Optimization of Activated Carbon from Corncob for Wastewater Treatment

*[1]Akuso, S. A., [2]Ajinomoh, C. S., [2]Olawale, A. S., [1]Abubakar, G., [1]Ayilara, S. I. and [1]Batari, M. L.

*[1]National Research Institute for Chemical Technology (NARICT), Zaria, Kaduna State

[2]Department of Chemical Engineering, Ahmadu Bello University, Zaria, Kaduna State

*Corresponding author: alkalisamuel1962@yahoo.com or alkaliakuso@gmail.com

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. A response surface methodology (RSM) technique was employed to optimize the operating parameters which were phosphoric acid, potassium hydroxide, and activation temperature and activation time. The optimal conditions for the preparation of AC using central composite design (CCD) software were 358.15 ^oC, 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 specific surface area of the AC was determined using Sear's method was 314.2 m^2/g. Corncob activated carbon can be used effectively for the treatment of wastewater effluent.

Key words: Activated carbon, adsorption capacity, CCD, corncob, optimization, specific surface area.

INTRODUCTION

Researchers have made efforts to develop cheaper, more effective, renewable and environmental friendly activated carbon [1] that can compete with commercially activated carbons. This has led to the exploitation of various materials such as agricultural waste materials, inorganic materials, waste papers, household waste etc. Different methods of preparations and activating chemicals were explored. Activated carbon has been in use as far back into history that its origin cannot be ascertained. However, the earliest known use of wood chars (charcoal) by Egyptians and Samarians were for the refining of copper, zinc, and tin ores in the manufacture of bronze [1], removal of colour and odour, oil spillage control, pesticides, storage, as well as domestic smokeless fuel [2, 3].

The unique structure of AC gives rise to its application ranges from liquid to gas phase adsorption. Activated carbon can be produced from agricultural residues that has low ash and high carbon content such as peanuts, rice husk, corncob, sugarcane bagasse, almonds, cherry stones, waste tea leaves, coconut bunch waste, groundnut shell, shells (such as chestnut, hazelnut) [2, 3, 4, 5], sugarcane bagasse, almonds, cherry stones, Canarium Schweinfuthii [6], papaya seeds, tamarind seeds, palm seed coat, pineapple stem, sunflower stalk, pearl millet husk, peels such as (banana, orange, mango, cassava, water melon), apricots stones, coconut shell, coir pith, olive wastes that has low ash content and reasonable hardness [7, 8, 9, 10, 11]

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. Activated carbon produced from agricultural waste materials has high potential adsorption capacity for the removal of different pollutants such as odour and taste from drinking water, metallic ions, and chemicals like herbicides and pesticides. The product obtained has a large internal surface area [8, 11]. Activated carbon has been widely used adsorbent in wastewater treatment globally. It is used for the removal of solutes from solutions and gases from industries and air atmosphere [2, 5, 12, 13].

AC has been the most popular and predominantly used adsorbent with great success [11] in liquid and gas treatment throughout the world. Wood charcoal being the pioneer of AC has been known as the ancient adsorbent in waste water treatment. The product obtained has a very porous structure with a large internal surface area. AC has versatile uses ranging from domestic usage to large scale industrial applications which can remove diverse pollutants such as metallic ions [11], anions, dyes, phenols, detergents, odour and taste from drinking water, food and pharmaceutical industries [2], chlorinated hydrocarbons and oil spillage [12], pesticides, herbicides and environmental chemistry [14] and many other chemicals and organisms. The two major methods for the production of activated carbon are physical and thermal. The processes consist of raw materials pre-treatment, carbonization and followed by activation with activating agent [8]. In chemical activation, the precursor is mixed with a chemical agent such as salts, acids or bases and then pyrolyzed at low temperature between 400-600^{o}C in the absence of air. It is carried out in a single step combining carbonization and activation processes, performed at lower temperatures and therefore, resulting in the formation of a better porous structure [4]. Using the

same raw materials and particle size distribution, it has been discovered that chemical activation gives products with higher surface area and yield than thermal activation [8].

