PREPARATION AND CHARACTERIZATION OF A CHEMICALLY ACTIVATED CARBON DERIVED FROM THE NATURAL PLANT GMC

T. Chandrasekaran, A. Arunkumar, K. Riaz Ahamed*

PG and Research Department of Chemistry, Jamal Mohamed College (Autonomous), Tiruchirappalli-620020, Tamil Nadu, India.

ABSTRACT
The present works show a preparation of novel adsorbent. The novel adsorbent was prepared from carbon based on a native lignocellulosic precursor. The precursor chosen for preparation of novel adsorbent was natural and easily available plant (Glycosmis Mauritania) from agricultural land. The activation process was carried out by two different process physical activation and chemical activation. Chemical activation was carried out by dipping the plant materials in different activating chemicals like phosphoric acid, sulphuric acid, potassium hydroxide and zinc chloride at certain concentration for 24 hours. The carbonization process of the precursor was carried out at 400°C and the activation taken at 600°C using muffle furnace for both physical and chemical activation. The prepared novel adsorbent was further made to characterize its physico-chemical parameters to determine the nature of the adsorbent. The surface group and surface morphology of the adsorbent can be identified using HRSEM and FTIR spectroscopy. Surface area of the activated carbon can be calculated by using nitrogen adsorption.

KEYWORDS: Adsorbent, SEM, FTIR.

INTRODUCTION
Adsorbent plays a vital role in many applications like the purification of water and waste water treatment. Many technical process have been applied for purification of water like reverse osmosis\textsuperscript{[1]} adsorption, membrane filtration, solvent extraction\textsuperscript{[2]} ion-exchange, etc., Several materials has been widely used as an adsorbent like the removal of impurities like...
heavy metal ions from contaminated aqueous solutions such as Bentonite\cite{3}, lignin\cite{4}, kerolite\cite{5}, zeolite, calcite, kaolinite, a-alumina\cite{6}, Al-pillared clay, Fe–Al pillared clays\cite{7}, etc.

Among these activated carbon plays a most important and convenient role in purification techniques. The main application of activated carbon used as an excellent adsorbent include the adsorptive removal of color, odor, taste, and other undesirable impurities from drinking waters; in the treatment of industrial waste water, air purification. In chemical industries it is used to remove many chemicals in food and pharmaceutical products and in a variety of other gas-phase applications. Nearly 85\% of the total activated carbon is consumed for liquid phase applications where, both granular and powdered activated carbons can be used\cite{8}. For gas-phase applications, granular activated carbon is usually the choice. Normally activated carbon is a black carbonaceous material with highly porous, surface area and amorphous in nature. It founds most useful in removal of toxic biodegradable and non-biodegradable substances from waste waters.

Sometimes the word “active” has been replaced for activated. The adsorption capacity of an adsorbent depends upon the pore structure and chemical nature of the carbon surface in connection with preparation conditions. Approximately 4000 square meters of surface area present in one kilogram of activated carbon. Based on the pore of the activated carbon it has been classified into three types namely, macropore, mesopore and micropore. (Micropores are carbon particles having pore width less than 2 nm, Mesopores carbon particles having porosity between 2 nm to 50 nm, Macropores are classified that particles having pore width greater than 50 nm).

Activated carbon can be prepared by physical activation and chemical activation. A physical activation method is a single step process in which the raw materials were heated at above 600\(^{\circ}\)C. The chemical activation method is a two step process in which carbonization process involved at 400\(^{\circ}\)C and activation process occurred at above 450\(^{\circ}\)C. By using a chemical activation process it reduces activation temperature. More porous activated carbon can be prepared by chemical activation process.

In the process of pyrolysis the dehydration and carbonization of the raw material were carried out followed by activation in the absence of air. During carbonization, volatile matters present in the raw materials were removed and the residue remained as carbon and hence it creates a large surface in carbon material. Based on the nature, size and structure of an
activated carbon it has been used as an adsorbent, nano materials, catalyst, etc. Activated carbon plays an important role in surface chemistry mainly in the adsorption process. Adsorption process is a surface phenomenon in which molecules bind in surface of an adsorbent.

Researchers interested in the preparation of environmental free, easily and cheaply available source material as an adsorbent. Attempt also made to prepare activated carbons prepared from biodegradable material were considered to be the main source for the activated carbon. This technique possesses some advantages of converting waste materials into renewable materials. Many available sources have been used for preparation of carbon like vegetable wastes, waste tires, pongam seed coat (pongamia pinnata L.), Albizia lebbeck\[9\], coconut shell carbon\[9\] Gelam wood bark, almond shell\[10\] cherry stones carbon, Bagasse fly ash\[11\] and rice husk \[12\] Chitosan\[13\] Neem husk, Carbon black, polymer binder, etc.

