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Study and modelling of kinetics biosorption of methylene blue on biomass material from waste mint

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ABSTRACT

This work involves the use of waste mint as a natural material value for the removal of dyes. Then we tested the power of removal of methylene blue in this material, the study of chemical kinetics in two hours for the initial concentrations C_0 = 10, 20, 30, 40 and 50 mg/L. All the experiments were conducted at a constant pH = 7.1 and at a constant temperature of 25±1 °C. The experimental results were modeled by theoretical models such as fractional power, pseudo-first order, pseudo-second order, Elovich and intraparticule diffusion. From the values of the correlation coefficients of these models we find the fractional power (R^2 between 90.9% and 96.9%), pseudo-second order model (R^2 between 80.6% and 98.5%) and Elovich model (R^2 between 90% and 97.6%) are closer to the experimental results of adsorption kinetics.

KEYWORDS

Sorption;
Methylene blue;
Waste mint;
Kinetics;
Modeling.

INTRODUCTION

In industrial water pollution, the color produced by minute amount of dyes in water is considered very important because, besides having possible harmful effects, the color in water is aesthetically unpleasant. Colored water can affect plant life, and thus an entire ecosystem can be destroyed by the contamination of various dyes in water. Some dyes are also toxic and even carcinogenic. This dictates the necessity of organic dye containing water to undergo treatment before disposal to the environment. The conventional methods for color removal are biological oxidation, chemical precipitation and other methods[1-3]. But these processes are not always effective and economic where the solute concentrations are very low. Moreover, most of the synthetic dyes undergo very slow biodegradation. Currently the adsorption technique is proved to be an effective and attractive process for the treatment of organic dye containing wastewater[4–6]. Also, this method will become inexpensive, if the sorbent material used is of cheaper cost and does not require any expensive additional pretreatment step.

In the present work, methylene blue is selected as a model compound in order to evaluate the capacity of the adsorbent for the removal of methylene blue from its aqueous solution. Methylene blue is a cationic organic dye having the structure:

For this, several studies have been devoted to finding new materials that can replace the activated car-

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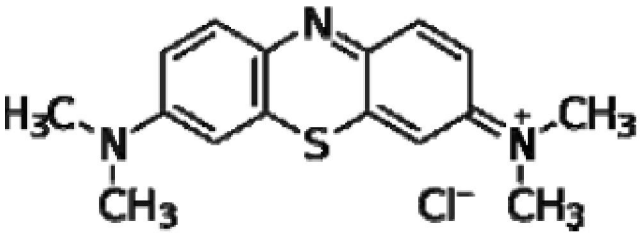

bon. The use of biological resources such as bacteria[7], sawdust[8], algae[9] and shells[10] has emerged as a potential alternative to conventional treatment methods (physico-chemical): The cotton[11], clay[12], bagasse[13] and chitosan[14].

In the present study, mint waste has been used as adsorbent for the removal of MB from its aqueous solution, hence the essential part of this work is the modeling of the kinetics by theoretical models to understand the phenomena of biosorption.

EXPERIMENTAL

Materials

The mint waste used in the present investigation as a biomass adsorbent was collected from household. The mint dust discarded after using is called mint waste. The collected materials were then washed with tap water and distilled water for several times to remove all the dirt particles. The washed materials were then dried at 60 æ%C for 3 days. The dried materials were then crushed and sieved at 200 µm and stored in bottles for uses.

Chemicals

Stock solution was prepared by dissolving 1.0 g of methylen blue (dye content 82%) supplied by Merck, Germany, in 1 L distilled water without further purification. The test solutions were prepared by diluting stock solution to the desired concentrations.

Experiments and analytical method

All the experiments were conducted at a constant temperature of 25±1 °C and at a constant pH = 7.1 to be representative of environmentally relevant conditions. Batch kinetics sorption experiments were carried out in 250mL Erlenmeyer flasks containing methylen blue solutions (100 mL) of known concentrations, which varied from 10 to 50 mg/L. Known amounts of biomass were added to each flask and the mixtures were agitated on the rotary shaker. After the sorption was reached, the change in methylen blue concentration due to sorption was determined colorimetrically (Shimadzu 1240 spectrophotometer) Absorbance was measured at wavelength (λ) 664 nm. For improving the results, all experiments were done in triplicate.

Methylen blue uptake capacities and kinetics models

The amount of methylen blue sorbed at equilibrium, q (mg.g^{-1}), which represents the metal uptake, was calculated from the difference in dye concentration in the aqueous phase before and after adsorption, according to the following equation:

$$q=\frac{(C_0-C_e)}{m}$$

C_0 and Ce respectively are the initial and equilibrium concentration of methylen blue in solution (mg/L), and m is the weight of biomass (g). Where V is the volume of methylen blue solution (L).

