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EFFECT OF KOH RATIO ON THE FORMATION OF ACTIVATED CARBON FROM PRESSED WOOD RESIDUES

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ABSTRACT: The present work concern the production of activated carbon of reasonably good properties from cheep sources. The results of preparation of activated carbon from compressed wood sheets residues used in the furniture industry are presented. The preparation method entails the conversion of the wood sheets to a small size pellets and reacting these pellets with the activating agent $FeCl_3$ (3% w/w). The mixture was heated at 300 $^{\circ}$C for a period of 3 hours. The product was allowed to cool to room temperature, followed by carbonization at high temperatures with KOH. The effects of carbonization time periods of 3 and 12 hours and the ratios of wood pellets to potassium hydroxide (1:0.5, 1:1, 1:1.5 and 1:2) were investigated in order to determine the best operating conditions. The quality of the activated carbon produced was assessed by different methods such as density, humidity, ash content, iodine adsorption and the ability for methylene blue pigment removal from aqueous solution. The density of product decreases with increasing the carbonizing agent ratio. Humidity increasing with increasing carbonizing agent ratio. The ash content also increasing with increasing KOH ratio. There was an increase in iodine number and methylene blue adsorption as carbonizing material increasing. All the values show on difference between the samples heated for 3 and 12 hours indicating that the time of carbonization has no clear effect.

INTRODUCTION: Activated carbon is a carbonaceous adsorbent that is highly porous suffers during its production a defect in the crystal structure leads to the appearance of inhomogeneous and unstable pores in terms of energy and activity. These pores can be found mostly on the outer surfaces of the activated carbon or can be internal. The size of the pores and their number exceeds the number and size of the pores in the ordinary carbon that is not activated, so its ability for adsorption is higher.

Activated carbon has a higher adsorption capacity than any other substance and has a high surface area ranging from 300 m^2/g and 5000 m^2/g [1, 2].

There are two types of activated carbon, first in the form of granules which is used for adsorption of gases and toxic vapors, for this purpose it is used in gas masks [3]. The second form is a powder which is used in different purposes such as adsorption of cylindrospermopsin and microcystin toxins from drinking water supplies [4].

There are many uses for activated carbon; it is used in the adsorption of gases and vapors such as ammonia and carbon dioxide [5], adsorption of nitrogen oxides NO_2 and NO [6] and the adsorption of carbon dioxide [7]. It is also used in the removal of elements like Cr(VI) [8]. Activated carbon is also used for medical purposes in the adsorption of odors from wounds, which can cause physiologic

disturbances such as increase in heart rate and respiratory rate. It can also cause nausea and vomiting [9]. It is used to treat poisonings and overdoses following oral ingestion [10]. Activated carbon usually found as tablets or capsules and used in many countries over-the-counter drug to treat diarrhea, indigestion and flatulence. Activated carbon has been used in the separation of proteins. The method depend on the differences in the size and effective charge of proteins. It is used to efficiently remove smaller proteinaceous impurities from larger proteins. It was found that smaller proteinaceous impurities are most efficiently removed at a solution pH close to the impurity's isoelectric point, where they have a minimal effective charge [11].

Due to the importance of activated carbon, several methods has been used for preparation from different sources. It is prepared from asphalt and heavy oil fly ash and coal fly ash by pyrolysis [12]. From petroleum coke using potassium hydroxide under nitrogen gas flow [13]. It is also prepared from damaged rubber using sulfur and a catalyst such as $FeCl_3$ at different temperatures [14]. From spent lubricating oils using oxidation condensation process. The oxidation of the spent lubricating oils conducted using 2% (wt%) of ($CoCl_2$, $ZnCl_2$ and $FeCl_3$) and in the presence of a stream of air or oxygen[15].

Activated carbon preparation from plant sources has been widely studied. It is prepared from Corncob by chemical activation with concentrated H_3PO_4 then pyrolysis at different temperatures [16]. It is prepared from Iraqi Khestawy date palm from three positions, the palm fronds, the date palm seeds and the palm fiber. It synthesized by a physiochemical activation method using H_3PO_4 as activating agent [17]. Activated carbon has also been prepared from softwood lignin which was isolated with polyethylene glycol. The results showed that activated carbon with more micropores exhibited high specific surface area and total pore volume which increased with the activation time prolonging; the highest ones were around 3100 m^2/g and 1.5 mL/g [18]. Wood bark was used to prepare activated carbon by steam activation at a temperature of 700 °C and 800 °C. The pore structures of the produced samples were analyzed by means of low temperature nitrogen adsorption [19]. Coconut shell is also used in the preparation of activated carbon by treatment with phosphoric acid (H_3PO_4) using the response surface methodology (RSM). Fifteen combinations of the three variables namely, impregnation ratio (1, 1.5 and 2), activation time (10, 20 and 30 min) and activation temperature (400, 450 and 500 °C) were optimized [20]. Different plant residues are used in the production of activated carbon through the reactance of these residues with zinc chloride and potassium carbonate as activated agents [21].

