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Evaluation of the Physicochemical Characteristics and Adsorption Efficiency of Activated Carbons Derived from Banana Peels and Coconut Shell: A Comparative Study

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Abstract: The physicochemical characteristics and adsorption efficiencies of the activated carbons prepared from banana peels and coconut shell were evaluated using physical activation method. Phosphoric acid (H_3PO_4) was used as an activating agent. The physicochemical characteristics (IAN, pH, attrition, porosity, titratable surface functional groups, bulk density, moisture and ash content) were determined using standard analytical procedures and the adsorption efficiencies were evaluated through batch adsorption studies using aqueous solution of Safranin-O dye as adsorbate. The results revealed that the physicochemical parameters played a vital role in the adsorption performance of the two adsorbents and contributed majorly to their differences in the adsorption efficiency. The batch adsorption process was carried out by varying initial dye concentration, pH, adsorbent dosage and contact time. CSAC was found to be better adsorbent than BPAC as it recorded higher percentage of Safranin-O dye removal under all the experimental conditions.

Keywords: Adsorption; Activated Carbon; Banana Peels; Coconut Shell; Safranin-O.

1. Introduction

In the course of searching for effective, simple, clean and more economical material that can be used in treating waste water, especially those containing heavy metals and dyes effluents, agricultural wastes had been found worthy among others. However, this has been achieved by many researchers through adsorption process either by direct use of the agricultural waste with little processing or by conversion into activated carbon.^[1]

Adsorption is the process by which some substances bind and concentrate selected ions or molecules onto to their surfaces from aqueous solutions.^[2] Some researchers had described adsorption process as an alternative technology used in removing heavy metals or dyes from effluents using both organic and inorganic materials which bind and accumulate these pollutants onto to their surfaces through different mechanisms.^[2,3]

Furthermore, adsorption of dye molecules onto the surface of absorbents is typically heterogeneous and complicated in nature as various mechanisms may be involved.^[3] Moreover, nature of the ions in the dye species and the functional groups on the absorbent surface play a vital role in the adsorption process.^[4] Thus, functional groups such as carboxylic and hydroxyl groups are commonly present in the structure of most natural absorbents.^[5] However, studies revealed that at suitable pH, these groups undergo dissociation,

forming negatively charged sites on the absorbent surface which hasten the adsorption of cationic dye on the adsorbent surface.^[6] This study used Safranin-O as an adsorbate. Safranin-O being a cationic dye, is readily soluble in water and used mostly in textile and pharmaceutical industries.^[7] Fig. 1 shows the structure of Safranin.

Activated carbon is a black, solid carbonaceous material having complex porous structures and high surface area. Their structural heterogeneity is as a result of existence of mesopores, micropores, and macropores of different sizes and shapes. These properties make activated carbon the most important adsorbent industrially. Furthermore, activated carbon, due to its high degree of microporosity, just one gram has a surface area in excess of 500 m² while some have surface area as high as 5000 m².^[8]

However, literatures revealed that conversion of agricultural wastes into activated carbon is more economical and best alternative for commercial activated carbon since they are abundant in nature and requires little processing.^[9] This research work therefore, aimed at comparing the adsorption efficiencies of the activated carbons prepared from banana peels and coconut shell.



Fig. 1. Chemical structure of Safranin-O (BR2).



2. Experimental Section

2.1. Preparation of Dye Solution

A stock solution of 1000 cm³ was prepared by dissolving 1.0 g of Safranin-O dye ($C_{20}H_{19}CIN_4$; MW, 350.84 g mol⁻¹) of analytical grade in 1000 cm³ volumetric flask and made up to mark with distilled water. Different concentrations were prepared by diluting the stock solution with suitable volume of distilled water and the natural pH of the stock solution was determined using pH meter (Jenway 3015).

2.2. Sample Collection and Treatment

Banana peels and coconut shells samples were collected from fruits sellers in Keffi, Nasarawa State. The samples were washed thoroughly with excess water and finally with distilled water to remove surface impurities. The samples were sun dried for one week and further dried in an oven at 105°C overnight. The dried samples were ground separately followed by sieving to 2 mm mesh size. The samples were then stored in an air tight container for further analysis.

