



## Removal of cationic dye from aqueous solution using melon peel as nonconventional low-cost sorbent

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### ABSTRACT

The ability of melon peel (*Cucumis melo L.*) (MP) for the biosorption of methylene blue (MB), a cationic dye, from aqueous solutions was investigated. Biosorption isotherm and kinetics of MB by MP were studied through a number of batch sorption experiments. The influence of operating conditions such as initial dye concentration, biosorbent dose, initial pH, stirring speed, temperature, and ionic strength on the removal of MB was examined. Equilibrium data were fitted to the Langmuir, Freundlich, and Temkin isotherm models. Experimental equilibrium data were best represented by the Langmuir isotherm with maximum monolayer sorption capacity of  $333 \text{ mg g}^{-1}$ . Biosorption kinetic obtained at different initial concentrations were analyzed using pseudo-first-order and pseudo-second-order equations. The pseudo-second-order model fit the kinetic data well and was better than the pseudo-first-order equation. The results revealed that the MP has the potential to be used as a biosorbent for the removal of MB from aqueous solutions.

*Keywords:* Biosorption; Methylene blue; Melon peel; Modeling; Kinetics; Isotherm

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### 1. Introduction

There are more than 100,000 types of dyes commercially available, with over  $7 \times 10^5$  tons of dyestuff produced annually, which can be classified according to their structure as anionic and cationic [1]. Dye removal from industrial effluents has been the subject of great attention in the last few years. Approximately, 10–15% of the overall production of dyes is released into the environment, mainly via wastewater [2]. The presence of low concentration of dyes in the effluent streams is highly visible and undesirable and it reduces the light penetration which leads to inhibit-

ing photosynthesis and stringent restrictions on the organic content of industrial effluents.

Methylene blue (MB) is selected as a model compound in order to evaluate the capacity of sorbents for the removal of dye from its aqueous solutions. MB is an important basic dye widely used for printing calico, dyeing, printing cotton and tannin, indicating oxidation-reduction, and dyeing leather, and in purified zinc-free form; it is also used as an antiseptic and for other medicinal purposes. Although, not strongly hazardous, MB can have various harmful effects. The dye causes eye burns, which may be responsible for permanent injury to the eyes of human and animals. If swallowed, the dye causes irritation to the

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gastrointestinal tract with symptoms of nausea, vomiting, and diarrhea. It may also cause methemoglobinemia, cyanosis, convulsions, tachycardia, and dyspnea, if inhaled. It is likely to cause irritation to the skin [3]. Hence, it is necessary to remove MB from wastewaters.

Various conventional methods of color removal from wastewater have been used. These include biological and physical-chemical process. However, these processes are difficult to handle and are not always effective and economical. Biosorption technology offers an efficient and cost-effective alternative compared to traditional chemical and physical remediation and decontamination methods [4–7]. The major advantages of this method include: low cost, high efficiency, minimization of chemical or biological sludge, no additional nutrient requirement, and possibility of effluent recovery [8–14]. A number of low cost biosorbents have been studied in the literature for their capacity to remove MB from aqueous solutions [15–22].

MP exhibits excellent sorption ability and it has been successfully used for the removal of cadmium from aqueous solutions [23]. Thus, utilizing MP for the removal of a cationic dye, MB, is an innovative idea for the water treatment process.

In this work, the potential of melon peel (MP) as novel biosorbent for the removal of MB from aqueous solution was investigated in batch processes. Kinetic data and equilibrium isotherms were determined and analyzed. The effects of various experimental parameters such as initial MB concentration, initial solution pH, stirring speed, biosorbent dose, temperature, and ionic strength on MB biosorption were examined. The biosorption data were analyzed and modeled using different models by linear regression method.

## 2. Materials and methods

### 2.1. Sorbate and biosorbent

The cationic dye, MB ( $C_{16}H_{18}N_3SCl$ ), was obtained from Sigma–Aldrich with analytical grade that was used without further purification. Required amount of dye was dissolved in distilled water to prepare  $1,000\text{ mg L}^{-1}$  stock solution that was later diluted to required concentrations.

The MP was collected in summer from the region of Batna (Algeria). The MP was dried at ambient air hangs 2–3 days and then it was ground and sieved using a vibrating sieve (diameter between 0.5 and 1 mm). The obtained material was washed several times with distilled water until the disappearance of

the color of the wash water. The MP was then dried at  $50^\circ\text{C}$  in an oven for 12 h and then cooled in a desiccator and packaged in sealed bottles.

### 2.2. Procedures

The initial concentration of MB solution was  $50\text{ mg L}^{-1}$  for all experiments, except for those carried out to examine the effect of initial dye concentration. For dye removal kinetic experiments, the batch method was used because of its simplicity. About 0.4 g of biosorbent was contacted with 200 mL of dye solution in a sealed agitated flask and the temperature was maintained constant using a water bath. The stirring speed was kept constant at 300 rpm, except for experiments carried out to investigate the effect of stirring speed. At predetermined intervals of time, samples of the mixture were withdrawn at suitable time intervals and analyzed by a UV–vis spectrophotometer (Jenway 6,405) for the concentration of MB.

