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Adsorption of methylene blue dye from industrial wastewater using activated carbon prepared from agriculture wastes

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ABSTRACT

The aim of the present work is to investigate the ability of activated carbon prepared from agriculture wastes (date palm fibers) (ACDPF) for the adsorption of methylene blue (MB) dye from industrial wastewater. To study the effect of factors affecting the removal efficiency of MB, experiments were conducted under a constant temperature. The batch adsorption process was examined at different parameters of initial MB dye concentration (100–1,000 mg/L), ACDPF dose (0.1–1 g/100 mL), pH (2–10), and mixing time (10–150 min). The optimum operating conditions of initial MB dye, ACDPF dose, pH, and mixing time were 100 mg/L, 0.7 g per 100 mL dye solution, 7, and 120 min, respectively. At the optimum conditions, the maximum removal efficiency was 98% and the adsorption capacity was 120 mg/g. The equilibrium data were analyzed using the Langmuir and Freundlich isotherm models. The data fitted very well into both isotherm models. The adsorption process for the removal of MB dye was proven favorable for monolayer on the surface of ACDPF.

Keywords: Agriculture wastes; Isotherm; Recycling; Removal; Wastewater

1. Introduction

In recent decades, dyes are commonly used in different applications such as textile, leather, paper, and plastic industries. The discharge of dye wastewater contains harmful compounds since it affects human health and marine life in rivers and lakes by decreasing light penetration. Methylene blue (MB) dye has been widely used in the dyeing of leather, cotton, and paper.

There are many methods for treating industrial wastewater effluents with synthetic dyes such as photocatalytic degradation [1,2], electrochemical degradation [3], electrocoagulation [4], and ion exchange [5], however, these methods cannot effectively treat wastewater content. On the other hand, the adsorption method can represent the best method to remove dye wastewater. Adsorption process has been proven to be a superior method for the treatment of industrial wastewater over other techniques. Moreover, it can represent a costly way if the adsorbent material used is expensive and not available [6]. Some of the researchers used polymeric bio-composites for efficient removal of acid black dye [7], sol–gel synthesis for the adsorption of Turquoise-Blue X-GB Dye [8], biogenic synthesis of nanoparticle for degrading Congo red [9], and biomass composite for removal of different dyes [10]. The other researchers used agriculture wastes without further chemical treatment like using date palm fiber (DPF)/rice husk/sawdust for adsorption methyl orange dye [11].

In recent decades, a lot of studies have used activated carbon as an adsorbent material for effective treatment but its high cost makes the process not economical. Recently, many researchers have undertaken the development of an eco-friendly and economic activated carbon derived from agriculture wastes [12–15].

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The objective of this study is to examine the ability of activated carbon which is derived from DPFs for adsorption of MB dye from industrial wastewater and to obtain a mathematical model for removal efficiency that assess the effect of four main operating factors such as the initial concentration of MB dye, agriculture wastes (date palm fibers) ACDPF dose, pH solution, and mixing time on this removal. The results were analyzed to obtain the optimum conditions that give higher adsorption uptake of MB dye. Finally, the equilibrium results were analyzed with Langmuir and Freundlich isotherm models to examine the fitness.

2. Materials and methods

2.1. Materials

DPF were used as precursors that were obtained from local agriculture orchards which locate at Al-Samawa city, Iraq. To prepare the adsorbent for the experimental work, it was removed the dust particles and color by washing continuously in water and then in double distillate water until the effluent water became clear. Next, the fibers were dried under the sun and then in an oven at 70°C for a period of time 24 h. The activated carbon of DPF was prepared by three steps. At first, DPF were crushed, milled, and sieved to obtain fiber particle size in the ranges between 1 and 2 mm using (Besmak Sieves, Turkey). Secondly, it was carbonized in a furnace at 600°C for 1 h, then it was cooled at room temperature. The final step represents chemical activation by impregnating DPF in KOH solution (45% purity) with IR ratio (2 KOH:1 DPF) w/w followed by heating under nitrogen gas into the microwave for 1 h. The activated carbon produced was cooled at room temperature and washed with hot double distillate water until the washing solution became neutral pH. The final activated carbon produced was dried in an oven at 100°C for 24 h, and stored in a glass container for future use. The properties of prepared ACDEF are listed in Table 1. According to the previous literature, activated carbon was prepared under these conditions, which represent the best operational conditions for preparing activated carbon from agricultural wastes [15].