Fractional power[15], Pseudo-first order[16], Pseudo-second order[17], Elovich[18] and Intraparticule diffusion[19] rate equations have been used for modeling the kinetics of methylen blue sorption (TABLE 1).

TABLE 1: Kinetic biosorption models

Model	Equation	linear expression
Fractional power	$q_t = k_p.t^v$	$\mathrm{Ln}\ q_t = v.\mathrm{Ln}\ t + \mathrm{Ln}\ k_p$
Pseudo-first order	$q_t = q_{e,1P}(1-e^{-k_{1p}.t})$	$\mathrm{Ln}(q_e-q_t) = -k_{1p}.t + \mathrm{Ln}\ q_{e,1P}$
Pseudo-second order	$q_t = \frac{k_{2p}.q_{e,2P}^2.t}{1+k_{2p}.q_{e,2P}.t}$	$\frac{1}{q_t} = \frac{1}{k_{2p}.q_{e,2P}.t} + \frac{1}{q_{e,2P}}$
Elovich	$q_t = \frac{1}{\beta_E}.\mathrm{Ln}(\alpha_E.\beta_E.t)$	$q_t = \frac{\mathrm{Ln}(\alpha_E.\beta_E)}{\beta_E} + \frac{1}{\beta_E}.\mathrm{Lnt}$
Intraparticle diffusion	$q_t = k_D.t^{1/2} + C_D$	$q_t = k_D.t^{1/2} + C_D$

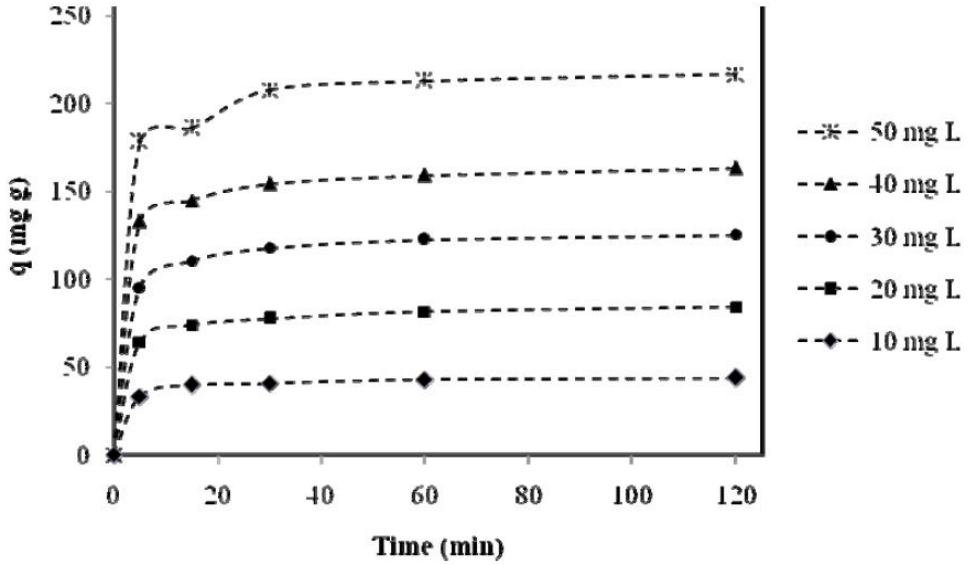

Figure 1: Kinetics (adsorption capacity q vs. time) of methylene blue on biomass waste mint

TABLE 2 : Kinetic model parameters for biosorption of methylene blue on biomass waste mint