Sorption equilibrium experiments were carried out by adding a fixed amount of MP (0.4 g) into a number of sealed glass flasks containing a definite volume (200 mL in each case) of different initial concentrations ( $25\text{--}500\text{ mg L}^{-1}$ ) of MB solution without changing their pH. The flasks were placed in a thermostatic water bath in order to maintain a constant temperature (25, 35, 45, or  $55^\circ\text{C}$ ) and stirring was provided at 300 rpm to ensure equilibrium was reached. Samples of solutions were analyzed for the remaining dye concentration with a UV–vis spectrophotometer.

## 3. Results and discussion

### 3.1. Effect of initial MB concentration

Fig. 1 shows the sorption uptake vs. the contact time at various initial MB concentrations at  $25^\circ\text{C}$ . The plots showed that the sorption of MB increases with time until it reached a constant value beyond which no more MB was further removed from the solution. The results revealed that the biosorption was fast at the initial stages of the contact period, and slowed down near equilibrium. The high sorption rate at the beginning of sorption was due to the sorption of dye molecules by the exterior surface of the biosorbent. When saturation was reached at the exterior surface, the MB molecules entered the pores of sorbent and were sorbed by the interior surface of the particles. The initial faster rates of sorption may also be attributed to the presence of large number of binding sites for sorption and the slower sorption rates at the end is due to the saturation of the binding sites and attainment of equilibrium. The necessary time to reach

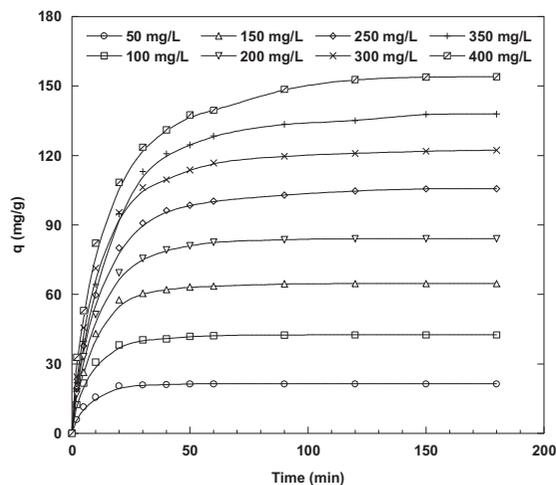


Fig. 1. Kinetics of MB uptake by MP for various initial dye concentrations (conditions: biosorbent dosage = 0.4 g (200 mL)<sup>-1</sup>; stirring speed = 300 rpm;  $T = 25^\circ\text{C}$ ; pH 5.3).

equilibrium is variable according to the initial dye concentration, about 50 min for 50 mg L<sup>-1</sup>, 60 min for 100 mg L<sup>-1</sup>, 90 min for 150 mg L<sup>-1</sup>, 120 min for 200 mg L<sup>-1</sup>, 150 min for 250 and 300 mg L<sup>-1</sup>, and 180 min for 350 and 400 mg L<sup>-1</sup>.

From Fig. 1 it was also shown that the biosorption of MB increased with increasing initial dye concentration, the amount of dye removed at equilibrium increased from 21.82 to 145.5 mg g<sup>-1</sup> with the increase in dye concentration from 50 to 400 mg L<sup>-1</sup>. This is due to increasing concentration gradient, which acts as increasing driving force to overcome all mass transfer resistances between the aqueous solution and solid phase [24].

### 3.2. Effect of solution initial pH

Fig. 2 shows the effect of initial pH on the sorption of MB by MP. It can be seen that the sorption decreases with the decrease in initial pH. As the pH of the system decreased, the number of negatively charged sorption sites decreased and the number of positively charged surface sites increased, which did not favor the sorption of positively charged dye cations due to electrostatic repulsion. At low pH values (2 and 3), the surface of sorbent is positively charged (pH < p*H*<sub>PZC</sub> = 4.2). This leads to electrostatic repulsion between the sorbent surface and MB cations. Additionally, lower sorption of MB at acidic pH is due to the presence of excess H<sup>+</sup> ions competing with dye cations for the sorption sites of MP.

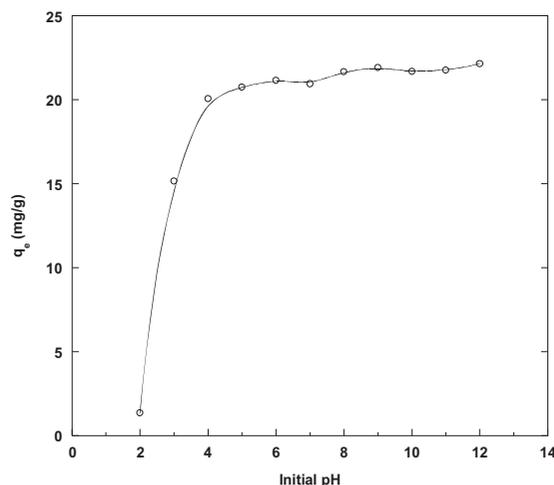


Fig. 2. Effect of initial pH on the biosorption capacity of MB (conditions: initial dye concentration = 50 mg L<sup>-1</sup>; biosorbent dosage = 0.4 g (200 mL)<sup>-1</sup>; stirring speed = 300 rpm;  $T = 25^\circ\text{C}$ ).

