Preparation of mesoporous activated carbon from Iraqi nabk twigs trees for the removal of methylene blue from aqueous solution

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Abstract

Mesoporous activated carbon was prepared from the twigs of Iraqi nabk trees (Zizyphus spina Christ Rhamnaceae family) as precursors using both of chemical activation which consisted of potassium hydroxide (KOH) treatment and physical activation using carbon dioxide (CO_2) gasification. It were found from the design of experiment software, that the optimum conditions for preparation nabk twigs activated carbon: activation temperature of 520 ^{o}C, activation time of 40 min and 1.0 for the chemical impregnation ratio.

The characterization of the prepared activated carbon from nabk trees twigs shows clear surface which contains well-developed pores and high surface area. The yield of activated carbon prepared was 23%.

The experimental data were analyzed using three isotherm models: Langmuir, Freundlich and the Temkin, it was found that the equilibrium data fitted well with the Langmuir model with maximum adsorption capacity of 182 mg/g with coefficients of correlation R^2 =0.990

***Keywords*:** Activated carbon; Adsorption; Al-Nabk trees (Zizyphus); Methylene blue; Isotherm models.

تحضير الكربون المنشط ميسوبوروس من أشجار الأغصان العراقية لإزالة الميثيلين الأزرق من محلول مائي

الخلاصة

تم تحضير الكربون المنشط Mesoporous من أغصان أشجار الزنبق العراقية) عائلة Zizyphus spina Christ Rhamnaceae)كسلائف تستخدم كلاً من التنشيط الكيميائي الذي يتكون من معالجة هيدروكسيد البوتاسيوم (KOH) والتنشيط الفيزيائي باستخدام تغويز ثاني أكسيد الكربون .(COO) وقد وجد من خلال تصميم برنامج التجربة ، أن الظروف المثلى لإعداد أغصان nabk من الكربون المنشط: درجة حرارة التنشيط 520 درجة مئوية ، ووقت التنشيط 40 دقيقة و 1.0 بالنسبة لنسبة التشريب الكيميائي.

يظهر توصيف الكربون المنشط المحضر من أغصان الأشجار سطحًا صافًا يحتوي على مسام متطورة ومساحة مرتفعة. كان محصول الكربون المنشط المحضر 23٪.

تم تحليل المعطيات التجريبية باستخدام ثلاثة نماذج متساوية :Langmuir و Freundlich و Temkin ، وقد وجد أن بيانات التوازن مزودة جيدًا بنموذج Langmuir مع قدرة امتزاز قصوى قدرها 182 مجم / جم مع معاملات الارتباط$R2 = 0.990$.

الكلمات المفتاحية: الكربون المنشط؛ الامتزاز؛ أشجار النبك (Zizyphus) ؛ الميثيلين الأزرق. نماذج الأيسوثرم.

1. **Introduction:**

Dyes are used in many industries in order to color their products such as textile industry. The presence of dyes in effluents is a major concern due to their adverse effect to many forms of life. The discharge of dyes in the environment is worrying about both toxicological and esthetical reasons [1]. Methylene blue (MB) is the most commonly used substance for dying cotton, wood and silk. Though MB is not strongly hazardous, it can cause some harmful effects where acute exposure to MB will cause increased heart rate, vomiting, shock, cyanosis, jaundice, quadriplegia and tissue necrosis in humans. Therefore, the treatment of effluent containing such dye is of interest due to its harmful impacts on the receiving waters. Adsorption onto activated carbon has been found to be superior compared to other techniques for wastewater treatment in terms of its capability for efficiently adsorbing a broad range of adsorbate and its simplicity of design [2].

Activated carbons obtained from various agricultural wastes, such as oil palm fronds [3], oil palm fiber [4], durian shell [5], oil palm shell [6], banana stalks [7], Olives stones [8], jute fiber carbon [9], coconut husks [10], pistachio nut shell [11], Cassava peels [12], palm date seeds [13], mangos teen peels [14], willow tree legs [15], and nabk twigs trees.