Model	Model parameters	C_0=10mg/L	C_0=20mg/L	C_0=30mg/L	C_0=40mg/L	C_0=50mg/L
Fractional power	linear expression	y = 0.084x + 3.407	y = 0.083x + 4.053	y = 0.086x + 4.446	y = 0.066x + 4.793	y = 0.067x + 5.074
	R^2(%)	90.9	96.1	93.5	96.9	91.8
	υ	0.084	0.083	0.086	0.066	0.067
	k_p	30.17	57.57	85.29	120.66	159.81
	υ. k_p ($mg.g^{-1}.min^{-1}$)	2.534	4.778	7.335	7.964	10.707
pseudo-first order	linear expression	y = -0.050x + 2.912	y = -0.048x + 3.585	y = -0.054x + 4.003	y = -0.051x + 4.129	y = -0.058x + 4.480
	R^2(%)	80.7	81.1	84.7	78.8	83.8
	k_{1P} (min^{-1})	0.05	0.048	0.054	0.051	0.058
	$q_{e.1P}$ ($mg.g^{-1}$)	18.39	36.05	54.76	62.12	88.23
pseudo-second order	linear expression	y = 0.036x + 0.022	y = 0.018x + 0.012	y = 0.012x + 0.008	y = 0.006x + 0.006	y = 0.005x + 0.004
	R^2(%)	98.5	96.8	98.3	93.7	80.6
	k_{2P} ($g.mg^{-1}.min^{-1}$)	0.611	0.667	0.667	1	0.8
	$q_{e.2P}$ ($mg.g^{-1}$)	45.45	83.33	125	166.67	250
Elovich	linear expression	y = 3.260x + 29.32	y = 6.210x + 55.75	y = 9.571x + 82.54	y = 9.799x + 118.3	y = 13.30x + 156.3
	R^2 (%)	92.9	97.4	95.2	97.6	92
	α_E ($mg.g^{-1}.min^{-1}$)	26427	49123	51407	1705523	1644204
	β_E ($g.mg^{-1}$)	0.307	0.161	0.104	0.102	0.075
Intraparticle diffusion	linear expression	y = 1.079x + 33.61	y = 2.096x + 63.67	y = 3.174x + 95.09	y = 3.319x + 130.7	y = 4.556x + 172.9
	R^2(%)	78.2	85.3	80.4	86	82.9
	k_D ($mg.g^{-1}.min^{-1/2}$)	1.079	2.096	3.174	3.319	4.556
	C_D ($mg.g^{-1}$)	33.61	63.67	95.09	130.7	172.9

RESULTS AND DISCUSSION

The kinetic study of biosorption of methylene blue was done during a time of two hours, with agitation, temperature T = 25 ° C and pH = 7.1 constants. A weight of 0.2 g/L of biomass waste mint was added in solutions of methylene blue to initial concentration C_0 = 10 to 50 mg/L. Figure 1 illustrates the variation in the adsorption capacity q versus at time t. These curves show two quite clear: A first branch reflects a rapid

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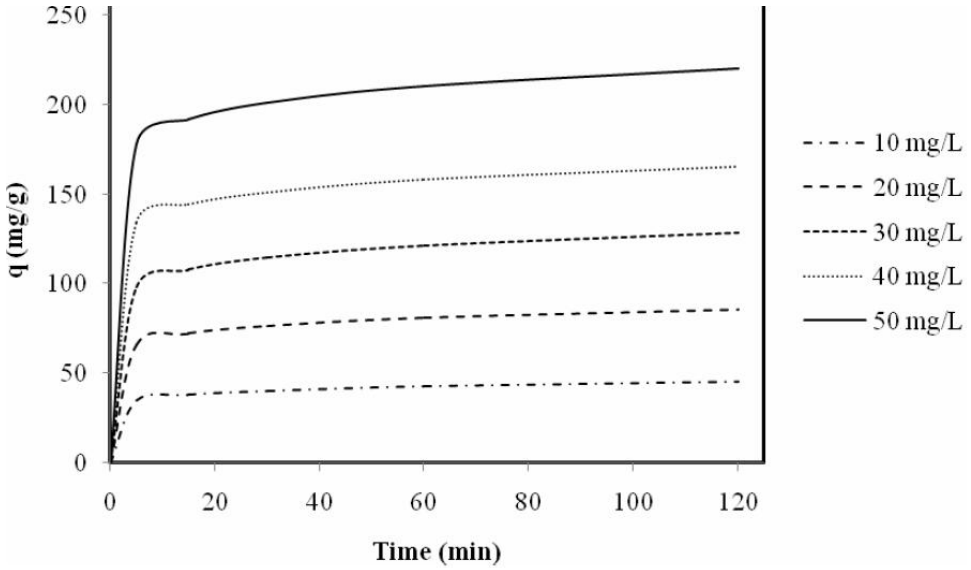