As shown in Fig. 2, the equilibrium uptake of dye increased notably with raising the pH from 2 to 4. Above this level, the sorption capacity did not change significantly up to pH 12. At higher pH, the sorbent surface is negatively charged which enhances the sorption of positively charged dye ions through electrostatic forces of attraction. Similar trend was reported for the sorption of MB by *Posidonia oceanica* (L.) fibers [25].

### 3.3. Effect of stirring speed

Agitation is a classic parameter in sorption phenomena, influencing the distribution of the solute in the bulk solution and the formation of the external boundary film [26]. Fig. 3 shows the sorption of MB by MP at different stirring speeds ranging from 0 (without stirring) to 600 rpm. The obtained results show that the higher sorption capacity was obtained for a stirring speed of 300 rpm. This agitation speed assures a good diffusion of dye cations toward biosorbent particles.

For the experiment conducted without agitation, a significant reduction in the sorption rate and capacity was noticed. The equilibrium time decreases from 25 to 1 h when the stirring speed increases from 0 (without stirring) to 300 rpm. When increasing the agitation speed, the diffusion rate of dye molecules from the bulk liquid to the liquid boundary layer surrounding particles became higher because of an enhancement of turbulence and a decrease of the thickness of the liquid boundary layer. The insignificant effect of

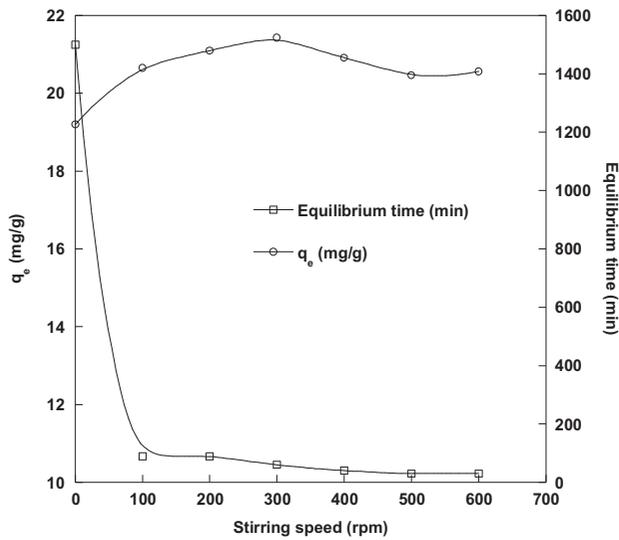


Fig. 3. Effect of stirring speed on the equilibrium time and biosorption capacity of MB by MP (conditions: initial dye concentration =  $50 \text{ mg L}^{-1}$ ; biosorbent dosage =  $0.4 \text{ g (200 mL)}^{-1}$ ;  $T = 25^\circ\text{C}$ ; pH 5.3).

agitation for the range 300–600 rpm can be attributed to the strong turbulence and the very small thickness of the boundary layer around the biosorbent particles and an induction in the mobility of system.

#### 3.4. Effect of biosorbent dosage

The effect of biosorbent dosage on the removal of MB is illustrated in Fig. 4. The result shows that an

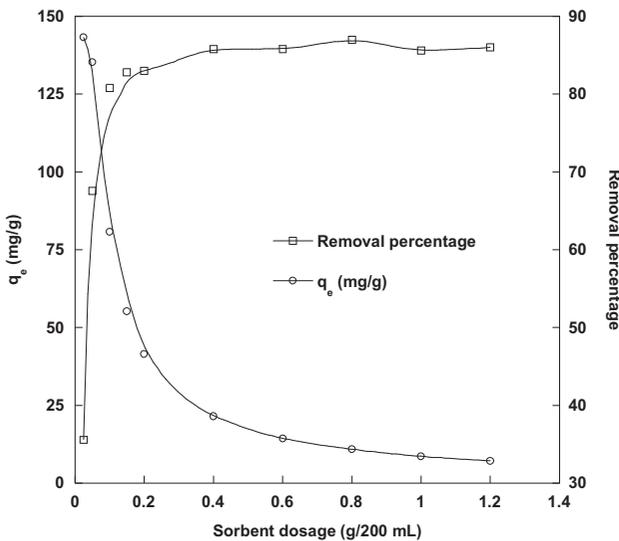


Fig. 4. Effect of biosorbent dosage on the removal and sorption capacity of MB by MP (conditions: initial dye concentration =  $50 \text{ mg L}^{-1}$ ; stirring speed = 300 rpm;  $T = 25^\circ\text{C}$ ; pH 5.3).

increase in the biomass quantity causes a decrease in the residual MB concentration at equilibrium time and consequently an increase in the biosorption removal efficiency. Indeed, the biosorption removal efficiency values increased from 35.6 to 86% as the sorbent dose was increased from 0.025 to  $1.2 \text{ g/200 mL}$ . Such a trend is mainly attributed to an increase in the sorptive surface area and the availability of more sorption sites. Quite similar tendency was reported for MB adsorption onto fly ash [27].

