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Investigation Study of Removing Methyl Violet Dye From Aqueous Solutions Using Corn-Cob as A Source of Activated Carbon

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Abstract

One of the most pollutants of water is organic dyes, which is usually come from industries of textile, leather and paper. In this work, activated carbon is used as adsorbent, which is prepared from the corn-cob (CCAC) to remove the methyl violet (MV) dye from prepared aqueous solutions. The amount of adsorption dyes were investigated by including the effect of different parameters such as, the agented time, initial dye MV concentration (10-50 g.L^{-1}), effect of pH (3,6,8,10 and 12), temperature (288,308,328) K and adsorbent dosage (0.01-0.1g). The percentage of removal of MV by the CCAC is increased significantly with increasing the amount of the adsorbent and the solution pH, and the maximum was at pH 11.5, but its decreased with increasing the temperature and initial concentration of the dye. The two adsorption isotherm models (Langmuir and Freundlich) were used to investigate the interaction between the dye and prepared activated carbon, while the adsorption equilibrium data were best represented by the Freundlich detect the type of adsorption, which implies that the adsorption of textile dye onto the (CCAC) is heterogeneous with multi – layers.

Keywords: Activated carbon, Corn-cob, Methyl violet, Adsorption isotherm, Textile dye.

Introduction

Many textile industries are used dyes to color its products. Some of these dyes are stable and nontoxic when to discharge by receiving water, but other dyes are not.[1, 2] In either case, it is need to remove these dyes form the wastewaters because it is affected directly to the human health and environment[3, 4]. Adsorption is one of the most important techniques, which is carried out by chemical and physical process to separate and purificate by using adsorbent materials[4]. Activated carbon (AC) is one of the great adsorption materials due to micro-porous structure, highly degree of surface reactivity and high surface area, which is ranging from 500 to 3000 m^2/g. On the other hand, AC is still considering a high cost as adsorbent Material [5, 6]. AC has a different application as adsorbent materials, for instance, can be used in the wastewater industries treatment, pharmaceutical industries and sugar refining.[6] There is a great interest from researchers to investigate the production of the AC from the waste and cheap material such as wood,[7] orange peel,[8] coffee husk,[9] sunflower seed hull[10] and Coconut husk[11, 12].

Methyl violate (MV) is an organic dye with high intensity of color, and is used in a wide range in textile industries [13]. MV is a toxic and harmful cationic dye, and according to the many reports, this dye was directly affect to the human heath due to their irritation, carcinogenic and damage (eye) affect. Also this dye was affect to the aquatic live and environment [14-17]. Because of the harmful properties of this dye, it is important to remove it from wastewater of textile industries before being discharged to the environment.

This study aims at discovering the adsorption efficiency of AC which, prepared in previous work from cheap martial (corn-cob), as low-cost adsorbent for removing MV dye from prepared aqueous solution and applied different types of conditions, which represented by, concentration, contact time, temperature and pH. The adsorption isotherm models were also investigated.

Experimental

Preparation of different concentration of adsorbate and adsorbent.

For all experiments the solutions are prepared by using the deionized water and all other reagents are used in analytical grade. However, the solutions of

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MV are prepared from a stock solution of (1000 mg /L) to get the required concentrations (10, 20, 30, 40 and 50) mg/L for all work experiments Fig.1 is shown the chemical structure of MV dye.
The CCAC has been prepared from the plant source of Corn-Cob and all details of work showing in our previous work [19].