Low cost activated carbon has been prepared from tea waste using sulphuric acid as activating agent, the effect of activation parameter such as temperature of carbonization, concentration of sulphuric acid and contact time on the final products was studied by varying the H_2SO_4 to tea waste ratio, activation temperature and preheats temperature [22]. It is also prepared by heating tea waste with boric acid as activating agent [23].

Snail shell waste (*Helix pomatia*) was used to prepare activated carbon material using $ZnCl_2$ and $CaCl_2$ compounds with the temperature ranging from 500˚C to 800˚C. The characterization of activated carbon produced was done by studying the effect of temperature on ash content, pore volume and porosity. The adsorption isotherm for methylene blue pigment was carried out on a batch study. The activated carbon exhibited excellent adsorption for methylene blue [24].

The preparation of activated carbon of good quality from cheep source for pharmaceutical uses is the main interest in this research.

MATERIAL AND METHODS: Chemicals were obtained from Sigma-Aldrich company, wood sheets were of the red oak type (*Quercus rubra*) collected from the residues of furniture factories. Experiments were carried out in the Chemistry Department, Serit University, Libya and University of Anbar, Iraq.

Preparation of Wood Pellets: The compressed wood sheets were chopped into small pieces. The small pieces then crushed and returned to its original small size pellets. In order to remove the resin materials used to hold the pellets with each other during composing the furniture wood, a stream of hot water passed through the vessel

containing the wood pellets for 1 hour. This step can be done by placing the vessel on a shaker for 1 hour. The resulting wood pellets then dried in a furnace at 100 ^{o}C for 3 hours.

Catalyzing with FeCl₃: 100 grams from the raw material were treated with ferric chloride FeCl$_3$ (3% wt/wt) as catalyzing agent. The mixture was heated at 300 ^{o}C for a period of 3 hours. The product was allowed to cool to room temperature.

Carbonization with KOH: The material from the last step was mixed with potassium hydroxide (KOH), as carbonizing agent, in weight ratios wood pellets to potassium hydroxide (1:0.5, 1:1, 1:1.5 and 1:2), and 20 ml of distilled water. The materials were mixed thoroughly till a thick bulk was obtained. The produced thick bulk was heated at 550 °C for periods of 3 and 12 hours. The activated carbon produced from this step was cooled to room temperature.

Purification of Activated Carbon: The activated carbon was washed after cooling with distilled water several times until neutral litmus paper test achieved. The product obtained was treated with 10% HCl solution under refluxed for 1 hour. The mixture was filtrated, washed with distilled water, crushed and dried at 110 ^{o}C for 24 hours.

Measurements of Activated Carbon Properties:
1- Density Measurement: The density of the prepared product was determined by placing the sample in 5 ml graduated cylinder to calculate the volume. The weight calculated using electronic balance. The density calculated using the equation:

$$\text{Density (g/cm}^3) = \text{Mass / Volume}$$

2- Humidity Measurement: One gram of activated carbon precisely weighed was heated in an oven at 130 ^{o}C for 3 hours. The difference in weight before and after heating was calculated as H$_2$O vapor in the sample.

3- Ash Content Measurement: The ash content of the produced activated carbon was measured by heating one gram of the sample in a porcelain crucible using an electrical furnace for two hours at temperature of 1000 ^{o}C. After cooling the sample, the remaining residue which was considered as the ash content is calculated using an electrical balance.

