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Preparation of Activated Carbon from (*Punica granatum .sp*) Wood by Chemical Treatment Using Potassium Hydroxide.

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ABSTRACT

In the present study, activated carbons were prepared from Punicagranatum .sp, using potassium hydroxide as activating agent. Punicagranatum .sp activated carbon(PGAC) was characterization using methylene blue number, iodine number and some physical properties such as humidity, ash content and density. The perfect measurement for this study was the proportion of (1:2.5)(wood : KOH) to give 560mg for iodine number and 67mg for methylene blue number which are good result.

1. Introduction

Activated carbon is a unique and versatile material that has a wide surface area, precise pore size, high surface activity and effective adsorption capacity. Activated carbon importance have emerged since the first world war where it was used as an adsorbent materials in poison gas masks [1]. Activated carbon is a black charcoal-like material, which has a well-developed pore structure, which leads to its large surface area; in addition, it possesses good mechanical strength. Activated carbon is commonly used as adsorbent in wastewater treatment and gas removal as well as a catalyst[2]. As an example of the raw materials, which used for preparation of activated carbon are coconut husks, walnut husks , Almonds husks, sawdust and other sources. The main uses of activated carbon are the treatment of contaminated water, air, water purification and effective removal of sulfur and mercury [3]. Wood is one of the materials that production of activated carbon and known as a natural material its components are cellulose and lignine and considered a renewable materials. Activated carbon has been synthesized from a variety of sources that included wood raw material [4]. However the literature has reported many studies that include preparation of activated carbon from plant sources. Jabbar prepared activated carbon by carbonizing albmb nuclei raw material, with

concentrated phosphoric acid[5]. The adsorption properties were studied and tested for good carbon specifications. Ramadan and his group synieszied activated carbon from carbonization of the India coconut shell with the presence of varying ratios of nylon (6.6) and fixed ratio of sodium hydroxide. The operation is carried out in the solid state apart from the air by melting [6]. Arie and his group prepared activated carbon by motivating Salacca peels using KOH as cheap and effective material to remove dyes. Metcalfe and his group were able to carbonizing a mixture of coconut husks wood those rich of lignin component[7]. The carbonization process gave activated carbon with equal sizes of high adsorption capacity of organic molecules [8]. Mao and his group prepared Activated carbon from pine wood by quick process with potassium hydroxide. The activation carried out by microwave technology [9].
In another study, Awaid and his group syntheszied activated carbon from a combination of (wood - polymer) using microwaves technique.
Other new types of activated carbon were prepared from asphalt after treated with recycled rubber[10]. The carbons was tested by adsorption of dyes employing kinetics and thermodynamic studies [11]. Ali was able to prepare activated carbon from coconut husks by carbonization with the presence of

fixed ratios of phenol and different ratios of bituminous substance and sodium hydroxide and changing the proportions of reactants for the purpose of obtaining the best result. Bhadusha and his group prepared activated carbon by carbonizing veneer of wood Apple outer shell and used to study the adsorption of the methylene blue dye from aqueous solution and PH [12] .Jabbar and his group manged to prepare activated carbon from Buckthorn nuclei as raw material by chemical activation [13]**.**

2. Experimental section

2.1.Synthesize of Activated Carbon :

The dry natural body of the raw material remnants (pomegranate wood, (Punicagranatum. sp) is crunched into a powder with the carbonization material in order to allow fully interaction and getting better results. Fixed weight of starting material is placed in stainless steel pot. Different ratio of the (KOH) is added. Carbonated(potassium hydroxide) (2.5:1, 2:1, 1.5:1, (0:1, 0.5:1, 1:1,1.5:1,2:1,2.5:1) (wood: base) The mixture is homogenized well and heated to a temperature of 300° c for half hour with continuous stirring. The next step is raised temperature to (550 + 25) ℃ for (1.5 hour) the heading become (2 hours) for accomplishing the carbonization and activation of the prepared samples of carbon. These samples are then cooled in to the room temperature. The activation carbon is washed with distilled water to of KOH until become neutral(using litmus paper). The samples are then dried by an oven at 100-120 C° for five hours. The samples are refluxed with (10%) HCl for one hour ,in order to remove any traces of ions. After that washed with distilled water for several times to the remove any traces of the acid remained(not reacted) KOH. The samples are then dried fore (24) hours and then crashed and separated by molecular sieve of(20-40) mesh and kept dry for use.

