Omar M. Ramadhan , Ammar A. Hamdon Dept. of Chemistry, College of Education, University of Mosul Kaanan R. Ahmed Dept. of Chemistry, College of Education, University of Dohuk

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#### Abstract

In this research work we aimed to graft lignin which a naturally oxygenated compound with different ratio of oxidized asphalt (contains synthetic oxygenated groups). Grafting aimed to allow the two type of the functional groups to react in the presence of small amount of base. The process conducted at 300 °C in the absence of air. Carbonization of the mixture was carried out in the presence of twice the amount of sodium hydroxide and at a temperature of 450-500 °C till no more gases evolved. The product carbon was activated by refluxing with 30% HCl. Evaluation of the activated carbon was conducted by adsorption of iodine and methylene blue. Other variables such as density, humidity, ash and surface area were also determined.

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#### Introduction

Activated carbon is defined as a group of materials with highly developed internal surface area and porosity due to the crystal defect in the structure and have a large capacity for adsorbing chemicals, gases and liquids. Activated carbons are extremely versatile adsorbents of great industrial significance in the removal of gas and purification of chemicals<sup>(1,2)</sup>.

Activated carbons are widely used as adsorbents in gas and liquidphase separation processes, removal of impurities from major products and purification of water. The activated carbon employed in water and waste water treatment has a relatively high surface area and a well developed porosity<sup>(3)</sup>.

Activated carbon can be prepared from a large number of sources using

many carbonization and activation methods. The Merck index divides activated carbons into four basic forms; Animal charcoal is obtained by charring bones, meat, blood, etc.; Gas black or furnace black is obtained by the incomplete combustion of natural gas; Lamp black is obtained by the burning various fats, oils, resins, etc. and activated charcoal is prepared from wood and wood waste<sup>(4)</sup>.

Among the other raw materials used as precursors to make activated carbons are sawdust, peat, lignite, coal, residues<sup>(5)</sup>. petroleum cellulose residues and coke, spent ion exchange resins such as, styrene-divinyl benzene polymers<sup>(6)</sup>, phenol formaldehyde resins<sup>(7)</sup>, old automobile tires<sup>(8)</sup> and sewage sludge<sup>(9)</sup>. Various binding agents may be added to improve the structure<sup>(10)</sup>. Commercial sources appear to be made from a variety of activating agents precursors, and binders<sup>(11)</sup>.

Carbon rich materials were pyrolysed or carbonized in an inert atmosphere in order to remove volatile organic constituents and hydrogen in the form of water,  $H_2S$ ,  $NH_3$ , ... etc., leaving behind a highly porous carboneacous residue. Activation of the carbonaceous materials usually carried out thermally under inert atmosphere or oxidizing atmosphere. On the other hand, chemical method of activation is also used. Evaluation of activated carbon usually carried out by their ability to adsorb iodine from aqueous phase, methylene blue. benzene vapour, carbon tetrachloride and toxic gas from gas stream $^{(12)}$ .

The oxygenated functional groups on the surface of activated carbon with their complex character has been conceived in different ways by many authors in the literature. The older literature has often emphasized the physical properties of the carbon interphase<sup>(13)</sup>. The chemical surface

feature also contribute to the selectivity of adsorption. Some authors have noted that the heterogenity of the carbon surface is a great relation to the adsorption properties<sup>(14)</sup>.

Activated carbon or activated charcoal are terms used for porous manufactured by two step method carbonization and oxidation. The structure consists of a distorted threedimensional array of aromatic sheets and strips of primary hexagonal graphic crystallines<sup>(15)</sup>. The structure creates angular pores between the sheets of molecular dimensions that give rise to many of the useful absorption properties of activated carbon<sup>(16)</sup>.