4- Carbon Activity Determination by Iodine Adsorption Method: The determination of the iodine number is a test for the internal surface area of the activated carbon. The iodine number (In), is defined as the number of milligrams of iodine compound adsorbed from an aqueous solution by one gram of activated carbon. The method was carried as follow:

One gram of the dried activated carbon produced was transferred to a dry glass 250 ml Erlenmeyer flask. 10 ml of 5% HCl was added to the flask and swirled until the carbon is wetted. The flask was placed on hot plate, until the contents started to boil, the mixture left boiling for exactly 30 minutes. The flask contents allowed to cool down to room temperature, then 100 ml of standardized 0.1 N iodine solution was added to the flask. The flask was closed immediately, and the contents mixed vigorously by shaking. The mixture was filtered by gravity immediately after shaking through filter paper. The initial 20-30 ml of filtrate was discarded and the remainder collected in clean beaker. The filtrate in the beaker was mixed with a stirring rod and 50 ml of the filtrate was transferred into 250 ml Erlenmeyer flask. The 50 ml sample was titrated with standardized 0.1 N sodium thiosulfate solution until the yellow color of the sample almost disappeared. About 1 ml of starch solution was added and the titration continued until the blue indicator color just disappeared. The volume of sodium thiosulfate solution used was recorded.

$$\text{Iodine number} = \frac{X}{M} A$$

Where
X= the mg of iodine adsorbed by the activated carbon
$X = (12.693\ N_1) - (279.246\ N_2\ V)$
Where:
N_1 = the normal concentration of iodine solution
N_2 = the normal concentration of sodium thiosulphate solution
V = the volume of sodium thiosulphate solution in ml
M = the mass of activated carbon in g
A = the correction factor

5- Carbon Activity Determination by Methylene Blue Adsorption Method: The value of methylene blue gives an indication of the adsorption capacity of an activated carbon for molecules having similar dimensions to methylene blue. It is defined as the numbers of milliliters standard methylene blue solution decolorized by 0.1 g of activated carbon.

An exactly weight (0.1 gm) of the activated carbon produced was added to an aqueous solution of 20 ppm methylene blue pigment in a conical flask. The flask content placed in an electrical shaker for 24 hours at 25 °C till adsorption of methylene blue from its aqueous solution was completed and reached a state of equilibrium (the color disappeared). The clear solution was separated and the absorbance was determined at λ_{max} 665 nm. The concentration of the adsorbed compound by activated carbon was calculated by standard curve using different concentrations of methylene blue (5, 10, 15, 20, 25 ppm).

RRSULTS AND DISCUSSION: Activated carbon is similar to graphite in structure, each of them consisting of hexagonal rings of carbon, the carbon rings in the activated carbon is not complete and irregular, especially at the edges, and this adds some characteristics for activated carbon. For example, the random distribution of carbon rings lead to the presence of holes (gaps) varies in size and shape. The surface area of one gram of activated carbon (the sum of these gaps) can be 5000 m^2/g which is equivalent to a football field area. The noncompletion of carbon rings at the edges leads to the presence of some atomic groups on the surface and this in turn determines the nature of the carbon surface as if it is acidic or alkaline or neutral.

The nature of the material used in the preparation of activated carbon in addition to the method of activation is the most important factors affecting the type and amount of surface groups.

The activated carbon adsorbs contaminants through the groups on the surface by chemical adsorption, here bonds are formed between adsorbent material (activated carbon) and the adsorbate (contaminants), or through the holes and gaps, and this is physical adsorption where the adsorbent moves between the

holes until it reaches the internal surface of these holes.

In this research we used the catalyzing agent $FeCl_3$ as Lewis acid which help in the oxidation process. Using KOH instead of NaOH also help in producing activated carbon with a great deal of gaps since potassium has bigger size than Na in NaOH.

By observing **Table 1** we found that the values of density decreases with increasing the carbonizing agent ratio, which reveals that the great amount of KOH produces high porous structure.

Humidity increasing with increasing carbonizing agent ratio which reveals increasing activity.

TABLE 1: PROPERTIES OF ACTIVATED CARBON FOR THE SAMPLE HEATED FOR 3 HOURS

Sample	Pellets: KOH Ratio	Density g/cm^3	Humidity %	Ash Content %
1	1:0.5	0.33	7.5	1.2
2	1:1	0.31	6.8	1.4
3	1:1.5	0.31	7.8	2.1
4	1:2	0.29	8.9	1.9

The results of ash content show an increase with increasing the carbonization agent ratio. The parameters of the sample heated for 12 hours are shown in **Table 2**.

Comparing **Table 1** and **2** shows no big differences between the samples heated for 3 and 12 hours, the 3 hours heating period was enough to develop the activated structure. If the carbonization time prolonged we assume that most volatile substances can be removed.

TABLE 2: PROPERTIES OF ACTIVATED CARBON FOR THE SAMPLE HEATED FOR 12 HOURS

Sample	Pellets: KOH Ratio	Density g/cm^3	Humidity %	Ash Content %
1	1:0.5	0.34	6.2	1.4
2	1:1	0.32	6.7	1.8
3	1:1.5	0.29	7.7	2.2
4	1:2	0.35	9	2

Studying the iodine number which is the number of milligrams of iodine adsorbed from an aqueous solution by one gram of activated carbon, which is in turn give an indication about the internal surface

area, showed an increase in iodine number as carbonizing material increasing.

