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Adsorption of cationic dye from aqueous solution by milk thistle seeds: isotherm, kinetic and thermodynamic studies

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ABSTRACT

The adsorption performance of milk thistle seeds (MTS), a low-cost and locally available biomaterial, for methylene blue (MB) removal from aqueous solutions was examined using a batch process. The effects of operational conditions such as initial dye concentration (50–250 mg/L), adsorbent dose (0.1–0.8 g/200 mL), temperature (25°C–45°C), ionic strength (0–500 mg/L) and pH 3–11 on the uptake of MB by MTS were examined. The adsorption of MB is favored by low temperatures. The ionic strength disfavors the sorption of dye. Near neutral and basic pHs are more favorable for the dye adsorption. Three models were employed to describe experimental adsorption isotherm data: Langmuir, Freundlich and Temkin equations. Experimental equilibrium data were best represented by the Freundlich isotherm model. The thermodynamic parameters such as $\Delta G°$, $\Delta H°$ and $\Delta S°$ were determined for the adsorption of MB. The removal kinetics of MB by MTS was analyzed using the pseudo-first-order, pseudo-second-order model equations and intraparticle diffusion model. Pseudo-second-order model was found to describe the adsorption process better than the pseudo-first-order equation. Analysis of adsorption kinetic results indicated that both film- and particle-diffusion are effective adsorption mechanisms. The results of the present work indicated that MTS was an attractive candidate for removing cationic dyes from wastewater.

Keywords: Adsorption; Methylene blue; Milk thistle seed; Kinetics; Mechanism; Isotherms; Thermodynamics

1. Introduction

Dyes and pigments present in wastewater have high visibility. Thus, even minor release into the environment may cause the appearance of color that attracts the critical attention of public and local authorities. Discharged effluent containing dyes are continuously released by textile, paper, wood and other dyeing industries into water sources. They are toxic to aquatic life and human beings, and also have a deleterious effect on the ecosystem [1].

In industries, the methods employed for treating dye wastewaters include coagulation and flocculation [2], oxidation or ozonation [3,4], membrane separation [5] and activated carbon sorption [6]. These technologies do not show significant effectiveness or economic advantage. In recent years, the applicability of biomass as low-cost adsorbent has been widely investigated for wastewater treatment [7–12].

Milk thistle (*Silybum marianum*) is a weed related to the daisy and ragweed family. This invasive species is native to Mediterranean countries. Some people also call it Mary thistle and holy thistle. This fairly typical thistle has red to purple flowers and shiny pale green leaves with white veins. Each flower can produce up to 190 seeds, averaging 6,350 seeds per plant in its life time. This great news led us to test the milk thistle seeds (MTS) as a novel adsorbent for the uptake of dyes from aqueous media. Methylene blue (MB) is selected as

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a model compound in order to evaluate the capacity of MTS for the removal of dye from its aqueous solutions. MB dye has wider applications, which include coloring paper, temporary hair colorant, dyeing cottons, wools and coating for paper stock.

The main focus of this work was to evaluate the adsorption aptitude of MTS as a novel, low-cost and renewable biomass for the removal of MB, as a model compound for basic dyes, from aqueous solutions. Batch adsorption studies were conducted to investigate the effects of various parameters such as contact time, initial dye concentration, adsorbent dose, pH, temperature and ionic strength on MB adsorption. Moreover, equilibrium isotherm, kinetic data are analyzed and modeled using different models.

2. Materials and methods

2.1. Adsorbate and adsorbent

MB is a basic cationic dye with the molecular formula $C_{16}H_{18}N_3ClS$ and molecular weight 373.91. The dye was procured from Sigma-Aldrich (USA), with analytical grade.

MTS was collected from the region of Batna, Algeria. Soluble and colored components were removed by washing with distilled water. This was repeated until the water was virtually colorless. The MTS was dried at ambient air hangs 2–3 d and then it was ground and sieved using a vibrating sieve (diameter between 0.5 and 1 mm). The MTS is then dried at 50°C in an oven for 12 h and then cooled in a desiccator and packaged in sealed bottles. Physicochemical characterization of MTS shows that the concentrations of acidic surface functions, mainly phenols and lactones groups, are more important than basic functions and the point of zero charge is 4.9 [13].