In this study, a hybrid chemical activation was implored comprising hydrolysis and chemical activation using phosphoric acid (H_3PO_4) for the hydrolysis process and potassium hydroxide (KOH) for the chemical activation process. The aim of the study was to optimize the operating conditions such as temperature, time, and concentration of activating agents H_3PO_4 and KOH for the production of AC from corncob using chemical activation technique.

MATERIALS AND METHODS

Raw Material Pre-treatment

The chemical reagents used in this work were all 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 dirt and oven dried for 24 hours at 110 ^oC, after which it was crushed in a local pestle and mortal and later processed in laboratory mill and then sieved using a 600μm 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 official Method of the Association of Analytical Chemist, (1984). Methylene Blue (MB) was used as an adsorbate. Distil water was used to prepare all solutions. Figure 1 shows the structure of methylene blue.

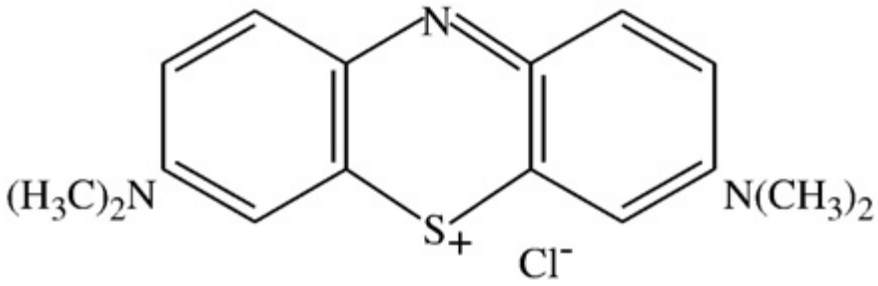


Figure 1: Chemical structure of methylene blue

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 was hydrolyzed with phosphoric acid on a magnetic stirrer at 85^oC for 1 hour, thereafter; the resulting sample was washed and dried in the oven at 105^oC for 12 hours. The dried hydrolyzed sample was activated with potassium hydroxide in a muffle furnace

at temperatures range of 100-500^{o}C and time range of 15-150 minutes. The activated sample produced was washed to get rid of any traces of the activating agent with distilled water and dried in an oven at 105^{o}C for 12 hours [15]. The experimental template used is given in [16].

Adsorption Capacity of Activated Carbon Samples

The adsorption capacity of the activated carbon samples produced was carried out using methylene blue solution of concentration of 10 mg/l and 0.5g of the activated carbons. The mixture was subjected to a mechanical shaker for a residence time of 20 minutes at 120 revolutions per minute (rpm). Thereafter, the mixture was filtered and the filtrate was centrifuge at 4000 rpm for 20 minutes. The cleared solutions were used to determine the residual concentrations of methylene blue in the solution at equilibrium using UV-vies spectrophotometer (UV-vies 1800 Shimadzu, Japan at a wavelength of 660 nm) [16].

The activated carbon yield was calculated by Equation (1).

$$\text{Yield } (\%) = w_{ac}/w_h \times 100 \quad (1)$$

Where w_{ac} and w_h are the dry weight of activated carbon and the dry weight of hydrolysate corncob, respectively.

The percentage removal of methylene blue at equilibrium was calculated by Equation (2).

$$\text{Removal } (\%) = (C_o - C_e)/C_o \times 100 \quad (2)$$

Where, C_o and C_e are the adsorbate (MB) initial and equilibrium concentration (mg/l), respectively.

Characterization of Samples

Chemical and structural characterization

The proximate analysis of the agricultural residue (corncob) was carried out on the best three activated carbon based on adsorption capacity using the official method of association of analytical chemist. The values of moisture and ash contents are: 5.8 and 9.3 wt%, 4.2 and 8.2 wt% and 5.3 and 12.3 wt% for activated carbons 8, 9 and 14. The specific surface areas of the selected activated carbon determined are 258.9, 215.0 and 314.2 m^2/g.

