

Production of Activated Carbon via Grafting and Chemical Activation

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Abstract

This research work was aimed to prepare active carbon from residual petroleum refining product obtained from northern Iraqi refinery in Beji . The process involve atmospheric oxidation through air blowing with constant flow rate for 48 hrs. at 350°C . The oxidized asphalt was grafted with different percentages of authentic lignin. The grafting process was carried out in the presence of limited amount of potassium hydroxide at a temperature of 350-400°C for 3 hrs. and till no more physical change in the nature of mixture was observed . Furthermore, Carbonization of the grafted asphalt was carried out in the presence of twice the original weight of potassium hydroxide . The process was carried out at 400-500°C , till no more evolution of gases or vapor was observed.

Carbonaceous materials obtained through the process were purified by washing with distilled water till the water eluate is neutral . Activation of the carbon was carried out by refluxing with 30% HCl , washed with water and dried in the oven . Evaluation of the active carbon was carried out through measuring its ability in the removing of iodine and methylene blue from their aqueous solution.

48

. 400-350
(:) 2 :1
. 500-400
. %30

500-400

. (B.D.H)

Introduction

Activated carbon is a black material and having pores of non crystalline texture. It could be granular or powder. Active carbon differs from most adsorbent in terms of surface area and

capacity . Active carbon is obtained from a wide range of high carbonaceous materials such as a coal, bitumen,etc. Preparation of the carbon is carried out by employing a

certain type of compounds that have an ability to remove the hydrogen from the structure in the form of H_2S , NH_3 and sometimes H_2O ⁽¹⁾.

In most cases the carbon produced is black to gray in color and have a certain texture differs from carbon black and charcoal in the porosity. Activation of the carbon produced usually carried out thermally or thermally in presence of steam. Activation usually carried out under inert atmosphere or oxidizing atmosphere. Some of the carbon sources are coal, bitumene, agricultural wastes and harvesting wastes⁽²⁾.

Activated carbon have many uses and applications specially in food processing, gases mask, ion exchange and pollutant removal. Also there are many types of activated carbon. Merck index divides these into four basic forms⁽³⁾:

- 1- Animal charcoal which is obtained by charring bones, meat, blood, ...etc.
- 2- Gas black obtained by the incomplete combustion of natural gas and liquefied petroleum gases.
- 3- Lamp black is obtained by the burning various fats, oils, resins, ...etc.
- 4- Activated carbon which is prepared from vegetables.

Activated carbon is produced by many methods of carbonization and in the presence of the required carbonizing agent and additives.

Looking back to the knowledge available in the literature, We find many workers in the field of activated carbon production and some of them are:

Aweed⁽⁴⁾ prepared activated carbon from some agricultural wastes by using excess amount of KOH at $550\pm 25^\circ C$. Aweed⁽⁵⁾ et al., carbonized the bituminous materials and high density polyethylene using catalytic oxidation with V_2O_5 to prepare activated carbon

at $550\pm 25^\circ C$. Al-Ghannam⁽⁶⁾ et al prepared activated carbon from (*Morus nigra*) using different amounts of KOH at $550\pm 25^\circ C$. Evans⁽⁷⁾ et al., prepared activated carbon from sugar (sucrose) by chemical methods. Ahmad and Do⁽⁸⁾ prepared activated carbon by chemical activation with KOH and zinc chloride. Garcia⁽⁹⁾ et al., prepared activated carbon from pine wastes gasified in a pilot reactor in the presence of (KOH), using different alkali/char ratio [from 1:1 to 1:4 (wt.:wt.) at $800^\circ C$]. Al-Ghannam⁽¹⁰⁾ et al., produced activated carbon from asphaltic materials using additives and chemical activation at $550\pm 25^\circ C$. Hamdon⁽¹¹⁾ et al., produced activated carbon by application of chemical oxidation using sodium periodate at $350^\circ C$ for 3 hours. The product was activated using excess amount of sodium hydroxide at $550\pm 25^\circ C$ for 3 hrs.

To the best of our knowledge and comparing the literature we did not find any research work employing grafted asphalt with lignin as feedstock for the production of active carbon.

Experimental

1-Oxidation of the Asphalt

The asphaltic materials were obtained from northern Iraqi refinery in Beji. The physical properties and the chemical composition of asphalt as. Two kilograms of the asphalt were placed in stainless steel reactor, heated gradually and a certain amount of air was blown into the mixture at $350^\circ C$. Addition of air continued till the asphalt and its weight decreased and no gases evolved from the reaction. The heating period for the oxidation required 48 hours. The oxidized asphalt was crushed into small volumes and kept for the next step.

2-Grafting of oxidized asphalt with lignin

Oxidized asphalt was mixed with lignin (ICI grade) in different ratios varied from 1:1 to 10:1 (Asphalt/Lignin). The two materials were mixed carefully and half the weight from potassium hydroxide was added.

