment. The product obtained has a large internal surface area. AC has broad uses ranging from domestic usage to large scale industrial applications which can remove diverse pollutants such as metallic ions [8, 11], anions, dyes, phenols, detergents, odours and tastes from drinking water, pesticides, humid substances, chlorinated hydrocarbons, and many other chemicals and organisms.

AC is also used in food processing industry, gas adsorption, dry cleaning recovery processes, pharmaceuticals, and oil removal, electroplating, alcoholic beverage production [9], and oil spillage clean-up [12].

The two broad processes for the production of AC from carbonaceous materials are thermal and chemical activation methods. Thermal activation involves carbonization of a cellulosic material followed by the activation of the resulting charcoal at a high temperature 700-1100°C in the presence of oxidizing gases such as CO_2, steam or N_2 [6]. In chemical activation, the cellulosic material is mixed with an activating agent such as salts, acids or bases and then pyrolyzed at low temperature range between 400-600°C at minimal amount of air. Chemical activation has several advantages over thermal activation. It takes place in a single step combining carbonization and activation. The process is always performed at lower temperatures and therefore, resulting in the development of a better porous adsorbent [1]. Given the same sample and particle size, it has been found that, chemical activation produces adsorbents with higher surface area and yield [6]. The present work is the pioneer of using hybrid chemical activation (hydrolysis and chemical activation) to optimize the operating conditions for AC production from corncob. Therefore, the work presented here is an optimization study of AC production from corncob. A chemical activation method for the production of activated carbon from corn cob using phosphoric acid (H_3PO_4) for hydrolysis and potassium hydroxide (KOH) as the activating agent was employed.

MATERIALS AND METHODS

Material Collection and Preparation

The chemical activating agents used in this work were of analytical grade. Corn cob samples were collected from the National Research Institute for Chemical Technology (NARICT) farms

in Basawa, Zaria, Nigeria. The corn cob was washed with tap water to remove impurity and oven dried, after which it was crushed in a local pestle and mortal and later processed in the laboratory mill and then sieved using a 600 μm mesh sieve. The corncob particles were subjected to proximate analysis to determine moisture content, ash and crude fibre, fat and protein as described by the procedure of American Society for Testing and Materials (ASTM), [13].

Hydrolysis, Impregnation and Activation of Corncob

Central composite design expert version 6.0.6 Stat-Ease, Inc. USA was used to design the experiment. The raw material with the desired particle size was first hydrolyzed with phosphoric acid in the ratios 0.07:1, 0.29:1, 0.50:1, 0.72:1 and 0.93:1 on a magnetic stirrer at 85°C for 1 hour. The resulting hydrolysate corn cob samples were washed and filtered by a vacuum pump and oven dried at 105°C overnight. The dry hydrolysate corn cob was then impregnated with KOH in the ratios 0.02:1, 0.08:1, 0.14:1, 0.20:1 and 0.26:1 and activated in a muffle furnace at temperatures range of 100-500°C, and activation time in the range of 15-150 minutes. The activated carbon was washed to a neutral pH of 7 and oven dried at 105°C overnight. The experimental template used is given in Table 1. Where, AC1, AC2.., AC30 are activated carbon samples code.

Table1: Experimental design matrix for the preparation of activated carbon using central composite design expert (CCD).

S/N	Sample Code	H$_3$PO$_4$ (mg/l)	KOH (mg/l)	Temperature (^{o}C)	Time (minute)
1	AC1	0.72	0.20	400	150
2	AC2	0.72	0.08	400	60
3	AC3	0.50	0.02	300	105
4	AC4	0.29	0.08	200	150
5	AC5	0.29	0.08	400	60
6	AC6	0.29	0.20	200	150
7	AC7	0.50	0.14	300	195
8	AC8	0.07	0.14	300	105
9	AC9	0.72	0.20	200	60
10	AC10	0.29	0.20	400	60
11	AC11	0.50	0.14	300	105
12	AC12	0.93	0.14	300	105
13	AC13	0.72	0.08	200	60
14	AC14	0.50	0.14	300	105

