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Batch adsorption of methylene blue from aqueous solutions by untreated Alfa grass

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ABSTRACT

In this study, adsorption capacities of untreated Alfa stems were tested for the removal of methylene blue (MB) as a dye in aqueous solutions. The effects of initial dye concentration (10–150 mg/L), contact time, adsorbent dose (0.25–12.5 g/L), solution pH (2–12), temperature (283–330 K) and ionic strength (5–100 mg/L) on MB adsorption were investigated. The thermodynamic parameters, the kinetics and the factors controlling the adsorption process were also calculated and discussed. The experimental data modelling showed that the models of Langmuir and pseudo-second order, describe perfectly the adsorption process. The maximum value of the adsorption capacity calculated according to the Langmuir model is 200 mg/g. The thermodynamic parameters showed that MB adsorption onto Alfa grass is a favourable endothermic and spontaneous phenomenon and confirms the Alfa grass affinity for MB. The Alfa stems in a rough state have good adsorption effectiveness with respect to dyes without a preliminary treatment. In addition, the availability and the low cost of the Alfa grass could lead to its use for the coloured wastewater treatment.

Keywords: Adsorption; Methylene blue; Alfa grass; Water treatment; Dyes; Isotherm; Kinetic; Thermodynamics

1. Introduction

Most of industrial processes consume water and produce wastewaters polluted by various substances hazardous to the environment. Wastewaters contaminated by dyes are generated by several industries such as textile, paper, plastics, leather, cosmetics, pharmaceutical and food industries.

The effluents discarded by the textile industry cause some problems to the environment due to the presence of a wide range of contaminants such as acids, bases, dissolved solids, and dyes. The dyes are substances non-degradable toxic and tend to be quite stable for long periods of time [1]. Moreover, color impedes light penetration, retards photo-synthetic activity, and inhibits the growth of biota. In addition, direct discharges of synthetic dyes into urban wastewaters in natural environments may cause the formation of toxic carcinogenic breakdown products [2].

Methylene blue (MB) is the most commonly used substance for dying paper, cotton, wood, and silk but can cause some harmful effects. It can cause eye burs which may be responsible for permanent injury to the eyes of human and animals. On inhalation, it can give

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rise to short periods of rapid or difficult breathing while ingestion through the mouth produces a burning sensation and may cause nausea, vomiting, diarrhea, and gastritis. Accidental large dose creates abdominal and chest pain, severe headache, profuse sweating, mental confusion, painful micturation and methemoglobinemia [3].

Dye effluents require especial treatment before their release in the environment. Physical, chemical, and biological methods have been used for the removal of dyes. These conventional methods are based on the treatment by oxidation or ozonation [4,5], coagulation and floculation [6], membrane separation [7], and adsorption on activated carbon [8,9].

For wastewater treatment, adsorption presents more advantages than the other methods [10]. The major advantages are low initial cost, simple design, easy operation, and free from or less generation of toxic substances [11]. Adsorption on activated carbon constitutes the most effective method for dyes removal from water; however it remains expensive especially in a large scale application.

In recent years, extensive research has been undertaken to develop effective and low cost adsorbents from natural materials, industrial wastes or agricultural by-products for wastewater treatment. Various low cost adsorbents from natural materials or agricultural wastes have been investigated for dye removal from aqueous solutions.

Some of these adsorbents are clays [12–14], zeolites [15], bioadsorbents like De-oiled Soya [16], algae [17,18], agricultural wastes hen feathers [19,20], fibers [21], fruits peels, husk, bark, and seeds [22–25], sawdust [26,27], industrial solids wastes such as sludge and granulated waste materials [28,29].

Alfa grass constitutes a natural and widely available material in Algeria and could be suggested as an interesting adsorbent for wastewater treatment processes. Widely distributed in semi-arid and arid regions like northwest Africa particularly Algerian highlands and southern Spain, Alfa grass grows to about 1 m height.

Called, *Stippa tenacissima*, or Esparto grass, Alfa grass is a tussock grass which belongs to the Graminaceae family. Alfa grass is mainly used as a fibre source in paper industry [30] especially for manufacturing high quality ink jet papers and for reinforcing biodegradable composite materials.

In the present paper, we propose this agro-industrial material as a low cost adsorbent to treat coloured wastewaters.

In this context, we carried out a study to test adsorption capacities of untreated Alfa stems for the removal of MB dye in aqueous solution.

The effects of initial dye concentration, contact time, adsorbent dose, solution pH and temperature on MB adsorption were evaluated. Thermodynamic parameters, the kinetics and factors controlling the adsorption process were also calculated and discussed.

2. Materials and methods

2.1. Materials

2.1.1. Preparation and characterisation of adsorbent

Alfa stems were collected in the highlands of Laghouat in Algeria during the period of March–June 2011. They are mainly composed by cellulose filaments bounded by lignin, pectins, and hemicelluloses [31].

The materials were washed several times with slightly warm water to remove dirt particles and to decrease its hardness. The washed materials were then dried at 105°C during 24 h, cut in small pieces, crushed in a knife mill and finally sieved to a desired size range (500–650 μm).

