# **Expulsion Methylene Blue MB Dye from Aqueous Solution by Using Activated Camel Thorn**

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## طرد صبغة الميثيلين الأزرق من محلول مائي باستخدام شوكة الجمل المنشط

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#### **ABSTRACT**

<u>Background:</u> The chance of camel thistle squander as eco-accommodating, accessible, and monetary adsorbent for adsorption methylene blue color from its watery arrangement was analyzed by utilizing clump and section framework. All experiments of the batch were achieving with modification camel thorn waste dye concentration 50 mg/L, pH6.5, Temp 25 °C.

Materials and Methods: Camel thorn (CT) waste were collected from AL-Mahaweel region, this region situated in Babylon city/Iraq. The waste were direct washed with running water tap to release all impurities, and rinsed with distilled water for 4 times, after then it dried under sunlight, and then in oven under 50 °C for two hours. The dried (CT) waste were ground and sieved BSS-60 mesh size particle Results: Methylene Blue(MB) dye was examined to remove from the aqueous solution by adsorption on the camel thorn waste added to the acidic adsorbent modification, thermal adsorbent modification on the decolonization dye efficiency was studies were investigated with the similar working condition contact time (2-90 min).

<u>Conclusion:</u> The current discoveries created the impression that the that normal adsorbent, camel thistle squander is altogether appropriate for the depolarization of methylene blue color from its watery arrangement. The outcomes show that the balance isotherm for the two modules that utilized in this work are of good kind, for being curved vertical

Key words: methylene blue dye, adsorption, camel thorn, Langmuir, isotherm



#### INTRODUCTION

Methylene blue is cationic dye, the degradation of this dye is difficult and unfavorable due to the harmful and toxic product fragments for environmental system[1,2]. The physical properties of this dye are listed in the table.1, and its structure is shown in the Figure.1. have variously utilized in the various fields, in the medical field use in the Cancer therapy: improving the percentage of tumor destruction in Photodynamic. And chemical in the chemical application: In analytical chemistry as a redox indicator. From other hand The MB dye is widely used in the Textile Industries, the effluents of all these application discharged to the eco-system with any treatment will create a serious of environmental problems [3,4,5].

Table-1: The physical properties of methylene blue dye.

No	Physical properties	
1	Molecular weight g/mol	319.85
2	Solubility in water / mL	1g/25
3	Type of dye	Cationic dye
4	Maximum absorbance/ nm	664
5	Molecular formula	C <sub>16</sub> H <sub>18</sub> N <sub>3</sub> SCl

Figure(1):Structure of methylene blue dye

Adsorption has played an important role in the removal impurities from wastewater, and considered to be one of the most effective treatment methods [5], especially in the case utilize natural material as adsorbents [6]. Because the use the natural adsorbents in the wastewater treatment is economical, safe because its nontoxic, and available [7]. By and large the actuated carbon is generally utilized as adsorbent however excessive cost contrasted with regular adsorbents [8]. Practically an adsorbent need to have some potential characteristics for acting as a good adsorbent such as (a) a great available pore volume (b) hydrophobicity (c) high thermal and hydrothermal stability (d) catalytic activity and (e) easy regeneration [9,10].

In the current paper a Continuous and Bach type adsorption has been investigated for treatment methylene blue dye from aqueous solution, that the solution of dye was supplied to the continuous treatment unit continuously, while in the Bach treatment unit solution of dye fed to the system periodically.



#### **Experimental procedure**

#### **Collection, Preparation, and Modification of Adsorbents**

Camel thorn (CT) waste were collected from AL-Mahaweel region, this region situated in Babylon city. The waste were direct washed with running water tap to release all impurities, and rinsed with distilled water for 4 times, after then it dried under sunlight, and then in oven under 50 °C for two hours. The dried (CT) waste were ground and sieved BSS-60 mesh size particle [11].

Specimen weighted 5g from (CT) was handled with 50ml 0.1M of hydrochloric acid for one hour with starrier, and rinsed with distilled water for 3 times, it was then dried at oven 50 °C for 24 hours.

Specimen weighted 5g from (CT) was heated at oven 120 °C for 4 hours [11].

#### **Preparation Adsorbate Solution**

The methylene blue color was provided by aldrch Chemicals, arranged criticized arrangement (100mg/L) the color by dissolving gauged measures of color powder in the refined water. The trial arrangements were ready by weakening at wanted fixations [12].