2.3. Preparation of Activated Carbon

A 100 g of the treated sample was placed in a separate crucible and introduced into a furnace at the temperature of 500°C for ten (10) minutes. The carbonized sample was transferred from the crucible into a bath of ice block after which it was removed, drained off and sun dried. The carbonized sample was further washed with 10% HCl to remove surface ash, followed by washing with distilled water to remove residual acid. The carbonized samples were sun dried and finally dried in the oven at 100°C for 1 hr. For the activation, 5 g of each carbonized sample was weighed followed by addition of 5 cm³ of 1M Phosphoric acid (H_3PO_4) which served as activating agent. The samples were kept for 24 hrs before they were introduced into a muffle furnace at 800°C for 5mins. The activated samples were removed from the furnace, washed with cold water, drained off and further washed with 10% HCl to remove surface ash. The carbonized samples were further washed distilled water to remove the residual acid, sun dried, and dried in an oven at 105°C for two hours.^[11] The prepared activated carbons were stored in air tight containers for further analysis.

2.4. Physicochemical Characterization

2.4.1. Moisture Content

Five grams (5 g) of activated carbon was weighed into a crucible and oven dried at 105° C for 2 hrs. It was then cooled in a desiccator for 30 minutes and weighed. This was repeated until a constant weight was obtained. The percentage moisture was calculated using equation 1.

% moisture =
$$W_1 - W_2/W_1 \times 100$$
 (1)

Where W_1 = weight of the sample before drying and W_2 = weight of sample after drying.

2.4.2. Ash Content

Another 5 g of the activated carbon was placed in a crucible and introduced into a furnace at 500°C for 3 hrs. It was cooled in a desiccator and weighed. The percentage ash content was determined using equation 2.

% ash =
$$W_3 - W_1 / W_2 - W_1 x 100$$
 (2)

Where W_1 = weight of empty crucible, W_2 = weight of empty crucible + fresh sample and W_3 = weight of crucible + ash content.

2.4.3. Determination of pH

0.5 g of the activated carbon each was weighed into a beaker and 15 cm³ of distilled water was added. The content was macerated with a glass rod to ensure uniform wet. It was allowed to stand for an hour. The extract (10 cm³) was decanted into a clean dry beaker and the pH was determined using pH meter (Jenway 3015).

2.4.4. Determination of Bulk Density

A 25 cm³ cylinder was filled to 20 cm³ with 2 mm mesh size activated carbon. The cylinder was tapped for at least 1-2 mm to compact the activated carbon and weighed.^[12] The bulk density was calculated using equation 3.

Bulk density
$$(g/cm^3) = W/V$$
 (3)

Where W = dry activated carbon (g) and V = volume of packed dry activated carbon (cm^3).

2.4.5. Determination of Porosity Based on Swelling

A Portion (0.5 g) each of the activated carbon was dispersed in 20 cm^3 of distilled water in a graduated tube with the aid of a shaker. This was centrifuged for 10 minutes at 400 rpm using centrifuge. The resulting volume each was read at VT and recorded. The equations (4) and (5) were used to calculate the porosity and density respectively.

Porosity (
$$\alpha$$
) = VW/VT (4)

Density (p) = Raw/1-
$$\alpha$$
 (5)

Where Raw = M/VW, M is the mass of activated carbon (g), VW is the volume of water, P is the apparent density and VT is the final volume of water after centrifugation.

2.4.6. Attrition

The attrition of the activated carbon samples was determined using a wet attrition test. A gram (1 g) of 40 mm mesh size was added 100 cm³ of acetate buffer (0.07 M) sodium acetate and 0.03 M acetic acid (pH 4.8) in a 250 cm³ Erlenmeyer flask. The solution was stirred for 6 hours at 25° C with a magnetic stirrer (model. REMI, 2MLH) at 200 rpm using 0.5 inch stir bar. It was poured onto a 40 mm mesh size and the residual activated carbon was washed with deionized water. It was transferred to a crucible and ovum dried at



90°C for 4 hrs. The samples were removed and allowed to cool in a desiccator and weighed.^[13] The percentage attrition was calculated using equation 6.

% attrition =
$$W_1/W_2 \times 100$$
 (6)

Where W_1 = weight of carbon retained by sieve (g) and W_2 = initial weight of the sample (g).