Looking at literature we find many research works as given below; Yamaguchi and Sato<sup>(17)</sup> prepared activated carbon using NaOH with lignin. The activation of the product was carried out thermally under  $N_2$ atmosphere at 600-900 °C. Hiavaly and Kavan<sup>(18)</sup> prepared activated carbon using carbon source and metallic powder of Na, Li and K by employing the catalyst as colloidal materials in toluene or normal hydrocarbon solvent. activity of metal ion The for carbonization is K > Na > Li. Measurements indicate that the carbon obtained in the study have a good adsorption property and large surface area. Carbonization of brown coal using hydroxide of Na and K at 500-700 °C was carried out by Kobayashi et al.<sup>(19)</sup>. The measurement of the characteristic of the activated carbon prepared such as surface area which is found to be 1000  $m^2/gm$ . Ramadhan and Rigib<sup>(20)</sup> prepared activated carbon using asphaltic materials polymerized by addition of Na<sub>2</sub>S and in the presences of Lewis acids [CoCl<sub>2</sub>, CrCl<sub>3</sub>, AlCl<sub>3</sub> and FeCl<sub>3</sub>]. The results indicate that such type of carbon has high ash content and moderate activity internally and externally.

## Experimental

### 1. Purification of Asphalt:

The asphaltic materials obtained from northern Iraqi refinery in Beji were purified by floating in boiling water for two hours with stirring to remove any sand and foreign materials contaminants. The bitumen was dried in an oven at 100 °C for 24 hours.

# 2. Treatment of Asphalt with Liquid Nitrogen:

1 Kg of the asphalt subdivided into small pieces was immersed in Dewar flask containing liquid nitrogen. The solidified asphalt was crushed in a mortar to small pieces and kept in refrigerator for use.

### 3. Oxidation of Asphalt:

500 gm of the asphalt was placed in a beaker immersed in a sand bath at a temperature of 350-400 °C. Air with constant flow was allowed to bubble into the asphalt till highly condensed and oxidized asphalt obtained. The oxidized asphalt was meshed through suitable sieve to constant particles.

### 4. Grafting of Lignin with Asphalt:

10 gm of pure lignin was mixed with different ratio of oxidized asphalt. The process was conducted by adding slight amount of NaOH (Ca. 0.25%) to the mixture and heating gradually with vigorous stirring at 300 °C. The sample was kept for additional two hours at the same temperature, cooled to room temperature and used in the preparation of activated carbon.

### 5. Preparation of Activated Carbon:

The grafted lignin and asphalt was mixed with twice the weight of NaOH and 10 ml of petroleum ether was added to the mixture. The mixture was heated gradually to 450-500 °C with continuous stirring. The mixture was allowed to stand at 450-500 °C for additional hour, 100 ml of distilled water was added to the carbonized product, filtered and washed thoroughly with distilled water. The product was dried at 120 °C and allowed to cool to room temperature. The sample was used in the next step.

# 6. **Purification of the Carbon Produced**:

The carbon produced was washed thoroughly with distilled water and heated with slightly acidified distilled water for 2 hours. The process was repeated till the (pH = 7.0-7.2).

## 7. Activation of the Carbon Product:

Dried carbon from step (6) was mixed with (30%) HCl and refluxed for 3 hours. The mixture was filtered and washed with distilled water, till the (pH = 7.0-7.2). The activated carbon was placed in an oven at 120 °C for 24 hours and kept in a closed contained for evaluation.

# 8. **Physical Evaluation of the Activated Carbon**:

### A. Measurement of the Density:

The density of the prepared activated carbon was determined by weighting  $(10 \text{ cm}^3)$  of carbon sample using graduated cylinder<sup>(21)</sup>.

### B. Determination of the Ash Content:

The ash content was measured by heating one gram of the prepared activated carbon in a porcelain crucible using an electrical furnace for five hours at a temperature of 1000-1100 °C. The remained residue was considered as the ash content<sup>(22)</sup>.

### C. Measurement of the Humidity:

One gram of air dried activated carbon was heated in an oven at 150 °C for 3 hours. The difference in weight before and after heating was calculated and considered as the amount of humidity in the sample<sup>(23)</sup>.

# D. Determination of Internal Porosity by Iodine Adsorption:

The iodine number (In), which is the amount (in milligrams) of iodine adsorbed from its aqueous solution by one gram of activated carbon, was determined for each sample using the following equation<sup>(24)</sup>:

$$In = \frac{x}{m}.D$$

where:

m = the weight of the activated carbon in gram

 $x = A - [2.2B \times m]$  of sodium thiosulfate solution used]  $A = N1 \times 12693$  N1 =

normality of iodine solution

 $B = N2 \times 126.93$  N2 =normality of sodium thiosulfate solution

D = correction factor

E. Determination of the External *Porosity by Methylene Blue*:

An exactly weight (0.1 gm) of the prepared activated carbon sample was added to an aqueous solution of 20 ppm methylene blue pigment in a conical flask. The solution was shaked by electrical shaker for 24 hours, at room temperature till adsorption of methylene blue from its aqueous solution was completed and a state of equilibrium was reached. The absorbance of the solution was determined using UV-Visible Spectrophotometer at  $\lambda_{max}$  665 nm. The procedure was carried out for the different types of the prepared samples for comparison purposes. The final concentration of methylene blue value for each activated carbon sample was calculated as the number of milligrams of methylene blue adsorbed by one gram of carbon<sup>(25)</sup>.