2.2. Chemical

The test solution of MB dye with the formula ($C_{16}H_{18}N_3SCl$) is represented by a basic dyestuff which was prepared by adding an accurate amount of MB dye (1 g) (99% purity) to double-distillate water in (1,000 mL) to obtain an aqueous solution with a concentration of (1,000 mg/L) MB dye. The desired MB dye concentration for the experiment was got by adding an accurate amount of distillate water using the dilution equation to the stock solution. A digital meter (model 2906, Jenway Ltd., UK) was used to adjust the pH solution by adding drops of either 0.01 N NaOH (97% purity) or 0.01 N HCl (37% purity). All chemicals used in the experimental studies were supplied by Merck Chemical Company, Germany.

Table 1
Physical properties of ACDPF

Surface area (m^2/g)	653
Pore volume (cc/g)	0.17
Yield (%)	34.8
Carbon (%)	82.37
Hydrogen (%)	1.15
Nitrogen (%)	0.14

2.3. Adsorption method

The isotherm batch experiments were carried out at a temperature range of 30°C ± 1°C by adding various amounts (0.1–1 g) of activated carbon prepared from agricultural wastes to 100 mL of aqueous MB dye solution at various initial concentrations (100–1,000 mg/L) along with changing of the acidity of the test solution (2–10) and contact time (10–150 min). A test flask of 250 mL was placed on a magnetic stirrer with a constant rotation of 150 rpm. The experiments were designed statistically using the Box–Wilson method. At the end of each experiment, a sample of 2 mL of MB dye solution was withdrawn at a specific time using a syringe to determine the final concentration of dye then filtered through Whatman filter paper. The equilibrium concentration of MB dye at the end of each experiment was determined by UV spectrophotometer (Shimadzu UV/V is 1800 spectrophotometer, Japan) at a wavelength of 664 nm. To calculate the percentage of removal efficiency, use Eq. (1):

$$\%R = \frac{C_0 - C_e}{C_0} \times 100 \quad (1)$$

The adsorption capacity of MB dye adsorbed on activated carbon at the equilibrium contact time, q_e (mg/g), was calculated using Eq. (2):

$$q_e = \frac{V \cdot \left(C_0 - C_e\right)}{W} \quad (2)$$

where C_0 (mg/L) in the above equations represents the initial concentrations of MB dye whereas C_e (mg/L) represents the equilibrium concentration of MB dye at the end of each experiment. The volume of the test solution is represented by V (L) and the weight of ACDPF used in the experiment is represented by W (g).

3. Results and discussion

The experimental results are analyzed to obtain a mathematical model which is describing the percentage of removal efficiency of MB dye on ACDPF at tested operating factors. The statistical analysis of the results obtained from experimental work was analyzed using STATISTICA version 7 to find the optimal values to obtain the highest removal efficiency of the MB dye. The mathematical model that includes the tested operating parameter such as initial MB dye concentration (X_1), ACDPF dose (X_2), pH (X_3), and mixing time (X_4) is shown in Eq. (3):

$$\begin{aligned}\%\ \text{Removal efficiency} = {} & 37.3815 + 0.0133847X_1 + 24.34597X_2 \\ & + 9.81498X_3 + 0.235969X_4 - 0.00001X_1^2 - 44.2387X_2^2 \\ & - 0.622396X_3^2 - 0.0004X_4^2 - 0.006173X_1X_2 - 0.000972X_1X_3 \\ & - 0.000056X_1X_4 + 3.194444X_2X_3 + 0.150794X_2X_4 \\ & - 0.027679X_3X_4 \end{aligned} \quad (3)$$

Correlation coefficient (R) = 0.9808;

Variance explained (S) = 96.2%;

To obtain the optimum values of tested parameters, optimizing the mathematical model by using a statistical program which has given the following optimum values:

- X_1^*: optimum initial MB dye concentration = 100 mg/L
- X_2^*: optimum ACDPF dosage = 0.7 g
- X_3^*: optimum pH = 7
- X_4^*: optimum mixing time = 120 min

At these optimum values, the maximum removal efficiency (% R) was 98% and the adsorption capacity of MB dye adsorbed (q_0) was 120 mg/g.