15	AC15	0.50	0.14	300	15
16	AC16	0.50	0.14	500	105
17	AC17	0.50	0.15	300	105
18	AC18	0.50	0.14	300	105
19	AC19	0.50	0.14	300	105
20	AC20	0.50	0.14	100	105
21	AC21	0.29	0.08	400	150
22	AC22	0.72	0.08	400	150
23	AC23	0.29	0.08	200	60
24	AC24	0.72	0.02	400	60
25	AC25	0.50	0.26	300	105
26	AC26	0.72	0.20	200	150
27	AC27	0.29	0.20	400	150
28	AC28	0.29	0.20	200	60
29	AC29	0.72	0.08	200	150
30	AC30	0.50	0.14	300	105

Adsorption Performance of Activated Carbon Samples

The adsorption capacity of the thirty samples produced using the design of experiment (DOE) template given in Table 1 on MB were carried out as follows: The adsorption capacity of the AC samples prepared were determined using MB concentration of 10 mg/l and 0.5g of the adsorbents were subjected to mechanical shaker at 120 revolution per minute (rpm) for a residence time of 20 minutes and centrifuged the cleared solutions at 4000 revolutions per minute (rpm). The cleared solutions were used to determine MB concentrations remaining in solution at equilibrium using UV-vis spectrophotometer.

Characterization of Materials and Samples

Chemical and structural characterization

The proximate analysis of the corncob particles was determined in accordance with the procedure of American Society for Testing and Materials (ASTM) [13]. Also, the best three of thirty activated carbon samples produced, in term of adsorption capacity, were subjected to Scanning Electron Microscope (SEM) and Fourier Transform Infra-red (FTIR) spectroscopy analysis. The moisture and ash contents were also determined for the samples using the method of American Society for Testing and Materials (ASTM) [13]. The values were: AC8 - 5.8 and 9.3 wt%, AC9 - 4.2 and 8.2 wt% and AC14 - 5.3 and 12.3 wt%.

Specific surface area

In determining the surface area of the selected activated carbons, Sear's method was employed. It is adapted BET method [14] which employed the resulting BET equation as expressed by Equation (1).

In this procedure, 1.5g of each of the activated carbon sample was acidified with dilute hydrochloric acid (HCl) drop-wise until a pH of 3-3.5 was attained. About 30g of sodium chloride (NaCl) was added to the acidified activated carbon samples with constant stirring; distilled water was added to make up the volume to 150ml. The solution was titrated with 0.1M sodium hydroxide (NaOH) till a pH of 9 was achieved [14]. The volume of sodium hydroxide used was noted. The specific surface area was determined using Equation (1).

$$S = 32V - 25 \tag{1}$$

where V is the volume of sodium hydroxide used to raise the pH of the solution to 9 and S is the specific surface area of the activated carbon sample.

Isotherm Study

The equilibrium adsorption behavior of the best AC samples was determined using tannery effluent containing 10 ppm of chromium (VI) solution as the adsorbate. 10 ml of the chromium (VI) solution was poured into each of five flasks containing 0.02, 0.04, 0.06, 0.08 and 0.10 g of the activated carbon samples [15]. The flasks were mechanically shaken for 20 minutes at a speed of 120 revolutions per minute, after which a clear solution was collected with a needle and syringe. These solutions were centrifuged for 10 minutes at 4000 revolution per minute. The cleared solutions from the centrifuge were then analyzed to obtain the chromium (VI) concentration of solution using atomic adsorption spectrophotometer (AAS). The adsorption data generated were fitted to the Langmuir and Freundlich adsorption isotherm model given in Equations (2-5).

The non-linear and linear forms of Langmuir isotherm model is given in Equations (2) and (3) respectively.

$$q_e = q_m b C_e / (1 + b C_e) \tag{2}$$

$$C_e / q_e = C_e / q_e + 1 / q_m b \tag{3}$$

where C_e is the concentration of chromium (VI) (adsorbate) at equilibrium (mg/l), q_m is the maximum adsorption capacity of adsorbate corresponding to monolayer coverage of the adsorbate on the surface of adsorbent (mg/g), q_e is the amount of adsorbate adsorbed per unit mass of adsorbent (mg/g) at equilibrium and b is Langmuir constant related to the affinity of adsorbent on adsorbate (l/mg).