The chemical reaction took place after mixing and heating the mixture below 400°C which leads to the elevation of H₂O and some other gases. After 3 hours the resultant asphalt-lignin co-polymer type was further carbonized in next step.

3-Carbonization of the Grafted Asphalt

The resulting grafted asphalt from step (2) was crushed to a small particles and twice weight of KOH was added to the original one (twice the weight). The mixture was heated to about 500°C till no gases evolved and a grayish product was indicated. The product was kept at room temperature to be processed in the next step.

4-Purification of the Carbon Produced

The carbon produced was washed thoroughly with distilled water and heated with distilled water for 2 hrs.. The process was repeated till the (pH=7-7.2)

5-Activation of the Carbon Product

Dried carbon from step (4) was mixed with (30%) HCl and refluxed for 3 hours. The mixture was filtered and washed with distilled water, till the (pH=7-7.2). The activated carbon was placed in an oven at 120°C for 24 hrs and kept in a closed container for further study.

6-Study of the Physical Evaluation of the Activated Carbon

A-Measurement of Density

The density of the prepared activated carbon was determined by weighing (10cm³) of carbon sample using graduated cylinder⁽¹²⁾.

B-Determination of 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⁽¹³⁾.

C-Measurement of Humidity

One gram of the air-dried activated carbon was heated in an oven at 150°C for 3 hrs. The difference in weight before and after heating was calculated and considered as the amount of humidity in the sample⁽¹⁴⁾.

D- Determination of Carbon Activity by Iodine Adsorption Method

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⁽¹⁵⁾:

$$I_n = \frac{X}{m} \cdot D$$

Where:

m= is the weight of the activated carbon in gram.

X=A- [2.2B X ml of sodium thiosulfate solution used]

A=N₁ X 12693

B=N₂ X 126.93

N₁=normality of iodine solution.

N₂= normality of sodium thiosulfate solution.

D= correction factor.

E- Determination of Carbon Activity by Methylene Blue (M.B.) Method

An exact weight (0.1gm) 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 shaken by electrical shaker for 24 hrs. at a temperature of 25°C 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 λ_{max} 665nm. 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⁽¹⁶⁾.

Results and Discussion

Activated carbon plays an important role in the removal of impurities from organic compounds, pollutants from air and water and many more applications.

In our research work we aimed to graft the asphalt and specially the oxidized asphalt that contain some oxygenated functional group which is recognized before. The grafting was introduced by adding lignin (ICI grade), Which is according to its structure contain many oxygen-carbon linkage, phenolic and carboxylic group which is expected to react with oxidized asphalt in the alkaline media. Grafting of the asphalt is carried out with different percent of lignin varied from 1:1 –10:1 and 0:1 (Asphalt/Lignin). The results of the varying of the lignin amount and keeping the asphalt constant indicated

that the density start to decrease as the amount of lignin decreased.

The ash content of the activated carbon samples prepared by grafting and fusion with alkaline potassium hydroxide lied between 1.7-2.7%, which is acceptable from the economical and industrial point of view when it is compared with B.D.H grade (3.2%).

Measurement of humidity content showed that grafting of asphalt with different amount of lignin does not affect the amount of humidity which may be due to the closing in the structure of the surface of the activated carbon that may adsorb water and retain it up to 350°C as a hydroxylic water⁽¹⁷⁾. On the other hand methylene blue adsorption decreased and reaches a high value in the oxidized asphalt and pure lignin. This may be explained by the surface oxidized functional groups which are very close to each other to give final large amount in the small pores and reduces the large pores. The aim of the variation of lignin by the grafting process is to produced surface material that may contain original surface oxygenated groups and synthetic groups. According to the obtained results we may conclude that as the amount of lignin decreases the iodine number increases. The results showed that lignin may affect the pores when its amount is increased due to presence of the original surface functional groups. The results of the study are given in the table below and figures(1,2).

Preliminary study for the removal of heavy metals from aqueous solution showed a good results and need some optimization which is the goal of the next paper.

Table
Properties of Prepared Activated Carbon

Sample	* asphalt: Lignin	Density gm/cm ³	Ash content %	Humidity %	Iodine Number mg/gm	Methylene Blue mg/gm
1	10:10	0.418	2.700	1.010	817	24.180
2	10:8	0.324	2.001	3.020	850	25.350
3	10:5	0.310	1.700	4.010	906	26.450
4	10:2.5	0.301	2.452	4.205	934	30.240
5	10:1	0.228	1.689	4.561	982	38.200
6	10:0	0.414	2.520	5.021	766	49.050
7	0:10	0.441	2.751	5.921	962	51.975
B.D.H		0.345	3.200	0.800	908	90

