

INFLUENCE OF SOME EXPERIMENTAL PARAMETERS ON METHYLENE BLUE SORPTION KINETICS FROM SYNTHETIC AQUEOUS SOLUTIONS USING THISTLE STALKS AS A LOW-COST SORBENT: EXPERIMENTAL AND MODELLING STUDIES

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ABSTRACT

The ability of thistle stalks, as an inexpensive sorbent for the removal of methylene blue (basic dye) from synthetic aqueous solutions, has been studied in batch conditions. The influence of some parameters such as: contact time, initial dye concentration, sorbent dose and agitation speed on dye sorption kinetics, has been studied. Dye uptake was time contact, initial dye concentration, sorbent dose and agitation speed dependent. The main parameters that play an important part in removal phenomenon were initial cadmium concentration and sorbent mass. Agitation speed showed a restricted effect on the dye removal kinetics. Two simplified kinetic models including a first-order and a pseudo second-order rate equation were selected to describe the dye sorption kinetics. Methylene blue sorption process followed a pseudo second – order rate kinetics. A multiple-stage diffusion of methylene blue onto thistle stalks particles was observed indicating that intraparticle diffusion was not a fully operative mechanism for this system and reflects some degree of boundary layer control. From these first results obtained under the investigated experimental conditions, the thistle stalks tested were shown to be promising sorbent material for removal/sorption of methylene blue from synthetic aqueous solution.

Keywords: Removal, Sorption, Methylene blue, Thistle stalks

1. INTRODUCTION

Nowadays, water pollution control has become one of the major environmental problems. Synthetic dyes are extensively used by various industries such as: textile, dyehouses, etc. Among the various types of dyes, various cationic dyes including methylene blue are used for dyeing cotton, wool and silk (Rafatullah et al. [1], Bielska

and Szymanowski [2]). Though methylene blue is not strongly hazardous, it can cause some harmful effects (eye burns, nausea, vomiting, etc. (Rafatullah et al. [1]). Thus, the treatment of effluent containing such dye is of major scientific interest, decolourization of dye-containing effluent becoming an obligation both environmentally and for water re-use. Although physical and/or chemical methods are efficient in treating a dye wastewater, they are quite expensive and have operational problems (Garg et al. [3], Kapdan et al. [4]). Adsorption processes using suitable adsorbents are proved to be an effective and attractive technique for removal of various dye types from wastewater (Robinson et al. [5], Aksu [6]). Most systems use activated carbon as adsorbent to remove dyes because of its excellent adsorption ability (Garg et al. [3], Kapdan et al. [4], Wang et al. [7]). Nevertheless, its widespread use is limited due to its cost and the problem of regeneration (Janos et al. [8]). In recent years, it has led to the search of alternative low cost adsorbents including biosorbents, waste from agriculture or industry and natural materials.

This study explores the possibility of using a natural plant waste material namely: thistle stalks, as an inexpensive sorbent for the removal of methylene blue, as a model of basic dyes, from synthetic aqueous solutions. This material is abundantly available in Algeria, hence cost effective sorbent. The effect of some experimental parameters such as: contact time, initial dye concentration, sorbent dose and agitation speed, on the kinetics of methylene blue sorption from synthetic aqueous solutions by this material, was studied in batch conditions. The experimental data of methylene blue sorption kinetics by this material tested were fitted by two current models namely: first-order and pseudo- second-order models. To identify the main rate controlling steps in the overall uptake mechanism, a single intra-particle mass transfer diffusion model was tested.

2. MATERIALS AND METHODS

2.1 Sorbents and dye

A natural plant waste material namely: thistle stalks, which is cheap and highly available lignocellulosic waste in Algeria, was used as a sorbent material in this work. This waste was collected from the region of Bensekrane (Tlemcen-Algeria-) at different periods: autumn-winter 2010 in the form of large flakes. It was sun/air dried at ambient temperature during many days, crushed and sieved to keep only the size range 1.25-2 mm. This waste was used as sorbent material after the following treatment chosen arbitrary: 10 g of each waste were contacted with 2 L of distilled water in a beaker agitated vigorously (at a speed of 400 rpm) by a magnetic stirrer at ambient temperature of $25 \pm 1^\circ\text{C}$ during 4 h, filtered, washed thoroughly with distilled water to remove all the adhering dirt particles until constant pH and no colour observed, then oven-dried at $85 \pm 5^\circ\text{C}$ for 24 h.