The non-linear and linear forms of Freundlich isotherm model is given in Equations (4) and (5) respectively.

$$q_e = KC_e^{1/n} \tag{4}$$

$$Log q_e = log K + 1/n \, log C_e \tag{5}$$

where q_e is the amount of adsorbate adsorbed per unit mass of adsorbent (mg/g), C_e is the equilibrium concentration of the adsorbate (mg/l), K is the Freundlich adsorption capacity of the adsorbate and n gives information on favorability of adsorption process.

RESULTS AND DISCUSSION

Characterization of Corncob and Activated Carbon

Composition of corncob and properties of the three best activated carbon sample produced are presented in Table 2.

Table 2: Properties of corncob and activated carbon samples

Properties	Corncob	Activated carbon 8	Activated carbon 9	Activated carbon 14
Moisture content, wt %	5.8	5.8	4.2	5.3
Ash content, wt %	3.9	9.3	8.2	12.3
Crude fibre, wt %	14	nd	nd	nd
Crude lipid, wt %	9.00	nd	nd	nd
Crude protein, wt %	2.84	nd	nd	nd
Carbohydrate (by difference), wt %	64.46	nd	nd	nd
Specific surface area of AC, m^2/g	nd	259.8	215.0	314.2

*nd - not determined

From the results in Table 2, it is indicated that at activation temperature of 300 ^{o}C and activation time of 105 minute and activating agent concentration of 0.14 mg/l, the specific surface area was 314.2 m^2/g. But at a lower temperature of 200 ^{o}C and time 60 minutes and activating agent concentration of 0.20 mg/l the specific surface area was 215.0 m^2/g, which shows that activation temperature and time has direct influence on the surface area formation and this parameters

agreed with the results from[1] that by increasing the impregnating time and temperature, the specific surface area and the pore volume increase.

Adsorption Performance and Yield of Samples

The yield of the hydrolysate and activated carbon produced as well as the adsorption performance of the activated carbon samples are given in Table 3.

Table 3: The yield of samples and adsorption performance of activated carbon using central composite design (CCD)

S/N	Sample Code	H_3PO_4 (mg/l)	KOH (mg/l)	Temperature (ºC)	Time (minute)	Hydrolysate yield (%)	Activated carbon yield (%)	Adsorption capacity of AC (mg/g)
1	AC1	0.72	0.20	400	150	48.15	7.12	1.22
2	AC2	0.72	0.08	400	60	48.70	5.00	1.25
3	AC3	0.50	0.02	300	105	67.03	19.32	1.30
4	AC4	0.29	0.08	200	150	76.59	18.87	1.72
5	AC5	0.29	0.08	400	60	77.67	18.73	1.91
6	AC6	0.29	0.20	200	150	74.60	8.99	1.28
7	AC7	0.50	0.14	300	195	70.14	14.20	1.90
8	AC8	0.07	0.14	300	105	85.27	18.30	1.92
9	AC9	0.72	0.20	200	60	47.72	15.69	1.97
10	AC10	0.29	0.20	400	60	70.27	18.78	1.88
11	AC11	0.50	0.14	300	105	67.01	19.00	1.74
12	AC12	0.93	0.14	300	105	41.98	6.67	1.71
13	AC13	0.72	0.08	200	60	47.42	15.72	1.67
14	AC14	0.50	0.14	300	105	67.04	18.52	1.98
15	AC15	0.50	0.14	300	15	68.21	13.57	1.89
16	AC16	0.50	0.14	500	105	69.41	7.33	1.91
17	AC17	0.50	0.15	300	105	68.16	18.50	1.79
18	AC18	0.50	0.14	300	105	70.27	18.78	1.88
19	AC19	0.50	0.14	300	105	68.18	18.66	1.88
20	AC20	0.50	0.14	100	105	68.41	18.67	1.83
21	AC21	0.29	0.08	400	150	73.67	20.48	1.87
22	AC22	0.72	0.08	400	150	47.89	7.83	1.47
23	AC23	0.29	0.08	200	60	74.34	25.39	1.73
24	AC24	0.72	0.02	400	60	48.55	7.65	1.73
25	AC25	0.50	0.26	300	105	67.52	10.00	1.17
26	AC26	0.72	0.20	200	150	47.56	12.05	1.66
27	AC27	0.29	0.20	400	150	74.91	15.00	1.90
28	AC28	0.29	0.20	200	60	75.39	13.83	1.23
29	AC29	0.72	0.08	200	150	47.00	11.59	1.90
30	AC30	0.50	0.14	300	105	68.93	18.69	1.89