## **Results and Discussion**

Activated carbon has an extraordinarily large surface area and pore volume that gives it a unique adsorption capacity<sup>(10)</sup>. The surface of activated carbon with various functional groups has been produced by various methods employed by many authors in the literature<sup>(13)</sup>.

In our study we aimed to graft lignin (ICI grade) with different percentages of asphalt. The amount of asphalt varied from [2:10 to 10:10 (asphalt:lignin)]. Grafting was conducted by mixing the lignin with asphalt at about 300 °C in the presence limited amount of sodium of hydroxide. The heating continued till slight carbonization was indicated by evolution of gases. Petroleum ether was added to help in the formation of pores as indicated by the National Organic Standard Board<sup>(2)</sup>. The results of investigation are given in the Table (1).

Looking at the results indicate that grafting the lignin with different amount of synthetic oxidized asphalt which contains some oxygenated functional groups in the presence of carbonizing agent, results in the formation of small pores that leads to iodine adsorption. The iodine number which is the term employed to indicate the internal pores or small pores. The results indicated that if we carbonized lignin and asphalt alone, the iodine number is (992 and 766 mg/gm) respectively, while activated carbon obtained from sample (1) indicate that a certain chemical reactions took place between the lignin and oxidized asphalt, which leads to formation of small pores. This small pores are mainly responsible for the adsorption of iodine from its aqueous solution (1129 mg/gm).

This result may through some light on the importance of gradual addition of the oxidized asphalt to lignin. When we move to next sample [sample (2)], the results of iodine number (908 mg/gm) compared to pure lignin (992 mg/gm) and pure asphalt (766 mg/gm). This results indicate that crowding effect of the functional groups and the electronic environmental released some retardation for the condensation reaction which lead to a small pore formation. On the other hand sample (3) and (4) indicate the same pathway in the process that may lead to the

instability of these group and no formation or little formation of the internal adsorption capacity as looking to the external pores which is determined by measuring adsorption of methylene blue pigment. Grafted lignin in sample (1) gives (69 mg/gm). The results of methylene blue adsorption varied between (69-27 mg/gm). This can be explained by the formation of a certain pores by the reaction of asphalt and lignin which may be result by changing the structure of the pores, if it compared with pure asphalt and pure lignin. Humidity content explained by the activity of functional groups on the surface of activated carbon. On the other hand the ash content which is

explain the amount of metal in the sample is slightly low in all the samples compared with B.D.H. sample. The density is very low in the sample (1) and then start to increase, which may be explain by the condensation reaction or due to the present of metal in the asphalt.

In order to be more specific about adsorption of activated carbon and the authentical one we employ developed multiple regration method by [Tharapong V. et al., 1999] which calculate the surface area from the amount of the adsorption iodine. The values of surface area are better than B.D.H. sample except in pure asphalt.

Sample	* Asphalt:lignin	Humidity %	Ash %	Density gm/cm <sup>3</sup>	Iodine number mg/gm	Methylene blue mg/gm	** Surface area m <sup>2</sup> /gm
1	2:10	8	1.289	0.168	1129	69.010	907.401
2	4:10	5	2.021	0.290	965	27.300	794.702
3	8:10	2	2.621	0.298	962	33.750	792.601
4	10:10	4	2.781	0.299	610	42.500	756.970
Lignin	-	8	1.921	0.214	992	59.059	813.304
Asphalt	-	3	2.512	0.414	766	49.050	658.042
B.D.H.	_	0.8	3.200	0.345	908	90	755.596

Table (	( <b>1</b> )	: Pro	nerties	of	prepared	activated	carbon
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\* by weight

\*\* calculated by equation adapted from Tharapong V. et al., 1999.

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