Methylene blue, as a commercial salt with known structure, was used as received without further purification, in single component aqueous solutions. 1000 mg/L stock solutions of this dye were prepared in distilled water. All working solutions of the desired concentration were prepared by successive dilutions.

2.3 Sorption experiments

The initial methylene blue concentration was 100 mg/L for all experiments except for that carried out to examine the effect of the initial concentration of dye. For dye removal kinetic studies, 1L of dye solution of known concentration was added to 1g of sorbent in a beaker agitated vigorously by a magnetic stirrer at 400 rpm using a water bath maintained at a constant temperature 25 °C. In all cases, the working pH was that of the original solution and was not adjusted. Samples from the clear supernatant, at appropriate time intervals, were pipetted from the beaker by the aid of the very thin point pipette, which prevented the transition of sorbent samples to solution. Their dye concentrations were determined using UV-visible spectrophotometer (HACH LANGE DR 5000) at λ_{\max} 664 nm. The dye uptake q_t (mg dye/g sorbent) was determined as follows:

$$q_t = (C_0 - C_t) \cdot V/m \quad (1)$$

where: C_0 and C_t are the initial and time dye concentration (mg/L), respectively, V is the volume of solution (mL), and m is the sorbent weight (g) in dry form.

Duplicate tests showed that the maximum standard deviation of the results was $\pm 5 \%$.

3. RESULTS AND DISCUSSION

3.1 Effect of contact time

A preliminary experiment was performed to obtain an idea on the equilibrium time. According to Fig. 1 obtained for an initial methylene blue concentration 100 mg/L, the kinetics of dye sorption by thistle stalks presents a shape characterized by a strong increase of the amount of dye sorbed during the first minutes of contact solution – thistle stalks, follow-up of a slow increase until to reach a state of equilibrium. The necessary time to reach this equilibrium is about 21 h and an increase of removal time to 30 h did not show notable effects. Under these experimental conditions, at equilibrium, about 36 % of initial dye solution were removed by thistle stalks corresponding to an equilibrium amount of $q_e = 36.56$ mg/g under these experimental conditions.

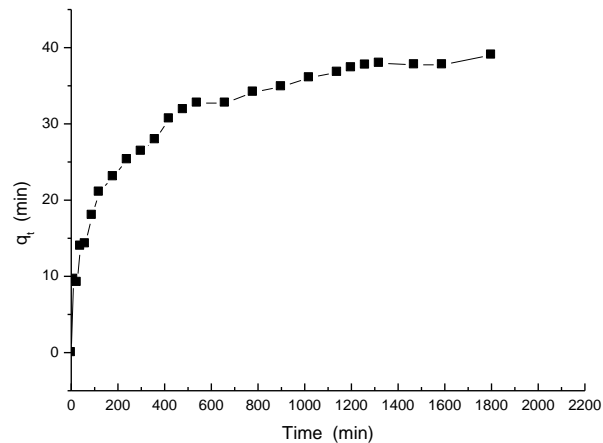


Fig. 1 Kinetic of methylene blue from aqueous solution by thistle stalks. (Experimental conditions: $C_0= 100$ mg/L, sorbent dose= 1 g/L, particle size= 1.25-2 mm, agitation speed= 400 rpm, natural pH of solution, $T= 25$ °C)

During the course of dye sorption by thistle stalks tested, an increase in the initial pH value of the solution followed by some equilibrium state was observed (see Fig. 2 shown here). This suggests that dye binding to thistle stalks tested is associated with the fixation of H_3O^+ ions from solution by the sorbent surface or a release of OH^- ions from the sorbent surface into the solution. At this stage, further investigations are required to understand the mechanisms involved in dye sorption by this type of complex natural materials.

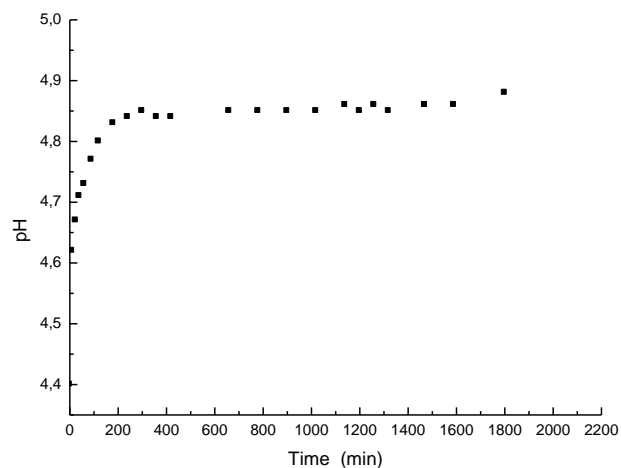


Fig. 2 pH profile of methylene blue sorption by thistle stalks. (Experimental conditions: $C_0= 100$ mg/L, sorbent dose= 1 g/L, particle size= 1.25-2 mm, agitation speed= 400 rpm, natural pH of solution, $T= 25$ °C)