In the present work to prepare novel adsorbent from the naturally occurring plant Glycosmis mauritiana and to characterize the general physico-chemical behavior of the prepared activated carbon. This plant commonly known as Ash-sheora, Orange berry, Rum Berry and Gin Berry. The plant Glycosmis mauritiana is native of India, Malaysia, China, Sri Lanka, Myanmar, Thailand, Indonesia and Malaya. Glycosmis mauritiana is a small tree or shrub, widely used in Hindu medicine\[14-16\].

The plant belongs to the family Rutaceae \[17\] and it possess a variety of medicinal properties. The leaves, flowers used as an antibacterial, anti-inflammatory and antioxidant. But the stem of the plant does not possess much important use. Hence the stem of this plant was chosen for the present work.

The objectives of the work to prepare carbon from the precursor material as an adsorbent, which is prepared from the stem of the plant Glycosmis mauritiana by physical and chemical activation. It is also planned to characterize the general properties like ash content, bulk density, matter soluble in acid, matter soluble in water, iron content, pH, iodine number and to characterize the BET surface area, pore size distribution (PSD) of activated carbon. The surface functional group can be identified using FTIR spectroscopy, morphology of the carbon can be identified using SEM analysis.
MATERIALS AND METHODS

Reagents and chemical activating agents
All the chemicals used in the study were from Merck (India) Ltd. analytical grade. The chemical used for activating process were potassium hydroxide, sulphuric acid, zinc chloride and phosphoric acid.

Instrumentation
FTIR was conducted for prepared carbon. Pellets were made by the mixture of carbon and KBr were pressed at high pressure and the pellet was scanned in transition mode using FT-IR spectrometer (FT-IR - Shimadzu IR Affinity 1) through a wavelength range from 4000 to 400 cm⁻¹. Surface and pore size distribution properties of the prepared activated was characterized by nitrogen adsorption at 77K using a Micrometrics ASAP 2020 Surface Analyzer.

Preparation of activated carbon
The activated carbon was prepared from Glycosmis mauritiana, collected from local agricultural lands in Tamil nadu. The stem of the plant was collected and dried in sunlight for one month and cut into pieces. The impurities attached in materials were removed manually, washed with distilled water and dried in oven at 110°C for 5 hours. The dried plant material was carbonized at 400°C and activation process was carried. Two types of activation process were carried for the preparation of activated carbon. A physical activation was carried out materials were heated at 600°C in a muffle furnace in the absence of air and the sample was cooled, sieved, stored in air tight container and named as GMC.

Chemically activated carbon can be prepared by dipping the material into different activating chemicals. The chemical used for activating process were phosphoric acid(50%), sulphuric acid(50%), potassium hydroxide(50%) and zinc chloride(50%). The chemical soaked materials were kept for 24 hours, at the end of the 24 hours the soaked materials were removed and dried in oven at 110°C for 4 hours. The dried samples were made to activate in a muffle furnace at 600°C for 3 hours in absence of air.

The activated samples were cooled and washed with distilled water until the pH of washed water become 7. The activated samples were crushed and sieved to obtain different size 0-53 μ, 53-106 μ, 106-300 μ, 300-500μ. The sieved samples were stored in air tight container and named as GMC-1, GMC-2, GMC-3 and GMC-3 used for further characteristics work.
Experimental techniques
The prepared activated carbon was subjected to physico-chemical characterization like moisture content, ash content, bulk density, matter soluble in water, matter soluble in acid, pH, iron content, loss on ignition, Iodine number. The experimental methods were followed by J.W. Hassler’s[18] method. The functional group present in the surface of activated carbon can be predicted by using FTIR spectroscopy, the surface morphology of the prepared carbon can be identified by using HRSEM. The surface and pore properties of the activated carbon can be identified by using N₂ adsorption.

Analysis of surface and pore properties of prepared activated carbon
Total Surface area
Total surface area of activated carbon can be determined using BET (Brunauer, Emmett and Teller) method using the nitrogen adsorption isotherm at 77K. The BET equation applicable to monolayer adsorption, can also provide a good insight into the surface area of an adsorbent.