2.2. Procedures

Batch mode adsorption studies of MB were carried out to investigate the effect of different operational parameters. Batch equilibrium studies were carried out in Erlenmeyer flask. A mass of 0.6 g of adsorbent was contacted with 200 mL of dye solution using a thermostatic water bath with initial dye concentration in the range of 50–200 mg/L. The stirring speed was kept constant at 300 rpm. Samples of the mixture were withdrawn at suitable time intervals and analyzed by a UV–Vis spectrophotometer (Jenway 6405) for the concentration of MB.

To study the effect of initial solution pH on MB adsorption, 0.6 g of MTS was agitated with 200 mL of MB solution of 50 mg/L dye concentration at 25°C. The experiment was conducted at different initial pH values ranging from 3 to 11. The initial solution pH was adjusted using 0.1 N HCl or NaOH aqueous solutions. Agitation was provided for a period which is sufficient to reach equilibrium with a constant agitation speed of 300 rpm.

The effect of temperature on the sorption of MB was studied by contacting 0.6 g of sorbent with 200 mL of dye solution of 50 mg/L initial concentration at different temperatures (25°C–45°C).

The influence of ionic strength on the sorption of MB by MTS was studied with a constant initial concentration of 50 mg/L, a sorbent mass of 0.6 g, a solution volume of 200 mL and a temperature of 25°C. The ionic strength of the dye solution was modified using different dosages of K_2SO_4 (0–500 mg/L).

Adsorption equilibrium experiments were carried out by adding a fixed amount of MTS (0.6 g) into a number of sealed Erlenmeyer flasks containing a definite volume (200 mL in each case) of different initial concentrations (50–250 mg/L) of MB solution. The flasks were placed in a thermostatic water bath in order to maintain a constant temperature (25°C, 35°C or 45°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. The adsorbed amount at equilibrium, q_e (mg/g) was calculated by:

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

where C_0 and C_e (mg/L) are the liquid phase concentrations of MB at initial and equilibrium time, respectively, V (L) is the volume of the solution and W (g) is the mass of used sorbent.

3. Results and discussion

3.1. Effect of initial MB concentration

The adsorption of MB onto MTS was investigated at different initial dye concentrations. It can be seen from Fig. 1 that the sorption of MB increased with time till it reached a constant value beyond which no more MB was further removed from the solution. Removal of MB for different initial concentrations (50, 100, 150, 200 and 250 mg/L) as a function of contact time was studied and the results are shown in Fig. 1. Obviously, the adsorption capacity of MTS toward MB is closely dependent on its initial concentration. In each case, the adsorption capacity significantly increases during the initial stage and then slowly reaches equilibrium within 150–420 min.

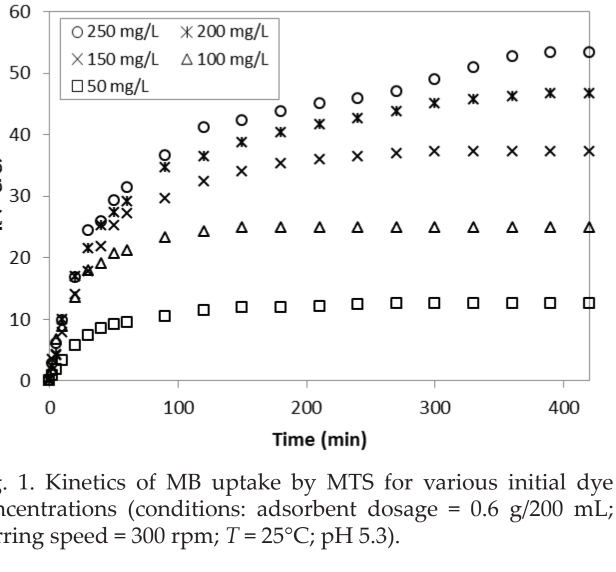

Fig. 1. Kinetics of MB uptake by MTS for various initial dye concentrations (conditions: adsorbent dosage = 0.6 g/200 mL; stirring speed = 300 rpm; T = 25°C; pH 5.3).

The phenomenon may be explained as follows. The high sorption rate at the beginning of sorption was due to the sorption of dye molecules by the large number of binding sites of the exterior adsorbent surface. During the adsorption process, the adsorption on the exterior surface should take place quickly, but it might be time consuming for the MB molecules to diffuse into the interior space of adsorbent [14].