Specific surface area

Sear's method was adapted for BET to determine the surface area of the best three activated carbons [16] was calculated using Equation 3.

1.5g of the activated carbons was acidified with hydrochloric acid until a pH of 3-3.5 was attained. 30g of sodium chloride was added to the acidified activated carbons with constant stirring and distilled water was topped up to make the volume to 150ml. The above volume was titrated with 0.1M sodium hydroxide till a pH of 9 was attained [15, 16]. The specific surface areas of the selected activated carbons were determined using Equation 3.

$$S = 32V - 25 \quad (3)$$

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 selected activated carbons.

RESULTS AND DISCUSSION

Characterization of Activated Carbon

From the results obtained for the selected activated carbons, it shows that activation temperature and time has direct influence on the surface area of activated carbon produced. These parameters agreed with the results obtained by [4] increasing activating agents, activation temperature and time, the specific surface area and pore volume increases.

Adsorption Performance and Yield of Samples

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 decreases.

The empirical model equations for the yields of hydrolysate (Y_H) and activated carbon (Y_{AC}) and adsorption capacity (Y_{ADS}) in term of coded factors are represented by Equations (4), (5) and (6), respectively.

$$Y_H = 64.13 - 12.59\ A \quad (4)$$

$$Y_{AC} = \text{AC yield} = 18.62 - 3.38A - 1.78B - 1.86C - 1.48\ A^2 - 0.93B^2 - 1.34C^2\ 1.12D^2 + 1.83AB - 2.07AC + 1.10BC + 1.21CD \quad (5)$$

$$Y_{ADS} = 1.84 - 0.053A - 0.049B - 0.16B^2 + 0.074AB - 0.19AC + 0.072BC - 0.069BD \quad (6)$$

where A, B, C and D represent phosphoric acid (mg/l), potassium hydroxide (mg/l), activation temperature (^oC) and activation time (min).

The coefficient with one parameter represents the effect of the particular factor, while the coefficients with two parameters and second order degree terms represent the interaction between two parameters and quadratic effect, respectively. The models developed were evaluated on the basis of correlation coefficients, R^2 which gave predicted values closer to the experimental values for the responses studied.

The R^2 values for the responses studied for Equations (4), (5) and (6) were 0.9045, 0.9360 and 0.9134, respectively. The adjusted R^2 values for the responses were 0.8893, 0.8762and 0.8326, respectively. The adjusted R^2 was closed to the experimental R^2 value, which showed that there is a strong agreement between the experimental value and the predicted value.

Analysis of Variance (ANOVA)

The ANOVA was used to further justify the significance and accuracy of the models. The mean squares in the ANOVA were obtained by dividing the sum of squares of each of the variation sources and the error variance by the respective degrees of freedom. The higher the F-value the greater is the significance of the independent variables to cause effect. If the Prob>F is less than 0.05, the model terms are considered significant [6]. The ANOVA for the hydrolysate corncob yield, the model F-value and Prob>F were 59.22 and 0.0001 implied that the model was significant. In this case, factor A is significant term, whereas B, C and D were insignificant terms to the response. R-squared 0.9045 and Adjusted R-squared 0.8893.

From the ANOVA for hydrolysate corncob yield, the model F-value and Prob>F were 59.22 and 0.0001 revealed that the model is significant. In this case, parameter A is a significant term, whereas, parameters B, C and D were insignificant terms to the response. In the hydrolysis step only factor A was involved in process.

A good correlation existed between experimental and predicted data with adjusted R-squared of 0.8893 which is close to the correlation coefficient of R^2 of 0.9045. This shows that the predicted data is in close agreement with the experimental data.