RESULTS AND DISCUSSION
Table.1 – Physico-chemical parameters for prepared activated carbon prepared by physical activation (GMC) and chemical activation (GMC-1, GMC-2, GMC-3, GMC-3)

<table>
<thead>
<tr>
<th>S.No</th>
<th>PARAMETERS</th>
<th>Units</th>
<th>GMC</th>
<th>GMC-1</th>
<th>GMC-2</th>
<th>GMC-3</th>
<th>GMC-4</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Ash content</td>
<td>%</td>
<td>4.05</td>
<td>23.48</td>
<td>6.16</td>
<td>6.53</td>
<td>13.65</td>
</tr>
<tr>
<td>2</td>
<td>Bulk density</td>
<td>g/cc</td>
<td>0.62</td>
<td>0.53</td>
<td>0.53</td>
<td>0.59</td>
<td>0.56</td>
</tr>
<tr>
<td>3</td>
<td>Iron content</td>
<td>%</td>
<td>0.36</td>
<td>-</td>
<td>0.04</td>
<td>0.02</td>
<td>0.02</td>
</tr>
<tr>
<td>4</td>
<td>Iodine number</td>
<td></td>
<td>293</td>
<td>276</td>
<td>419</td>
<td>366</td>
<td>406</td>
</tr>
<tr>
<td>5</td>
<td>Loss on ignition</td>
<td>%</td>
<td>91.45</td>
<td>93.17</td>
<td>91.46</td>
<td>93.02</td>
<td>92.47</td>
</tr>
<tr>
<td>6</td>
<td>Matter soluble in acid</td>
<td>%</td>
<td>2.59</td>
<td>1.68</td>
<td>0.47</td>
<td>4.9</td>
<td>3.11</td>
</tr>
<tr>
<td>7</td>
<td>Matter soluble in water</td>
<td>%</td>
<td>0.93</td>
<td>0.57</td>
<td>0.36</td>
<td>3.11</td>
<td>0.72</td>
</tr>
<tr>
<td>8</td>
<td>Moisture content</td>
<td>%</td>
<td>0.44</td>
<td>0.42</td>
<td>0.40</td>
<td>1.13</td>
<td>0.86</td>
</tr>
<tr>
<td>9</td>
<td>pH</td>
<td></td>
<td>6.9</td>
<td>5.8</td>
<td>6.8</td>
<td>7.2</td>
<td>5.7</td>
</tr>
</tbody>
</table>

The physico-chemical parameters for activated carbon prepared by physical and chemically modified carbons were listed in table-1. The results of this parameter the investigator finds that the ash content of the carbon prepared by sulphuric acid modified contain very small compared to the other carbons. The moisture content does not affect the adsorption capacity for carbon. It is necessary the use of additional weight of an adsorbent of the carbon. The moisture content of the carbon GMC-2 possesses relatively low compared to that of other carbon.
Ash content shows the percentage of inorganic compound present in prepared raw activated carbon. The high level of matter soluble in acid was obtained in GMC-4 this is due to the presence of inorganic matters present in the compound. Iodine number is a measure of the iodine adsorbed in the pores and it is used to calculate the pore volume available in the prepared activated carbon. Experiment results show that carbon prepared with the sulphuric acid activation show that treatment with 50% acid concentration at 600°C possess good properties for iodine number. The results of BET surface area have revealed the porosity and surface area of the carbon GMC-2.

**Table 2 – Analysis of surface and pore properties of prepared activated carbon**

<table>
<thead>
<tr>
<th>SURFACE AREA</th>
<th>PORE VOLUME</th>
<th>PORE SIZE</th>
<th>NANO PARTICLE SIZE</th>
</tr>
</thead>
<tbody>
<tr>
<td>BET surface area</td>
<td>Total pore volume (cm²/g)</td>
<td>t-plot micropore area</td>
<td>t-plot external surface area</td>
</tr>
<tr>
<td>262.941 3 m²/g</td>
<td>0.1567</td>
<td>200.9348 m³/g</td>
<td>62.006 5 m³/g</td>
</tr>
</tbody>
</table>

The high resolution scanning electron microscope (HRSEM) analysis has been carried out on the dried carbon adsorbents to obtain textural and surface information of the adsorbent before adsorption and shown in fig-2.