3.2 Effect of initial dye concentration

According to Fig. 3, for all methylene blue concentrations studied in the range 50-200 mg/L, the obtained curves present the same shape characterized by a strong increase of the amount of dye sorbed during the first minutes of contact solution – sorbent, follow-up of a slow increase until to reach a state of equilibrium.

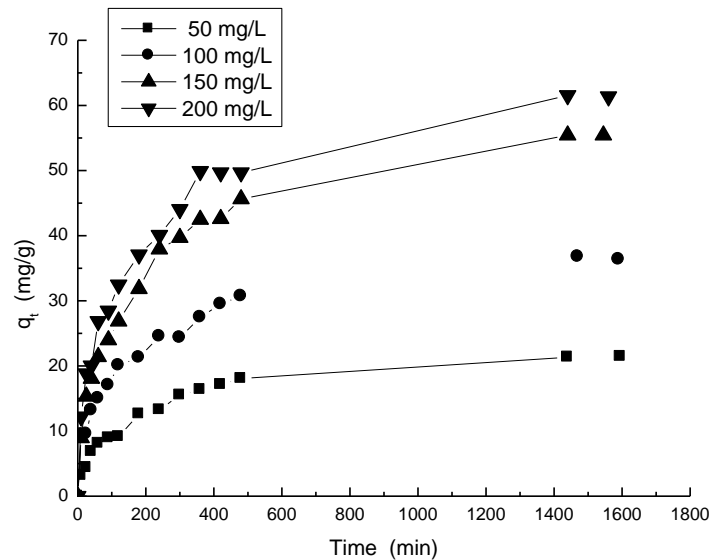


Fig. 3 Effect of initial methylene blue concentration on dye sorption kinetics by thistle stalks. (Experimental conditions: sorbent dose = 1g/L, particle size: 1.25-2 mm, agitation speed= 400 rpm, natural pH of solution, T= 25 °C)

Under these experimental conditions, from the results obtained at equilibrium, the necessary time to reach equilibrium was 21 h, independent on initial dye concentration, and an increase of dye removal time to 30 h did not show notable effects. The amount of methylene blue sorbed at the equilibrium increases with the initial dye concentration: about 21.40 mg/g ($C_0 = 50$ mg/L) and 61.44 mg/g ($C_0 = 200$ mg/L). Initial dye concentration provides an important driving force to overcome all mass transfer resistances of the dye between the aqueous and solid phases. Hence, a higher initial concentration of dye will enhance the sorption process (Gulnaz et al. [9]).

3.3 Effect of sorbent dose

In the goal to determine the necessary thistle stalks dose for a maximal removal of methylene blue, the effect of sorbent mass on the kinetics of dye removal was studied. Fig. 4 shows that the quantity of dye sorbed at equilibrium by thistle stalks increases with the quantity of

sorbent introduced: 30.33 mg/g ($m = 0.5$ g/L) and 38.02 mg/g ($m = 2$ g/L)

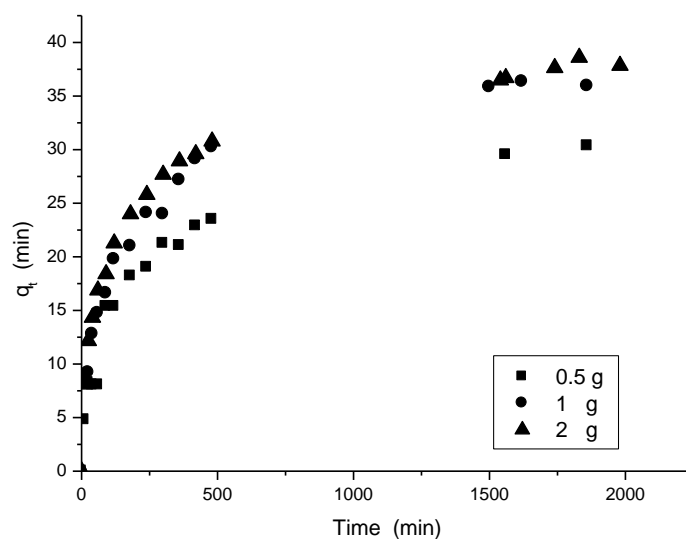


Fig. 4 Effect of sorbent dose on methylene blue sorption kinetics by thistle stalks.
(Experimental conditions: $C_0 = 100$ mg/L, particle size: 1.25-2 mm, agitation speed= 400 rpm, natural pH of solution, $T = 25$ °C)