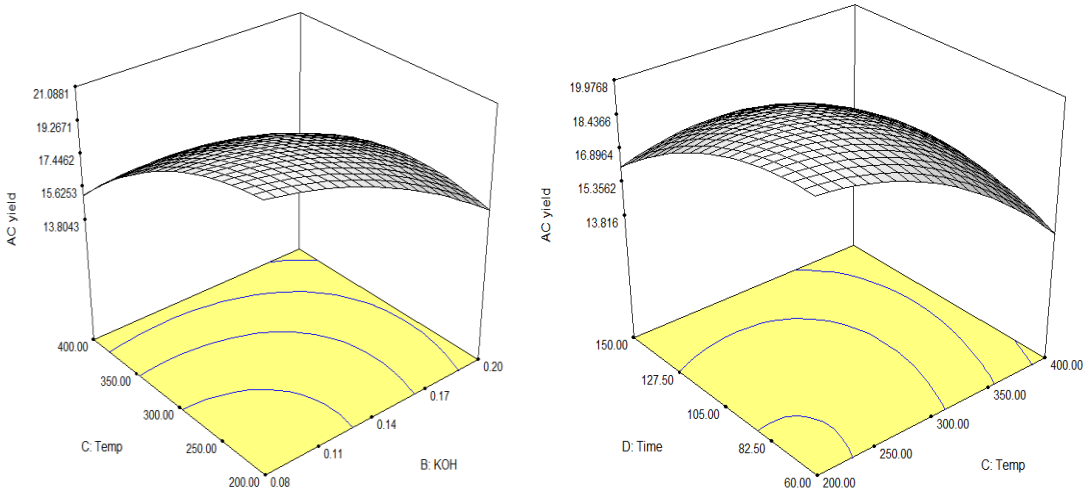
From the ANOVA for activated carbon yield, the model F-value and Prob>F were 15.66 and 0.0001 revealed that the model is significant. In this case, A, B, C, A^2, B^2, C^2, D^2, AB, AC, BC

and CD were significant terms, whereas, D, AD and BD were insignificant to the response. R-squared 0.9360 and Adjusted R-squared 0.8762.

From the ANOVA for methylene blue adsorption capacity of the activated carbon samples, the model F-value and Prob>F were 11.31 and 0.0001 revealed that the model is significant. In this case, A, B, B^2, AB, AC, BC and BD were significant terms, whereas, C, D, A^2, C^2, D^2, AD and CD were insignificant terms to the response. R-squared 0.9134 and adjusted R-squared 0.8326.

Activated carbon yield

From the F-value of activated carbon yield, phosphoric acid has greater effect on activated carbon yield followed by the activation temperature and potassium hydroxide. The interaction effects between potassium hydroxide and temperature as well as activation temperature and activation time were considered. Figures 2a and 2b shows the three-dimensional response surfaces which were plotted to show the effects of activated carbon samples preparation conditions on the yield. Figure 2a shows the effect of activation temperature and potassium hydroxide on the yield of activated carbon, whereas Figure 2b shows the effect of activation temperature and activation time on the yield of activated carbon.