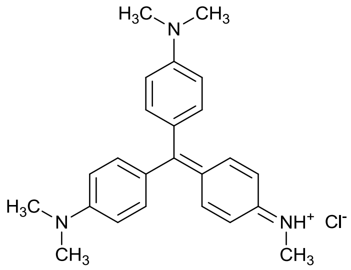

Fig. 1. The structure of methyl violet [18]

Adsorption Study

Batch adsorption experiments was performed by taking (100 mL) from the stock solution of the dye for all different concentrations and treated with (0.05 g) of CCAC. The flask were agitated onto water-bath shaker for 1 hour until equilibrium was achieved and after that the treatment samples were centrifuged, and measured at specific wavelength 582 nm using the UV/ vis. (Spectrophotometer shimadzu, 1650). The amount of MV dye up take onto the (CCAC) was calculated using the following mass balance equation [20, 21]:

$$q_e = \frac{(C_0 - C_e)V}{W} \qquad 1$$

where the q_e the amount of MV dye that adsorbed onto the surface of (CCAC) at equilibrium state in the, in mg/g D.W., C_0 and C_e are the intial and final concentrations of MV (M), respectively, W adsorbent weight (g) and V volume of solution (L).
On the other hand, the percentage removal %E of MV dye was calculated as shown below [20, 21]:

$$\%E = \frac{C_0 - C_e}{C_o} * 100 \qquad (2)$$

Effect of several parameters on the adsorption process of MV on to the CCAC
Effect of Initial MV dye concentration
The initial dye concentrations are carried in this work (10, 20, 30, 40 and 50) mg.L^{-1}onto the CCAC and shaking using the water-bath shaker at temperature of 308K and constant speed at130 rpm.

Effect of weight activated Carbone
To study the effect of the CCAC weight, several weight (0.01, 0.025, 0.05, 0.057, and 0.1) g was investigated at 308K, 130 rpm, 30 mg of (particle size 75 µm) Corn-cob (AC) concentration of (MV) dye (10–50) mg/L in100 mL.

Effect of pH
The effect of pH is studied using many solutions at several pH (3, 6, 8, 10, and 12) at 308 K, 130 rpm, 0.05 gm (particle size 75 µm) of CCAC, MV concentration. (10–50) mg.L^{-1} in 100 mL.

Effect of temperature
The other parameter can affect on the adsorption process is the temperature of solution therefore, this study is carried with different temperatures (288, 308, and 328) K using water-bath shaker at solution pH 6 at constant the agitation speed of 130 rpm and for 60 min contact time.

Adsorption isotherm
The adsorption isotherms refer to the relation between the equilibrium concentrations of a solute with the quantity adsorbed by a given amount of adsorbent at a particular temperature. However, the adsorption isotherm is consider very important to understand the interactions behaviour between adsorbate molecules (MV) and the adsorbent surface (CCAC) also its play an important role especially in the plan design and of any adsorption systems, as well as the analysis.
There are a different types of adsorption isotherms, and the adsorption isotherm that have been used in the present study included the Langmuir and Freundlich adsorption isotherms [22]. In the present study, the adsorption isotherm of MV dye by CCAC was studied at different temperatures 288, 308, and 328 K and the initial concentration of MV is fixed at 30 mg/L. The adsorption experimental data was expressed with Freundlich and Langmuir adsorption equation.
The Langmuir isotherm can be express mathematically as follows [22]:

$$\frac{C_e}{q_e} = \frac{C_e}{qm} + \frac{1}{K_L q_m} \qquad (3)$$

q_m is the maximum adsorption capacity for the adsorption process, K_L is Langmuir constant.
While Freundlich model isotherm can be express as shown in the following equation [22]:

$$\log qe = \log K_f + \left(\frac{1}{n}\right) \log C_e \qquad (4)$$

Results and Discussion
Effect of weight adsorbent (CCAC)

One of the most important parameters that can impacts the adsorption process is the weight or the dose of adsorbent that used. Hence, in this work the influence of the adsorbent dose CCAC on the adsorption process for removing the MV was investigated in the range of 0.01-0.1 g at 308K, while the volume and concentration of the dye solution is keeping constant. The results graphically represented in Fig. 2.

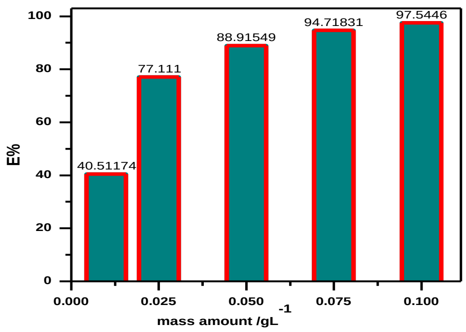

Fig.2. Relation between the percent removal of adsorbed MV and the weight of CCAC.