3.4 Effect of agitation speed

In the goal to determine the optimal speed of agitation, the kinetics of methylene blue removal by thistle stalks was studied using different agitation speeds: 200, 400 and 600 rpm. Fig. 5 shows that the high quantity of dye removed at equilibrium, that is about of 37.71 mg/g, is obtained with a agitation speed of 400 rpm (speed besides chosen for further study of the various experimental parameters influence on the kinetics of dye removal and for the continuation of this work), that assures a good diffusion of dye toward thistle stalks particles. For a weak agitation speed, a reduction in the capacity of dye sorption by thistle stalks is observed: 29.98 mg/g for 200 rpm. On the other hand, in the case of high agitation speed, a reduction in the capacity of dye removal at equilibrium is also observed: 33.17 mg/g for 600 rpm.

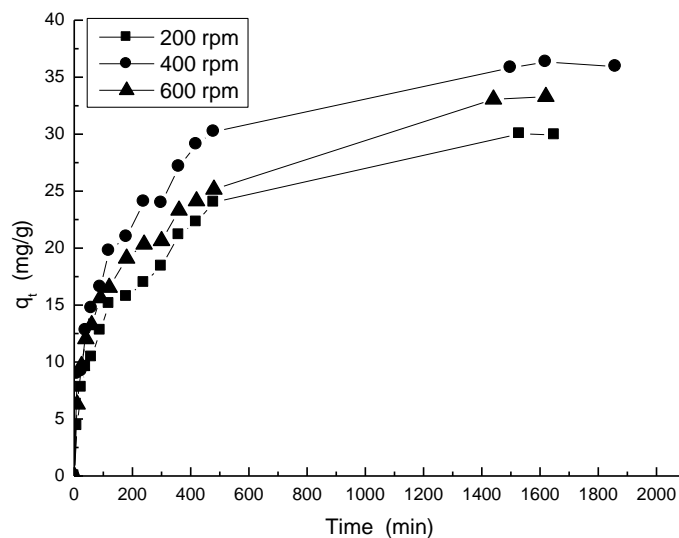


Fig. 5 Effect of agitation speed on methylene blue sorption kinetics by thistle stalks. (Experimental conditions: $C_0 = 100$ mg/L, dose sorbent= 1g/L, particle size: 1.25-2 mm, natural pH of solution, $T = 25$ °C)

During the course of dye sorption by this sorbent tested (Fig. no shown here), for all experimental parameters studied, an increase in the initial pH value of the solution followed by some equilibrium state was observed.

3.5 Modelling

To analyze the kinetic data of bezanyl red sorption by each variety of almond peel under the experimental conditions tested, two common models from the literature, namely: the first-order rate model of Lagergren (Lagergren [10]) and the pseudo second-order rate model (Ho and McKay [11,12]) were chosen and shown below as Eqs. (2) and (3) in their linear forms:

$$\log (q_e - q_t) = \log q_e - k_L t / 2.3 \quad (2)$$

$$t/q_t = 1/k \cdot q_e^2 + t/q_e \quad (3)$$

where: k_L is the Lagergren rate constant of sorption (min^{-1}) and k the pseudo second-order rate constant of sorption ($\text{g} \cdot \text{mg}^{-1} \cdot \text{min}^{-1}$); q_e and q_t are the amounts of dye sorbed ($\text{mg} \cdot \text{g}^{-1}$) at equilibrium and at time t , respectively. For all initial dye concentrations, the different values of constants from the slope and intercept of linear plots of $\log (q_e - q_t)$ vs. t and t/q_t vs. t (see Fig. 6 as a typical example) are summarized in the Table 1.