The surface functional groups of Alfa were detected by Fourier transform infrared (FTIR) spectroscope. Surface aspects of Alfa particles were observed by optical microscope type ZEISS equipped with a numerical camera (Nikon 500).

2.1.2. Adsorbate

The characteristics and chemical structure of the adsorbate MB of the adsorbate MB are regrouped in Table 1 and Fig. 1, respectively.

2.2. Method

Adsorption experiments were carried out, at a fixed temperature in batch mode, by putting in

Table 1
Properties and characteristics of MB

Generic name	MB
Chemical name (IUPAC)	3,7-bis(dimethylamino)-phenazathionium chloride tetramethylthionine chloride
Chemical formula	$C_{16}H_{18}\,ClN_3S$
Molecular weight (g/mol)	319.86
Maximum wavelength (nm)	665
Colour index number	52,015

200 mL glass Erlenmeyer flasks 100 mL of MB solution of known initial concentration, pH and adsorbent dose. The mixtures were then capped and agitated mechanically at 500 rpm using a rotary orbital shaker during 180 min to attain equilibrium conditions. Solution pH was adjusted to desired values with dilute HCl or NaOH solution and tested by Hanna HI-8224 pH-meter equipped with a combined pH electrode.

After centrifugation and filtration, MB solutions concentration was measured by spectrophotometry using a Shimadzu UV/Vis spectrophotometer model 1800 over the wavelength of 665 nm. The effects of parameters such as initial dye concentration, contact time, solution pH, adsorbent dose and solution temperature were investigated.

3. Results and discussion

3.1. Characterisation of Alfa adsorbent

3.1.1. Optical microscope analysis

Alfa stems structure is complex. The smallest parts in the stems are the cellulose filaments or the fibrils. These fibrils are tied in a dense way by hemicelluloses, which are bounded by lignin and pectins to give beams of stems. The bond of these beams forms finally the stem [32].

Alfa particles were observed under optical microscope before and after adsorption. The given photographs (not shown) reveal that stems structure is heterogeneous and their longitudinal section has an irregular form. Furthermore, the presence of fine spines on Alfa particles surface was examined, which indicates a certain degree of roughness.

After adsorption, it was observed that adsorbent surface had been loaded significantly by MB but it was not fixed in a homogeneous manner. Someparts were more coloured than the others, due to the surface heterogeneity.

3.1.2. FTIR analysis

FTIR spectra of Alfa stems presented several absorption peaks indicating complex structure of the adsorbent. This analysis shows broad band at 3,400 cm^{-1} representing bonded –OH groups and corresponding to the alcohols, phenols and acids carboxylic functions being mainly in lignins, pectins and cellulose.

The peaks observed at 2,900–2,850 cm^{-1} and which correspond to –CH_2- and –CH-groups, appear more marked after adsorption.

A vibration peak was detected at 1,740 cm^{-1} related to the carbonyl groups C=O of pectins. The spectra presented also a peak at 1,100 cm^{-1} related to C–O–C stretching groups. The large band located at 700 cm^{-1} is related to the alkene group C=C.

The large band between 1,000 and 1,900 cm^{-1} presents several peaks clearly more marked after adsorption indicating that –OH groups, C–O–C stretching, C=O stretching, C–O stretching and C–OH stretching groups are particularly involved in MB adsorption [33].

3.1.3. BET surface area

The textural characterization of Alfa grass particle was carried out by N_2 adsorption and the specific surface estimated is 3.2783 m^2/g was determined by BET method with an area surface analyser (NOVA 2000E).

3.1.4. pH of point of zero charge (pH_{ZPC})

The pH_{PZC} of Alfa stems was determined using the method described by Barka et al. [34]. This method consists to add HCl (1 N) or NaOH solution (1 N), to 50 mL of NaCl solution (0.01 M), contained in a thermostated cell maintained at 25°C. When the pH of the NaCl solution is fixed, we add 0.05 g of Alfa stems. The equilibrium pH was measured after 6 h of shaking.

The pH_{PZC} can be used to characterize an adsorbent material, since it indicates the pH at which the adsorbent material has a net zero surface charge [35].

The adsorbent surface has a net positive charge at $pH < pH_{PZC}$, while at $pH > pH_{PZC}$, the surface has a net negative charge. Therefore, the adsorption of cationic dyes is favored when the pH is greater than the pH_{PZC}, while the adsorption of anionic dyes is favored at pH values lower than the pH_{PZC} [36]. The pH value for the potential of zero charge for Alfa stems was 6.8, indicating that when the pH of the solution is greater than the pH_{PZC}, the adsorbent has a negatively charged surface that can attract MB (see Fig. 1) positively charged dye [37].

3.2. Influence of adsorption parameters

3.2.1. Effect of initial dye concentration and contact time

Fig. 2 shows the amount of dye adsorbed vs. time for various initial MB concentrations at 293 K. It appears that MB adsorption was rapid in the initial phase and gradually decreased with time until equilibrium was reached.

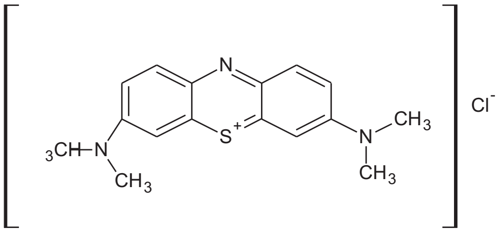

Fig. 1. Chemical structure of MB.

