SYNTHESIS AND CHARACTERIZATION OF GOETHITE, ACTIVATED CARBON AND THEIR COMPOSITE

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ABSTRACT

Iron oxide nanoparticles, goethite (G), activated carbon (AC) and their composite (G-AC) are prepared and characterized. The goethite was synthesized under inert atmosphere and characterized by physicochemical and spectroscopic methods. The physico-chemical results show bulk density values of 0.4408 g/ml, 0.3316 g/ml and 0.3638 g/ml, pH values of 8.9, 7.2 and 5.5 and a point of zero charge referring to 8.8, 7.6 and 7.9 for G, AC and G-AC, respectively. The spectroscopic analyses used include X-ray Diffraction (XRD), Scanning Electron Microscopy (SEM), Transmission Electron Microscopy (TEM), X-ray Fluorescence (XRF) and Fourier Transmission Infrared (FTIR) spectroscopies. The XRF results show 96.97 % purity of goethite nanoparticles and 73.18 % of iron oxide in the composite. The SEM and TEM data revealed that the goethite is in the form of smooth needles of a diameter of 97.89 nm. These results suggest that goethite nanoparticles, activated carbon and the composite based on them are multi-purpose adsorbents due to the presence of carbon and iron oxide active adsorption sites and large surface areas.

Keywords: synthesis, goethite, activated carbon, composite, characterization.

INTRODUCTION

Goethite is a very common mineral of the chemical formulae of FeO(OH). It is a frequent matrix material for other more aesthetic minerals. It is usually a golden brown or golden yellow, though specimens from a handful of locations (especially Colorado) are remarkable for their delicate and beautiful crystal or oddly formed botryoidal and stalactitic velvety growth. An activated carbon is a highly porous amorphous solid of a graphite lattice, usually prepared in small pellets or a powder. It is non-polar and cheap. One of its main drawbacks is that it is combustible. Because of the great pore size of the activated carbon and the highly developed surface area per weight of the nanoparticles, e.g. in case of goethite, magnetite and hematite, etc., researchers continue to direct their application to waste water treatment. In this fastest growing area of an environmental application they are used for purification, decolorization and removal of toxic heavy metal ions [1 - 3]. Most of the other methods have some shortcomings such as a high cost of operation, high investments required and disposal of the metal sludge. Therefore, attempts are made to develop cheap materials for pollutants removal from aquatic environments [4 - 6]. The new advancement referring to nanoparticles use has solved some of the problems in this regard [7]. Having an appropriate adsorption surface, they exhibit unique characteristics [8, 9]. The present investigation focuses on the use of the cost-effective material Deniella oliveri stem bark for the preparation of an activated carbon incorporated by synthesized goethite particles. The aim is to improve the performance of the materials.
EXPERIMENTAL
Material collection and preparation
The material used to produce an activated carbon referred to the stem bark of \textit{Deniella oliveri}. It was collected from the trees growing around the Chemical Engineering Laboratory building of the University of Ilorin, Nigeria. The tree bark was washed, sun and air dried for 6 days to a constant weight.

Synthesis of Goethite nanoparticles
The method of Schwertmann and Cornell [10] of the synthesis of goethite was used. It was slightly modified. The preparation was carried out under N\textsubscript{2} atmosphere. 100 ml of 1M Fe(NO\textsubscript{3})\textsubscript{3} solution (freshly prepared by dissolving unhydrolysed Fe(NO\textsubscript{3})\textsubscript{3}.9H\textsubscript{2}O in deionized water) were rapidly added to 180 ml 5M KOH solution. Red brown ferrihydrite was immediately precipitated. The suspension was diluted to 2 L with doubly distilled water and held in a closed polyethylene flask in an oven at 70\textdegree C for 60 h. The vessel was removed from the oven, centrifuged and the precipitate was subjected to dialysis, filtered by Millipore glass membrane vacuum filtration system and dried. A polyethylene container was used since the glassware contained dissolved Si.

The dialysis was carried out by decanting the prepared iron oxide precipitate in a dialysis tubing cellulosic membrane (Sigma co.) and placed in a 2 L beaker filled with deionized H\textsubscript{2}O (resistivity of 18.2 M\textOmega). The iron oxide suspension was then dialyzed using deionized water until the conductivity of the water was equal to that of the initial deionized H\textsubscript{2}O used. The nitrate and chloride ions present in the suspension were slowly removed by osmosis through a membrane. The water in the beaker was replaced several times until it became free of chloride or nitrate ions. The existence of Cl-ions in the water of the beaker was tested with AgNO\textsubscript{3}(0.1 M) solution. The resulting water of the beaker cake was isolated from the mother liquor by decanting, filtered by a millipore glass membrane vacuum filtration system and oven dried at 40\textdegree C.