The optimal conditions for the production of activated carbon from corncob in the investigation were 358.15 ^{o}C, 116.90 minutes, 0.29 mg/l H_3PO_4 acid and 0.09 mg/l KOH gave rise to hydrolysate yield of 77.67 %, activated carbon yield of 25.39 % and adsorption capacity of the activated carbon of 1.98 mg/g. At constant concentrations of activating agents, high activating temperature and time, yield and adsorption capacity decreased.

FTIR Spectral Analysis of Corncob, Hydrolysate and Activated Carbon Samples.

Figure 1a-c shows spectral of corncob, hydrolysate and activated carbon samples.
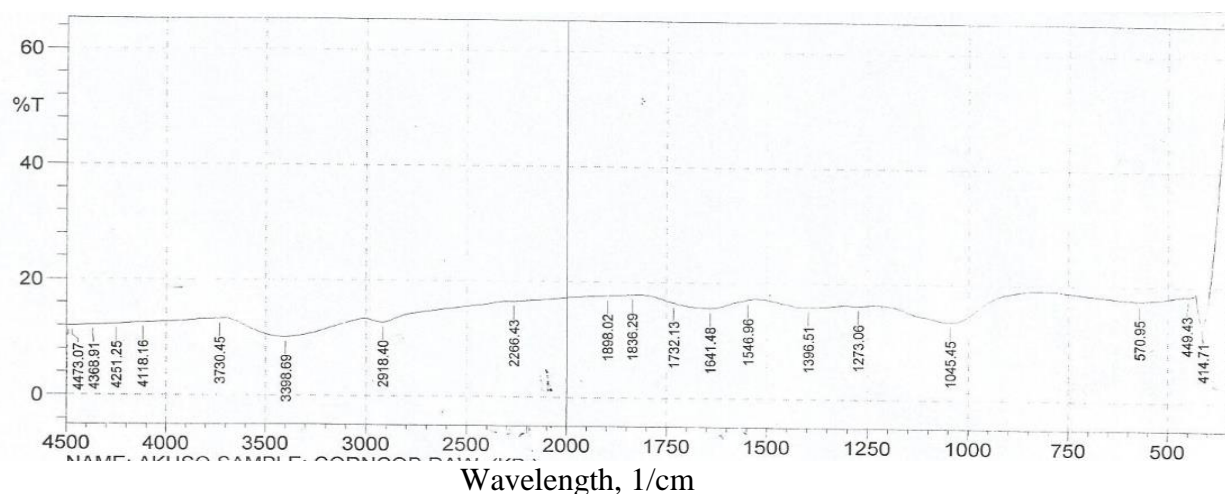
Figure 1: FTIR spectra of corncob
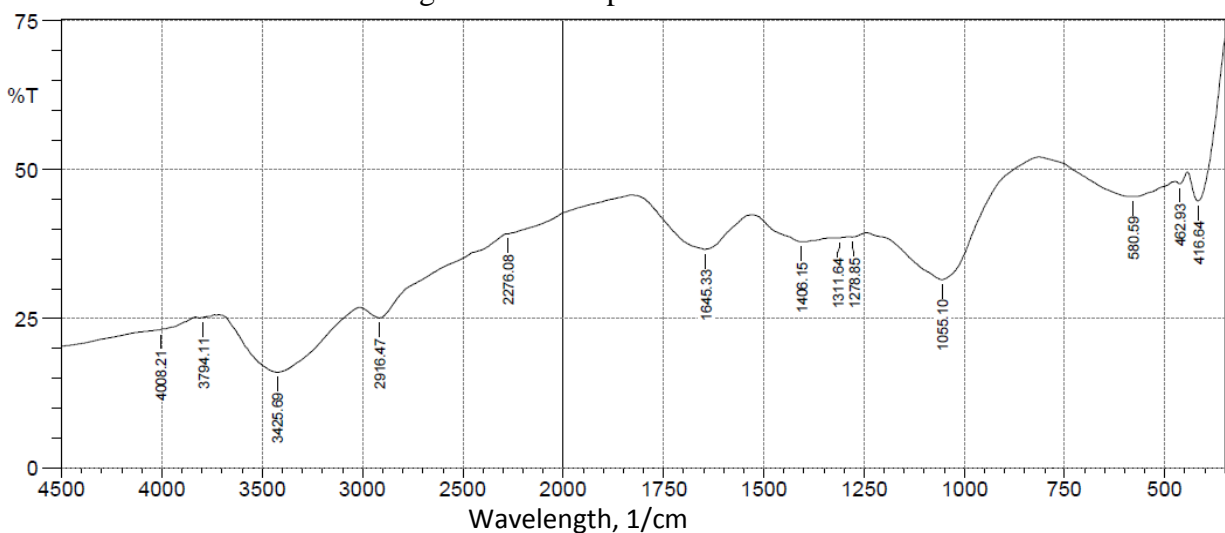
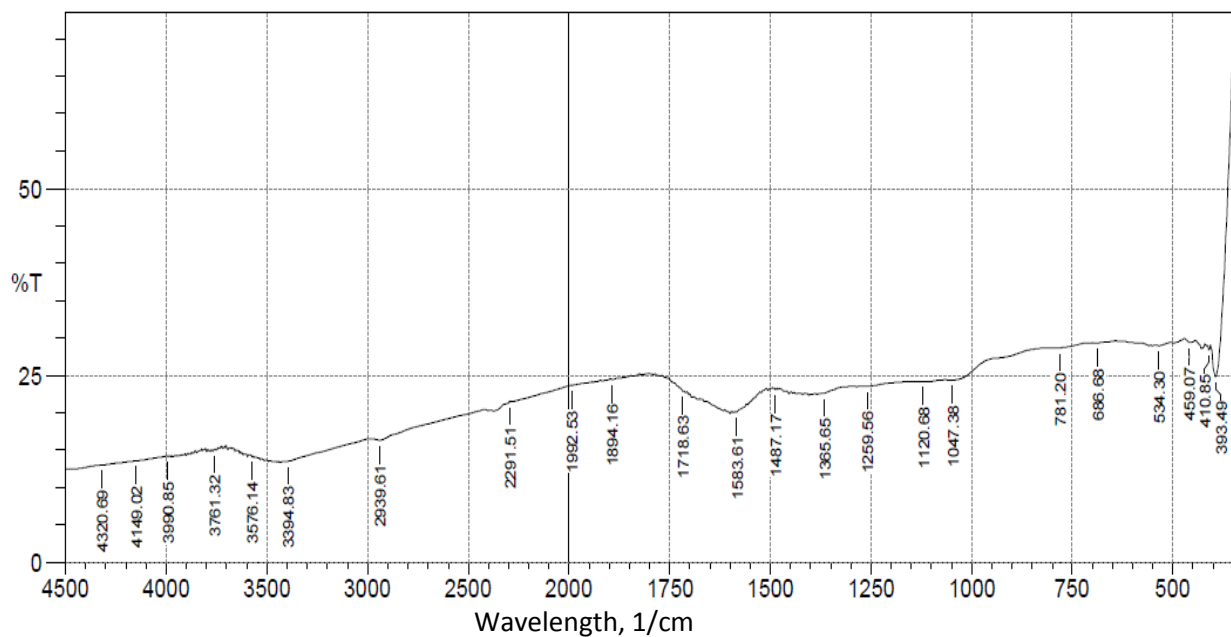Figure 2: FTIR spectra of hydrolysate corncob