The high adsorption rate in the initial period may be due to the large number of sites available in the initial phase, resulting in a concentration gradient which tends to increase the adsorption of dyes in the early stages. As time passes, this concentration gradient is reduced due to the accumulation of dye particles on the adsorption sites, leading to a decrease in adsorption in the later stages [38].

Moreover, these results show that the removal of dye depends on dye concentration. At equilibrium, the quantity of MB removed increased from 2.24 to 113.77 mg/g with an increase in dye concentration from 10 to 520 mg/L.

The initial dye concentration provides the necessary driving force to overcome the resistances to the mass transfer of MB between the aqueous and solid phases [36]. Hence a higher initial concentration of dye will enhance the adsorption process.

Similar tendency was observed by Hasnain Isa et al. [39] for disperse dyes adsorption on palm ash and by Hameed et al. [22,33] for MB adsorption on respectively banana stalk waste, pomelo and garlic peel.

The results show also that equilibrium time increased from 30 to 60 min with an increase in dye concentration from 10 to 155 mg/L and it reached a value around 120 min for both concentrations of 315 and 520 mg/L. Equilibrium time is thus attained more quickly for low concentration solutions. Further experiments were performed with 180 min contact time to guarantee the maximum adsorption and a complete equilibrium condition.

3.2.2. Effect of adsorbent dose

In order to determine the Alfa amount which gives an optimal MB adsorption, experiments were carried out by varying adsorbent dose from 0.25 to 12.5 g/L and the other parameters were fixed.

The effect of adsorbent dose on equilibrium adsorption capacity is presented in Fig. 3. It appears that MB quantity adsorbed on Alfa particles is significant when adsorbent dose is low.

When adsorbent dose increases from 0.25 to 6.5 g/L the equilibrium quantity q_e retained decreases from 228.31 to 14.62 mg/g and for doses higher than 6.5 g/L, the amount of MB adsorbed tends to remain almost constant.

Similar phenomenon was observed by Barka et al. [34] for the adsorption of MB, yellow basic 28, and reactive yellow 125 on natural phosphate. He explained this trend by the fact that for low doses, the free superficial area of adsorbent grains is more exposed and consequently MB removal by adsorption is more favoured.

Di Toro et al. [40] and Serverston and Banerjei [41] allotted this reduction to desorption of the unstable fraction of adsorbed compound resulting from interparticle collisions which are more important and intense when adsorbent dose increases.

In addition, Van Hoff and Andreus [42] explained the reduction in amount of MB removal by a reduction in molecular diffusion of adsorbate when adsorbent dose increases. Consequently, time necessary to equilibrium establishment is longer.

3.2.3. Effect of solution pH

The pH is a significant factor in any adsorption study; it influences the adsorbent material charge and

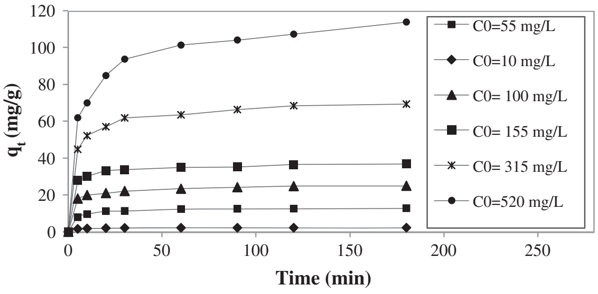

Fig. 2. Adsorption capacity evolution at various initial MB concentrations ($T = 293$ K; $W = 400$ mg; pH = 12; $N = 500$ rpm).

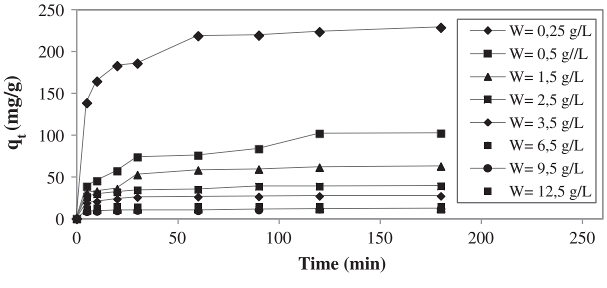

Fig. 3. Adsorption capacity evolution at various adsorbent doses ($T = 293$ K; $C_0 = 100$ mg/L; pH = 12; $N = 500$ rpm).

controls the sorption phenomenon. For this reason, the adsorption effectiveness was tested with different MB solutions adjusted at pH from 2 to 12 by adding dilute HCl or NaOH solution.

The results in Fig. 4(a) show that the pH evolutes with time. Initially it decreases rapidly then remains almost constant with time. As shown in Fig. 4(b), the pH solution influences considerably the amount of dye adsorbed. The equilibrium adsorbed quantity of MB by Alfa grass increases from 7.49 to 24.97 mg/g when the pH increases from 2 to 12. The removal of MB is enhanced at high pH values.

This behaviour can be explained by considering the pH evolution during the free process and the adsorbent pH corresponding to zero charge point, determined experimentally, and equal to 6.8.