From Fig. 1, it can be observed that the amount of dye removed at equilibrium increased from 12.52 to 53.33 mg/g with the increase in dye concentration from 50 to 250 mg/L. 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.

3.2. Effect of initial solution pH

At values of pH < pH_{pzc}, the surface charges of the sorbent are positive and susceptible to electrostatic interactions with anionic dye molecule. At pH > pH_{pzc}, the adsorbent surface is negatively charged and available to bind cationic dye such as MB.

Fig. 2 presents the influence of pH of the initial dye solution on sorption of MB onto the tested adsorbent. It can be seen that the adsorption of MB decreased with the decrease of initial solution pH. As pH of the system decreased, the number of negatively charged sorption sites decreased contrary to the number of positively charged surface sites, which did not favor the sorption of positively charged dye cations due to electrostatic repulsion. Also, the change of pH affects the adsorptive process through dissociation of functional groups on the adsorbent surface active sites [15]. Additionally, lower sorption of MB at acidic pH is due to the presence of excess H^+ ions competing with dye cations for the sorption sites of MTS.

As shown in Fig. 2, the equilibrium uptake of dye increased notably with raising the pH from 3 to 5.3. Above these levels, the sorption capacity did not change significantly up to pH 11. Similar trend was reported for sorption of MB by *Posidonia oceanica* (L.) fibres [16] and melon peel [9].

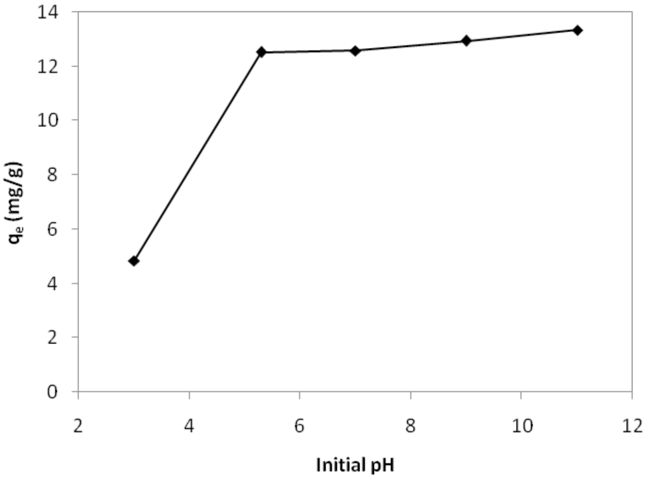

Fig. 2. Effect of initial pH on the adsorption capacity (conditions: initial dye concentration = 50 mg L^{-1}; adsorbent dosage = 0.6 g/200 mL; stirring speed = 300 rpm; *T* = 25°C).

3.3. Effect of adsorbent dosage

Fig. 3 shows that an increase in the biomass quantity causes an increase in the adsorption removal efficiency. At equilibrium time, the adsorbed amount decreased from 37.68 to 9.55 mg/g for an increase in sorbent dose from 0.1 to 0.8 g, respectively. On the other hand, the removal of dye increased with an increase in sorbent amount. The adsorption removal efficiency values increased from 37.68% to 76.4% as the biomass dose was increased from 0.1 to 0.8 g. This may be attributed to an increase of the sorbent surface area and to the availability of more sorption sites resulting from the increase of the sorbent dosage. But the amount of dye adsorbed per unit mass of sorbent decreased with an increase in sorbent amount (Fig. 3). Quite similar tendency was reported for MB adsorption onto fly ash [17]. By increasing the adsorbent dosage the number of active sites available for adsorption increased, facilitating the adsorption of dyes, which explain the increase of removal percentage. The decrease of adsorption capacity by increasing the adsorbent dosage (higher weight of adsorbent per dye ratio) is maybe due to the unsaturation of adsorbent sites, during the adsorption process. Similar results have been reported by other authors [18–21].

3.4. Effect of temperature

Temperature of the solution is one of the important parameters affecting the adsorption process. Three different temperatures were tested. According to Fig. 4, it was observed that an increase in temperature from 25°C to 45°C decreased the sorption capacity from 12.52 to 11.17 mg/g, indicating the exothermic nature of the adsorption process, and decreased the equilibrium time from 300 to 180 min, respectively.