2.4.7. Determination of Iodine Adsorption Number (IAN)

From each sample, 0.5 g was weighed into a beaker and 25 cm³ of iodine solution (0.05 M) was added. The mixture was swirled vigorously for 10 minutes and filtered by means of a funnel impregnated with a clean filter paper. 20 cm³ of the filtrate was titrated with 0.1 M thiosulphate solution until a persistence pale yellow colour was obtained. 5 cm³ of a freshly prepared starch indicator solution was added and titrated slowly until a colourless solution appeared. The titration was also repeated with 25 cm³ portions of the standard iodine solution (not treated with AC from the precursor) to serve as blank titration.^[14] The iodine adsorption number (IAN) was calculated from the relationship using equation 7.

$$IAN = Ms (Vb - Vs)/2Ma$$
⁽⁷⁾

Where Ms = molarity of thiosulphate solution (mol/dm³), Vs = volume of thiosulphate (cm³) used for titration of the AC aliquot, Vb = volume of thiosulphate (cm³) used for blank titration and M = mass of activated carbon (g)

2.4.8. Determination of Titratable Surface Functional Groups

Boehm titration was employed in the determination of titratable surface functional groups. Three bases; sodium hydroxide (NaOH), sodium trioxocarbonate IV (Na₂CO₃) and sodium hydrogen trioxocarbonate IV (NaHCO₃) were formulated to a 0.05 M solution. One gram (1.0 g) of the adsorbent was taken into 100 cm³ conical flask and 35 cm³ of the base added. The flask was vigorously shaken for about five (5) minutes and left for 3 days. The samples were filtered thereafter and 10 cm³ of 0.1 M HCl (aq) was added each in excess to 10 cm³ aliquot of the filtrate. The solution of the excess HCl (aq) was allowed to react with residual base in the filtrate then boiled and cooled. The remaining HCl was back titrated with 0.1 M NaOH (aq) with few drops of methyl orange as indicator. The result was expressed as mmoles H⁺ ions neutralized by excess OH⁻ per gram adsorbent.^[14]

2.5. Batch Equilibrium Method

The experiments were carried out in a batch system at ambient temperature. A known mass of the activated carbon, 0.2 g was added into 100 cm³ conical flask containing 30 cm³ aqueous solution of Safranin-O dye. The contents were thoroughly shaken in an orbital shaker rotating at a speed of 250 rpm. This was carried out by varying initial concentrations of dye solution (10-50 mg/L) while other experimental factors include pH; adsorbent dosage and contact time were kept constant. Similarly, effects of varying these factors; adsorbent dosage (0.2-1.0 g), pH (2-10), contact time (20-100 min.)



The unadsorbed dye concentrations were determined using UV/visible spectrophotometer.

The amount of Safranin-O adsorbed at equilibrium Q_e , the amount adsorbed at any time t, Q_t (mg/g) and the percentage removal (%RE) were calculated using equations 8, 9 & 10 respectively.^[15]

$$Q_e = \frac{(c_o - c_i)V}{W}$$
(8)

$$Q_{i} = \frac{(c_{o} - c_{i})V}{W}$$
(9)

$$%RE = \frac{\left(c_{e} - c_{e}\right)}{C} x_{100}$$
(10)

3. Results and Discussions

3.1. Physicochemical Characterization of the Derived Activated Carbons

Table 1 shows the data of the physicochemical parameters obtained from the derived activated carbons. The results obtained indicate that coconut shell activated carbon (CSAC) had 0.10% while banana peels activated carbon (BPAC) 0.20% moisture content which in any case was found to be minimal. Moisture content determines the shelf-life of the activated carbons. Thus, the lower the moisture content the longer the shelf life and the better it's in terms of storage. This implies that the two adsorbents have the potential to be stored for a long period without deterioration. This result is also in agreement with the one reported on evaluation of the Physicochemical and adsorptive properties of adsorbents prepared from guinea corn husks carbon.^[16]