The surface of Alfa grass particles contains a large number of active sites; in fact for pH greater than 6.8, the Alfa particle surface becomes negatively charged which favours electrostatic attraction of positively charged cations and adsorbent sites negatively charged. Whereas for a pH lower than 6.8, the particles surface becomes positively charged, which do not favours the adsorption of dye cations and leads then to an electrostatic repulsion between the cations and adsorbent sites. In addition, lower adsorption of MB at acidic pH might be due to the presence of excess H^+ ions competing with dye cations for the available adsorption site [43].

The same phenomenon was observed by Dogan et al. [44] for the adsorption of methyl purple and MB on the sepiolite and by Al-Ghouti et al. [45] for MB adsorption on diatomite.

3.2.4. *Effect of ionic strength*

Since real time waste water contains salts; it is important to study the ability of adsorbent for MB removal in presence of ionic salts. For this purpose, ionic strength of dye solutions was adjusted in a range between 5 and 100 g/L by adding known amount of NaCl solution. Fig. 5 shows the amount of MB adsorbed vs. time for various NaCl concentrations. It appears that the presence of salt in adsorption medium significantly inhibited dye adsorption capacity of Alfa stems. The adsorption capacity decreased from 24.65 to 16.06 mg/g with an increase in NaCl concentration from 5 to 100 mg/L.

Al-Degs et al. [46] reported that if electrostatic forces between the adsorbent and solute ions were attractive, adsorption capacity will decrease with an increase in the ionic strength. The decrease in dye removal efficiency may also be attributed to the competition between Na^+ and dye cations for the negatively charged sites on the adsorbent surface. It was reported that generally, the adsorption mechanism of ion exchange is ionic strength-dependent [47].

3.2.5. *Effect of temperature and thermodynamics of MB adsorption*

The effect of solution temperature on equilibrium adsorption of MB onto Alfa grass was investigated at six temperatures 283, 293, 303, 313, 323 and 333 K.

Fig. 6 depicts the effect of temperature on MB removal by Alfa grass in terms of adsorption capacity.

The adsorption capacity is more significant when medium temperature is high. The adsorption process is rapid at the beginning of contact and becomes faster with increasing temperature. An increase of temperature leads to shorter equilibrium time.

This trend could be explained by an increase of diffusion rate of adsorbate molecules across the external boundary layer and in the internal pores of the adsorbent particle, owing to the decrease of solution viscosity [48].

Furthermore, MB adsorption capacity increased from 17.78 to 26.99 mg/g when solution temperature increased from 283 to 333 K indicating that the adsorption process is endothermic. The rise in temperature

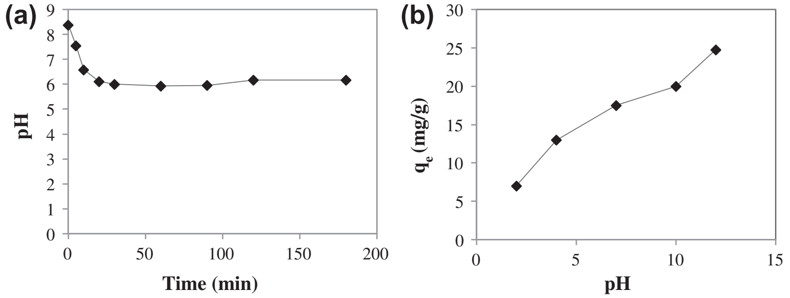

Fig. 4. (a) Evolution of pH solution and (b) evolution of equilibrium adsorption capacity with pH ($T = 293$ K; $C_0 = 100$ mg/L; $N = 500$ rpm; $W = 400$ mg).

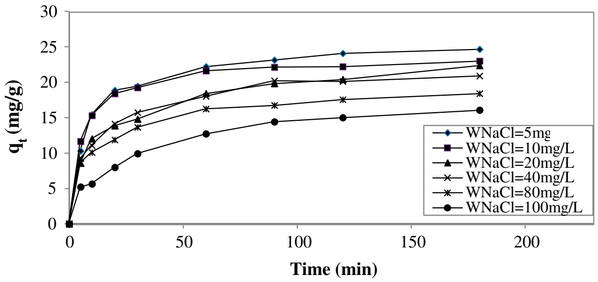

Fig. 5. Adsorption capacity evolutions at various ionic strengths ($T = 293$ K; $C_0 = 100$ mg/L; pH = 12; $N = 500$ rpm; $W = 400$ mg).

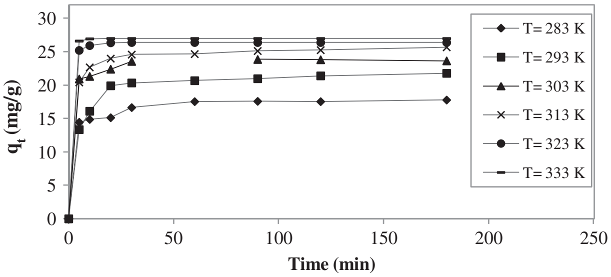

Fig. 6. Effect of temperature on the amount of MB adsorbed on Alfa grass ($C_0 = 100$ mg/L; pH = 12; $N = 500$ rpm).

would favour the mobility of dyes ions and would produce a swelling effect within the internal structure of Alfa. It will also allow the dye molecules to further penetrate [34]. Therefore, the capacity of adsorption should depend mainly on the chemical interaction between functional groups on adsorbent surface and adsorbed molecules.