Ziziphus spina-christi — known as the Christ's Thorn Jujube — is an evergreen tree or plant native to northern and tropical Africa, southern and western asia. It is native to the countries Chad, Djibouti, Eritrea, Ethiopia, Gambia, Mali, Mauritania, Nigeria, Pakstan, Saudi Arabia, Iraq, Palestine, Sengal, Somalia, Tunisia, Turkey, Uganda and Zimbabwe. In arab countries, especially in Palestine, hundred years ago it was called sidr (associated with the Lot trees of the Koran) and was common in the Jordan Valley and around Jerusalem. There were some folklore traditions that said the trees were protected by benevolent spirits or dead saints. Easton argues that the spina-christi is too brittle to be bent into a crown, and suggests another local plant which he says is called Nabk (16, 17).

This research was mainly focus on the preparation of activated carbon under the optimum conditions from Iraqi nabk trees for the purpose of removal of methylene blue from aqueous solution.

2. Experiment

2.1. Materials

Methylene blue (MB) supplied by Sigma–Aldrich was used as an adsorbate and was not purified prior to use. Distilled water was used to prepare all solutions. Table 1 listed the properties of MB dye used.

Table 1: Some properties of the MB used

Properties	
Chemical formula	$C_{16}H_{18}ClN_3S.3H_2O$
Molecular weight	373.9 g/mol
Type	Basic dye
Solubility	Soluble in water
Wave length	668 nm

2.2 Preparation and characterization of activated carbon

Al-Nabk trees twigs (collected from Iraqi agriculture fields) used as precursors for preparation of activated carbon. The precursor was firstly cleaned and cutting into small pieces (around 2 cm), the precursors was carbonized at 250 ^{o}C under purified nitrogen (99.995%) flow of 150 cm^3/min for 90 min in a stainless steel vertical tubular reactor placed in a tube furnace. The heating rate was fixed at 10 ^{o}C/min. Then according to the optimum conditions for preparation activated carbon, the carbon produced was then soaked in potassium hydroxide (KOH) solution with 1.0 impregnation (KOH: char) ratio. The mixture was then dehydrated in an oven overnight at 105 ^{o}C to remove moisture and was then activated under the same condition as carbonization, but to a different final temperature (520 ^{o}C), once the final temperature was reached, the nitrogen gas flow was switched to CO_2 and activation was held for 40 min. The activated carbon produced was then cooled to room temperature under nitrogen flow and then washed with warm distilled water and 0.1 molar hydrochloric acid until the pH of the washing solution reached 6–7.

2.3 Characterization of the prepared activated carbon

Scanning electron microscopy (SEM) analysis was carried out on the prepared activated carbon under optimum conditions, to study its surface texture and the development of porosity. Brunaeur, Emmett and Teller (BET) suggested to determine the pore size distributions, the surface area and pore characteristics of activated carbons using Micromeritics (Model ASAP 2020, US).

2.4 Design of experiments for preparation of activated carbon

Response surface methodology (RSM) is a collection of mathematical and statistical techniques that are useful for modeling and analysis of problems in which a response of interest is influenced by several variables [19]. A standard design called a central composite design (CCD) was applied in this work to study the variables for preparing the activated carbons. This method is suitable for fitting a quadratic surface and it helps to optimize the effective parameters with a minimum number of experiments, as well as to analyze the interaction between the parameters [20]. Generally, the CCD consists of a 2^n factorial runs with $2n$ axial runs and n_c center runs (six replicates). The activated carbons were prepared using physiochemical activation method by varying the preparation variables using the CCD. The activated carbon preparation variables studied were (x_1) activation temperature; (x_2) activation time and (x_3) KOH: char impregnation ratio. These three variables together with their respective ranges were chosen based on the literature and preliminary studies. Activation temperature, activation time and impregnation ratio are the important parameters affecting the characteristics of the activated carbons produced [21]. The number of experimental runs from the central composite design (CCD) for the three variables consists of eight factorial points, six axial points and six replicates at the center points indicating that altogether 20 experiments were required, as calculated from equation 1:

$$N = 2^n + 2n + n_c = 2^3 + 2 \times 3 + 6 = 20 \qquad (1)$$

where N is the total number of experiments required and n is the number of process variables.