2.2. Iodine number

The determination of specification of the prepared models of activated carbons are as follow:

Measurement of adsorption of (mgs.) of iodine from aqueous solution by one (gm) of activated carbon is done. This method was achevied for providing information about the internal surface area(S.A.) as follow:

One gram of activated carbon and 10 ml of (5%) HCl were placed in conical flask of 250ml, than the flask is heated to boiling temperature, stayed for (0.5 hour) and then cooled to the room temperature. 100 ml of iodine solution is added to the flask than shaked for (0.5 hour) by electrical shaker, the next step is filtteration of activated carbon from iodine solution with negligence of first (20-25)ml of filtrate than the rest are collected in clean flask. 50 ml of iodine solution filtrate is transported in to a conical flask and titrated with (0.1N) of sodium thiosulfate solution until the color become pale yellow. Starch solution(1ml) was added as an indicator, the color become blue, the titration is complete until disappear

the blue color and the volume of thiosulfate is calculated.

the iodine number is calculated using the following equations[14]:-

$X = A- [2.2B * V]$

$A = N_1*12693$

$B = N_2 * 126.93$ ……(1)

Where, X = adsorbed iodine weight (measured in milligrams) by activated carbon.V = volume of sodium thiosulfate from pipette .N1 = standard concentration of iodine solution (0.1N).N2 = standard concentration of sodium thiosulfate solution (0.1N).

The iodine number is calculated from the following equation:

I.N. =X/M .D ………(2)

Where,M = Weight of activated carbon model used.D = correction factor (value close to one).

2.3. Metheylene blue number:

This is a common method which carried out by placing (0.1) grams of activated carbon in a conical flask . Certain volume is the dye solution of concentration (20ppm) was shaked for (24) hours(the room temperature. The dye color start to disappear, and when it reach constant color the solution was left to settle down then separated by decantation to measure its absorbance at 665 nm. The concentration of adsorbed dye is calculated from the difference between the initial and remained concentration .This is determined by calibration cure which made for the dye at Wavelength (665),by employing various concentration (5, 10, 15, 20, 25ppm) The capacity of activated carbon to adsorb the dye is calculated using the equation below[15]

$$qe = \frac{Ci - Ce}{m} v ………(3)$$

Where, q_e : is (mg/g) is adsorption capacity of carbon (mg) to adsorbed dye (g). C_i :is the initral cocetration of dye (mg/L). C_e :is the concentration of dye at equilibrium (mg/l). M: is the weight of. V= is the volume of shaked dye(l)

2.4. Measurement of moisture content: -

This method involves exposing certain weight of the activated carbon at lab temperature for(24) hours, then its dried at 110 ℃ for 2 hours. The sample is cooled and weighed. The molar content is calculated from the weight difference as percentage(ISO,5.62) [16].

2.5. Measurement of the Ash percentage:

One gram of activated carbon is placed in a crucible and then heated by oven up to at 1000 ℃ for an hour. The sample is then cooled to lab temperature in a desiccator .The weight of the remaining model represents the weight of ash. The ash percentage is then calculated (ASTM-D2866-70).

2.6.Measurment of Activated Carbon Density

Acertan amount of activated carbon is placed in a volumetric flask (5) ml. The sample is precisely for the purpose of getting rid of the pores size in the molecules, so that the carbon molecule filled the volumetric flask to the mark. The weight of carbon is

calculated from the difference between the weight of the flask filled and empty(ASTM-D2854-70).The density of carbon is calculated using the following equation[17].

Density = mass \ Size (gm / cm³) ………(4)

3. Results and discution

3.1.Optimazation of parameters to prepare activated carbon

Activated carbon is considered as a porous material that has a large surface area which makes it with high adsorption capacity for various chemicals. The first step in the preparation of activated carbon is chooses the starting material which must be of high carbonic content. The second step includes heating of the raw material in isolation from air atmosphere. The heating leading to the removal of element other than carbon such as hydrogen,oxygen,nitrogen and sulfur as gases and volatile materials. The free carbon atoms are then arranged as graphite structure in a way allow the presence of pores among the carbons layers of graphite. The carbonization process produces primary porous structures. The carbonization process continues until the total removal of liberated gases. The product is then activated either thermally in an inert atmosphere or with the presence of activation materials such as oxygen, carbon dioxide and water vapor or chemical activation by using $AlCl_3,ZnCl_2$ or Cr [18]. In this study, the pomegranets tree wood was selected as a raw material (starting material) and KOH as a carbonization and activation material. Table (1) illustrates the achieved measurements on the prepared activated carbon models.