An increase of temperature increases the rate of diffusion of the adsorbate molecules across the external boundary layer and within the internal pores of the adsorbent particle, due to the decrease in the viscosity of the solution [22].

3.5. Effect of ionic strength

Generally, various salts and metal ions exist in dye containing wastewater. The presence of salt may significantly

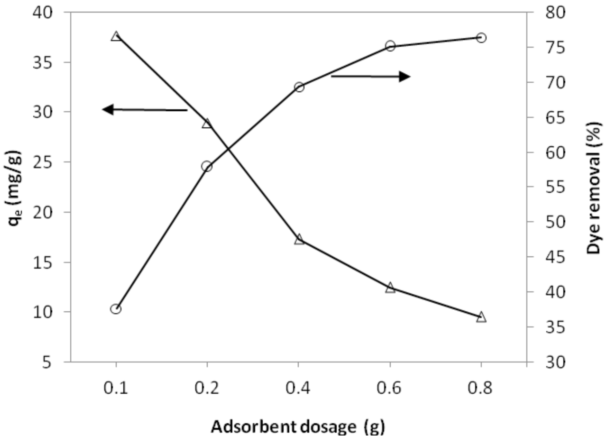

Fig. 3. Effect of adsorbent dosage on the removal of MB and adsorption capacity of MTS (conditions: initial dye concentration = 50 mg L^{-1}; stirring speed = 300 rpm; *T* = 25°C; pH 5.3).

affect the performance of the adsorption process. To investigate the effect of ionic strength on MB adsorption, equilibrium adsorption studies were performed by gradually increasing K_2SO_4 concentration in adsorption solution from 0 to 500 mg/L.

As shown in Fig. 5, the adsorption capacity decreases slightly as K_2SO_4 concentration increases. The ionic strength of the solution is of significance for its effect on the adsorbent, as well as the adsorbate [23]. At high ionic strength, adsorption sites are surrounded by counter ions which partially lose their charge, and this weakens the binding force by an electrostatic interaction [24].

3.6. Adsorption isotherms

To further interpret the adsorption behaviors, three common isotherm models Langmuir, Freundlich and Temkin were applied to fit the experimental data.

The Langmuir isotherm is described as homogeneous, assuming that all the adsorption sites have equal adsorbate affinity and that the adsorption at one site does not affect the adsorption at an adjacent site [25–27]. The Langmuir equation may be written as follows:

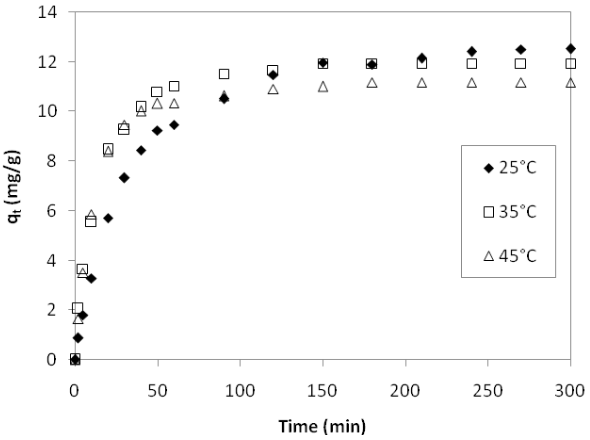

Fig. 4. Effect of temperature on the adsorption of MB by MTS (conditions: initial dye concentration = 50 mg L^{-1}; adsorbent dosage = 0.6 g/200 mL; stirring speed = 300 rpm; pH 5.3).

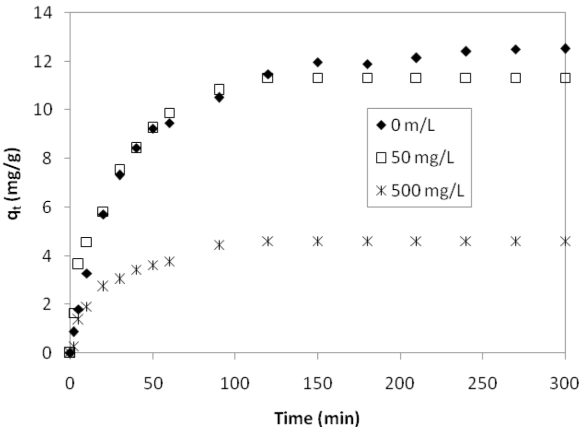

Fig. 5. Effect of salt (K_2SO_4) concentration on the adsorption of MB by MTS (conditions: initial dye concentration = 50 mg L^{-1}; adsorbent dosage = 0.6 g/200 mL; stirring speed = 300 rpm; T = 25°C; pH 5.3).