It can be seen from Fig. 2, that the percentage removal% of MV dye by the CCAC is directly proportional with CCAC dose, which is increased from 40.51% to 97.5% and this increasing in the values of percentage removal of the dye with the adsorbent dose it could be to an increase in the active site surface of the adsorbent, which will be available for the adsorption process as reported previously in other state [23, 24].

Effect of solution pH on adsorption

The effect of pH solution is playing a vital role of the adsorption of MV dye onto the surface of CCAC. However, the adsorption of MV was studied over a pH range of 3.5-11.5 as shown in Fig.3. The removal percentage of the MV by CCAC is significantly increase with increasing the solution pH, whereas the optimum adsorption of MV dye was achieved at pH 11.5 whereas the lowest adsorption at pH 3.5.

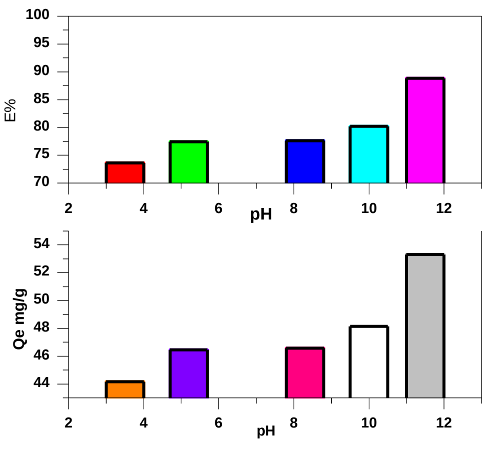

Fig. 3. Effect of the pH solution on to percentage of removal (E%) and amount of adsorbed MV on to the CCAC (methyl violet MV primary concentration 30 mg/L, Temp. = 308 K, and weight of adsorbent 0.05 g/L).

The solution pH has been affecting both the surface binding-sites of the adsorbent and the degree of ionization as well. The adsorption capacity (q_e) at pH 2 was minimum (44.1mg/g) and increase above to solution pH10, reached maximum (53.3mg/g) through the primary pH 3.5–11.5. When pH value is low, its easily to protonate the functional groups which are existing on the surface of adsorbent, then the adsorbent surface will have more of a positive charge, thus will lead to decrease the adsorption of the ions of the dye which have a positive charge as well through the effect of the repulsion forces. As the pH of the dye solution increases, then a proportional increase in the value removal percentage of the adsorption dye process and that due to the sequential deprotonation for the sites with a positive charge on the surface of adsorbent also the electrostatic attraction between the negative charged groups exist in the CCAC and MV cation [22].

Effect of initial methyl violet MV concentration and Temperature

Fig. 4 shows the effects of various initial concentrations on the adsorption process of MV dye by calculating the removal efficiency and adsorption capacity. The results shown that the adsorption capacity (qe) increases with increasing the initial concentration of MV dye, whereas the removal of percentage was decreased with increasing initial concentrations of MV dye, as result of the increasing of the MV concentration, the interaction which occur between the surface of adsorbent and the dye is increased and this will lead to increase the producer of adsorption process [25, 26].

On the other hand, the temperature effect on the adsorption process to remove the MV dye by the CCAC was studied at different temperatures (288, 308, and 328) K and the results shown in Fig.4. It observed that the temperature influenced the adsorption process by affecting on the value of the adsorption capacity which also increased, while percentage removal of the dye was decreased and that could be attributed to the weakening of the existing bonds between the functional groups of the dye molecules and the active sites of the adsorbent surface [27].

Adsorption isotherm

All the experimental parameters and their correlation coefficients that obtained from experiments have been tested using the two model of adsorption isotherms, Langmuir and Freundlich models and listed in Table.1 and shown in the Fig.5 that the adsorption of MV by CCAC followed the Freundlich isotherm because it's fitted the adsorption data best with the highest correlation ($R2 \geq 0.9941$).