Table 1: proximate analysis of prepared activated carbon(PGAC)

Sample	Wood: KOH	Percentage of results%	Density gm/cm³	Moisture Content%	Ash Content%	Iodine number mg	Blue methylene number mg
1	1 : 0	23.75	0.268	0.97	0.03	247	9.62
2	1 : 0.5	6.65	0.174	0.98	0.03	366	20
3	1 : 1	15.65	0.166	0.99	0.02	376	32
4	1 : 1.5	17.6	0.11	1.01	0.02	430	44
5	1 : 2	22.42	0.22	0.96	0.03	454	53
6	1 : 2.5	34.87	0.138	0.99	0.01	560	67

The results of Table (1) show that, the percentage of the produced carbon is increased with the increase of the base: wood (Figure1). This can be illustrated by the fact that ,increasing the amount of KOH used as a catalyst it is getting interfered with a greater quantity of wood used in the carbonization process. After learning the base leaves a great number of pores and makes the carbon prepared more porous. This agrees with the resulting carbon density decrease with increasing the amount base.

The value of density is decreased with the increase of the used base until getting to model(5) [(1:2) (wood: base)].Then the density started increasing. The density values were the commercially accepted range (0.325) (Figure2).

The moisture content, is slightly increased with the increased base used, until the use get to model (5),because the increased humidity reduces the efficiency of activated carbon as adsorbent since the active sites qualified for adsorption are occupied by water molecules. The humidity content for model [(1:2) (wood : base)] is decreased (%0.096) where in the model (6) [(1:2.5) (wood: base)] is slightly increased to reach (% 0.099) (Figure 3).The values of the ash content was differentiated in terms of increase and decrease (Figure 4). Development of porous structure of activated carbon is depending on the interaction of carbon atoms present in the starting material with the KOH under the reaction condition ,which lead to the formation of K_2O, K‚ CO and CO2 and K_2CO_3 .The presence of these products in the reaction mixture enlarges the pores formed in the carbonization process. The removel of these base increases the number of pores in the prepared carbon as mentioned before. The presence of metal oxides increases the distance among the carbon atoms in the structure which lead to increasing the sizes of pores and the surface area as a result which improves the adsorption properties and the activity of carbon .For this purpose. The removal of gases during activation process also gives more activity. For the pores available for adsorption since these location were occupied by these gases and decreases the activity of carbon toward adsorption. The reaction occurred during activation process can be expressed by the following reaction. The increase of the amount of KOH with respect to the starting material (pomegranate wood) will lead to the formation of microspores and new transition mesopores formed among the wall of the origin pores[19]. This was noticed in Table. The number of iodine number is increasing with the increase of the amount of the base KOH used. The increase of the amount of the base work as a catalyst increasing the sizes of the internal surface area that available for adsorption leading to the increase of adsorbed iodine as a result. Iodine number values ranged from 247 mg/g for model(1) [(wood: base)] in to 560 mg/g model (6) [(1:2.5) (wood: base) (Figure (5) and (6) respectively). This proves that as the base KOH used increases, the internal and external surface area increase. That means that the KOH leading to the expansion and development of porous structure models of activated carbons prepared. There are a large number literatures, referring to the effect of base on the wood containing cellulose. Choosing this type of wood in this study being locally available materials and grow in the ways of obtaining it with suitable parries in

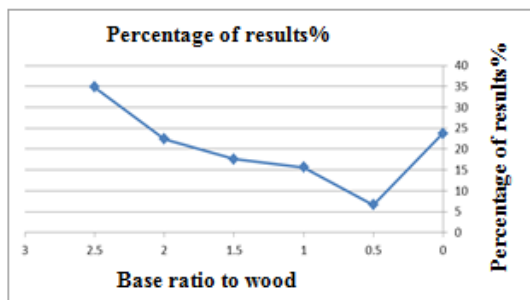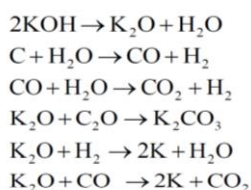addition to its carbon contents which increase the prepared activated carbon ratio.

$$2KOH \rightarrow K_2O + H_2O$$
$$C + H_2O \rightarrow CO + H_2$$
$$CO + H_2O \rightarrow CO_2 + H_2$$
$$K_2O + C_2O \rightarrow K_2CO_3$$
$$K_2O + H_2 \rightarrow 2K + H_2O$$
$$K_2O + CO \rightarrow 2K + CO_2$$