Preparation of an activated carbon
The \textit{Deniella oliveri} tree bark was crushed and carbonized using a muffle furnace. It was weighed in a crucible and then introduced to the muffle furnace. The sample was carbonized at a temperature of 400\textdegree C for 3 h. The pyrolyzed sample was grounded to a granulated size and then activated [11]. The activation was carried out by using orthophosphoric acid (H\textsubscript{3}PO\textsubscript{4}) as an activating reagent. This was done by mixing the char sample with 75 \% concentrated orthophosphoric acid in a beaker using a H\textsubscript{3}PO\textsubscript{4}/char weight ratio of 1.0. The slurry formed was evaporated within 24 h at 60\textdegree C to give a dried mixture [12]. The purification of the sample was done by pouring it into a beaker containing 250 ml of 0.1 M H\textsubscript{2}Cl\textsubscript{3} and stirring for 1 h. It was then rinsed to pH 6 - 7. The resulting activated carbon material was kept in a tightly closed container for a further application [13, 14].

Preparation of a composite
The composite sample was prepared using the method of Kosmulski et al. [15] after a slight modification. A mixture of iron oxides and activated carbon powders of a ratio of 1:5 was dispensed in 0.1 M HNO\textsubscript{3} solution and subsequently vigorously stirred at 1800 rpm for 1h. Then it was aged for 24 h at 80\textdegree C. The precipitate was centrifuged and washed with milli Q water (resistivity of 18.2M\textOmega) to neutrality and dried in an oven.

Physico-chemical characterization of the adsorbents
\textbf{pH}
A mass/volume ratio of 1:10 was used. 1mg of the adsorbent was placed in 10 ml of deionized water and stirred with a glass rod. The suspension was left standing for 30 min and subsequently filtered. Then pH was determined [16].

\textbf{An iodine number of the activated carbon}
A sample of 0.5 g was placed in 20 ml of 5 wt. \% HCl and then boiled. After cooling to a room temperature 100 ml of 0.1 N iodine solutions were added. The content was shaken vigorously and filtered. 25 ml of the filtrate were titrated with 0.1 N sodium thiosulphate in presence of starch as an indicator. The color changed from pale yellow to colorless [17]. The iodine number was calculated using Eq. (1):

\begin{equation}
\text{Iodine No} = \frac{12.69 (B-A)}{W}
\end{equation}

where B was the volume of the blank sample, A was the volume adsorbed, while W was the weight of the sample used.

\textbf{Ash content of the activated carbon}
An empty dry crucible was weighed, and a sample
of 0.5 g was introduced. The crucible was placed in a furnace and was heated for 2 h at 500°C. It was cooled in a dessicator and weighed [18]. The amount of ash in % was estimated on the ground of Eq. 2:

\[
\% \text{ Ash} = \frac{W_3 - W_2}{W_2 - W_1} \times 100\%
\]  

(2)

where \( W_1 \) was the weight of the empty crucible, \( W_2 \) was the weight of the crucible and the sample prior to ashing, while \( W_3 \) was the weight of the crucible and the sample after the ashing.

**Moisture content of the activated carbon**

The weight of the dry empty crucible was taken, and 0.5 g of the sample were weighed. The crucible was placed in an oven at a temperature of 105°C until a constant weight was obtained. Then the content was cooled in a dessicator and reweighed. The procedure was repeated until a constant weight was obtained [19]. The moisture content was calculated on the ground of:

\[
\% \text{ moisture content} = \frac{W_3 - W_2}{W_2 - W_1} \times 100\%
\]  

(3)

where \( W_1 \) was the weight of dry crucible, \( W_2 \) was the weight of crucible and the sample prior to drying, while \( W_3 \) was the weight of the crucible and the remaining sample after the drying.