#### **Continuous Adsorption**

The adsorption of persistent stream tests was coordinated in a glass section made from glass tube have 40 cm and an inward breadth 15cm. At the lower part of the segment, spotless sifter was append trailed by a layer of glass dots. A proper measure of the pre-arranged camel thistle fiber was full in the segment to create the required thickens of the adsorbent fibers(0.1,0.15, and 0.2) m, and afterward an upper holding strainer was confined on top of a section to give a homogeneous progression of the arrangement during the entirety of the segment locales. The solution of dye (with concentration 50ppm at pH5.5) was allowed to flow through the column at a wanted rating of flow  $3.3*10^{-6}$ m³/Sec. The specimens of dye solution at the exit from the column were collected at fixed times and measured the concentration [13]. Treatment system and process flow used in the study is shown in Figure (1).





Figure(2): The treatment system and process flow.

#### **RESULTS AND DISCUSSION**

#### **Activation Adsorbent (Bach adsorption)**

MB dye was examined to remove from the aqueous solution by adsorption on the camel thorn waste added to the acidic adsorbent modification, thermal adsorbent modification on the decolonization dye efficiency was studies were investigated with the similar working condition contact time (2-90 min), dye concentration 50ppm, pH-6.0, the temperature was  $(25\pm2~^{\circ}\text{C})$  and adsorbent dosage 5g/L.At first the removal procedure was completed with actively as appeared in the Figure(3).

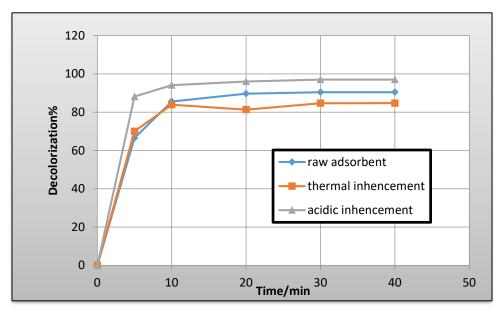


Figure (3): Decolonization methylene blue dye from aqueous solution on the surface of camel thorn waste, dye concentration 50 ppm, pH-6.0, the temperature was (25±2 °C) and adsorbent dosage 5g/L.

Beginning the expulsion information that were found from adsorption examines uncovered explain a similar conduct, such conduct as at the principal minutes of adsorption tests the evacuation interaction was solid and the pace of expulsion was quick this close was distinguished from the expulsion rate, that found there are 60% from dye was removed at the first 10 min. This due to the active site available on the adsorbent surface [13,14]. Active sites were will passed saturation stage by dye molecules by progress adsorption contact time for this reason removal process was decreased progressively till reach equilibrium situation. (5, 19, 20) [15] As a comparison between surface adsorbent modifiable sample (acidic and thermal absorbents modifications`1), the acidic more active comparing with thermal activation to adsorption MB dye from aqueous solution. Generally the results that found is explained in the Figure (4).

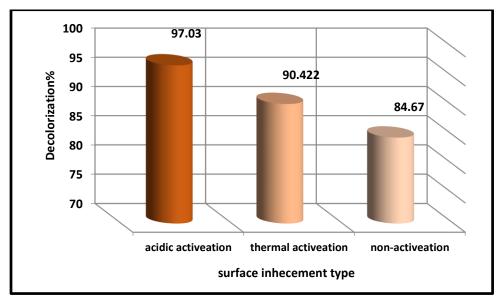


Figure (4): Decolonization percentage of methylene blue dye from aqueous solution, by use raw and enhancements (acid, thermal) camel thorn waste, dye concentration 50 ppm, pH-6.0, the temperature was (25±2 °C) and adsorbent dosage 5g/L.

#### **Adsorption Isotherm**

The adsorption isotherm is represent relationship between adsorbents and adsorbet, there are numerous models to selective it to this studies, so we select Freundlich and Langmuir models. The adsorption isotherm is essentially play important role due to explain how dye molecules (adsorbent)interact with the adsorbent particle, and is critical in optimizing the use of adsorbents .The performance of camel thorn waste as adsorbent was investigated via valuing the Equilibrium isotherm and adsorption percentage of MB dye in the batch model. The process was operated at the similar working condition contact time (2-90 min), dye concentration 50ppm, pH-6.0, temperature was (25±2 °C) and adsorbent dosage 5g/L. Generally by applying Freundlich and Langmuir equations obtain Figure(5), and Figure(6) which are appears fitted to the Freundlich and Langmuir models for the adsorption of MB dye on the prepared surface adsorbent.

#### Langmuir model

The equation (1) describes the Langmuir model [15,16]:

Where the  $q_{\text{max}}$  is maximum adsorption capacity.