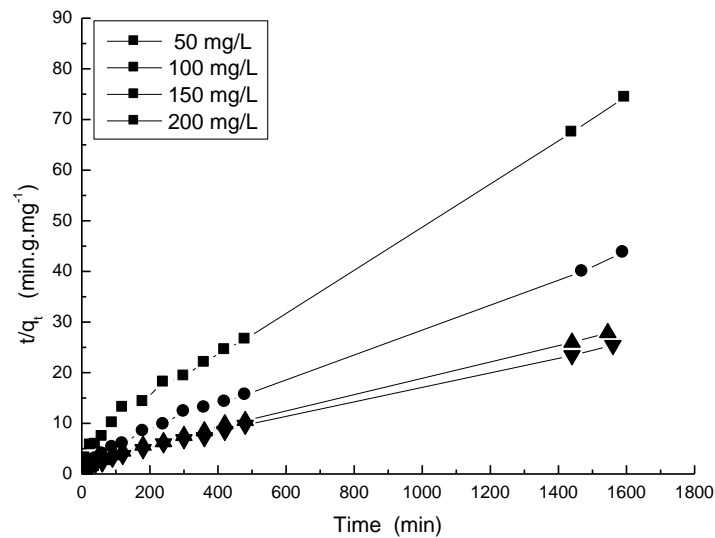


Fig.6 Pseudo-second order model for methylene blue sorption kinetics by thistle stalks.
 (Experimental conditions: sorbent dose = 1 g/L, particle size: 1.25-2 mm, agitation speed= 400 rpm, natural pH of solution, T= 25 °C)

Compared to the first-order rate model ($0.9679 < R^2 < 0.9955$), the pseudo second-order rate model adequately described the kinetics of dye sorption with acceptable correlation coefficients ($0.9945 < R^2 > 0.9960$). The equilibrium dye sorption capacity, q_e , increases with the increase in the initial dye concentration. The values of q_e obtained from the fitting to the pseudo second-order rate model are very similar to the experimental values obtained from the sorption kinetics at equilibrium: consequently, it was further used to describe all the kinetics of dye sorption by obtained under other experimental conditions. The results obtained and also presented in Table 1, confirm that the kinetic data obtained follow the pseudo-second order kinetic model. In this model, all the steps of sorption such as: external diffusion, internal diffusion, and sorption are lumped together and it is assumed that the difference between the average solid phase concentration and the equilibrium concentration is the driving force for sorption, and that the overall sorption rate is proportional to the square of the driving force (Wu et al. [13]).

Table 1 Models rate constants for methylene blue sorption kinetics by thistle stalks: effect of some experimental parameters.

		First-order kinetics model			Pseudo second order kinetics model			
		$q_{e,exp}$ (mg/g)	$q_{e,cal}$ (mg/g)	$k_L \cdot 10^3$ (min^{-1})	R^2	$q_{e,cal}$ (mg/g)	$k \cdot 10^4$ ($\text{g} \cdot \text{mg}^{-1} \cdot \text{min}^{-1}$)	R^2
C_0 (mg/L)		Initial dye concentration						
50	21.40	19.35	3.96	0.9955	23.09	3.29	0.9960	
100	36.56	27.50	3.10	0.9932	38.74	2.32	0.9945	
150	55.43	44.37	3.29	0.9679	59.28	1.39	0.9956	
200	61.44	52.36	3.96	0.9899	65.15	1.41	0.9956	
m (g/L)		Sorbent dose						
0.5	30.33				32.01	2.34	0.9950	
1	37.71				38.74	2.32	0.9945	
2	38.02				39.59	2.50	0.9980	
N (rpm)		Agitation speed						
200	29.98				32.24	2.12	0.9910	
400	37.71				38.74	2.32	0.9945	
600	33.17				35.30	2.14	0.9889	

3.6 Rate determining steps

From a mechanistic viewpoint, to interpret the experimental data, it is necessary to identify the steps involved during the sorption process. It is generally agreed that there are four consecutive steps which describe the overall sorption process of solute from a solution by a sorbent particle (Furusawa and Smith [14]). These steps, as adapted to apply to the sorption dye by a sorbent particle, are as follows:

1. Transfer of dye from the solution bulk to the boundary layer recovering the surface of the solid phase: bulk diffusion.

10 Sixteenth International Water Technology Conference, IWTC 16 2012, Istanbul, Turkey

2. Dye diffusion through the boundary film to the surface of the sorbent particle: film diffusion.
3. Diffusion of dye from the solid phase surface to the sorption sites: intraparticle diffusion.
4. Final uptake of dye at the sorption sites, via complexation, sorption, ion-exchange, complexation or precipitation, which is fast.