**A volatile component of the activated carbon**

A dry crucible was weighed, 1 g of sample were added, and the total weight was noted. The crucible was placed in a furnace at 100°C for 20 min. Then it was cooled and reweighed. At every 20 min, the furnace temperature was increased by 100°C and the sample was weighed. The procedure was repeated until a temperature of 500°C was reached [20]. The presence of a volatile component was estimated on the ground of:

\[
\% \text{ volatile} = \frac{W_0 - W_f}{W_0} \times 100
\]  

(4)

where \( W_0 \) was the initial weight of sample, while \( W_f \) was the weight of the activated carbon following the pyrolysis.

**A bulk density of the samples**

The samples bulk density was determined gravimetrically. An empty 10 ml measuring cylinder was weighed \( (W_c) \) and then filled with water to determine its exact volume \( (V) \). The measuring cylinder was emptied, dried and then filled with the sample. This was followed by tapping to ensure compactness. It was reweighed \( (W_s) \). The bulk density was obtained by the ratio of the masses difference to the volume of the cylinder [18]. The bulk density was calculated as:

\[
\text{Bulk Density} = \frac{W_s - W_c}{V}
\]  

(5)

**A point of zero charge (a potentiometric - mass titration method)**

Two solutions were prepared by mixing 30 ml of 0.1 M KNO\(_3\) and 10 ml of 0.01 M HNO\(_3\) in two beakers and the pH of the two solutions was measured. The first solution was tagged blank, while the other one containing 0.5 g of a sample was called a sample solution. The two solutions were titrated against 0.01 M NaOH and the resulting pH was recorded at every 0.5 ml addition of the titrant till the equivalence point was reached. The results of both titrations were plotted on a single graph. The point of intersection marked the point of a zero charge [21].

**Spectroscopic characterization**

The elemental composition of the sample was determined by X-ray Fluorescence spectroscopy (XRF). X-ray Diffraction Spectroscopy (XRD) was carried out to reveal the phases present. The functional groups present in each sample were determined by Fourier Transform Infra-red Spectroscopy (FTIR). The surface morphology of each adsorbent was revealed by Scanning Electron Spectroscopy (SEM). Transmission Electron Microscopy (TEM) was used to determine the particle sizes and the morphology of the samples.

**RESULTS AND DISCUSSION**

The physicochemical properties of the adsorbent are an essential feature. They are indicative of its potential to remove pollutants (organic or inorganic) from the environment. The results obtained are summarized in Table 1.

The color of goethite is yellowish brown which is in line with the color of different iron oxides reported [22]. Carbon is black in nature, while the composite of both is greenish-black in appearance.
The yield is a term used mostly in industries/industrial processes to refer to the quantity of a product formed per quantity of starting materials (reactants) and is usually expressed in percentage (%). Table 1 shows that the yields of the adsorbents refer to 76.65%, 54.6% and 94.5% for G, AC and G-AC, respectively. This gives the line of G-AC > G > AC.

The pH values of the adsorbents solutions in deionized water are equal to 8.9, 7.2 and 5.5 for G, AC and G-AC, correspondingly. The pH value (8.9) of G shows that it is basic. This alkalinity nature can be associated with the dissociation of OH⁻ present in the compound because of the hydrolysis. The pH value found for G-AC is within the pH ranges (7-9) reported [16, 24]. The pH value (7.92) of the composite shows that it does not change much through impregnation by iron hydroxide. This is in line with ref. [25].

The bulk density (0.3638 g/ml) of G-AC is found between those of G and AC. This is expected since it refers to a composite of the two adsorbents. The bulk density values found in this study show that the samples might be of a great potential for wastewater treatment purposes as they are higher than 0.25 g/ml, which is the minimum requirement for adsorbents [23].

The pH

pzc values of G, AC and G-AC amount to 8.8, 7.6 and 7.92, respectively (Table 1). That of goethite is within the pH

pzc ranges (7 - 9) reported in the literature [16, 24]. The pH

pzc value (7.92) of the composite shows that it does not change much through impregnation by iron hydroxide. This is in line with ref. [25]. The volatile matter obtained for the AC adsorbent is equal to 44.3%, which is higher than the value (20.96 %) reported elsewhere [26].

The moisture content of the AC adsorbent (10.23%) is close to that (9.7 %) reported by Mane et al. [27], and higher than the value (4.5 %) reported by Salman et al. [28] and that (2.2 %) found by Elnasri et al. [24]. The latter values refer to agricultural materials used.

The percentage ash contents of AC is found equal to 26.83 %, which is lower than the value (29.24 %) reported by Aloko and Adebayo [29], but higher than those (10.5 %, 5.6 %, 5.9 %) reported by Salman et al. [28], Mane et al. [27] and Elnasri et al. [24], correspondingly. The latter values refer to agricultural materials used.