With high temperatures, the adsorbent would contribute to the MB adsorption, since the diffusion is an endothermic process.

In order to explain and confirm the mechanism of MB adsorption onto Alfa, the thermodynamics of adsorption were evaluated using ΔG°, ΔS° and ΔH° given by Eqs. (2) and (3):

$$K_D = \frac{C_0 - C_e}{C_e} \tag{1}$$

$$G^\circ = -RT \ln K_D \tag{2}$$

$$\ln K_D = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT} \tag{3}$$

Thus, ln K_D vs. $1/T$ plot allowed ΔH° and ΔS° calculus from slope and intercept respectively.

Free energy (ΔG°), entropy (ΔS°) and enthalpy (ΔH°) obtained from Eqs. (1)–(3), are presented in Table 2. For all temperatures studied, (ΔG°) values are negative which indicates that a spontaneous physisorption process occurred. The decrease of (ΔG°) with temperature increase indicates more efficient adsorption at higher temperatures.

The numerical value of the enthalpy (55.03) < 60 kJ/mol, shows that the adsorption of the MB on Alfa stems is in extreme cases of a physisorption.

The activation energy (E_a) for MB adsorption onto the Alfa stems surface was also calculated from the rate constants (K_2) obtained for reactions performed at 283, 293, 303, 313, 323 and 333 K (section 3.4) with 100 mg/L dye solutions. Arrhenius equation was used for this purpose:

$$K_2 = A\, e^{\frac{-E_a}{RT}} \tag{4}$$

where A is the Arrhenius frequency factor, R is the ideal gas constant (8.314 $\text{J}\,\text{mol}^{-1}\,\text{K}^{-1}$) and T is the adsorption temperature in Kelvin. The activation energy calculated from the slope of the linear plot of ln K_2 vs. $1/T$ (not shown) was found to be 115.28 kJ/mol. This value existing at chemisorption (60–800 kJ/mol) range [49] revealed that the chemisorption take place.

3.3. Isotherm studies

The adsorption isotherm equilibrium of MB on Alfa was tested by Langmuir model expressed by the following equation:

$$\frac{1}{q_e} = \frac{1}{q_m} + \frac{1}{K_L q_m} \times \frac{1}{C_e} \tag{5}$$

where C_e (mg/L) is the equilibrium concentration, q_e (mg/g) the amount of adsorbate adsorbed per unit mass of adsorbent, q_m and K_L are Langmuir constants

Table 2
Thermodynamic parameters for MB adsorption at equilibrium on Alfa

T (K)	ΔH° (kJ/mol)	ΔS° (J/mol K)	ΔG° (kJ/mol)
283	55.03	199.44	−1.14
293			−3.40
303			−5.40
313			−7.12
323			−9.39
333			−11.38

related to the adsorption capacity and energy of adsorption respectively.

The plot of $1/q_e$ vs. $1/C_e$ gave straight line (Fig. 7) with slope $1/K_L\ q_m$ and an intercept $1/q_m$, indicating that MB adsorption on Alfa grass follows the Langmuir isotherm.

The Langmuir constants q_m and K_L were calculated from this isotherm and their values are presented in Table 3.

For the Langmuir equation the favourable nature of adsorption can be expressed by a dimensionless separation factor called equilibrium parameter R_L defined by:

$$R_L = \frac{1}{1 + K_L C_0} \tag{6}$$

where K_L is the Langmuir constant and C_0 is the initial concentration of adsorbate in solution.

The value of R_L indicates whether an isotherm is unfavourable ($R_L > 1$), linear ($R_L = 1$), favourable ($0 < R_L < 1$) or irreversible ($R_L = 0$). R_L values mentioned in Table 4 are included between 0.15 and 0.90 at 293 K and confirm that Alfa grass is favourable for MB adsorption under operating conditions used.

In order to situate Alfa grass capacity with other adsorbents, Table 5 compares maximum monolayer adsorption capacity of MB onto various agro adsorbents. It is clear that Alfa grass used in this work had a relatively suitable adsorption capacity which is 228.31 mg/g if compared to other agro adsorbents tested and mentioned in the literature.

Table 3
Langmuir isotherm parameters at 293 K

Langmuir isotherm	C_e range (mg/L)	K_L (L mg^{-1})	q_m (mg/g)	R^2
	1.034–65.25	0.011	200.00	0.999

Table 4
R_L values at different initial concentration

C_0 (mg/L)	10	55	100	155	315	520
R_L	0.90	0.62	0.47	0.37	0.22	0.15

Table 5
Comparison of maximum monolayer adsorption of MB onto various agro adsorbents

Adsorbents	Maximum adsorption capacity (mg/g)	References
Alfa grass	228.31	This work
Garlic peel	82.64	[33]
Rice husk	40.50	[50]
Oil palm trunk fibre	149.35	[51]
Date pits	80.31	[52]
Activated rice husks	0.21	[53]
Pistachio hull waste	389.00	[54]
Saw dust	195.70	[55]

3.4. Kinetics studies

The kinetic data were analyzed by using pseudo-first order model and pseudo-second order model proposed respectively by Lagergren [56] and Ho [57].