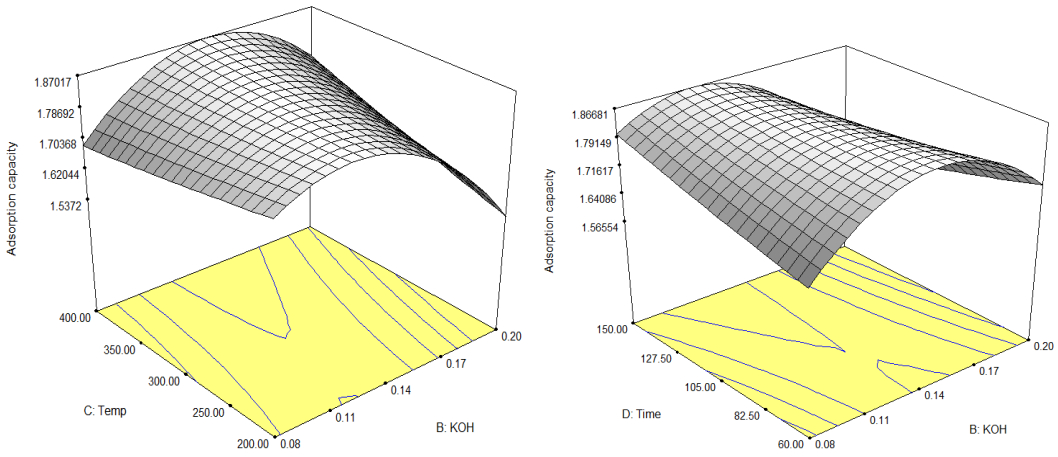


a b

Figure 2: Three-dimensional response surface plot of activated carbon yield; (a) effect of potassium hydroxide and activation temperature, (b) effect of activation temperature and activation time.

Adsorption of methylene blue on activated carbon

Based on the F-value, phosphoric acid has significant effect compared to potassium hydroxide and temperature on the adsorption of methylene blue on activated carbon. Figure 3a shows the interaction effects between potassium hydroxide and activation temperature, whereas Figure 3b shows the interaction effects of the potassium hydroxide and activation time on the adsorption of methylene blue.



a b

Figure 3: Three-dimensional response surf ace plot of methylene blue adsorption; (a) effect of potassium hydroxide and activation temperature, (b) effect of potassium hydroxide and activation time.

Process Optimization

The operating parameters for the production of activated carbon from corncob were, phosphoric acid, potassium hydroxide, activation temperature and activation time were studied to optimize the yields of hydrolysate and activated carbon and the adsorption performance of the activated carbon samples and the removal of methylene blue from aqueous solution. The central composite design expert software version 6.0.6 (STAT-EASE Inc., Minneapolis, USA) was used to optimize the responses under same operating conditions. The resulting responses; hydrolysate yield, activated carbon yield, and adsorption performance of the activated carbon samples were obtained using the software were 76.93 % hydrolysate yield, 21.84 % activated carbon and 1.98 % adsorption capacity, respectively. The optimal preparation conditions obtained were 0.29 mg/l phosphoric acid, 0.09 mg/l potassium hydroxide, 358.15 ^{o}C activation temperature and 116.90 minutes activation time.

Chemical and Structural Characterization of Activated Carbon Samples

The three best activated carbon samples based on adsorption performance were characterized as described in section 2.4. The most important parameters of activated carbons is their surface area and porosity. The specific surface area of the best activated carbon sample produced was found to be 314.2 m^2/g and this was compared with the commercial activated carbon (animal charcoal) having specific surface area of 109.4 m^2/g.

The Scanning Electron Microscope (SEM) of Selected Activated Carbon Samples

The selected activated carbon samples were texturized using the scanning electron microscope (SEM) analysis as shown in Figures 4-6. The surface textures of the activated carbon samples were almost homogeneous type pores structure distributed on the surface of the activated carbon samples as shown in Figures 4-6. This result revealed that the combination of the operating conditions were effective in creating well-developed pores resulting to high surface area of activated carbon with good porosity for adsorption.