* By grams

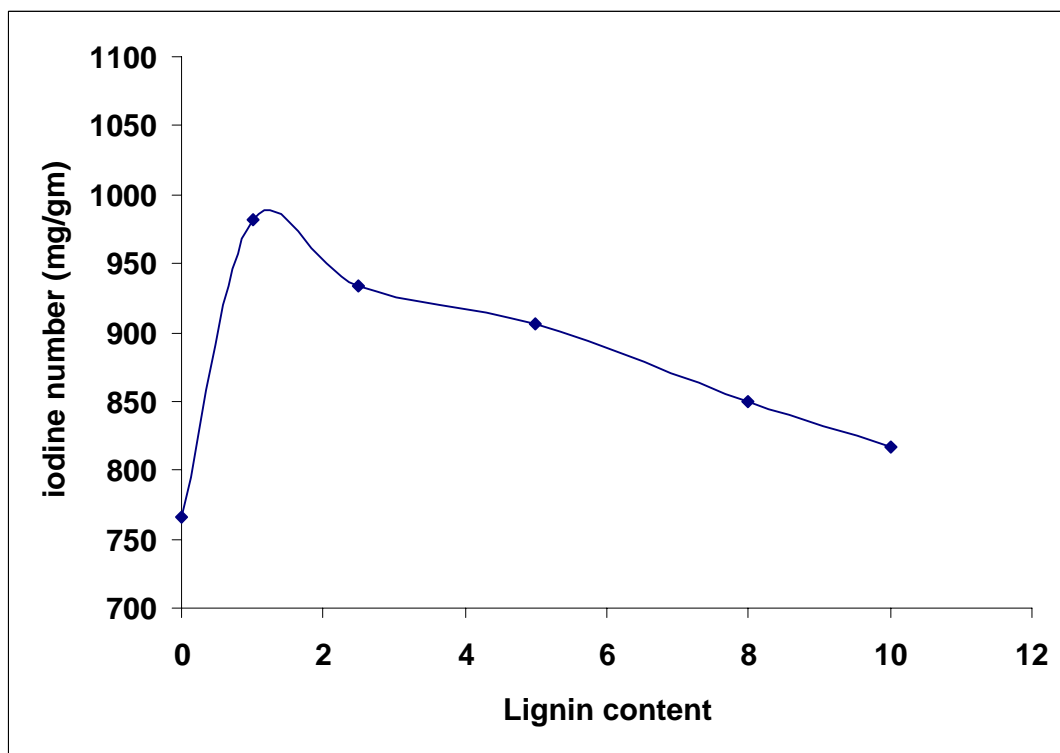


Figure (1): effect of lignin ratios on adsorption of iodine.

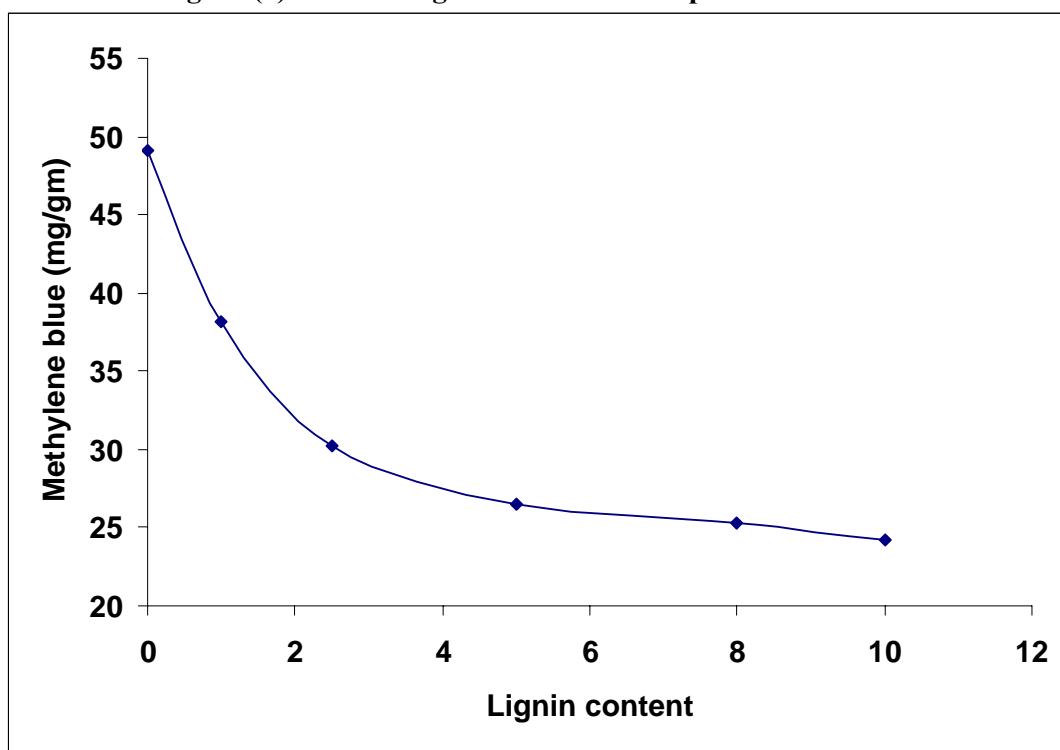


Figure (2): effect of lignin ratios on adsorption of methylene blue pigment.

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