Figure 2 : Modeling the kinetic biosorption by fractional power model

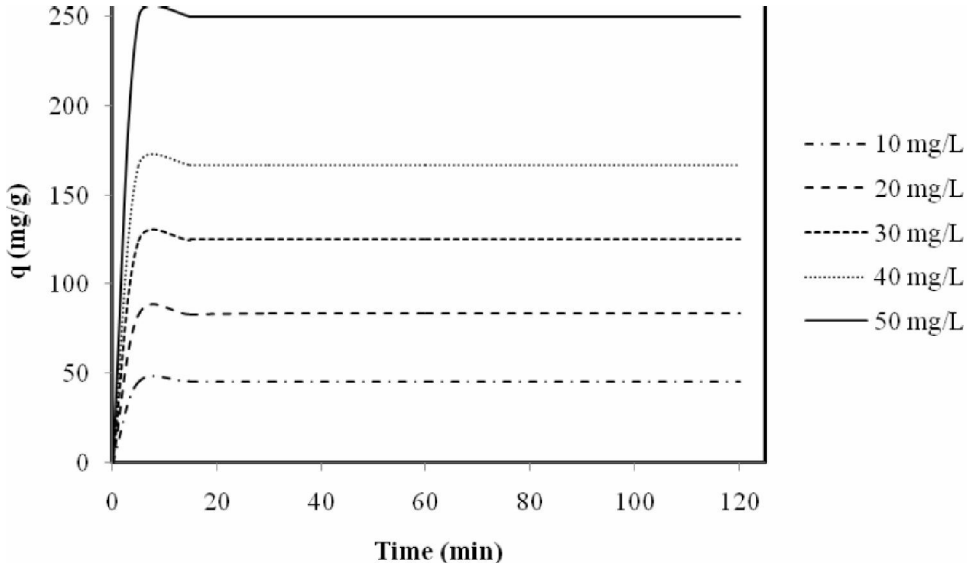

Figure 3 : Modeling the kinetic biosorption by pseudo-second order model

decrease of the adsorption capacity q of methylene blue for 5 minutes. A second branch from 15 minutes at 120 minutes is characterized by a gradual change of the adsorption capacity q of methylene blue until equilibrium of biosorption.

The experimental adsorption capacities of biomass mint waste are higher, then the values of the absorption capacity at equilibrium (2 hours) of the initial concentrations for C_0 = 10, 20, 30, 40 and 50 mg/L, are respectively 44.05±0.88, 84.23±1.23, 125.46±1.62, 163.22±5.87 and 216.84±1.21 mg/g.

All the kinetic parameters of biosorption media biomass waste mint are determined from the straight linearity according to the equations of the models described in TABLE 1. In considering the reliability of the proposed kinetic models, we calculated the correlation coefficients of the equations and the kinetic constants of each model. These are grouped in TABLE 2.

From the values of correlation coefficients R^2 of these tables we can conclude that the model of fractional power (R^2 between 90.9% and 96.9%), pseudo-second order model (R^2 between 80.6% and 98.5%) and Elovich model (R^2 between 90% and 97.6%) are closer to the experimental results of adsorption kinetics. By cons, we note that the theoretical data from other models move away from the experimental data.

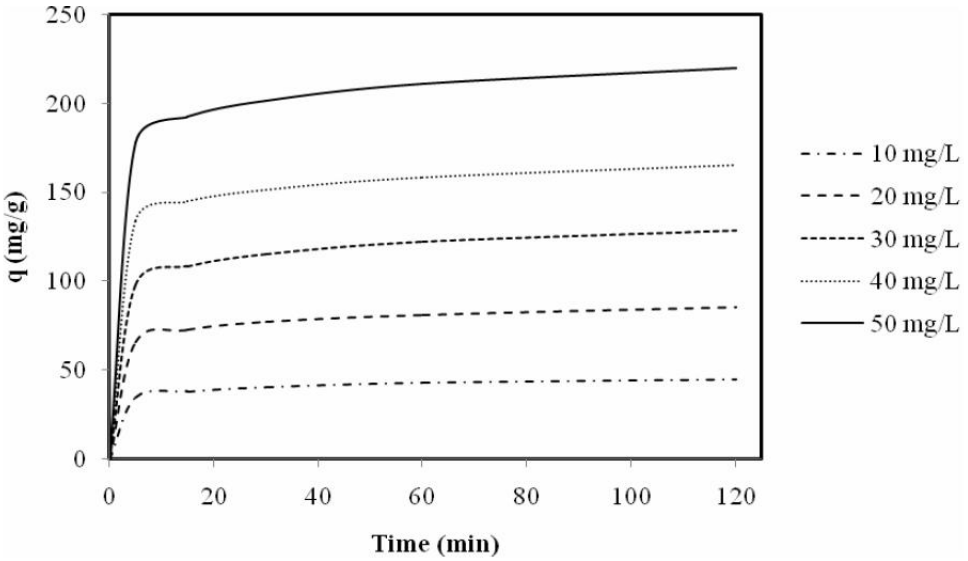

Figure 4 : Modeling the kinetic biosorption by Elovich model.

To better demonstrate the effectiveness of the fractional power model, pseudo-second order model and Elovich model, we reported in Figures 2, 3 and 4 modeling the kinetics of methylene blue biosorption of these 3 models respectively on biomass waste mint.

CONCLUSION

The results obtained during the adsorption of methylene blue on biomass waste mint show that:

- The waste mint can be used as good adsorbent particularly for the removal of methylene blue and generally for all dyes.
- The adsorption kinetics could be considered consistent with models of fractional power, pseudo-second order and Elovich.

All the results obtained in this work, we have discovered new ways of valuing the waste mint, giving new biomass in the field of environmental applications.

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