$$\frac{1}{q_e} = \frac{1}{q_m} + \frac{1}{bq_m} \times \frac{1}{C_e} \tag{2}$$

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

The Freundlich [28] empirical isotherm is applicable to the adsorption on heterogeneous surfaces with interaction between adsorbed molecules. In this case, the heat of adsorption exponentially decreases with the coverage of adsorbent surface. The Freundlich isotherm can be expressed as follows:

$$\ln q_e = \ln K_F + \frac{1}{n} \ln C_e \tag{3}$$

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 ($[\text{mg}^{1-1/n}\ \text{L}^{1/n}]$/g).

Temkin [29] isotherm was also applied to evaluate the experimental data. Unlike the Langmuir and Freundlich models, the Temkin isotherm model takes into account the interactions between adsorbent and dye to be adsorbed and is based on the assumption that the free energy of sorption is a function of the surface coverage. Temkin model is given by the following equation:

$$q_e = \frac{RT}{b_t} \ln a_t + \frac{RT}{b_t} \ln C_e \tag{4}$$

where b_t is the Temkin constant related to the heat of adsorption (J mol^{-1}), a_t is the Temkin isotherm constant (L mg^{-1}), R is the ideal gas constant (8.314 J mol^{-1} K^{-1}) and T is the absolute temperature (K).

The linear forms of Langmuir, Freundlich and Temkin models were plotted in Figs. 6–8, respectively. The models parameters are shown in Table 1. Langmuir simulation showed that the monolayer adsorption capacities of MTS were 264.55 mg/g at 25°C. The determination coefficients (r^2) showed the fit between experimental data and isotherm equations.

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

$$\text{APE}(\%) = \frac{\sum_{1}^{N} \left| \frac{(q_e)\text{exp} - (q_e)\text{cal}}{(q_e)\text{exp}} \right|}{N} \times 100 \tag{5}$$

where the subscripts 'exp' and 'cal' show the experimental and calculated values and N is the number of experimental data. The APE indicated the fit between the experimental and predicted values of adsorption capacity used for plotting isotherm curves.

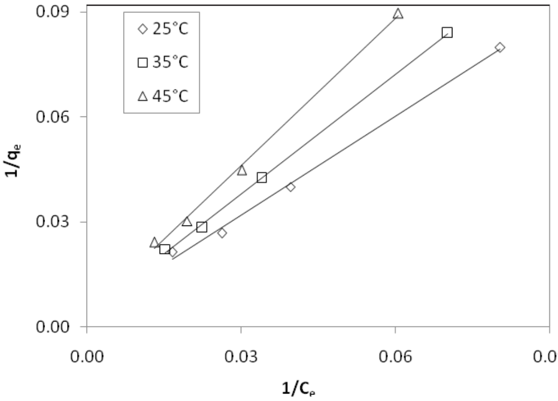

Fig. 6. Langmuir isotherm for MB dye adsorption onto MTS adsorbent at different temperatures (conditions: initial dye concentration = 50–250 mg L^{-1}; sorbent dosage = 0.6 g/200 mL; stirring speed = 300 rpm; pH 5.3).

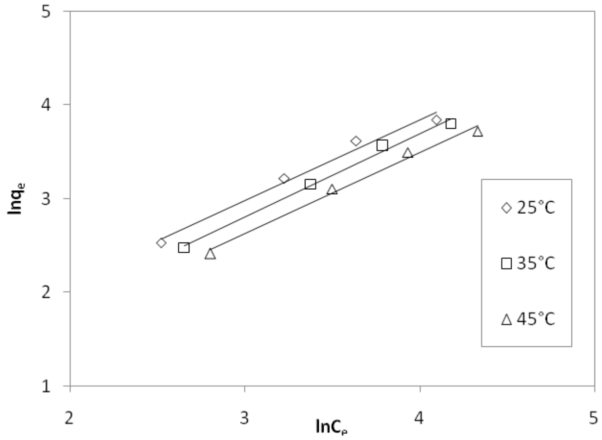

Fig. 7. Freundlich isotherm for MB dye adsorption onto MTS adsorbent at different temperatures (conditions: initial dye concentration = 50–250 mg L^{-1}; sorbent dosage = 0.6 g/200 mL; stirring speed = 300 rpm; pH 5.3).