The experimental sequence was randomized in order to minimize the effects of the uncontrolled factors. Each response (Y_i) for carbon yield and MB removal was used to develop an empirical model which correlated the response to the three preparation process variables using a second degree polynomial equation (equation 2) [22].

$$Y = b_o + \sum_{i=1}^{n} b_i x_i + \sum b_{ii} x_i^2 + \sum_{i=1}^{n-1} \sum_{j=i+1}^{n} b_{ij} x_i x_j \qquad (2)$$

where Y is the predicted activated carbon yield or MB removal response, b_o the constant coefficient, b_i the linear coefficients, b_{ij} the interaction coefficients, b_{ii} the quadratic coefficients and x_i, x_j are the coded values of the activated carbon preparation or MB removal variables. The activated carbon was derived from these precursors by physiochemical activation method which involved the use of KOH treatment and followed by gasification with CO_2. The parameters involved in the preparations were varied using the response surface methodology (RSM). The three variables studied were x_1, activation temperature, x_2, activation time and x_3, KOH/char impregnation ratio (IR). These three variables together with their respective ranges were chosen based on the literature and the results obtained from the preliminary studies where the activation temperature, activation time and IR were found to be important parameters affecting the characteristics of the activated carbon produced [23]. The most important characteristic of an activated carbon is its adsorption uptake or its removal capacity which is highly influenced by the preparation conditions. Besides, activated carbon yield during preparation is also a main concern in activated carbon production for economic feasibility. Therefore, the responses considered in this study were Y_1 activated carbon yield, Y_2 removal of MB.

2.5 Activated carbon yield

The experimental activated carbon yield was calculated based on the following equation (3):

$$\%Yield = \frac{w_c}{w_o} \times 100 \qquad (3)$$

where w_c and w_o are the dry weight of final activated carbon (g) and dry weight of precursor (g), respectively.

2.6 Adsorption studies

2.6.1. Batch adsorption study

Batch adsorption was performed using 5 Erlenmeyer flasks (250 ml). In a typical adsorption run, 200 ml of methylene blue solution with initial concentrations of 100–500 mg/l were placed in these flasks. Fixed amount (0.30 g) of the prepared activated carbon, with particle size of 2 mm, was added to these flasks and kept in an isothermal shaker (120 rpm) at 30^{o}C until equilibrium was attained. The concentrations of dye solution before and after adsorption were determined using a double beam UV–Vis spectrophotometer (UV-1700 Shimadzu, Japan). The maximum wavelength of the methylene blue was found to be 668 nm. The amount of adsorption at equilibrium, q_e (mg/g), was:

$$q_e = \frac{(C_o - C_e)V}{W} \qquad (4)$$

where C_o and Ce (mg/l) are the liquid phase concentrations of methylene blue at the initial and equilibrium conditions, respectively. V (l) is the volume of the solution and adsorbent mass W (g). [24].

The percentage removal of dye at equilibrium was calculated by the following equation:

$$\% \, Removal = \frac{(C_o - C_e)}{C_o} \times 100 \qquad (5)$$

2.6.2. Isotherm study

2.6.2.1. Langmuir isotherm

The linear form of Langmuir isotherm equation is given as:

$$Ce/qe = Ce/qm + 1/Ka \, q_m \qquad (6)$$

where *Ce* is the equilibrium concentration (mg/l); q_e the amount of methylene blue adsorbed at equilibrium (mg/g); q_m the adsorption for complete monolayer (mg/g); *Ka* is the sorption equilibrium constant (l/mg).

2.6.2.2. Freundlich isotherm

The well-known logarithmic form of the Freundlich isotherm is given by the following equation:

$$\ln q_e = \ln K_F + (1/n) \ln Ce \qquad (7)$$

where *Ce* is the equilibrium concentration of the adsorbate (mg/l), q_e is the amount of methylene blue adsorbed per unit mass of adsorbent (mg/g), K_F and *n* are Freundlich constants with n giving an indication of how favorable the adsorption process.

2.6.2.3 Temkin isotherm

The Temkin isotherm has been used in the form as follows:

$$q_e = \mathrm{B} \ln \mathrm{A} + \mathrm{B} \ln C_e \qquad (8)$$

where *B = RT/b*, *b* is the Temkin constant related to heat of sorption (J/mol); *A* is the Temkin isotherm constant (l/g), *R* the gas constant (8.314 J/mol K) and *T* the absolute temperature (K).