3.1. Effect of initial MB dye concentration

The initial concentration of MB dye can be considered a primary factor that affected the adsorption process. Thus, to evaluate the influence of this factor on the removal efficiency, the experiments were designed to study this factor by varying ACDPF dose (0.1–1 g/100 mL) and optimum values of pH at 7 and mixing time at 120 min. The experimental results were analyzed to obtain a mathematical model as shown in Eq. (3) that describes these effects, then were plotted in Fig. 1.

The results indicate that the removal efficiency, as well as the adsorption capacity of MB dye, decreases slightly with increasing initial dye concentration. The maximum removal efficiency was noticed at the 100 mg/L of MB dye concentration, while after that the removal efficiency decreased due to the decreasing of vacant sites and accumulation of MB dye molecules on the surface of ACDPF. This result is a similar phenomenon that was noticed in the removal of textile dye on different agricultural wastes [16].

Fig. 2 illustrates the impact of the initial concentration of dye on the removal efficiency by changing of pH range between 2 and 10 at an optimum ACDPF dosage of 0.7 g/100 mL and contact time of 120 min. The maximum removal efficiency of MB dye is established at a neutral medium of test solution (pH = 7).

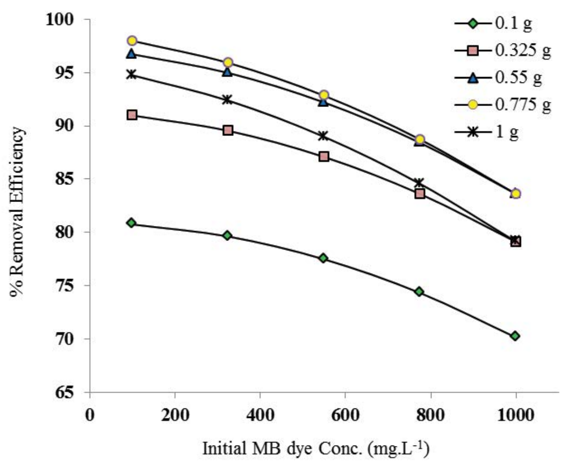

Fig. 1. Effect of initial MB dye concentration at different ACDPF dose.

Fig. 3 shows the effect of contact time (10–150 min) at optimum values, ACDPF dose of (0.7 g/100 mL), and pH value of 7. In Fig. 3 as is clearly illustrated, the percentage of MB dye removal decreases when the initial MB dye concentration was increasing.

3.2. Effect of ACDPF dose

The influence of the ACDPF dose on the removal efficiency of MB dye was illustrated in Figs. 4–6. It can be seen from these figures that the removal percentage increases with increasing ACDPF dosage until an optimal ACDPF dose of 0.7 g/100 mL was reached, after this point, the removal of MB dye curves were nearly continuous in smooth lines which indicated reaching saturation of ACDPF surface by MB dye molecules. This result is similar to that noticed for almost all previous studies such as the removal of MB on rejected tea [17] and on treated marble powder [18].

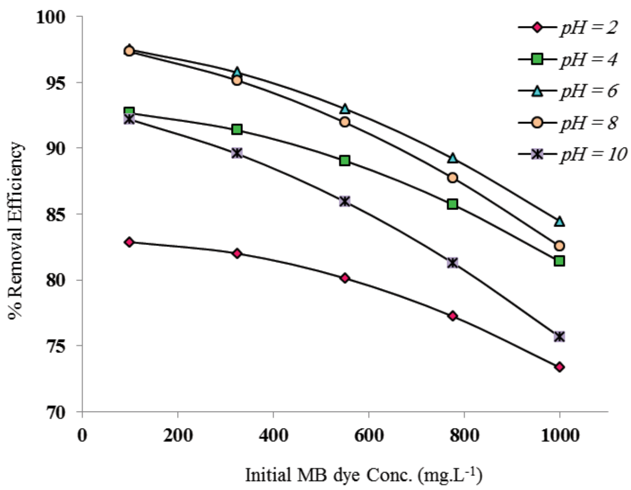

Fig. 2. Effect of initial MB dye concentration at different pH.