The linear form of pseudo-first order model is given by the following equation:

$$\log(q_e - q_t) = \log(q_e) - \left(\frac{K_1}{2.303}\right)t \tag{7}$$

where q_e and q_t (mg/g) are the amounts of adsorbate adsorbed at equilibrium and at time t (min) respectively, and k_1 (min^{-1}) is the rate constant of adsorption.

If log (q_e–q_t) vs. time plot gives straight line, the slope and intercept lead to k_1 and q_e calculus.

The pseudo-second order model is expressed by:

$$\frac{t}{\mathrm{q}_t} = \frac{1}{K_2 q_e^2} + \frac{t}{q_e} \tag{8}$$

where q_e is the equilibrium adsorption capacity and K_2 (g/mg min) is the pseudo-second order constant. K_2 and q_e are determined from the slope and intercept of plot t/q_t vs. t.

The rate constants of pseudo-first order and pseudo-second order with linear regression coefficients are regrouped in Tables 6 and 7.

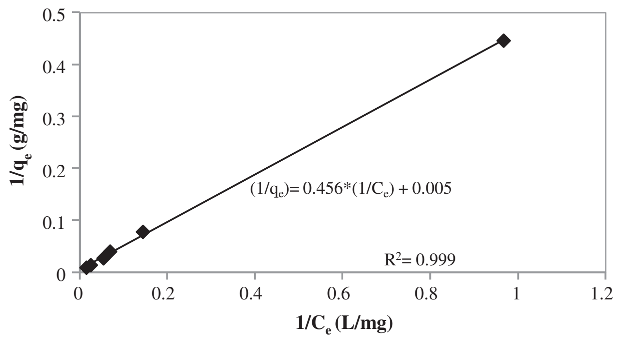

Fig. 7. Linear transform of Langmuir isotherm.

Table 6
Kinetic parameters of MB adsorption onto Alfa grass at 293 K

Pseudo-first order kinetic			Pseudo- second order kinetic	
C_0 (mg/L)	K_1 (min^{-1})	R^2	K_2 (g/mg min)	R^2
10	0.033	0.83	0.1950	1
55	0.033	0.86	0.0220	0.999
100	0.032	0.91	0.0110	0.999
155	0.027	0.81	0.0096	0.999
315	0.029	0.90	0.0033	0.999
520	0.020	0.85	0.0012	0.999

According to the results on Tables 6 and 7, the pseudo-second order model fits the kinetic data better than the pseudo-first order model. This means that the adsorption of MB onto Alfa grass may be best described by the pseudo-second order kinetic model.

A pseudo second-order suggests that this adsorption depends on the adsorbate as well as the adsorbent and involves chemisorption process in addition to physisorption. The chemisorption might be the rate limiting step where valency forces are involved via electrons sharing or exchange between the adsorbent and the adsorbate [57].

Moreover, we see that K_2, the pseudo-second order constant decreases when initial MB concentration increase. There exists an inverse trend between initial MB concentration and pseudo-second order constant K_2.

This tendency was also observed by Kumar and Porkodi [58] for the biosorption of MB using *Paspalum notatum* as biosorbent.

For the range of the considered parameters in this study, K_2 and q_e have been correlated vs. C_0 by the following equations:

Table 7
Kinetic parameters of MB adsorption onto Alfa grass for $C_0 = 100$ mg/L

Pseudo-first-order kinetic			Pseudo-second-order kinetic	
T (K)	K_1 (min^{-1})	R^2	K_2 (g/mg min)	R^2
283	0.044	0.85	0.0255	0.999
293	0.028	0.76	0.0141	0.999
333	0.12	0.87	0.0586	0.999
343	0.025	0.68	0.0223	0.999
353	0.304	0.93	0.2760	1.000
363	0.629	0.96	1.5200	1.000

$$K_2 = 1.859 C_0^{-1.039} \tag{9}$$

$$q_e = 1.53 + 0.216 C_0 \tag{10}$$

Eqs. (9) and (10) were substituted in Eq. (8) relative to the pseudo-second order model. A generalized kinetic expression that predicts MB uptake kinetics for the range of initial dye concentration studied is then obtained and expressed by:

$$q_t = \frac{(1.859 C_0^{-1.039})(1.53 + 0.216 C_0)^2 t}{1 + (1.859 C_0^{-1.039})(1.53 + 0.216 C_0)} t \tag{11}$$

Fig. 8 shows the kinetic experimental data with predicted pseudo second order kinetics for the range of initial dye concentrations studied.

As shown by Fig. 8, the pseudo second order model well represents the experimental data by using Eq. (11).

3.5. Adsorption mechanisms

For a solid liquid sorption process, the solute transfer is usually characterized by either external mass transfer (boundary layer diffusion) or intraparticle diffusion or both. The sorption dynamics can be described by the following three consecutive steps which are as follows:

- Transport of the solute from bulk solution through liquid film to the adsorbent exterior surface;
- Solute diffusion into the pore of adsorbent except for a small quantity of sorption on the external surface; parallel to this is the intraparticle transport mechanism of the surface diffusion; and
- Sorption of solute on the interior surfaces of the pores and capillary spaces of the adsorbent.