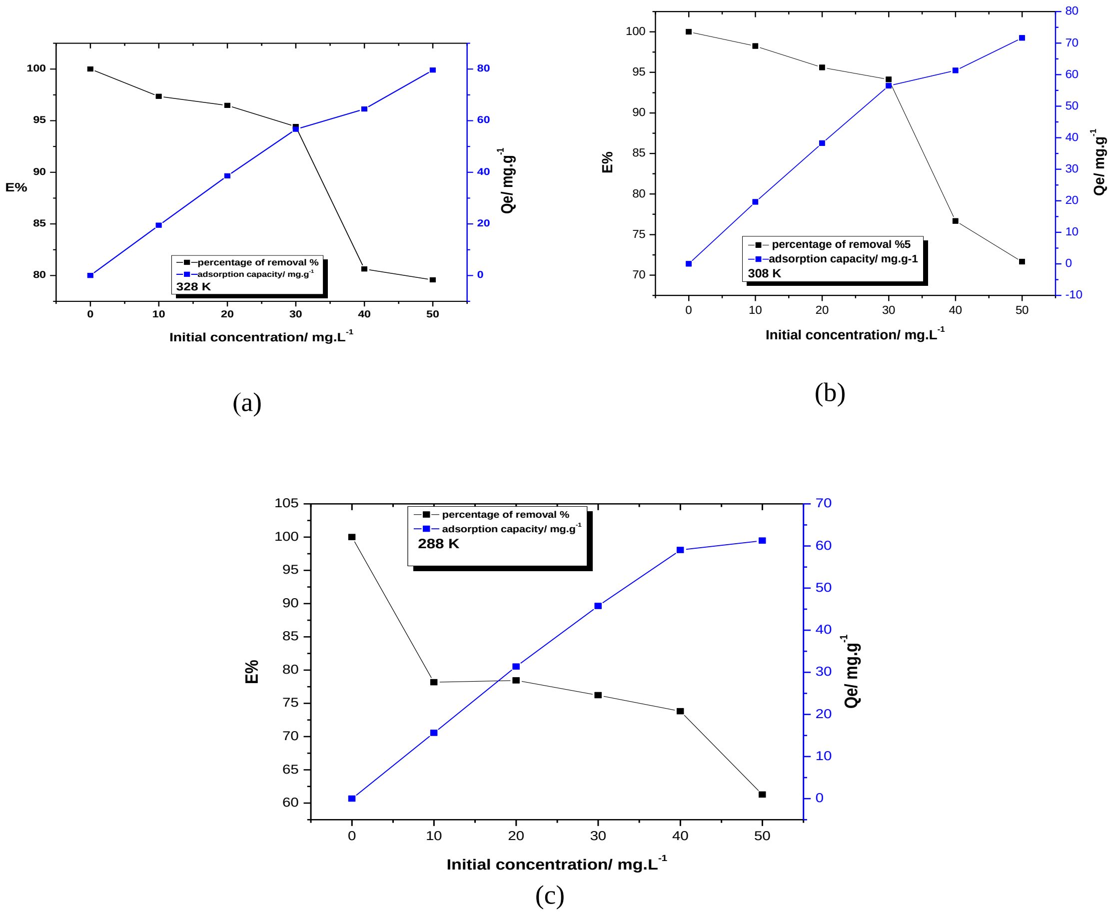

Fig. 4. Effect of initial concentration on to percentage removal and amount of adsorbed methyl violet MV dye on to CCAC at: a) 328 K, b) 308 K, c) 288 K (Exp. Condition: contact time 24 h, and solution pH 6)

Table 1: Thermodynamic parameters of MV dye on the surfsve of CCAC

T/K	Equilibrium Cons.	ΔS ($J.mol^{-1}.K^{-1}$)	ΔH ($KJ.mol^{-1}$)	ΔG ($kJ.mol^{-1}$)
288	1285.714286	49.71772	11.0227012	-16.84430307
308	1428.571429			-17.69616655
328	1612.244898			-18.60482808