On the other hand, the amount of sorbed dye per unit mass of sorbent decreased with the increase in sorbent dosage. The biosorption capacity values decreased from  $143.2$  to  $7.2 \text{ mg g}^{-1}$  as the sorbent dose was increased from 0.025 to  $1.2 \text{ g/200 mL}$ . The decrease in the amount of dye sorbed with increasing sorbent mass is due to the split in the flux or the concentration gradient between solute concentration in the solution and the solute concentration in the surface of the sorbent. Thus, with increasing sorbent mass, the amount of dye sorbed onto unit weight of sorbent is reduced, thus causing a decrease in sorption capacity with increasing sorbent dosage. Additionally, this decrease may be attributed to overlapping or aggregation of sorption sites resulting in decrease in total sorbent surface area available to dye molecules and an increase in diffusion path length.

#### 3.5. Effect of temperature

Fig. 5 shows the effect of temperature on the biosorption of MB by MP. It was observed that the sorption uptake slightly decreases with increasing temperature, indicating the exothermic nature of the sorption process. An increase in temperature from 25 to  $55^\circ\text{C}$  decreased the sorption capacity from  $21.43$  to  $15.3 \text{ mg g}^{-1}$ , and decreased the equilibrium time from 60 to 30 min, respectively. The decrease in sorption with the rise in temperature may be due to the weakening of sorptive forces between the active sites of the sorbent and sorbate species [28]. Additionally, this may be attributed to a relative increase in the escaping tendency of the solute from the solid phase to the bulk phase with the rise in temperature of the solution. On the other hand, the temperature has two main effects on the sorption process. An increase in temperature is known to increase the diffusion rate of the sorbate across the external boundary layer and within the pores. This could be the result of decreasing solution viscosity. Furthermore, changing the temperature will modify the sorption capacity of the sorbent for a particular sorbate.

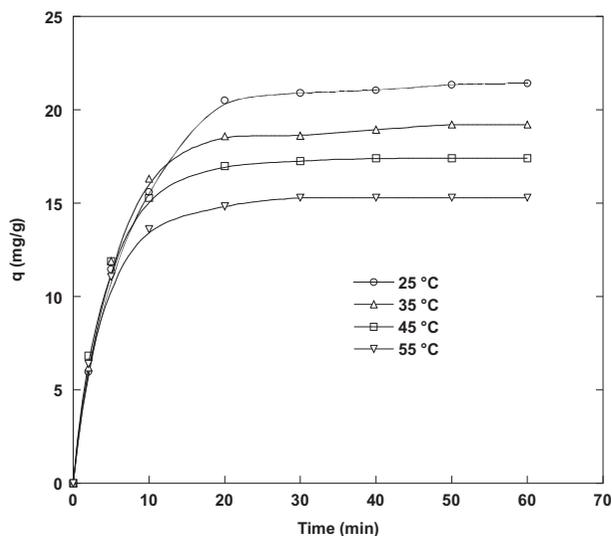


Fig. 5. Effect of temperature on the biosorption of MB by MP (conditions: initial dye concentration = 50 mg L<sup>-1</sup>; biosorbent dosage = 0.4 g (200 mL)<sup>-1</sup>; stirring speed = 300 rpm; pH 5.3).

### 3.6. Effect of ionic strength

The presence of salt leads to high ionic strength, which may significantly affect the performance of the biosorption process. Fig. 6 shows clearly that the variation of K<sub>2</sub>SO<sub>4</sub> concentration exhibits a major effect on the extent of MB sorption. The reason for this is that K<sup>+</sup> ions in the aqueous phase compete effectively with positively charged dye molecules for the same binding