The equation (1) has linearization form given by equation (2):

$$\frac{C_e}{q_e} = \frac{1}{Kq_{max}} + \frac{C_e}{q_{max}} \dots \dots \dots \dots \dots \dots (2)$$

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The  $(1/q_{max})$  value is the result from plot $(\frac{C_e}{q_e})$  vs  $C_e$ , that the slope of straight line is represented  $(1/q_{max})$  while the value of intercept is $(\frac{1}{Kq_{max}})$ 

One of the main properties of the Langmuir isotherm have been characterized

By the term detachment factor, or balance steady R<sub>L</sub>, which is depicted by the situation (3):

$$R_L = \frac{1}{1 + K C_o} \dots \dots \dots \dots (3)$$

Where the K is Langmuir constant, and the C<sub>o</sub> adsorbate initial concentration. The Langmuir constant indicates the adsorption nature as show in the table (2) [17]:

Table-2: The Langmuir constant indicates.

Values of R <sub>L</sub>	Type of isotherm
1 >R <sub>L</sub>	Un favorable
$1 = R_{L}$	Linear
$1 \qquad < R_L < 0$	Favorable
$0 = R_L$	Irreversible

#### Freudlich model

The freudlich model is given by the equation (4) [16],[17]:

$$q = \frac{X}{m} = K_F C^{1/n} \dots \dots \dots \dots \dots (4)$$

Where:

 $q_e$ : adsorbed amount mg/g.

x: adsorbate mass(mg).

*m* : adsorbent mass (mg).

 $C_e$ : concentration of adsorbate at equilibrium (mg/L).

KF: indicator of adsorption capacity of the adsorbent.

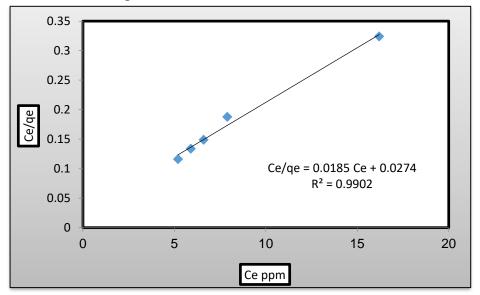
1/n: heterogeneity of the surface.

Generally by linearize the equation (5) by take logarithms can obtain the equation (5):

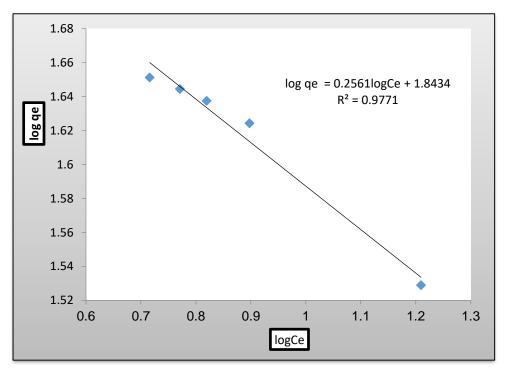
$$\log q_e = \log K_F + \frac{1}{n} \log C_e \dots \dots \dots \dots \dots (5)$$

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The (1/n) value is the obtain by plot  $\log q_e$  vs  $\log C_e$ , that the slope of straight line is represented (1/n) while the value of intercept is (K) [17].



Figure(5):Langmuir isotherm for methylene blue dye adsorption on the camel thorn waste, dye concentration 50 ppm, pH-6.0, the temperature was (25±2 °C) and adsorbent dosage 5g/L.



Figure(6):Freundlic isotherm for methylene blue dye adsorption on the camel thorn waste, dye concentration 50 ppm, pH-6.0, the temperature was (25±2 °C) and adsorbent dosage 5g/L.

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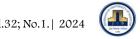


Table-3: Parameter of Freundlich and Langmuir isotherm for methylene blue adsorption on the camel thorn west surface.

Model	Langmuir		Freundlic	
No	Parameter	Value	Parameter	Value
1	q <sub>m</sub> (mg/g)	54.05	$K_{\rm F}({\rm mg/g})(1/{\rm mg})^{1/{\rm n}}$	83.6
2	K (L/mg)	0.71	1/n	0.398
3	RL	0.08-0.0075	$\mathbb{R}^2$	0.9513
4	$\mathbb{R}^2$	0.992		

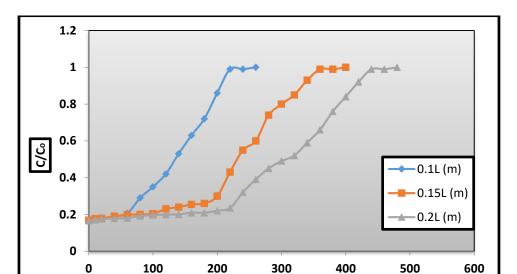
The current discoveries created the impression that normal adsorbent, camel thistle squander is altogether appropriate for the depolarization of methylene blue color from its watery arrangement. The outcomes show that the balance isotherm for the two modules that utilized in this work are of good kind, for being curved vertical. In order to assess the different isotherms and their fitness to relate with exploratory information the coefficient of assurance, R<sup>2</sup> used to decide the attack of the use isotherm with trial results.