Fig. 1: The relationship between the added base ratio and the percentage of output..
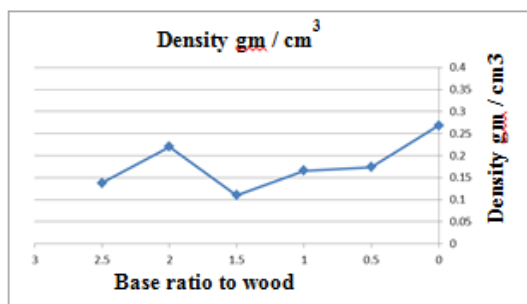
Fig. 2: The relationship between the added base ratio and the density of g / cm ^{3}
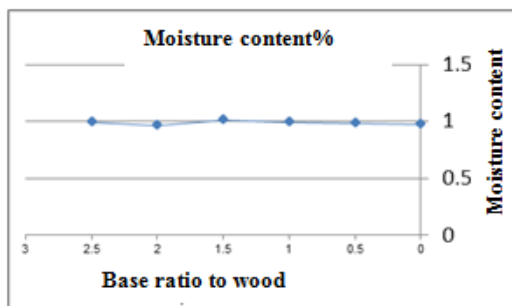

Fig. 3: The relationship between the ratio of the added base and moisture content
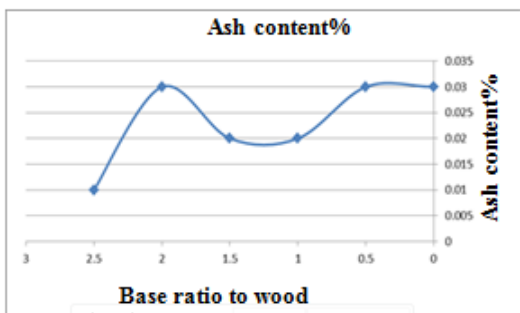

Fig. 4: The relationship between the ratio of the added base and ash content.
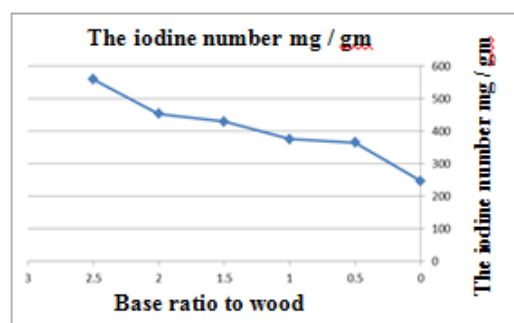

Fig. 5: The relationship between the base ratio added and the iodine number mg / gm
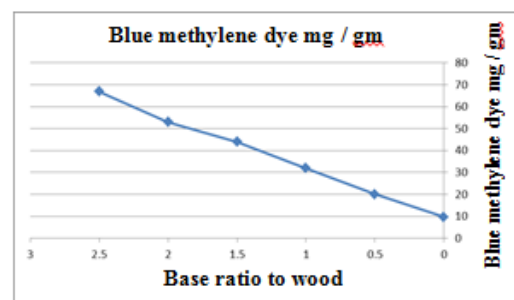

Fig. 6: The relationship between the ratio of the added base and blue methylene dye mg / gm

3.2.Adsorption Isotherms:
Adsorption isotherms are empirical equation developed in order to describe the distribution of the solute (adsorbate) between the solid and liquid phases at equilibrium in the unit component system depending on some assumption .

In this study, two of the most common isotherm namely, Freundlich and Langmuir were applied in the empirical data of the studied dye adsorbed on the prepared activated carbon on follow:

1. Freundlich isotherm:
The main assumption of this isotherm is, the active sites those available for adsorption on the adsorbent surface with nonequivalent energies, the adsorption on the solid surface is not the rate determining step of the adsorption ,and the adsorption can occur with a multilayer[20].The isotherm can be represented by the following equation:

Log q_e=Logk_f+1\n Log Ce………(5)

Where n and k_f are the Freundlich isotherm constant and related to the intensity and capacity of adsorption respectively.

k_f and n are calculated from the intercept and steps of plotting logq_e versus log C_e.

The data obtained from applying this isotherm on the empirical result of this study are presented in Table (2) and Figure (7).