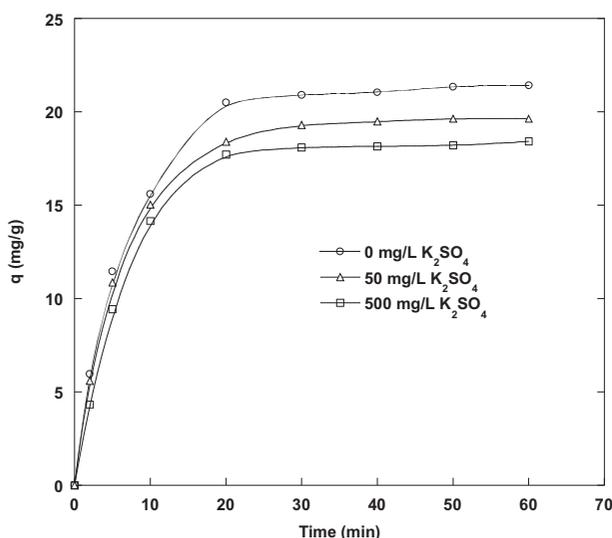


Fig. 6. Effect of salt (K<sub>2</sub>SO<sub>4</sub>) concentration on the biosorption of MB by MP (conditions: initial dye concentration = 50 mg L<sup>-1</sup>; biosorbent dosage = 0.4 g (200 mL)<sup>-1</sup>; stirring speed = 300 rpm; T = 25 °C; pH 5.3).

sites on the biosorbent surface [12,29]. Additionally, salt screens the electrostatic interaction between sorbent and sorbate and the great ionic strength influences on the activity coefficient of MB, which should decrease the sorbed amount with the increase in salt concentration [12,29].

### 3.7. Biosorption isotherms

The analysis of the isotherm data by fitting them to different isotherm models is an important step to find the suitable model that can be used for design purpose. In this work, three sorption isotherms namely the Langmuir, Freundlich, and Temkin isotherms in their linear forms were applied to the equilibrium data of MB sorption by MP.

The Langmuir model [30] assumes uniform energies of sorption onto the surface and no transmigration of sorbate in the plane of the surface. The Langmuir equation may be written as:

$$\frac{1}{q_e} = \frac{1}{q_m} + \frac{1}{bq_m} \times \frac{1}{C_e} \quad (1)$$

where  $q_e$  is the amount of solute sorbed per unit weight of sorbent at equilibrium (mg g<sup>-1</sup>),  $C_e$  is the equilibrium concentration of the solute in the bulk solution (mg L<sup>-1</sup>),  $q_m$  is the maximum sorption capacity (mg g<sup>-1</sup>), and  $b$  is a constant related to the free energy of sorption (L mg<sup>-1</sup>).

The Freundlich isotherm is an exponential equation and therefore, assumes that as the sorbate concentration increases, the concentration of sorbate on the sorbent surface also increases. The Freundlich equation [31] can be written as:

$$\ln q_e = \ln K_F + \frac{1}{n} \ln C_e \quad (2)$$

where  $n$  is a constant indicative of the intensity of the sorption and  $K_F$  is a constant indicative of the relative sorption capacity of the sorbent (mg<sup>1-1/n</sup>L<sup>1/n</sup>g<sup>-1</sup>).

The Temkin [32] isotherm model assumes that the heat of adsorption of all the molecules in the layer decreases linearly with coverage due to adsorbent-adsorbate interactions, and that the adsorption is characterized by a uniform distribution of the binding energies, up to some maximum binding energy. Temkin model is given by the following equation:

$$q_e = \frac{RT}{b_t} \ln a_t + \frac{RT}{b_t} \ln C_e \quad (3)$$

where  $b_t$  is the Temkin constant related to the heat of adsorption (J mol<sup>-1</sup>),  $a_t$  is the Temkin isotherm

constant ( $\text{L mg}^{-1}$ ),  $R$  is the gas constant ( $8.314 \text{ J mol}^{-1} \text{ K}^{-1}$ ), and  $T$  is the absolute temperature (K).

In this work, three isotherm equations namely Langmuir, Freundlich, and Temkin were fitted to the experimental equilibrium data for MB at different temperatures by their linear forms and the obtained results are plotted in Figs. 7–9. The models parameter values are shown in Table 1.

In order to compare the validity of isotherm equations more definitely an average percentage errors (APE) is calculated as follows:

$$\text{APE (\%)} = \frac{\sum_{i=1}^N \left| \frac{(q_e)_{\text{exp}} - (q_e)_{\text{cal}}}{(q_e)_{\text{exp}}} \right|}{N} \times 100 \quad (4)$$

where the subscripts “exp” and “cal” show the experimental and calculated values and  $N$  is the number of experimental data. The determination coefficients ( $r^2$ ) showed the fit between experimental data and isotherm equations, while the APE was calculated according to Eq. (4) indicated the fit between the experimental and predicted values of sorption capacity used for plotting isotherm curves.

The values of APE and determination coefficients given in Table 1 attest that the sorption isotherm data could be well simulated by Langmuir isotherm model; determination coefficients ( $r^2$ ) and APE for Langmuir model were determined in the range 0.996–0.999 and 3.6–5.13, respectively, for all the studied temperatures.