Figure 3: FTIR spectra of activated carbon

FTIR spectroscopy is a technique that uses infra-red light to ascertain the properties of a solid, liquid, or gas. The spectra analysis for corncob, hydrolysate corncob and activated carbon samples are shown in Figures 1-3. One of the most vital parameters that influence the uptake of metal ions from aqueous solutions by activated carbon is the carbon-oxygen and carbon-hydrogen functional groups present on the activated carbon surface. FTIR analysis shows adsorption band's at 3394.83 cm^{-1}, 3398.69 cm^{-1} and 3425.69 cm^{-1} which are associated with the stretched vibration of the O-H groups in alcohols, phenols and carboxylic acids, N-H groups in amines (includes primary and secondary) and amides. Also, bands at 2916.47 cm^{-1}, 2918.40 cm^{-1} and 2939.61 cm^{-1} are associated with the stretched vibration of the C-H in alkanes and alkyl groups and O-H in carboxylic acids. While bands of 2266.43 cm^{-1}, 2276.08 cm^{-1} and 2291.51 cm^{-1} are associated with the stretched vibration of the C≡C and C≡N in alkynes and nitriles. Spectrum bands at 1583.61 cm^{-1}, 1641.48 cm^{-1} and 1645.83 cm^{-1} are associated with the stretched vibration of the N-H groups in amines and amides bend, C-C and C=C in alkenes and aromatics and C=O in inorganic carbonate. While bands at 1045.45 cm^{-1}, 1055.10 cm^{-1} and 1047.38 cm^{-1} which are associated with stretched vibration of the O-H groups in alcohols, esters, carboxylic acids and ethers, and C-N stretched in amines. Bands at 781.20 cm^{-1} and 1120.68 cm^{-1} are associated with

stretched of C-O in aromatic, esters and ethers. Bands at 686.68 cm^{-1}, 781.20 cm^{-1} and 1487.17 cm^{-1} are associated with stretched of C-H in alkanes, alkynes and aromatic.

Isotherm Study on Activated Carbon Sample

Study was performed on the best activated carbon sample produced to establish the appropriate isotherm model for the sample. The adsorption isotherm studied showed that Langmuir isotherm gave a better correlation than Freundlich isotherm. The b-value was 0.025 (l/mg), the closer the value to unity indicated that significant adsorption took place. However, the R^2 for the Langmuir isotherm was 0.9974 while that of Freundlich isotherm was 0.7691. The AC formulation showed the best correlation with Langmuir isotherm. The higher the b and qm values, the better the adsorbent. Isotherm plot for chromium (VI) adsorption on the activated carbon produced are shown in Figures 4 and 5. The Langmuir and Freundlich models gave the following parameters: Langmuir isotherm (b - 0.0251 (l/mg), qm - 133.88 (mg/g) and R^2- 0.9974; Freundlich isotherm (n- 0.0670, K_F- 15.601 (mg/g) and R^2- 0.7691.
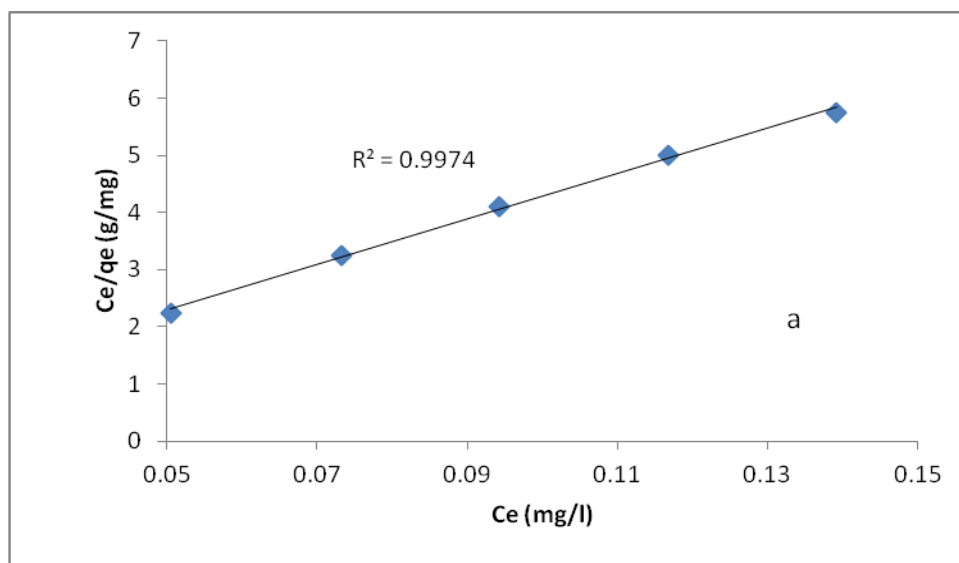