It was observed from the Table 1, that the values of the ash content fell within the range of 3.80-15.10% with BPAC having higher percentage (15.10%) than CSAC (3.80%). The higher percentage ash content recorded in BPAC could be attributed to the constituents of the starting material.^[17] High ash content reduces the overall activities of the activated carbon by reducing its performance efficiency in terms of adsorption and re-activation.^[18] It therefore means that, the lower the ash content of the activated carbon the higher its adsorption the efficiency and vice versa. However, the results obtained for the ash content could be a reason why BPAC had lower adsorption performance than CSAC since ash content also plays a vital role in the a adsorption of the adsorbent.

lodine adsorption number (IAN) is the most fundamental parameter usually used to characterize the performance of activated carbon. High value indicates high degree of activation. It's also employed as a measure of porosity of an active carbon and as an indicator for the total surface area.^[19] The results displayed on Table 1 for IAN (mg/g) of the two absorbents varied in order: BPAC (0.14) < CSAC (0.48). This implies that CSAC had higher degree of activation than BPAC. This also justifies its adsorption performance in this study. It also implies better performance in removing small size contaminants than BPAC. Although, the two adsorbents gave fairly



Parameters	BPAC	CSAC
Moisture content (%)	0.20±0.010	0.10±0.08
Ash content (%)	15.10±1.2	3.20±0.11
рН	9.80±0.02	6.08±0.01
IAN (mg/g)	0.26±0.08	0.48±0.02
Attrition (%)	1.53±0.21	11.27±1.05
Porosity	0.76±0.16	0.85±0.04
Titratible surface functional	2.84±0.02	4.01±0.12
(mmol/g)		



high values of IAN when compared with a study reported on commercial activated carbon. $^{\left[20\right] }$

Bulk density is an important physical characteristic of an activated carbon which depends invariably on the nature of the starting material.^[21] From the Table 1, it could be seen that CSAC had higher bulk density of 0.50 g/cm³ than BPAC (0.36 g/cm³). It has been reported that the rate of volatilization during activation depends on the bulk density which affects the hardness, strength and the porosity of the activated carbon produced. Also, low bulk density enhance trapping of impurities inside porous structure of the activated carbon.^[22] From the results obtained, it could be inferred that lower volatility will be observed in BPAC (0.36 g/cm³) than in CSAC (0.50 g/cm³) while for trapping impurities, BPAC will be higher than CSAC.

The values of attrition for the two adsorbents followed the order: CSAC (11.27%) > BPAC (1.53%). Attrition is the measure of the mechanical strength or abrasion of an activated carbon, it's an important parameter which indicates the ability of activated carbon to maintain its physical integrity and withstand frictional forces impose during handling and regeneration or back washing.^[22] The results indicate that CSAC had higher attritional value than BPAC. The high and low values observed in CSAC and BPAC respectively, could be attributed to their carbon density or starting materials. Also, from the result obtained in Table 1, it could be suggested that CSAC has higher physical integrity to withstand its relative loss during handling or regeneration than the BPAC.

The porosity obtained for both the activated carbons fell within the range of 0.76-0.85 which is higher than minimum requirement (0.25) for application in the removal of pollutants from waste water.^[23] This implies that both the prepared adsorbents are good for adsorption studies.

The titratable surface functional groups (mmol/g) obtained from this study shows that CSAC had 2.84 mmol/g while BPAC had 2.84 mmol/g. The type of charge on the functional groups bonded to the



carbon's surface is important in adsorption and even the understanding of the mechanism of adsorption of adsorbates onto the activated carbons. The surface functional groups that dominate the adsorption behaviour of activated carbon are mainly carbon-oxygen structures which include carbonyl, carboxyl, and phenolics.^[24] However, presence of these structures in activated carbon enhances adsorption of charged species of both organic and inorganic substances (adsorbates). The percentage burn off was found to be higher in CSAC (72.10%) than BPAC (64.13%). The result is also in agreement with the studies reported on activated carbon prepared from peanut shell.^[25] Thus, the higher the percent burn off the lower the yield of the activated carbon. This justifies the values obtained from this study.