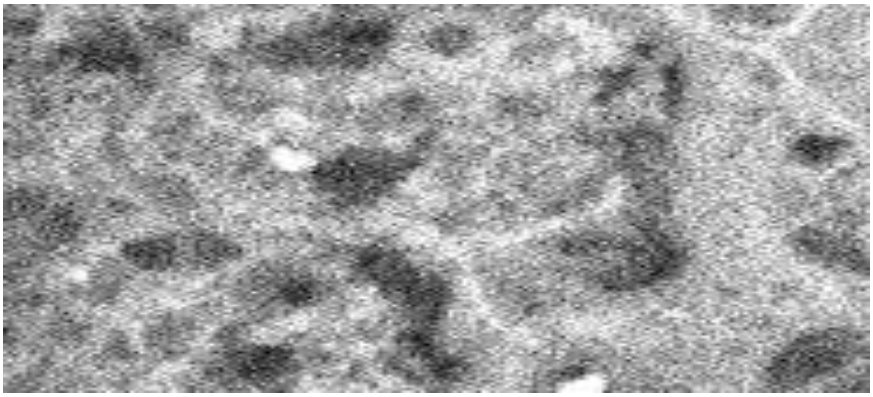


Figure 4: Scanning electron microscope for AC 8 at a magnification of 600x

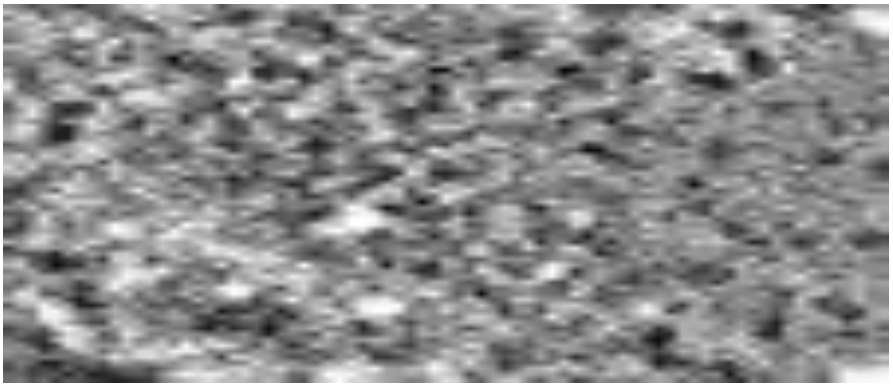


Figure 5: Scanning electron microscope for AC 9 at a magnification of 600x

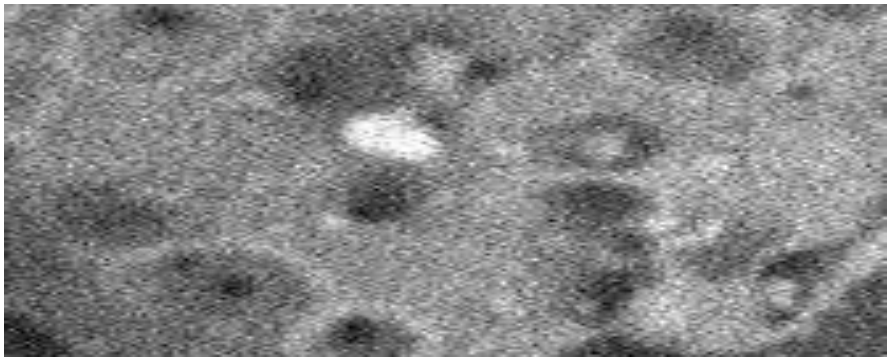


Figure 6: Scanning electron microscope for AC 14 at a magnification of 600x

From the SEM images of the activated carbon samples in Figures 4-6, the pores were visible. The pores are somehow homogeneous with specific surface areas of 314.2 m^2/g, 259.8 m^2/g and 215.0 m^2/g. The higher the specific surface area of the adsorbent; the higher the adsorption capacity.

CONCLUSION

Central composite design expert was successfully used to study the effects of the operating conditions on the yield and adsorption of methylene blue in aqueous solution. Activated carbons prepared from corncob at different activation temperatures between 100-500 ^oC and activation time of 15-195 minutes, phosphoric acid of 0.07- 0.93 mg/l and potassium hydroxide of 0.02 – 0.26 mg/l resulting to 1.98 mg/g of methylene blue adsorption . The optimal preparation conditions were 0.29 mg/l hydrolysate, 0.09 mg/l potassium hydroxide, 358.15 ^oC temperature and 116.90 minutes activation time. This formulation gave the highest specific surface area of 314.2 m^2/g compared to the other formulations.

Recommendations

1. Application of the activated carbons produced should be tested on real industrial effluent.
2. Effect of mixing activating agents in one step should be investigated and compare their specific surface areas and adsorption capacity of the activated carbon produced in this study.
3. Kinetics study of the activated carbon samples should be investigated.
4. Economic analysis of preparation of activated carbon using hybrid chemical activation should be carried out.

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