The iodine number of the AC adsorbent is found to be 152.06. This value is relatively lower when compared

Table 1. Physicochemical properties of G, AC and G-AC adsorbents.

<table>
<thead>
<tr>
<th>Physicochemical Parameters</th>
<th>Goethite (G)</th>
<th>Activated carbon (AC)</th>
<th>G-AC composite</th>
</tr>
</thead>
<tbody>
<tr>
<td>Appearance</td>
<td>Golden yellow</td>
<td>Black</td>
<td>Greenish-black</td>
</tr>
<tr>
<td>% Yield</td>
<td>76.65</td>
<td>54.6</td>
<td>94.5</td>
</tr>
<tr>
<td>Bulk Density (g/ml)</td>
<td>0.4408</td>
<td>0.3316</td>
<td>0.3638</td>
</tr>
<tr>
<td>pH</td>
<td>8.9</td>
<td>7.2</td>
<td>5.5</td>
</tr>
<tr>
<td>PZC</td>
<td>8.8</td>
<td>7.6</td>
<td>7.92</td>
</tr>
<tr>
<td>Surface area(m²/g)</td>
<td>130.098</td>
<td>ND</td>
<td>ND</td>
</tr>
<tr>
<td>Particle size (mm)</td>
<td>0.113</td>
<td>ND</td>
<td>ND</td>
</tr>
<tr>
<td>Volatile component</td>
<td>ND</td>
<td>44.3</td>
<td>ND</td>
</tr>
<tr>
<td>Moisture content</td>
<td>ND</td>
<td>10.23</td>
<td>ND</td>
</tr>
<tr>
<td>Ash content</td>
<td>ND</td>
<td>26.83</td>
<td>ND</td>
</tr>
<tr>
<td>Iodine Value</td>
<td>ND</td>
<td>152.06</td>
<td>ND</td>
</tr>
</tbody>
</table>

(ND – Not Determined)
with that reported in the literature [26], where all the adsorbents studied have a higher iodine number and a higher degree of micropores development treated as an indication of a better performance. It is evident that the adsorbents considered possess most of the desirable characteristics.

The surface area and the micropore volume are key factors in determining whether the material is suitable for metal ions removal from aqueous solutions. In addition, the nature of the adsorbent-adsorbate interaction must also be considered. It is recognized that the pore volume contributes to the accommodation of the metal ion in the adsorbent [30]. The surface area of goethite found in this study is equal to 130.098 m$^2$/g. The value obtained is within the specific surface area range of 8 m$^2$/g - 200 m$^2$/g stated by Cornell and Schwertmann [31]. The micropore volume is 6.3847x 10$^{-3}$ cm$^3$/g, while the micropore area amounts to 26.3089 m$^2$/g.

Several instrumental techniques are utilized in this study to elucidate the surface morphology, the pore and the particle size, the chemical structure and the chemical composition of the three adsorbents. The results obtained are duly discussed below.

**X-ray Diffraction (XRD) Analyses**

The X-ray diffraction patterns of G, AC and G-AC are shown in Fig. 1 (a-c) respectively. The three adsorbents show characteristic peaks at an angle of 2θ. They are found at 21.40°, 34.50°, 35.80°, 40.70°, 41.80°, 54.60°, and 59.10° for goethite, which is in good agreement with refs. [32 - 34]. The activated carbon spectra show low appearance of crystallites on the surface. The spectrum of the composite is almost identical with that of the goethite particle. There is a little difference because of the slight shift of the peaks. Those of G-AC are recorded at 21.60°, 34.50°, 37.10°, 42.80°, 54.50° and 59.40°. The X-ray diffraction analysis provides an information on the crystallographic nature of the adsorbents. The diffractograms obtained for G show that, it has a higher degree of crystallinity than that of the composite G-AC. This is also in agreement with the literature [35].

**X-ray Fluorescence (XRF) Analyses**

The oxides present in goethite (G), the activated carbon (AC) and their composite (G-AC) are listed in Tables 2(a), 2(b) and 2(c), respectively. The X-ray fluorescence analyses show that 96.97 % and 73.18 % of iron oxide are present in the goethite and the goethite-
activated carbon composite particles, respectively. This indicates that the iron oxide is of high purity.