3. Results and discussion

3.1 SEM, BET analysis and carbon yield

The surface morphology of the prepared activated carbon was examined using scanning electron microscope (SEM). Plate 1 show the SEM image (magnification ×1000) of activated carbon prepared under optimum conditions. It can be seen that the surface of prepared activated carbon contains a well-developed pores where there is a good possibility for dye to be absorbed into the surface of the pores. The (BET) surface area was 806 m^2/g using Micromeriticsue (Model ASAP 2020, US).According to equation (3) the yield of prepared carbon was 23%.

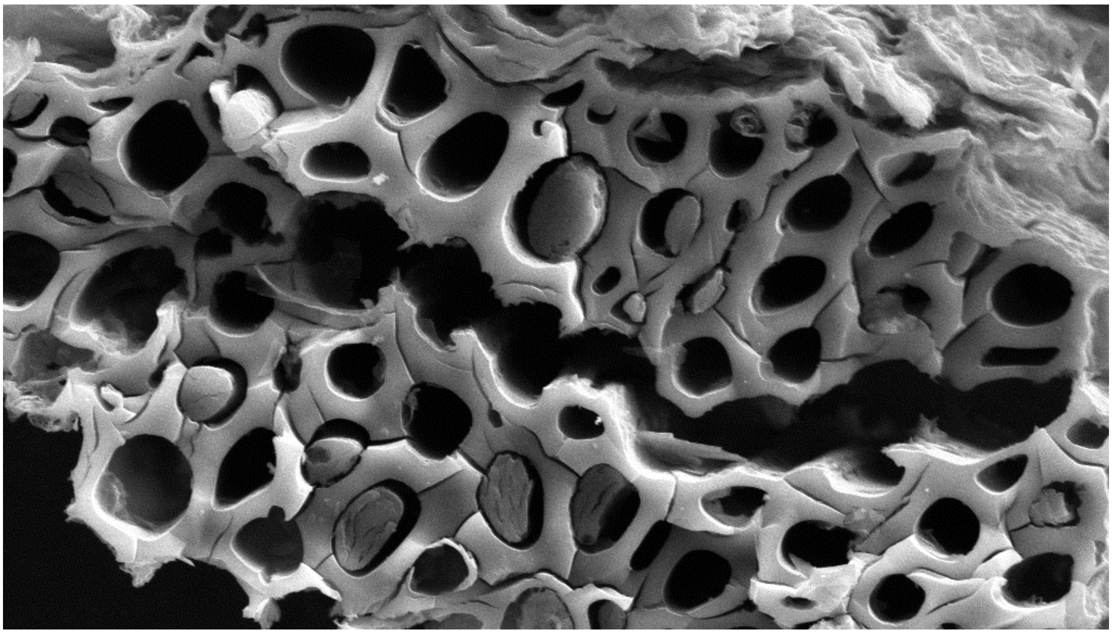

Plate 1: SEM image (magnification ×1000) of activated carbon prepared

3.2 Adsorption isotherms

The adsorption data have been subjected to Langmuir, Freundlich, and Temkin isotherm models (Table 2). The applicability of the isotherm models to fit the adsorption data was compared by judging the correlation coefficients, R^2 values. The closer the R^2 value to unity, the better the fit. The analysis of the isotherm data was done by fitting them to these isotherm models to find the suitable model that can be used for design purposes. Based on the correlation coefficient, R^2 (0.99) it can be concluded that the adsorption process of our system was demonstrated well by Langmuir isotherm model with maximum monolayer adsorption capacity of 182 mg/g at 30 ^oC. It can be seen from Figures (2&3) that an increase in initial concentration of

MB includes increasing the uptake of dye from aqueous solution onto the prepared activated carbon. The equilibrium adsorption capacity increases with the increase of initial concentration of MB (50-300 mg/l) as (32.77, 65.11, 96, 123, 147 and 170 mg/g, respectively.