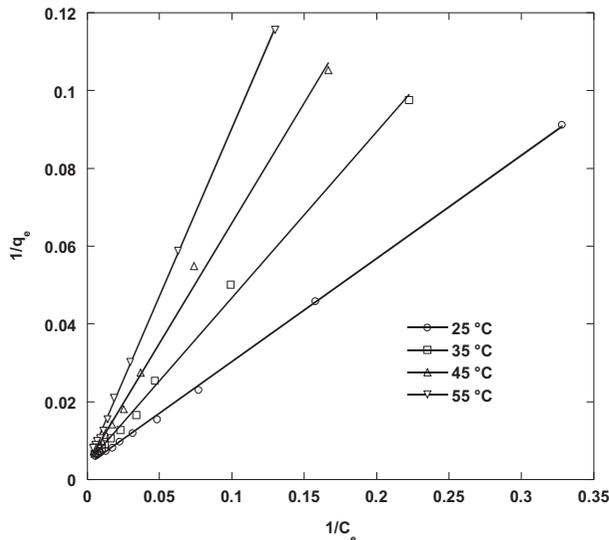


Fig. 7. Langmuir isotherm for MB sorption by MP at different temperatures (conditions: initial dye concentration =  $25\text{--}500 \text{ mg L}^{-1}$ ; sorbent dosage =  $0.4 \text{ g (200 mL)}^{-1}$ ; stirring speed =  $300 \text{ rpm}$ ; pH 5.3).

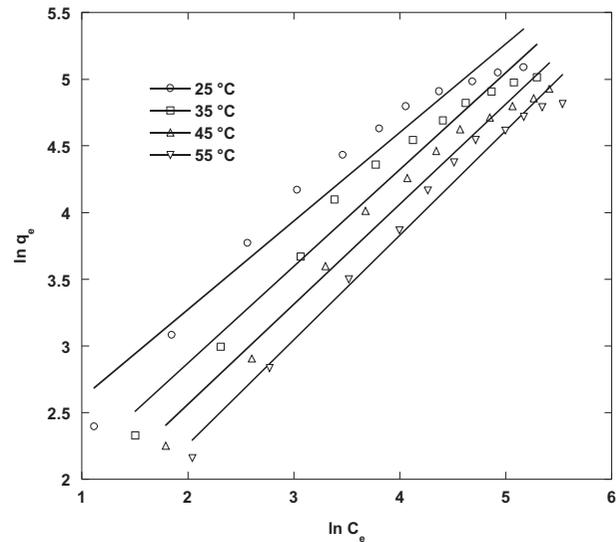


Fig. 8. Freundlich isotherm for MB sorption by MP at different temperatures (conditions: initial dye concentration =  $25\text{--}500 \text{ mg L}^{-1}$ ; sorbent dosage =  $0.4 \text{ g (200 mL)}^{-1}$ ; stirring speed =  $300 \text{ rpm}$ ; pH 5.3).

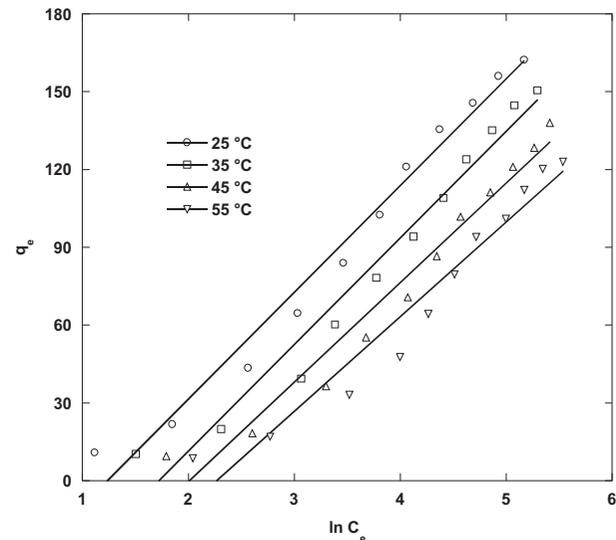


Fig. 9. Temkin isotherm for MB sorption by MP at different temperatures (conditions: initial dye concentration =  $25\text{--}500 \text{ mg L}^{-1}$ ; sorbent dosage =  $0.4 \text{ g (200 mL)}^{-1}$ ; stirring speed =  $300 \text{ rpm}$ ; pH 5.3).

It appears that the sorption of MB is conducted by monolayer coverage on the homogeneous surface of MP.

The Freundlich and Temkin equations were not suitable for the description of equilibrium isotherms obtained at different temperatures because of the relatively higher values of average percentage error.