Table 2: Application of Freundlich isotherm on data of adsorption of activated carbon(PGAC)

A	C(mol/L)	Ci(mg/L)	Ce(mg/L)	qe(mg/g)	LOG qe	LOG Ce
0.175	0.0001	31.985	14.221	17.764	1.249541	1.15293

0.230	0.0003	95.955	45.381	60.574	1.782286	1.656874
0.241	0.0004	127.94	51.613	76.326	1.882673	1.712759
0.242	0.0005	159.925	52.18	82.8	1.91803	1.717504
0.286	0.0006	191.910	66.911	125	2.09691	1.825498
n=0.831808, k_f=1.165791,Temp(**25 ºC**)						

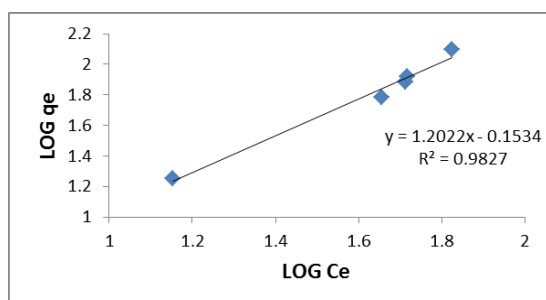**Fig. 7: Freundlich isotherm of activated carbon (PGAC)**

Fig. 8: Langmuir isotherm of activated carbon (PGAC)

3.2.2. Langmuir Isotherm:

This isotherm assumes that ,the adsorption is occurred as a single layer on an energetically equivalent surface contain active site available for adsorption with equal energies [21].

Langmuir isotherm can be represented with the following equation.

$$C_e \backslash q_e = 1/b.Q_{max} + C_e \backslash Qmax \ldots \ldots (6)$$

Plotting the relation between $C_e \backslash q_e$ versus C_e gives strength Line with a slope $1/ Q_{max}$ and intercept $1/b.Q_{max}$ when the values of b and Q_{max} are the Langmuir constants and related to strength of connection of the dye to the carbon surface and the theoretical adsorption of the dye on the carbon surface(mg/g). related to the intensity and capacity of adsorption respectively. k_f and n are calculated from the intercept and slope of plotting.

The experimental result s obtained from the application of this isotherm are listed in table (3) as illustrated in figure(8).

Table 3: Langmuir isotherm of prepared activated carbon(PGAC)

Ce	qe	Ce/qe
14.221	17.764	0.800552
51.613	76.326	0.676218
52.18	82.8	0.630193
66.911	125	0.535288
b(L/mg)=0.005346,Qmax(mg/g)=212.766, Temp(**25 ºC**)		

The results obtained from both isotherms show that, the Langmuir isotherm fit better the experimental data of these study, indicated the value of R^2(0.9292). The value of n (freundlich constant)(1.0) referee to a favorable adsorption (physical adsorption). Fitting of Langmuir isotherm on the studied system may indicate that the prepared activated carbon follow the assumption of Langmuir and a single adsorbed layer on the carbon surface are obtained distributed on the surface with equivalent energy homogenously distributed.

4. Concolison

The study so far remark that an activated carbon is successfully prepared form low cost and locally available material (PGAC) wood by carbonization at 550 ºC using KOH as a catalyst. A starting material representing a source of pollution to the environment is converted to a new material used for controlling pollution, the application of two isotherms Freundlich and Langmuir on experimental data of adsorption of dye showed better fitting to Langmuir isotherm indicating to that, a single layer of dye molecules is adsorbed on the carbon surface with equivalent energy homogenously distributed on the carbon surface. The value of Freundlich constant(n=1) indicates that the adsorption is the forward type

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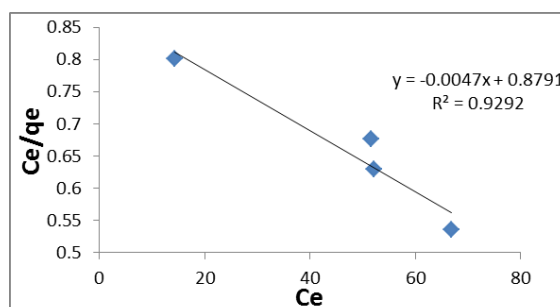
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تحضير الكاربون المنشط من خشب شجرة الرمان (*Punicagranatum .sp*) بالمعالجة الكيميائية باستخدام هيدروكسيد البوتاسيوم

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الملخص

في هذه الدراسة، تم تحضير الكربون المنشط من خشب شجرة الرمان، باستخدام هيدروكسيد البوتاسيوم كعامل منشط. الكاربون المنشط الذي تم تحضيره تم تشخيصه ودراسته باستخدام رقم صبغة الميثيلين الزرقاء والرقم اليودي وبعض الخصائص الفيزيائية مثل الرطوبة ومحتوى الرماد والكثافة، القياسات المثالية لهذه الدراسة وجدت ان النسبة (1: 2.5) (خشب: هيدروكسيد البوتاسيوم) التي اظهرت نتائج 560mg للرقم اليودي و 67mg لرقم صبغة الميثيلين الزرقاء.