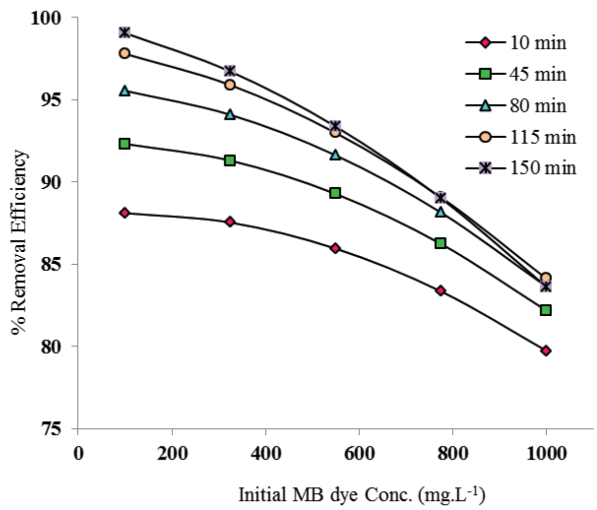

Fig. 3. Effect of initial MB dye concentration at different contact time.

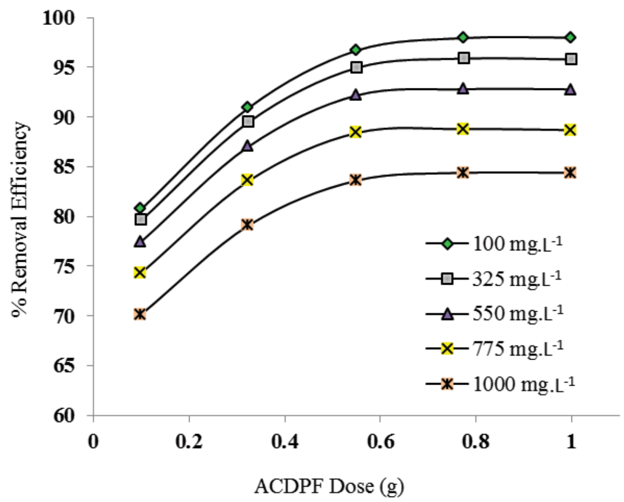

Fig. 4. Effect of ACDPF dose at a different initial MB dye concentration.

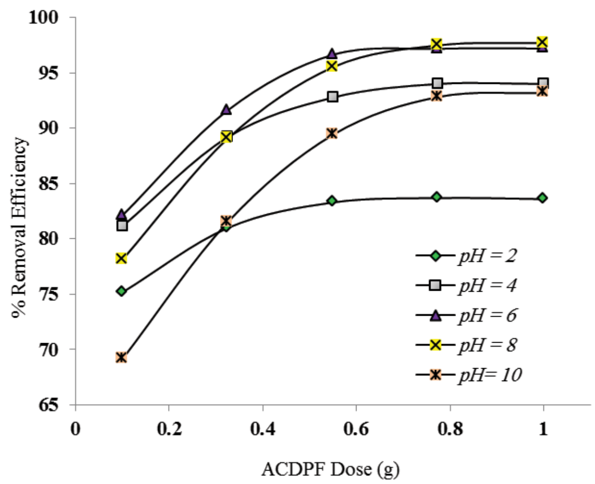

Fig. 5. Effect of ACDPF dose at different pH.

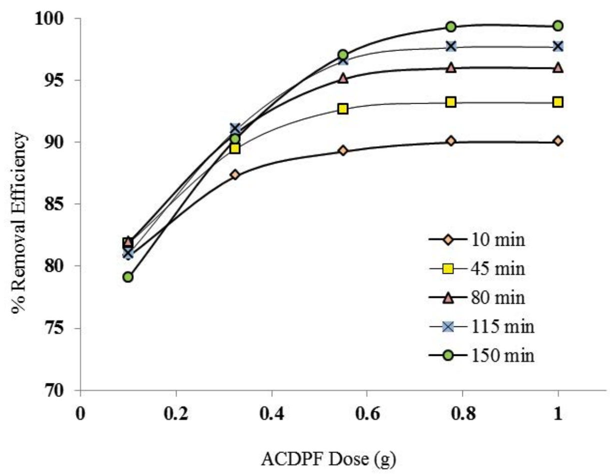

Fig. 6. Effect of ACDPF dose at different contact time.