Methylene blue adsorption has the same style of iodine number; it is increasing as the amounts of KOH increased. **Table 3** shows the parameters of the sample heated for 3 hours.

TABLE 3: PARAMETERS FOR IODINE AND METHYLENE BLUE ADSORPTION FOR THE SAMPLE HEATED FOR 3 HOURS

Sample	Pellets: KOH Ratio	Iodine Number (mg/g)	Methylene Blue (mg/g)
1	1:0.5	650	35
2	1:1	730	44
3	1:1.5	980	62
4	1:2	1110	110

The increased adsorption means a great internal surface area of the activated carbon. **Table 4** shows the parameters of the sample heated for 12 hours period. Again there is no differences in the iodine and methylene blue adsorption between the two samples.

TABLE 4: PARAMETERS FOR IODINE AND METHYLENE BLUE ADSORPTION FOR THE SAMPLE HEATED FOR 12 HOURS

Sample	Pellets: KOH Ratio	Iodine Number (mg/g)	Methylene Blue (mg/g)
1	1:0.5	630	36
2	1:1	680	45
3	1:1.5	910	60
4	1:2	1154	107

Fig. 1 and **2** show the relationship between iodine number and methylene blue adsorption and the amounts of KOH used in the carbonizing the carbon.
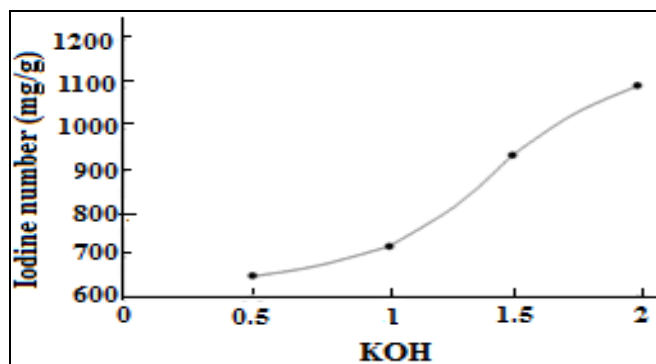

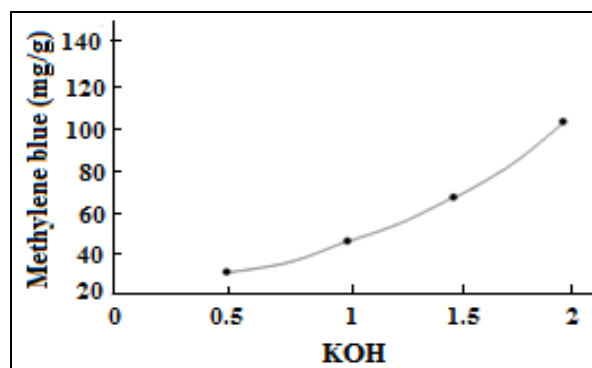FIG 1: THE RELATIONSHIP BETWEEN KOH ADDED AND IODINE NUMBER FOR THE SAMPLE HEATED FOR 3 HOURS

FIG 2: THE RELATIONSHIP BETWEEN KOH ADDED AND METHYLENE BLUE ADSORPTION FOR THE SAMPLE HEATED FOR 3 HOURS

CONCLUSION: Activated carbon can be prepared from Pressed wood residues by chopping the wood sheets to a small size pellets and reacting these pellets with the activating agent $FeCl_3$ followed by carbonization at high temperatures with KOH. The effects of carbonization time periods of 3 and 12 hours and the ratios of wood pellets to potassium hydroxide (1:0.5, 1:1, 1:1.5 and 1:2) were investigated in order to determine the best operating conditions. The quality of the activated carbon produced was assessed by different chemical methods such as density, humidity, ash content, iodine adsorption and the ability for methylene blue pigment removal from aqueous solution.

There was an increase in iodine number and methylene blue adsorption as carbonizing material increasing. The density of product decreases with increasing the carbonizing agent ratio. Humidity increasing with increasing carbonizing agent ratio. The ash content also increasing with increasing KOH ratio. No big differences between the samples heated for 3 and 12 hours, the 3 hours heating period was enough to develop the activated structure.

CONFLICT OF INTEREST: The author does not have any conflict of interest.

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