**Fourier Transmittance Infrared Spectroscopy Analyses (FTIR)**

This instrumental technique serves as an important tool in the investigation of the functional groups present. The latter are of importance in respect to the interaction of the wastewater heavy metals and the adsorbents used for the treatment.

The FTIR spectra obtained for goethite show a broad absorption band at 3132.40 cm$^{-1}$ which is due to O-H stretching frequency. The H$_2$O intramolecular bending frequency determines the adsorption band at 1647.21 cm$^{-1}$.

![FTIR spectra of Goethite (a), AC (b) and the composite studied (c).](image)

![SEM micrographs of Goethite (G) at magnifications of 4.86 kX and 14.10kX.](image)
The stretching frequency of Fe-OH is found at 863.04 cm\(^{-1}\). The peak at 769.60 cm\(^{-1}\) is due to the presence of O-H deformation. The adsorption band at 453.27 cm\(^{-1}\) and 638.44 cm\(^{-1}\) indicate the stretching frequency of Fe-O due to H\(_2\)O.

The spectrum of the AC adsorbent shows a broad absorption band at 3444.87 cm\(^{-1}\) due to the surface O-H stretching frequency. The C-H stretching vibration at 2926.01 cm\(^{-1}\) indicates the presence of an alkane (SP\(^3\)) functional group. The peaks at 2366.66 cm\(^{-1}\) and 2339.65 cm\(^{-1}\) correspond to C≡C of the alkyne functional group. The C=C stretching vibration at 1620.21 cm\(^{-1}\) is indicative of alkenes and aromatic functional groups. The peaks at 1317.38 cm\(^{-1}\) and 1128.36 cm\(^{-1}\) correspond to C-H rock and C-H bend of the aliphatic functional group.

**Scanning Electron Microscopy Analyses (SEM)**

This analytical technique is used to investigate the visual confirmation of the surface morphology of the adsorbents. The SEM images of all adsorbents studied are presented in Fig. 3. The synthesized goethite particle is found to be needle-like and irregular in shape. The micrographs show that the diameter of the rod is within the range of 97.89 nm - 182.77 nm. The micrograph of AC shows a network of shallow pores. The composite micrograph shows the needle-like goethite particle embedded on the activated carbon surface.
Transmission Electron Microscopy Analyses (TEM)

The TEM micrographs of goethite (G) shown in Fig. 4(a) reveal rod-shaped particles of varying diameters. They have a rough surface which would enhance the adsorption properties. The TEM micrographs of the activated carbon (AC) shown in Fig. 4(b) reveal that it has a spherical surface covered by few tiny micropores. The TEM micrographs of the composite adsorbent pre-

<table>
<thead>
<tr>
<th>Adsorbents</th>
<th>C</th>
<th>O</th>
<th>Fe</th>
<th>Ca</th>
<th>Cu</th>
<th>K</th>
<th>Total</th>
</tr>
</thead>
<tbody>
<tr>
<td>G</td>
<td>29.44</td>
<td>42.71</td>
<td>27.23</td>
<td>0.28</td>
<td>0.28</td>
<td>0.06</td>
<td>100</td>
</tr>
<tr>
<td>AC</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>GAC</td>
<td>27.46</td>
<td>26.88</td>
<td>45.45</td>
<td>0.21</td>
<td>-</td>
<td>-</td>
<td>100</td>
</tr>
</tbody>
</table>
sented in Fig. 4(c) indicate that the needle-like goethite particles are found on the surface of AC providing their blunt rod shape.

**Energy Dispersive X-ray Spectroscopy (EDS) Analyses**

Table 3 shows the EDX results referring to the adsorbents G, AC and G-AC. It is seen that Fe, O and C are the major elements present in G and G-AC, while Ca, Cu, and K are the minor elements. The EDX spectra show also that the higher peaks correspond to a greater quantity of the corresponding element in the sample. It is evident that iron and oxygen are dominant in the goethite and composite samples. The peaks are more intense in the goethite due to its high purity. It can be deduced that the composite has a lower crystallinity than that of goethite because of the presence of an activated carbon.

**CONCLUSIONS**

The results obtained in this study lead to the following conclusions:

All adsorbents investigated have a high potential of removing any environmental pollutants.

The XRF, FTIR, SEM, TEM, EDX and XRD analyses carried out show that all adsorbents studied are very good. It can be deduced that the composite has a lower crystallinity than that of goethite because of the presence of an activated carbon.

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