3.3. Effect of pH

The pH parameter can be considered an important factor to control adsorption processes as shown in Figs. 7–9 which show the influence of pH on the removal efficiency of MB dye at different initial MB dye concentrations, ACDPF dose, and mixing time, respectively, with the optimum conditions of other operating factors. From Figs. 7–9, the capacity of MB dye removal increases rapidly with the increasing pH of the test solution. The maximum removal efficiency is established at a neutral solution medium (pH = 7), the low adsorption capacity at the acidic medium can be attributed to competition of MB dye cation with an excess amount of H^+ ions in the MB dye solution. After this point, with an increasing pH value of the test solution, the adsorption capacity decreases again with increasing of pH value. This result can be ascribed to the electrostatic attraction. This phenomenon is similar to that reported for removal of MB dye on rejected tea [17], on rice husk [19], and on garlic peels [20].

3.4. Effect of contact time

One of the most important factors that must be studied in adsorption processes is the contact time. These influence

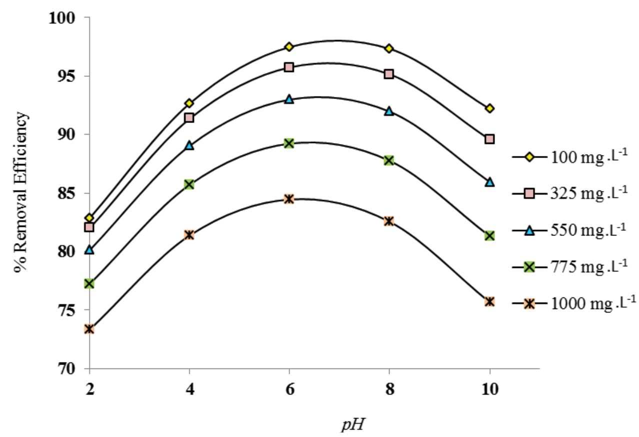

Fig. 7. Effect of pH at a different initial MB dye concentration.

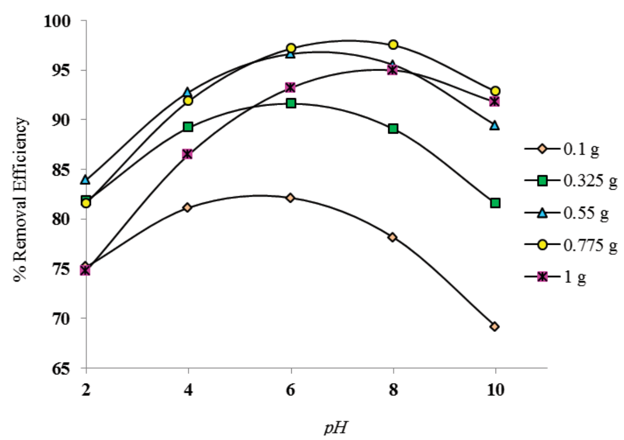

Fig. 8. Effect of pH at different ACDPF dose.

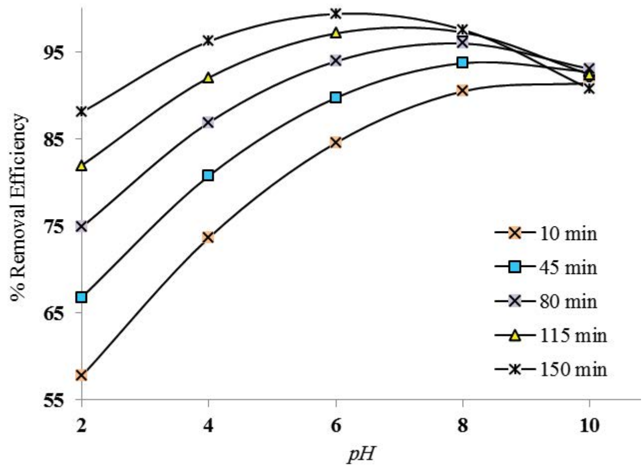

Fig. 9. Effect of pH at different contact time.