Table 2. Modal factors for MV dye onto CCAC at 308 K

Adsorption isotherm models	**Parameters**	**MV dye**
Langmuir	qm ($mg.g^{-1}$)	40.8121±3.11175
	k_L($L.mg^{-1}$)	8.609 ± 3.5575
	R^2	0.888
Freundlich	k_F	27.3018 ±2.01855
	1/n	0.19368 ±0.03244
	R^2	0.9941

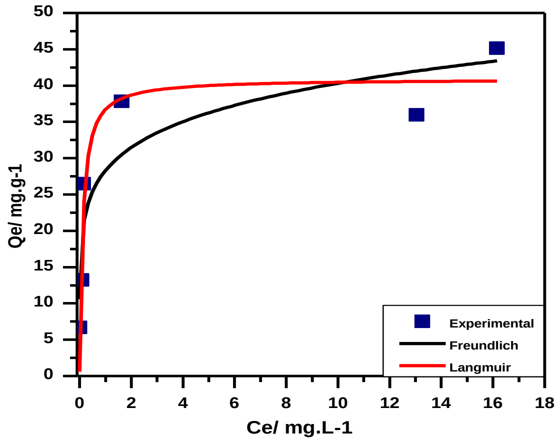

Fig.5. Adsorption isotherm models (Langmuir and Freundlich)

Conclusion

This study shows that the activated carbon which prepared from corn-cob is an effected the removal percentage of the MV from aqueous solutions and the amount of Methyl violet (MV) dye removed was dependent on adsorbent dose, the initial concentration, temperature and the pH of the solution as well. The adsorption process was depended on the temperature and the pH of the solution, whereas the MV is maximum adsorbed at pH=11.5. And the two adsorption isotherm models, Langmuir and Freundlich are used to describe the interaction behavior between the adsorbent and adsorbate and found that the adsorption of MV by CCAC followed the Freundlich isotherm because it's fitted the adsorption data best with the highest correlation (R2 ≥ 0.9941). In conclusion, the CCAC can be used for removing dye from aqueous solution because it's considering inexpensive, environmentally benign adsorbent for water purification and alternative.

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دراسة بحثية لإزالة صبغة الميثيل البنفسجي من المحاليل المائية باستخدام كوز الذرة كمصدر للكربون النشط

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الخلاصة

تعد الأصباغ العضوية من أكثر الملوثات للمياه، والتي تأتي عادة من صناعات النسيج والجلود والورق. في هذا العمل، يتم استخدام الكربون المنشط كسطح ماز، والذي يتم تحضيره من كوز الذرة لإزالة صبغة الميثيل البنفسجي (MV) من المحاليل المائية المحضرة. تم التحقق من كمية صبغات الامتزاز من خلال تضمين تأثير العوامل المختلفة مثل، عامل الوقت، تركيز الصبغة، تأثير الرقم الهيدروجيني (3، 6، 8، 10 و 12)، درجة الحرارة (288، 308، 328 كلفن) وكذلك جرعة الممتزات. تمت زيادة النسبة المئوية لإزالة MV بواسطة الكاربون الفعال بشكل كبير مع زيادة كمية المادة الماصة ودرجة الحموضة في المحلول، وكان الحد الأقصى عند الرقم الهيدروجيني 11.5، ولكنه انخفض مع زيادة درجة الحرارة والتركيز الأولي للصبغة. تم استخدام نموذجي متساوي الامتزاز (Langmuir وFreundlich) للتحقيق في التفاعل بين الصبغة والكربون المنشط المحضر، بينما تم تمثيل بيانات توازن الامتزاز بشكل أفضل بواسطة نموذج Freundlich، مما يعني ضمناً أن امتزاز صبغة النسيج على الكاربون النشط غير متجانس مع الطبقات المتعددة.