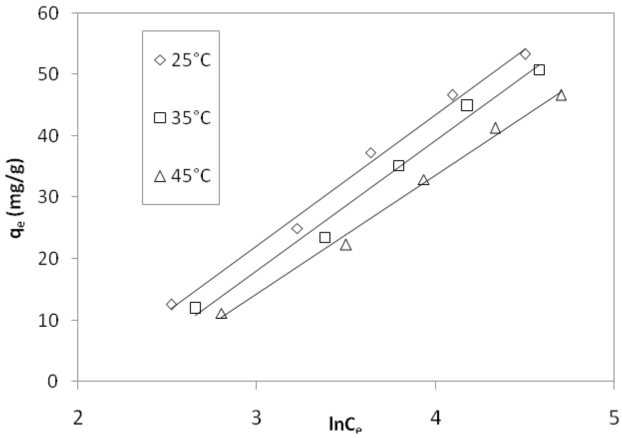

Fig. 8. Temkin isotherm for MB dye adsorption onto MTS adsorbent at different temperatures (conditions: initial dye concentration = 50–250 mg L^{-1}; sorbent dosage = 0.6 g/200 mL; stirring speed = 300 rpm; pH 5.3).

Table 1
Langmuir, Freundlich and Temkin isotherm models constants and determination coefficients for the sorption of MB by MTS at three different temperatures

Model	Parameters			
Langmuir	q_m (mg/g)	b (L/mg) × 10^3	r^2	APE (%)
25°C	264.55	4.028	0.996	4.668
35°C	257.73	3.415	0.999	2.181
45°C	251.26	2.841	0.997	3.740
Freundlich	K_F ([mg$^{1-1/n}$ L$^{1/n}$]/g)	n	r^2	APE (%)
25°C	1.1533	1.167	0.982	1.873
35°C	1.1554	1.127	0.994	1.026
45°C	1.0120	1.149	0.989	1.616
Temkin	a_t (L/mg)	b_t (J/mol)	r^2	APE (%)
25°C	0.1412	116.10	0.992	4.760
35°C	0.1172	121.03	0.988	6.394
45°C	0.1044	136.54	0.994	4.450

The values APE and r^2 given in Table 1 attest that the adsorption isotherm data could be well simulated by Freundlich isotherm model and then Langmuir and Temkin models, respectively. Similar results were observed in the literature [30].

3.7. Adsorption kinetics

The adsorption kinetics is an important parameter for designing adsorption systems. The pseudo-first-order and the pseudo-second-order models were applied to understand the sorption kinetics. The linear form of the pseudo-first-order equation is given as follows [31]:

$$\ln(q_e - q) = -k_1.t + \ln q_e \tag{6}$$

where k_1 is the pseudo-first-order rate constant (min^{-1}), q_e is the amount of adsorbate adsorbed at equilibrium (mg/g), q is the amount of adsorbate on the surface of adsorbent at any time t (mg/g) and t is the time (min).

The experimental data were examined by the pseudo-second-order kinetic model which is given by the following equation [32,33]:

$$\frac{t}{q} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \tag{7}$$

where q_e and q_t have the same meaning as mentioned previously, and k_2 is the rate constant for the pseudo-second-order kinetics.

Figs. 9 and 10 show the pseudo-first-order and pseudo-second-order plots for the adsorption of MB, respectively. The corresponding model constants along with regression coefficient and percentage error values are presented in Table 2.

Based on the high regression coefficients and low APE, pseudo-second-order model fit the experimental data well and was best than the pseudo-first-order model. Similar results were obtained in the MB adsorption onto clay [34].

The intraparticle diffusion model is given by the following equation [35]:

$$q = K_p t^{1/2} + C \tag{8}$$

where q (mg/g) is the amount of MB dye adsorbed at time t and K_p (mg/g/min$^{1/2}$) is the rate constant for intraparticle diffusion.