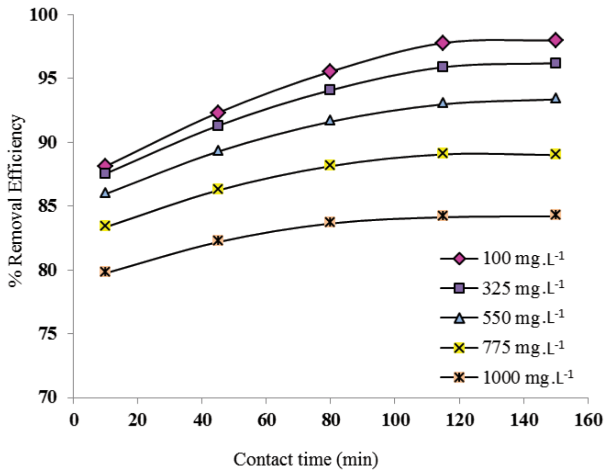

Fig. 10. Effect of contact time at a different initial MB dye concentration.

on the removal of MB capacity was studied at different initial MB concentrations (Fig. 10), ACDPF dose (Fig. 11), and pH (Fig. 12).

Figs. 10–12 show that the removal efficiency, as well as the adsorption capacity of MB dye, increases with increasing contact time and equilibrium was reached at 120 min for all examined factors. The rapid increase of removal efficiency at the first contact time intervals can be attributed to available more vacant sites on the surface of activated carbon. After this period, the curves were continuous in a straight line which represented reaching an equilibrium state due to saturation of vacant sites on the surface of adsorbent with MB dye molecules. These results are quite similar to those in other previous studies such as an equilibrium contact time of 120 min for removal of MB on rejected tea [20].

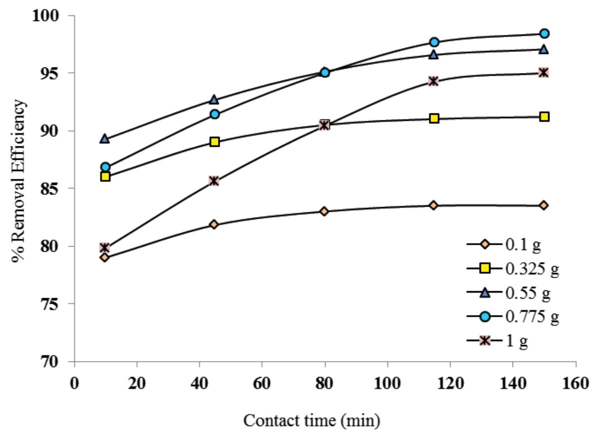

Fig. 11. Effect of contact time at different ACDPF dose.

3.5. Adsorption isotherm models

To illustrate the distribution of MB dye molecules on the surface of ACDPF adsorbent at equilibrium state, the standard adsorption isotherm models were used to describe this distribution. The best popular adsorption isotherm models are Langmuir and Freundlich which were used to describe the distribution of MB dye molecules on the ACDPF surface at optimum conditions of examined parameters. The Langmuir model is a linear form which represents monolayer dye sorption on to ACDPF surface as shown in Eq. (4) [21]:

$$\frac{1}{q_e} = \frac{1}{q_0} + \frac{1}{q_0 \cdot K_1} \cdot \frac{1}{C_e} \tag{4}$$

Eq. (4) contains Langmuir constants which are represented by q_0 and K_l. C_e is the final concentration of MB dye at equilibrium time and q_e is the equilibrium adsorption capacity of the adsorbent. It can be estimated the Langmuir constants by plotting $1/q_e$ against $1/C_e$ and then the value of q_0 can be obtained from intercept and K_l from the slope. Fig. 13 illustrates the equilibrium data which were obtained from a mathematical model plot of $1/q_e$ against $1/C_e$.