The last step is considered to be an equilibrium reaction. The third step is assumed to be rapid and considered to be negligible. The overall rate of sorption will be controlled by the slowest step, which would be either film diffusion or pores diffusion. However, the controlling step might be distributed between intraparticle and external transport mechanisms. Whatever the case, external diffusion is involved in the sorption process.

For the sorption process, the external mass transfer controls the sorption process for the systems that have poor mixing, dilute concentration of adsorbate, small particle sizes of adsorbent, and higher affinity of adsorbate for adsorbent. Whereas the intraparticle diffusion will control the sorption process for a system

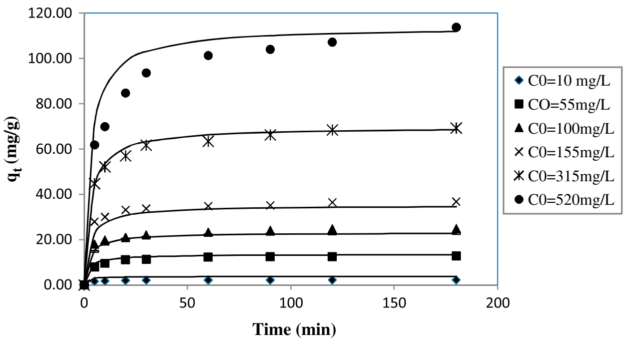

Fig. 8. Experimental data and simulated kinetics for various initial MB concentrations.

with good mixing, large particle sizes of adsorbent, high concentration of adsorbate, and low affinity of adsorbate for adsorbent [24,58].

The most commonly used technique for identifying the mechanism involved in the sorption process is by fitting the experimental data in an intraparticle diffusion plot. Previous studies by various researchers showed that the plot of q_t vs. $t^{1/2}$ represents multilinearity, which characterizes the two or more steps involved in the sorption process.

According to Weber and Morris [59], rate parameters for intraparticle diffusion were determined by the following equation:

$$q_t = K_p t^{1/2} + C \tag{12}$$

where q_t (mg/g) is the amount of adsorbate adsorbed at time t (min), K_p is the intraparticle diffusion rate constant (mg/g min$^{1/2}$) and C is a constant related to boundary layer thickness and the presence of an external resistance in liquid film.

K_p and C can be evaluated from the slope and intercept of the linear plot of q_t vs. $t^{1/2}$.

The values of these constants are listed in Table 8.

Fig. 9 shows that the curves do not pass through the origin and they present two successive linear stages. This indicates that the intraparticle diffusion is not only rate controlling step. In fact, the first stage represents the intraparticular diffusion and the second step shows that the equilibrium is gradually reached and corresponds to a slowdown of adsorption process [43,60].

Therefore, the external diffusion also takes part in adsorption process; particularly, in the first 2 min, when the MB molecules are fixed quickly on active sites being at external surface of the adsorbent [61].

3.5.1. Determination of diffusivity

The kinetic model of intraparticle diffusion is based on a developed theoretical approach. This approach was included in the recent literature by several authors, e.g.: Srivastava et al. [36] and Rudzinski et al. [62].

With diffusion rate controlling for adsorption on spherical particles, the solution of the simultaneous set of differential and algebraic equations lead to:

$$F(t) = 1 - \frac{6}{\pi^2} \sum_{n-1}^{\infty} \frac{1}{n^2} \exp\left[\frac{-n^2\pi^2 Dt}{R_a^2}\right] \tag{13}$$

where $F(t) = q_t/q_e$ is the fractional attainment of equilibrium at time t, D the effective diffusion coefficient of adsorbate in the adsorbent phase (m^2/s), R_a the radius of the adsorbent particle assumed to be spherical (m), and n is an integer.

Table 8
Kinetic parameters of MB adsorption onto Alfa grass

C_0 (mg/L)	First step			Second step		
	K_p (mg/g min$^{1/2}$)	C (mg/g)	R^2	K_p (mg/g min$^{1/2}$)	C (mg/g)	R^2
10	0.16	1.27	0.98	0.01	2.07	0.92
55	1.08	5.86	0.91	0.16	10.77	0.80
100	1.20	15.64	0.96	0.37	20.4	0.92
155	1.86	24.09	0.95	0.41	31.6	0.95
315	5.02	34.62	0.97	1.03	56.12	0.95
520	10.02	39.08	0.99	2.44	81.02	0.99
T (K)	K_p (mg/g min$^{1/2}$)	C (mg/g)	R^2	K_p (mg/g min$^{1/2}$)	C (mg/g)	R^2
283	0.61	12.90	0.84	0.84	16.27	0.70
293	2.25	8.77	0.94	0.94	19.26	0.99
333	0.82	18.91	0.97	0.97	21.54	0.96
343	1.24	18.16	0.92	0.92	23.68	0.95

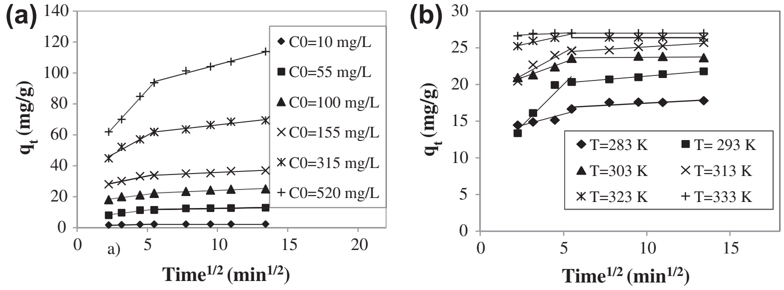

Fig. 9. Intraparticule diffusion plots for MB adsorption on Alfa grass.