In the process of establishing the rate limiting step, the fourth step is assumed to be very rapid and is therefore not considered in any kinetic analysis (Findon et al. [15]): sorption is a quasi-instantaneous process (Tsezos and Volesky [16]). The first and the second step are external mass transfer resistance steps, depending on various parameters such as agitation and homogeneity of solution. In this study, the agitation given here to the solution (400 rpm) is considered as sufficient to avoid steps 1 and 2 being controlling steps. In a well – agitated batch system, the boundary layer surrounding the particle is much reduced, reducing the external mass transfer coefficient; hence, the third intraparticle diffusion resistance step is more likely to be the rate controlling step (Sag and Aktay [17], McKay [18]). This possibility was tested in terms of a graphical relationship between q_t and the square root of time, $t^{1/2}$, according to the intraparticle diffusion model proposed by Weber and Morris [19] which is commonly expressed by the following equation:

$$q_t = K_i t^{0.5} \quad (4)$$

where: q_t is the solute concentration in the solid (mg g^{-1}) and K_i is the slope of the plot defined as an intraparticle diffusion rate parameter ($\text{mg g}^{-1} \text{min}^{-1/2}$).

If the intraparticle diffusion is involved in the solute sorption process, then the plot of q_t vs. $t^{0.5}$ would result in a linear relationship, and the intraparticle diffusion would be the controlling step if this line passed through the origin (McKay and Poots [20], Ho [21]). Fig. 7, as a typical example of results obtained, shows plots of q_t vs. $t^{0.5}$ for methylene blue sorption kinetics by thistle stalks at an initial dye concentration 100 mg/L. For the sorbent tested, three linear portions are observed in the same experiment before achieving the equilibrium confirming that straight lines do not pass through the origin with correlation coefficients ranging from ? to ? values without definite meaning (see Table 2). This observation is indicative of a multiple-stage diffusion of methylene blue onto thistle stalks particles: external-mass transfer followed by intraparticle diffusion in macro, meso and micropores (Ho and McKay [22]). Such a multiple nature of the curve confirms that intraparticle diffusion is not a fully operative mechanism for this system and reflects some degree of boundary layer control.

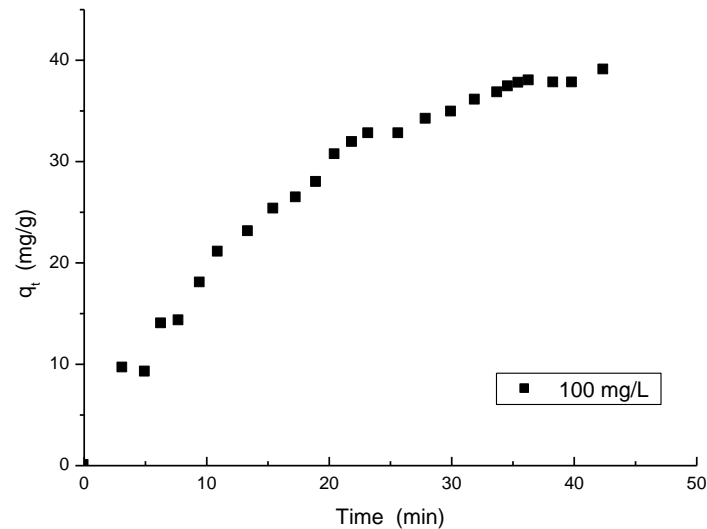


Fig. 7 Intraparticle diffusion model for methylene blue sorption kinetics by thistle stalks. (Experimental conditions: $C_0 = 100$ mg/L, sorbent dose = 1 g/L, particle size: 1.25-2 mm, agitation speed= 400 rpm, natural pH of solution, $T = 25$ °C)

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CONCLUSION

The present study shows that thistle stalks tested can remove methylene blue from synthetic aqueous solutions under the experimental conditions tested. The quantity of dye sorbed at equilibrium depends on contact time, initial dye concentration, dose sorbent and agitation speed. It increases with an increase in the values of initial dye concentration and sorbent dose. The kinetics of methylene blue sorption was well described by a pseudo-second order rate model. A multiple-stage diffusion of methylene blue onto thistle stalks particles was observed indicating that intraparticle diffusion was not a fully operative mechanism for these systems and reflects some degree of boundary layer control. These results obtained stimulate the prosecution of this research because there are still several very important aspects to clarify.

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