The percentage yield obtained (Table 1) in this study followed the order: BPAC (33.16%) > CSAC (24.34%). The values indicate that there is a trend between the yield and the burn off as reported by Ahmedna.^[26]

The pH values for the two investigated derived activated carbons fell within the range of 6.08-9.24. The results indicate that CSAC had pH value 6.08 while BPAC had pH value of 9.24. This implies CSAC is acidic while BPAC is basic. The acidic and basic properties observed in the two adsorbents CSAC and BPAC could be attributed to either the nature of their starting materials or their treatment with phosphoric acid (H₃PO₄) as an activating agent during activation process. The pH also affects the rate of activated carbon adsorption. Thus, activated carbon at low pH is more effective than at high pH.^[27] This implies that CSAC will be more effective in terms of adsorption performance than BPAC which is justified in this study.

3.2. Equilibrium Studies

3.2.1. Effect of Initial Concentration

The effect of varying concentration (10-50 mg/L) of Safranin-O dye in aqueous solution using a fixed mass of the adsorbents (0.2 g) from coconut shell activated carbon (CSAC) and banana peels activated carbon (BPAC) was studied. It was observed from both Fig. 2 and 3 that as concentration of the Safranin-O dye increases from 10 mg/L to 50 mg/L, the percentage removal decreases from 96.40-60.28% in CSAC and 82.40-42.26% in BPAC respectively. This implies that as the concentration of the Safranin-O dye in the solution increases the percentage of dye removed decreases. This may be due to the saturation of adsorption sites on the adsorbent surface as the concentration increases. Thus, at low concentrations, there will be





more unoccupied active sites on the adsorbent surface which decrease with increase in initial dye concentration. It was also observed that the percentage removal in CSAC is higher than in BPAC, this could be attributed to more adsorption sites and the porosity in CSAC than in BPAC.^[28]

Fig. 6. Effect of pH using BSAC.

3.2.2. Effect of Adsorbent Dosage (g)

The results from the Fig. 4 and 5 shows that as the adsorbent dosage increases, the percentage removal of Safranin-O dye from the solution also increases from 0.20 to 0.60 g in both BPAC and CSAC after which no significant changes in the percentage of Safranin-O dye removal were recorded as adsorbents dosage increased. This means, the CSAC and BPAC attained adsorption equilibrium at the dosage of 0.60 g.^[29]

3.2.3. Effect of pH

The effect of pH on the adsorption study is highly significant especially on the adsorption of dyes because it controls the magnitude of electrostatic charges which are imparted both by the ionized dye molecules and the charges on the surface of the



adsorbent. As a result, rate of adsorption varies with both the pH of an adsorbate and the adsorbent.^[29] Fig. 6 and 7 showed the effect of varying pH (2, 4, 6, 8 and 10) on the adsorption efficiency of the two adsorbents. The results reveal that highest percentage of Safranin-O dye removed was observed at the pH of 10 in CSAC and as the pH of the Safranin-O dye solution increases the percentage of Safranin-O dye removal increases (2-10) while in the case of BPAC, reverse is the case, the highest percentage of Safranin-O dye removed was observed at the pH of 2 and it decreases as the pH increases (2-10). The difference in the trends of the adsorption processes observed by the two adsorbents with respect to varying pH could be traced to their differences in the pH as shown in Table 1.

3.2.4. Effect of Contact Time

Fig. 8 and 9 showed the effect of contact time on the adsorption of Safranin-O using BPAC and CSAC respectively. It was observed that the percentages of Safranin-O removed were between the range of 59.95-90.70% in CSAC and 50.65-78.75% in BPAC respectively. It was also observed that highest percentage removal of Safranin-O dye was recorded at 80 mins for both CSAC and BPAC. This signifies that both CSAC and BPAC attained maximum adsorption equilibrium at 80



mins.^[30] But, the CSAC recorded higher percentage removal of Safranin-O dye.

4. Conclusions

The physicochemical characteristics of the derived activated carbons played a vital role in the adsorption of Safranin-O dye from aqueous solution and contributed significantly to the differences in the percentage of Safranin-O dye removal by the derived activated carbons. The effects of experimental parameters which include initial dye concentration were inversely proportional to percentage of dye removal while dosage and contact time were directly proportional to the percentage of Safranin-O dye removal. From the results obtained, CSAC was found to be more effective than BPAC since it recorded the highest percentage of Safranin-O dye removal under the experimental parameters. This implies that CSAC was better adsorbent than BPAC; reason could be attributed to the differences in the data obtained from their physicochemical parameters.

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Conflicts of Interest

The authors declare no conflict of interest.

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