Figure 4: Effect of adsorbent dosage on chromium (VI) adsorption for Langmuir isotherm models for AC sample
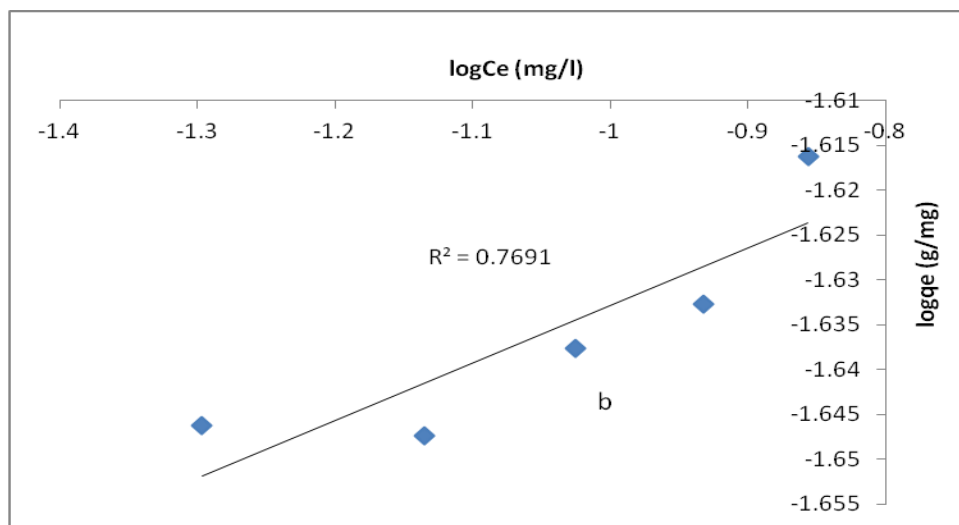
Figure 5: Effect of adsorbent dosage on chromium (VI) adsorption for Freundlich isotherm models for AC sample

CONCLUSION

Activated carbons were prepared from corncob at different activation temperatures between 100-500 $^{\circ}$C and activation time of 15-195 minutes. This formulation gave the highest specific surface area of 314.2 m^2/g compared to the other formulations.

The isotherm studied for chromium (VI) removal showed Langmuir isotherm model gave a fitted curve of the adsorption data obtained for chromium (VI) uptake on AC sample. This study showed that activation conditions for the preparation of (AC) adsorbent had a significant effect on the adsorption capacity of the adsorbent. The data obtained from the batch adsorption experiments for chromium (VI) best fit Langmiur model than Freundlich model with R^2 value of 0.9974. Langmuir model best described the adsorption equilibrium data with a maximum adsorption capacity of 133.876 mg/g for chromium (VI). The adsorbents were found to be a potential adsorbent for the removal of methylene blue and chromium (VI) ions.

FTIR analysis showed the presence of O-H, C-H, C-Br, N-H, C-C, C-N, C=C and C≡C groups which aid adsorbing adsorbate onto the adsorbent.

Recommendation

1. Effect of not washing the hydrolyzed corncob before impregnation should be investigated.

2. Effect of high activation temperatures above 500 $^{\circ}$C should be investigated to compare the yield and its adsorption capacity of the AC.

Akuso, S. A., Abubakar, G., Nwobi, B. E., Abdullahi, M., Ayilara, S. I., Batari, M. L. and Umar, M.: Production and Characterization of Activated Carbon (Ac) from Corncob for Methylene Blue and Chromium (VI) Adsorption

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