Table 1

Langmuir, Freundlich, and Temkin isotherm models constants and determination coefficients for the sorption of MB by MP at four different temperatures (conditions: initial dye concentration = 25–500 mg L<sup>-1</sup>; sorbent dosage = 0.4 g (200 mL)<sup>-1</sup>; stirring speed = 300 rpm; pH 5.3)

Model	Parameters				
Langmuir (°C)	$q_m$ (mg g <sup>-1</sup> )	$b$ (L mg <sup>-1</sup> ) × 10 <sup>3</sup>	$r^2$	APE (%)	
	25	333	11.30	0.999	5.08
	35	250	9.36	0.997	4.57
	45	250	6.48	0.996	4.55
	55	250	4.64	0.999	3.73
Freundlich (°C)	$K_F$ (mg <sup>1-1/n</sup> L <sup>1/n</sup> g <sup>-1</sup> )	$n$	$r^2$	APE (%)	
	25	6.99	1.51	0.954	16.83
	35	4.13	1.38	0.969	12.94
	45	2.89	1.33	0.974	12.42
	55	2.00	1.27	0.981	9.44
Temkin (°C)	$a_t$ (L mg <sup>-1</sup> )	$b_t$ (J mol <sup>-1</sup> )	$r^2$	APE (%)	
	25	0.29	55.08	0.978	20.67
	35	0.179	55.26	0.965	26.53
	45	0.134	59.12	0.962	27.07
	55	0.104	62.3	0.947	28.28

### 3.8. Biosorption kinetics

Various sorption kinetic models have been used to describe the uptake of sorbate depending upon the time. Understanding of biosorption kinetics is much less than theoretical description of biosorption equilibrium. The pseudo-first-order kinetic equation or

the so-called Lagergren equation has the following formulation [33]:

$$\ln(q_e - q) = -k_1 t + \ln q_e \quad (5)$$

where  $k_1$  is the pseudo-first-order rate constant (min<sup>-1</sup>),  $q_e$  is the amount of sorbate sorbed at equilibrium

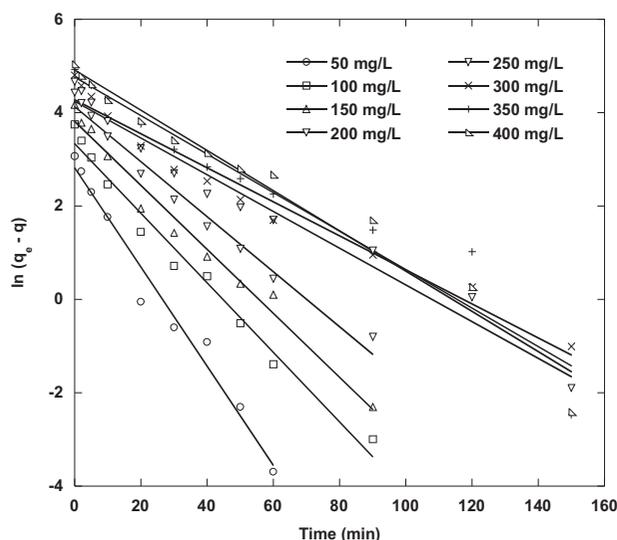


Fig. 10. Modeling of MB sorption kinetics at various initial dye concentrations using the pseudo-first-order kinetic expression (conditions: biosorbent dosage = 0.4 g (200 mL)<sup>-1</sup>; stirring speed = 300 rpm;  $T = 25^\circ\text{C}$ ; pH 5.3).

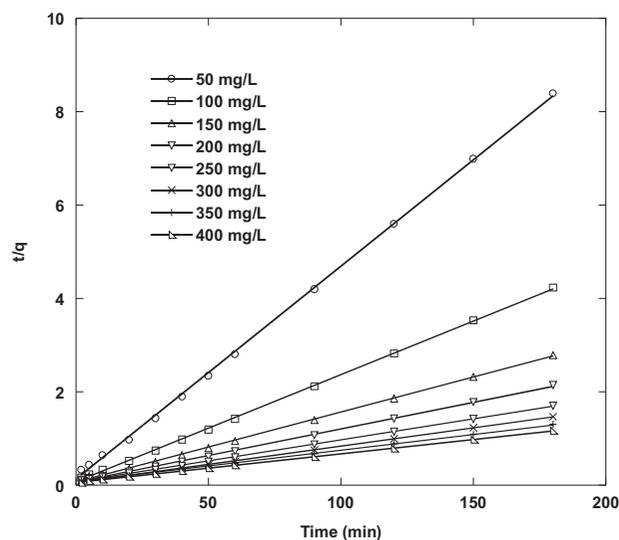


Fig. 11. Modeling of MB sorption kinetics at various initial dye concentrations using the pseudo-second-order kinetic expression (conditions: biosorbent dosage = 0.4 g (200 mL)<sup>-1</sup>; stirring speed = 300 rpm;  $T = 25^\circ\text{C}$ ; pH 5.3).