The Langmuir correlation coefficient (R^2) of this equation was (0.9971). The experimental data were fitted with

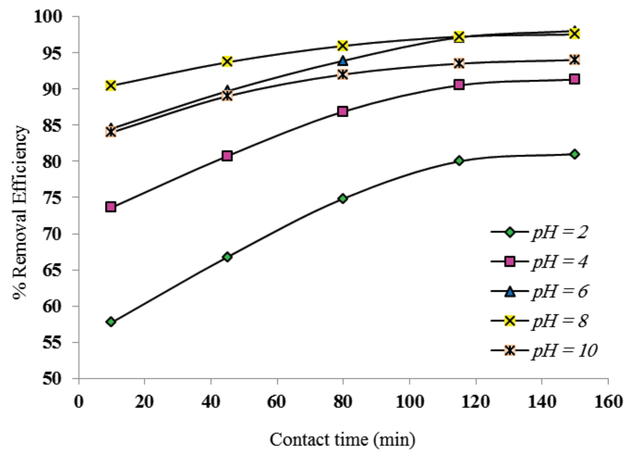

Fig. 12. Effect of contact time at different pH.

the Langmuir model with a high value of correlation coefficient. R_L is a dimensionless constant of separation factor for equilibrium factors that indicate the favorability of using

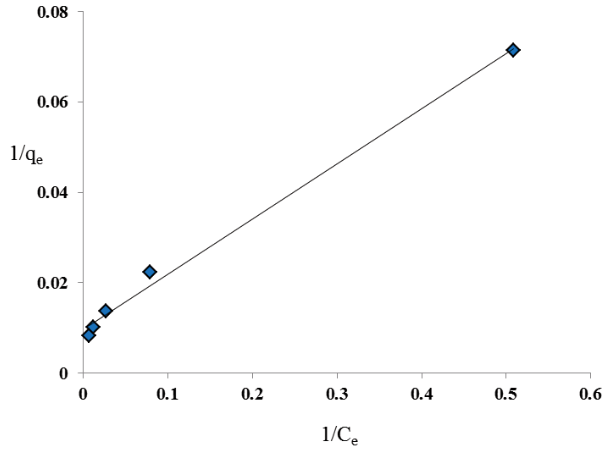

Fig. 13. Langmuir isotherm for adsorption of MB dye.

ACDPF for adsorption of MB dye when its value lies between ($0 < R_L < 1$). R_L can evaluate its value by applying Eq. (5) [6]:

$$R_L = \frac{1}{1 + K_l \cdot C_0} \quad (5)$$

Fig. 14 illustrates the values of R_L which confirmed that the ACDPF is favorable for the removal of MB dye at optimum operating conditions.

The Freundlich model has represented a non-uniform distribution of MB dye on the heterogeneous surface of ACDPF as shown in Eq. (6) [22]:

$$\ln q_e = \ln K_f + \frac{1}{n} \cdot \ln C_e \quad (6)$$

where K_f has represented the Freundlich constant which is mean the adsorption capacity whereas the n is represented the intendancy of adsorption that measures the heterogeneity of the adsorbent surface whenever its value

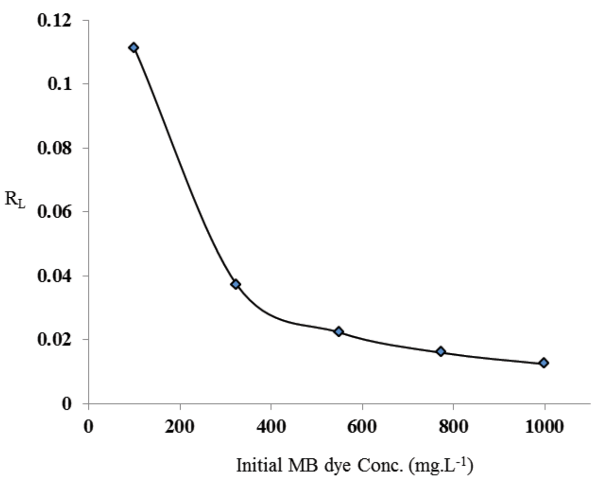

Fig. 14. Separation factor for MB dye adsorption.

close to zero [20]. Fig. 15 illustrates the experimental data of $\ln q_e$ against $\ln C_e$.