From the table. 3. The worth coefficient were higher for Langmuir than for freundlich, This coordinates that the Langmuir isotherm is greater concurrence with the exploratory outcomes, and this demonstrates that the outer layer of utilized adsorbents has homogeneous nature.

#### **Experiments of Column**

The influence of the flow rate of the dye solution and the adsorbent modification on the removal efficiency was studied. The effect of solution flow rate on the removal of methylene blue dye by utilized camel thorn fibers was achieved by experimenting different solution flow rate m<sup>3</sup>/Sec, and constant another condition like the fiber height, dye concentration 50ppm, pH5.5 as illustrated in the curve in the Figure(8). Form this Fig can investigate that the breakthrough that the breakthrough is generally happening quicker with a greater rate of flow. This result, because of reduced contact time among dye molecules and active sites on the fiber of adsorbents at higher flow rate, this lead to Lower active sites employment [18,19,20,21]. Generally, when the rate of flow is lower the contact time is greater and the removal dye efficiency is higher [22].

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Figure(8): Experimental breakthrough results of methylene blue dye adsorption on surface acid activated camel thorn fiber in changing fiber highest, Q=3.33 \*10<sup>-6m3/s</sup>, C<sub>0</sub>=50ppm pH=6.5.

time/min

In the current paper, the activity of utilize camel thorn waste as adsorbent was investigated. The data results found in the batch adsorption explained the equilibrium isotherms for methylene blue adsorption on the surface of camel thorn waste was favorable type and description by the Langmuir and Freundlich model. The experimental data show that the fitting Langmuir model compared with Freundlich model. The maximum adsorption capacity was 54.4mg/g. The removal percentages were the obey to the following sequence at dosage 5g/L:

97% acid activation > 90 thermal activation > 84 raw material

The data of the experiments of continuous flow rate appeared that, as the flow rate increased, the time essential to achieve saturation camel thorn waste decreases more quickly.

### **Conclusion**

The current discoveries created the impression that the that normal adsorbent, camel thistle squander is altogether appropriate for the depolarization of methylene blue color from its watery arrangement. The outcomes show that the balance isotherm for the two modules that utilized in this work are of good kind, for being curved vertical



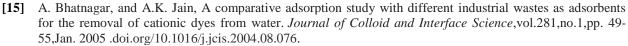
#### Conflict of interests.

There are non-conflicts of interest.

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ابل للعلوم الصسرفة والتطبييقية مجلة جسامعة بسابل للعلسوم الصبرفة والتط



#### الخلاصة

المقدمة: تم دراسة فرصة تبديد شوك الجمل كممتصات بيئية ، ويمكن الوصول إليها ، وممتازات نقدية لامتصاص اللون الأزرق الميثيلين من ترتيبها المائي من خلال استخدام إطار الكتلة والقسم. أجريت تجارب الدفعة بتحويل تركيز نفايات أشواك الإبل إلى 50 جزء في المليون ، ودرجة الحموضة 6.5 ، ودرجة الحرارة 25 درجة مئوية.

طرق العمل: تم جمع نفايات شوك الجمل من منطقة المحاويل في مدينة بابل. تم غسل النفايات مباشرة بحنفية مياه جارية لإخراج جميع الشوائب ، وشطفها بالماء المقطر لمدة 4 مرات ، ثم تجفيفها تحت أشعة الشمس ، ثم في الفرن تحت 50 درجة مئوية لمدة ساعتين. كانت النفايات المجففة (CT) عبارة عن جسيمات بحجم شبكة BSS-60 مطحونة.

النتائج: تم فحص صبغة الميثيلين الأزرق (MB) لإزالتها من المحلول المائي عن طريق الامتزاز على نفايات شوك الجمل المضافة إلى تعديل المادة المادة الممتصة الحرارية على كفاءة صبغة إزالة الاستعمار مع ظروف العمل المماثلة زمن الاتصال (2- 90 دقيقة).

الاستنتاجات: خلقت الاكتشافات الحالية انطباعًا بأن المادة الماصة العادية ، وهي عبارة عن بذر شوك الجمل مناسبة تمامًا لإزالة استقطاب لون الميثيلين الأزرق من ترتيبها المائي. تظهر النتائج أن التوازن متساوي الحرارة للوحدتين المستخدمتين في هذا العمل من نوع جيد ، لكونهما منحنيًا رأسيًا

<u>الكلمات المفتاحية:</u> صبغة الميثيلين الزرقاء ، الامتزاز ، شوكة الجمل ، لانجموير ، متساوي الحرارة