Table 2

Pseudo-first- and pseudo-second-order kinetic models constants and determination coefficients at various initial dye concentrations for the sorption of MB by MP (conditions: biosorbent dosage = 0.4 g (200 mL)<sup>-1</sup>; stirring speed = 300 rpm; T = 25 °C; pH 5.3)

Model	Parameters			
Pseudo-first-order model (mg L <sup>-1</sup> )	$K_1$ (min <sup>-1</sup> )	$q_e$ (mg g <sup>-1</sup> )	$r^2$	APE (%)
50	0.106	16.69	0.976	28.53
100	0.074	27.88	0.98	43.83
150	0.068	45.15	0.978	40.18
200	0.058	61.86	0.98	36.92
250	0.039	69.69	0.97	46.53
300	0.036	72.02	0.964	53.97
350	0.041	116.16	0.935	26.83
400	0.043	136.45	0.964	23.82
Pseudo-second-order model (mg L <sup>-1</sup> )	$K_2$ (g mg <sup>-1</sup> min <sup>-1</sup> ) × 10 <sup>3</sup>	$q_e$ (mg g <sup>-1</sup> )	$r^2$	APE (%)
50	15.94	22.22	0.999	6.76
100	2.75	45.45	0.999	4.19
150	3.69	66.66	0.999	5.49
200	1.83	90.9	0.999	4.83
250	0.88	111.11	0.999	2.93
300	0.88	142.85	0.999	2.66
350	0.49	166.6	0.999	3.78
400	0.62	166.6	0.999	1.45

Table 3

Thermodynamic parameters for the sorption of MB by MP

T (K)	$\Delta H^\circ$ (kJ mol <sup>-1</sup> )	$\Delta G^\circ$ (kJ mol <sup>-1</sup> )	$\Delta S^\circ$ (J mol <sup>-1</sup> K <sup>-1</sup> )
298		-20,30	-14,40
308	-24,59	-20,50	-13,28
318		-20,20	-13,81
328		-19,90	-14,30

(mg g<sup>-1</sup>),  $q$  is the amount of sorbate on the surface of biosorbent at any time  $t$  (mg g<sup>-1</sup>), and  $t$  is the time (min).

The sorption of MB by MP was also analyzed using the pseudo-second-order equation or the so-called Blanchard equation [34] using linear fitting analysis method proposed by Ho [35]:

$$\frac{t}{q} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \quad (6)$$

Figs. 10 and 11 show, respectively, the Lagergren and Blanchard plots for the biosorption of MB. Table 2 shows the pseudo-first-order and pseudo-second-order kinetic parameters for different initial concentrations of MB obtained by utilizing the linear regression analysis method. From Figs. 10 and 11 and Table 1, it seems that the pseudo-second-order model fit the

experimental data well and was better than the pseudo-first-order equation because of the low average percentage error values and good coefficients of determination.

### 3.9. Thermodynamic parameters

In environmental engineering practice, both energy and entropy factors must be considered in order to determine which process will occur spontaneously. The Gibbs free energy change ( $\Delta G^\circ$ ) is the basic criterion of spontaneity, and a negative value indicates the reaction to be spontaneous. By using the equilibrium constant ( $b_M$ ) obtained for each temperature from the Langmuir model using the linear method (Table 1),  $\Delta G^\circ$  can be calculated according to Eq. (7):

$$\Delta G^\circ = -R_g T \ln b_M \quad (7)$$

$$\Delta G^\circ = \Delta H^\circ - T \Delta S^\circ \quad (8)$$

where  $T$ (K) is the absolute temperature,  $R_g$  (kJ mol<sup>-1</sup> K<sup>-1</sup>) is the gas constant,  $b_M$  (L mol<sup>-1</sup>) is the Langmuir equilibrium constant, and  $\Delta G^\circ$  (kJ mol<sup>-1</sup>),  $\Delta H^\circ$  (kJ mol<sup>-1</sup>) and  $\Delta S^\circ$  (kJ mol<sup>-1</sup> K<sup>-1</sup>) are the changes in free energy, enthalpy and entropy, respectively.

The thermodynamic parameters obtained for the sorption of MB by MP are given in Table 3. The values demonstrate spontaneous and favorable sorption processes. The negative values of change in enthalpy are due to the exothermic nature of sorption. Furthermore, the negative values of the change in free energy depict the feasibility and spontaneous nature of the process. Finally, negative values of the entropy change are not very large and correspond to a decrease in the degree of freedom of the sorbed species.

#### 4. Conclusion

The sorption of MB from aqueous solution using MP was investigated in batch mode. Increasing the initial concentration of MB leads to an increase in sorption. The removal of MB increased by increasing sorbent dosage. The sorption of MB is favored by low temperatures. The ionic strength disfavors the sorption of dye. The pH values in the range of 4–12 are more favorable for MB sorption. Effect of stirring speed seems to be negligible for agitation speeds higher than 300 rpm.

The sorption of MB dye onto MP was better described by the Langmuir model than by the Freundlich and Temkin isotherms. The maximum sorption capacity calculated by using the Langmuir isotherm at 25 °C was 333 mg g<sup>-1</sup>.

Kinetic data were modeled using the pseudo-first and pseudo-second-order kinetic models. Kinetic results were adequately fitted by the pseudo-second-order model.

MP used in this work is freely and abundantly available, do not require an additional pretreatment step such as activation before application and possess high sorption capacity for MB. Therefore, the sorbent is expected to be economically feasible for the removal of MB dye from aqueous solutions.

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