The Alfa particles are not spherical; they may be taken as cylindrical particles. If one assumes that the diffusion takes place radially with diffusion in the angular and axial direction to be negligible, one gets the solution given by Skelland [63], which after rearrangement is:

$$F(t) = 1 - \frac{4}{\pi^2} \sum_{n-1}^{\infty} \frac{1}{b_n^2} \exp[Db_n^2 t] \tag{14}$$

where b_n's are roots of $J_0(b_n R) = 0$. Vermeulen's approximation [64] of Eq. (14) fits the whole range $0 < F(t) < 1$, for adsorption on spherical particles.

$$F(t) = \left[1 - \exp\left(\frac{-\pi^2 Dt}{R_a^2}\right)\right]^{1/2} \tag{15}$$

This equation could further be simplified to cover most of the data points for calculating effective particle diffusivity.

$$\ln\left[\frac{1}{1 - \mathrm{F}^2(t)}\right] = \frac{\pi^2 Dt}{R_a^2} \tag{16}$$

Thus the slope of $\ln[1/(1 - F^2(t))]$ vs. t plot would give D. Table 9 presents the effective diffusion coefficient values D as calculated from Eq. (16) and according to the operating parameters.

Table 9
Effective pore diffusivity for MB adsorption on Alfa

C_0 (mg/L)	$D \times 10^{10}$ (m^2/s)	T° (C)	$D \times 10^{10}$ (m^2/s)
10	0.1083	10	0.0957
55	0.1022	20	0.1012
100	0.0980	30	0.1618
155	0.0940	40	0.1673
315	0.0752	50	0.4180
520	0.0523	60	0.7955

We notice, according to Table 9 values, that the diffusion coefficient *D* decreases with increasing initial MB concentration. This phenomenon could be due to MB molecules interactions which create a steric obstruction when their concentration increases.

For rice husk as adsorbent Vadivelan et al. [24] found diffusion coefficient D values as 3.10601×10^{-09}, 2.41449×10^{-09}, and 5.48534×10^{-09} m^2/s for an initial MB concentration of 50, 70, and 100 mg/L.

In addition, we note an increase of diffusion coefficient *D* with increasing temperature. This fact indicates that the mobility of dye molecules increased with temperature.

4. Conclusions

According to this study, Alfa grass, a natural material widely available, is effective for MB adsorption from aqueous solutions.

The amount of MB adsorbed was found nearly dependant with initial dye concentration, adsorbent dosage, pH and temperature. This amount is more significant with the increase of the initial dye concentration, pH and temperature.

The experimental data modelling showed that the models of Langmuir and pseudo-second order, describe perfectly the process of adsorption. The maximum value of the adsorption capacity calculated according to the Langmuir model is 200 mg/g.

The thermodynamic parameters showed that MB adsorption onto Alfa grass is a favourable endothermic and spontaneous phenomenon and confirms the Alfa grass affinity for MB.

The detailed study of the present work shows that the adsorption involves chemical reactions in addition to physisorption.

The Alfa stems in a rough state, without preliminary treatment, have good adsorption effectiveness with respect to dyes. Moreover, the availability, and the low cost of the Alfa grass can lead this agro-industrial material to be used for treating coloured wastewaters.

List of symbols

C	constant related to boundary layer thickness	(mg/g)
C_0	initial dye concentration	(mg/L)
C_e	equilibrium liquid phase concentration of dye solutions	(mg/L)
D	effective diffusion coefficient of adsorbate in the adsorbent phase	(m^2/s)
K_1	pseudo-first-order constant	($\min^{-1}$)
K_2	pseudo-second-order constant	(g/mg min)
K_D	distribution coefficient of the adsorbate	(L/g)
K_L	Langmuir constant related to the energy of adsorption	(L/mg)
K_p	intraparticle diffusion rate constant	(mg/g $\min^{1/2}$)
q_t	amount of MB adsorbed onto Alfa at time t	(mg/g)
q_e	equilibrium amount of adsorbate adsorbed per unit mass of adsorbent	(mg/g)
q_m	Langmuir constant related to the adsorption capacity	(mg/g)
R	universal gaz constant (8.314)	(J/mol K)
R (%)	MB percent removal	(%)
R^2	correlation coefficient	–
R_a	radius of the adsorbent particle assumed to be spherical	(m)
R_L	equilibrium parameter of Langmuir	–
T	absolute temperature	(°C, K)
V	volume of solution	(L)
W	adsorbent dose	(g)
W_{NaCl}	ionic strength	(g/L)
ΔG°	standard free energy change	(kJ/mol)
ΔH°	enthalpy change	(kJ/mol)
ΔS°	entropy change	(J/mol K)

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