The active functional group present in the surface of the carbon can be identified using FTIR spectroscopy. The active sites are the responsibility for attracting metal ion from the water. The FTIR spectra were collected in the range from 4000 to 400 cm⁻¹ for the prepared different type of activated carbon prepared by different chemicals from *Glycosmis mauritiana* stem as precursor. In physical activation (GMC) the absorption peaks observed in the range of 3705.26 cm⁻¹ and 3630.03 cm⁻¹ indicates the presence of OH groups in alcohol or phenol groups. The peaks observed in 2822.16 and 2856.58 cm⁻¹ show the appearance of carboxylic acid group. The peaks observed in 1583.56 cm⁻¹ shows the presence of N-H group in amine.O-H group carboxylic acid shows in the region at 1431.18 cm⁻¹ as shown in fig-3.
In chemical activation, The FTIR spectrum of carbon prepared by chemical activation (GMC-1, GMC-2, GMC-3, GMC-4) shows a large number of active functional groups. Fig-4 shows the IR spectra of GMC-1 carbon. The absorption peaks at 3442.94 cm\(^{-1}\) is attributed to the absorption of O-H stretching vibration. The band at 2924.09 cm\(^{-1}\) is connected with C-H stretching vibration. The bands around 1743.65 cm\(^{-1}\) C=O group in configurations such as lactones, quinone and COOH groups. The appears at 1379.10 cm\(^{-1}\) is associated with C-H bending in alkane or alkyl groups and peak at 677.01 cm\(^{-1}\) shows the presence of NO\(_2\) in nitro groups.

In compound GMC-2 the band at 3597.24 cm\(^{-1}\) indicates the appearance of stretching O-H group. The band in the region between 1400-1600 cm\(^{-1}\) shows the presence C=O, O-H and aromatic ring. The peak in the range of 1743.65 indicates the presence of acetyl and ester group present in hemicelluloses. The band at 2881.65 -CH\(_3\) and CH\(_2\) attributed to the aliphatic compound and the band at 1573.91 cm\(^{-1}\) implies NH\(_2\) group in primary alkyl amide as shown in fig-5.

Fig-6 show IR spectra for compound GMC-3, the peaks at around 3444.87 cm\(^{-1}\) correspond to the O-H stretching vibration. The appearance of the bands at 2922.16 and 2852.72 cm\(^{-1}\) can be attributed to the CH\(_3\) and CH\(_2\) in aliphatic compounds. The band located at 1712.79 cm\(^{-1}\) is assigned to the stretching vibration of C=O group in carboxylic acid. The absorption at around 1651.07 cm\(^{-1}\) is assigned to conjugated carbonyl bond in lignin. The OH group possibly attributed carboxylic acid caused the absorption at around 1435.04 cm\(^{-1}\). The band occurred at 1161.15 cm\(^{-1}\), which corresponds to the C-O groups. The band appeared in 675.09 which corresponds to the C-OH group present in alcohol.

Fig-7 shows the IR spectra for GMC-4, the IR band in the region 3444.87 cm\(^{-1}\) represents the O-H stretching vibration. The absorption band at 2362.80 cm\(^{-1}\) indicates the position of asymmetric and symmetric stretching vibration of the methylene group in aliphatic and cyclic hydrocarbon. The (C=O) of ketone occurs in the region of 1701.22 cm\(^{-1}\). The band at 1745.58 cm\(^{-1}\) shows the C=O in an ester group of hemicelluloses. The band at 1653 cm\(^{-1}\) represents C=O and NH\(_2\) in primary amides. The peak near 1496.76 cm\(^{-1}\) corresponds to C-C stretching in aromatic rings. The IR peaks at 1427.32 cm\(^{-1}\) are due to O-H in carboxylic acid. The Ar-OH in phenol band appeared in the region at 719.45 cm\(^{-1}\). The C-OH in alcohol was identified at 615.94 cm\(^{-1}\).
Fig. 1 – BET surface area plot for prepared activated carbon

Fig. 2 – SEM micrographs for prepared activated carbon

Fig. 3 – IR spectrum of GMC
Fig. 4 – IR spectrum of GMC-1

Fig. 5 – IR spectrum of GMC-2

Fig. 6 – IR spectrum of GMC-3
CONCLUSION
The investigator prepared various chemically modified activated carbons. The FTIR spectrum shows the presence of active functional groups is considered to be connected to the mechanism in the adsorption techniques. From these investigations it has been proven that carbon prepared by sulphuric acid (GMC-2) modified carbon possess more surface area while compared to other carbon. Therefore it can be chosen as adsorbent for removing the metal ion and used in purification techniques. Since trees used in this investigation, are free, abundantly and locally available and the preparation of adsorbents from these trees are cheap and economically viable for wastewater treatment. Hence they are recommended to be used as low cost, efficient adsorbents.

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REFERENCES