Table 2: Isotherm parameters for removal of MB onto prepared AC

Isotherm model	**Value**
Langmuir	
Q_m (mg/g)	182
b (l/mg)	0.208
R^2	0.990
Freundlich	
K_F	42.86
N	2.6
R^2	0.954
Temkin	
A	3.33
B	32.85
R^2	0.994

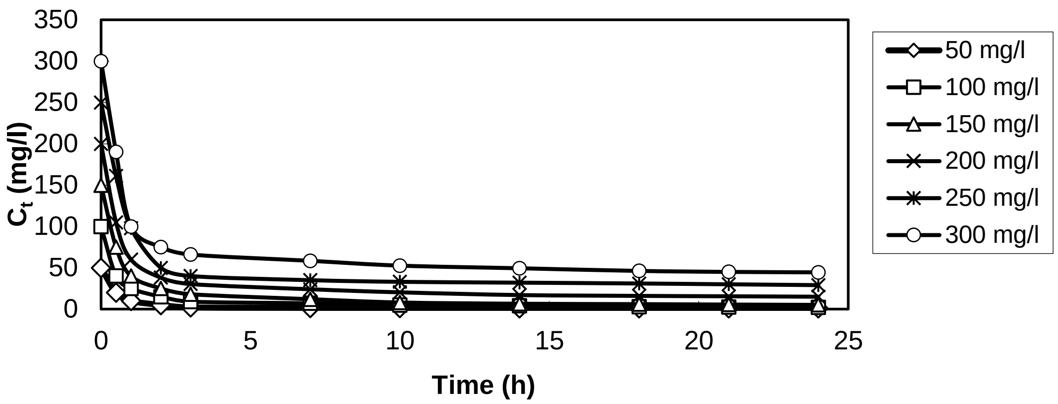

Fig. 2: Initial concentration Vs contact time of MB adsorption

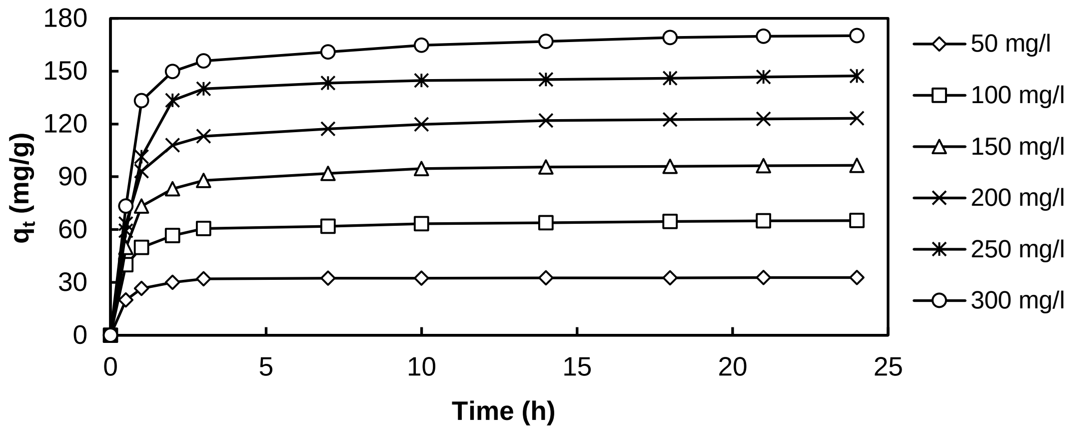

Fig. 3: Adsorption capacity of MB for different initial concentration and contact time

4.0 Conclusion:

Iraqi nabk trees twigs were used as precursor to prepare mesoporous activated carbon with sufficient yield of carbon and high methylene blue dye removal. The optimum conditions for prepare Nabk twigs AC was obtained using 520 ^{o}C activation temperature, 40 min activation time and 1.0 KOH: char impregnation ratio.

According the optimum conditions the activated carbon prepared from nabk trees twigs used to adsorb methylene blue with different initial concentrations from aqueous solutions with carbon yield of 23%. Equilibrium data were fitted to Langmuir, Freundlich and Temkin isotherms and the equilibrium data were best described by the Langmuir isotherm model, with maximum monolayer adsorption capacity of 182 mg/g at 30 ^{o}C.

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