The value of C explains the thickness of the boundary layer, the larger the intercept the greater the boundary layer effect [36]. A plot of q vs. $t^{0.5}$ should give a linear graph if intraparticle diffusion is involved in the sorption process and if the plot passes through the origin then intraparticle diffusion is said to be the sole rate-limiting step. However, q vs. $t^{0.5}$ could give a multilinear plot which suggests that two or more steps govern the sorption process [37].

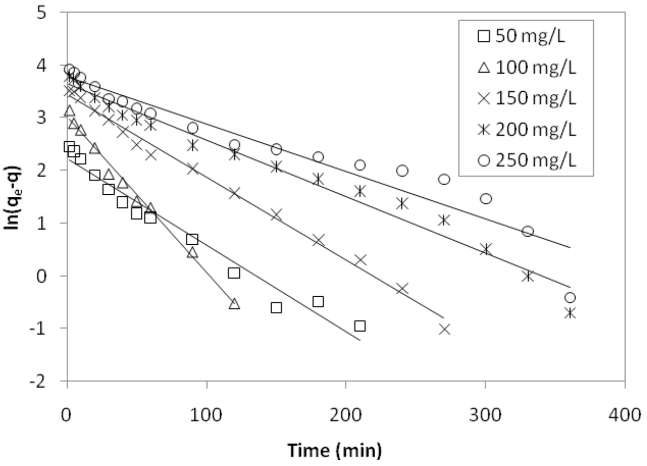

Fig. 9. Modeling of MB sorption kinetics by MTS at various initial dye concentrations using the pseudo-first-order model.

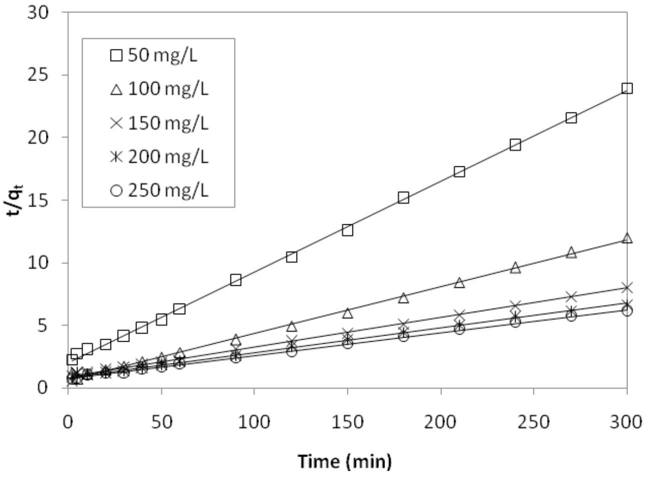

Fig. 10. Modeling of MB sorption kinetics by MTS at various initial dye concentrations using the pseudo-second-order model.

Diffusion intraparticle model parameters (Table 3) suggest that the adsorption is consistent with a multistage processes (Fig. 11). The first stage is driven by the rapid diffusion of the MB molecules from the bulk dye solution to the surface of the adsorbent. When external adsorption sites became saturated, the MB molecules start to enter into the adsorbent pore. As consequence, the diffusion rate (K_p) decreases and intraparticle diffusion starts and becomes increasingly limiting. Also, in the second stage when the initial dye concentration increased, the values of the intercept (C) increased, indicating that intraparticle diffusion is less and less involved in the adsorption process with increasing the initial dye concentration. In the last stage, MB molecules diffuse with low diffusion rate until the system attains the equilibrium. A multilinear profile was previously reported for the uptake of Congo red dye onto ackee apple seed [38].

Table 2
Pseudo-first-order and pseudo-second-order kinetic models constants and determination coefficients at various initial dye concentrations for the sorption of MB by MTS

Model	Parameters			
Pseudo-first-order model	k_1 (min^{-1})	q_e (mg/g)	r^2	APE (%)
50 mg/L	0.01646	9.29	0.966	40.76
100 mg/L	0.02969	20.85	0.991	28.58
150 mg/L	0.01576	31.84	0.993	28.57
200 mg/L	0.01074	38.59	0.977	34.69
250 mg/L	0.00901	44.07	0.924	36.46
Pseudo-second-order model	k_2 (g/mg/min) × 10^3	q_e (mg/g)	r^2	APE (%)
50 mg/L	2.57	13.83	0.999	2.82
100 mg/L	2.15	26.85	0.998	5.76
150 mg/L	0.644	42.16	0.997	4.36
200 mg/L	0.453	50.71	0.998	3.01
250 mg/L	0.433	54.67	0.999	3.34