From this figure, we can obtain the values of K_f from its intercept and the value of $1/n$ from its slope. The Freundlich model is fitted very well with equilibrium data at a correlation coefficient of "0.9914." The constants of Langmuir and Freundlich models are presented in Table 2.

The maximum adsorption capacity of MB dye on different agriculture wastes are listed in Table 3.

It is clearly noticed that ACDPF is proven to be an efficient material for the adsorption of MB dye from wastewater compared with other adsorbents in previous studies which were found in the literature. Fig. 16 shows the relationship between the removal efficiency of MB dye

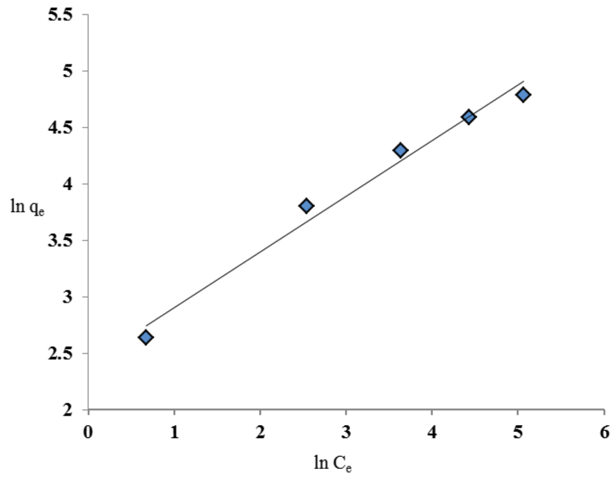

Fig. 15. Freundlich isotherm for adsorption of MB dye.

Table 2
Constants of adsorption isotherm models

Langmuir constants			Freundlich constants		
q_0	K_l	R^2	K_f	n	R^2
102.3	0.0800	0.997	11.16	0.4918	0.9914

Table 3
Adsorption capacity of different agriculture waste adsorbents

Adsorbent	q_{max} (mg/g)	Reference
Activated carbon from date palm fibers	120	This study
Activated carbon from wood	200	[23]
Activated carbon from coffee waste	185.7	[24]
Tea waste	85.16	[22]
Rice husk	40.59	[25]
Banana peel	20.8	[26]
Wheat shells	16.56	[27]

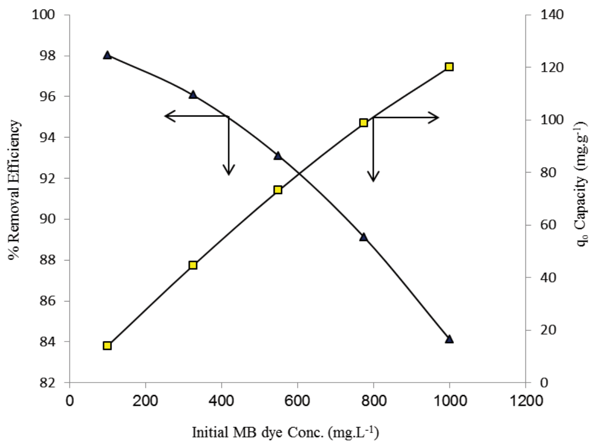

Fig. 16. Removal efficiency and the maximum adsorption.

on ACDPF at the optimum conditions and the maximum amount of MB dye adsorbed.

4. Conclusion

The ability of activated carbon prepared from ACDPF to remove methylene blue (MB) from industrial wastewater was proved. Activated carbon was prepared by carbonization of date palm fibers at 600°C followed activation using KOH solution then it was heated under nitrogen gas. The mathematical model was obtained to describe the ability of using ACDPF for removing of MB dye and to study the effect of tested parameters that examined like initial MB dye concentration, ACDPF dose, pH, and contact time on the removal capacity. The statistical analysis was conducted to get optimum values of operating parameters for maximum removal dye efficiency. The equilibrium results were fitted with a high correlation coefficient and it was satisfied with both Langmuir and Freundlich isotherm models.

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