Table 3
Intraparticle diffusion kinetics model parameters for the adsorption of MB onto MTS

C_0 (mg/L)	K_p (mg/g min$^{1/2}$)	C (mg/g)	r^2
50	1.63052	–1.66614	0.9952
	0.62215	4.6532	0.9896
100	3.7927	–2.98593	0.9860
	1.29603	11.17033	0.9645
150	4.02511	–3.84536	0.9872
	1.56197	15.07892	0.9934
200	4.5083	–4.24171	0.9896
	1.31478	22.35338	0.9964
250	4.43991	–3.00878	0.9829
	1.30388	26.34852	0.9718

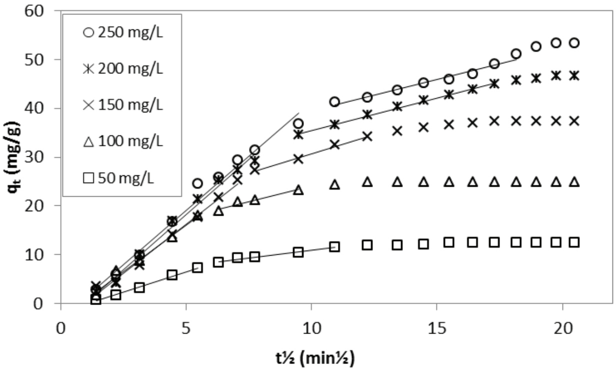

Fig. 11. Modeling of MB sorption kinetics by MTS at various initial dye concentrations using the intraparticle diffusion model.

Table 4
Thermodynamic parameters for the uptake of MB

T (K)	$\Delta G°$ (kJ/mol)	$\Delta H°$ (kJ/mol)	$\Delta S°$ (J/mol/K)
298	–17.742	–13.743	13.46
308	–17.915		
318	–18.010		

3.8. Thermodynamic parameters of sorption

According to the following equation, it is possible to calculate Gibbs energy changes for the sorption process at different temperatures:

$$\Delta G° = -RT \ln b \tag{9}$$

where R is universal gas constant, b is the equilibrium constant, T is the temperature (K) and $\Delta G°$ is the free energy change (J/mol).

The enthalpy and entropy changes of sorption can be determined through the slope and intercept of the line produced by drawing ln$b$ vs. 1/T (Van't Hoff equation). Table 4 summarizes these parameters.

According to Table 4, the negative values of the standard Gibbs free energy at various temperatures indicated the spontaneous nature of the sorption of MB from the solution by the sorbent. The negative values of the standard enthalpy indicate the exothermic nature of the sorption of MB on the sorbent. Similar thermodynamic values for MB removal were found in the literature [9]. The positive values of standard entropy changes reflect the increasing randomness at the solid/liquid interface during the sorption of MB on the sorbent.

4. Conclusion

Removal of MB from aqueous media using MTS as nonconventional and low-cost adsorbent was investigated in batch mode. Effects of operating parameters on the sorption of MB by MTS have been studied and discussed. Increasing the initial concentration of MB leads to an increase of sorption. The removal of MB increases by increasing sorbent dosage. On the other hand, the sorbed amount per unit mass of MTS decreased when the sorbent dose increases. The sorption of MB is favored by low temperatures. The ionic strength disfavors the sorption of dye. Strong acidic pHs are unfavorable for MB sorption. The adsorption of MB dye onto MTS was better described by the Freundlich isotherm model followed by Langmuir and Temkin models. The maximum adsorption capacity calculated by using the Langmuir isotherm was 264.55 mg/g. Enthalpy variation is negative indicating that the sorption process is exothermic. The change in free energy is negative showing that the sorption of MB by MTS is spontaneous and favorable. The positive values of standard entropy changes reflect the increasing randomness at the solid/liquid interface during the sorption of MB on the sorbent. The process kinetics was found to follows the pseudo-second-order rate equation and both film- and particle-diffusion are effective adsorption mechanisms.

From this investigation, it was concluded that, MTS can be successfully utilized as low-cost, alternative, eco-friendly and effective adsorbent for the treatment of dye-bearing industrial wastewater.

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