ELSEVIER

Chemical Engineering Journal 143 (2008) 73–84

Chemical Engineering Journal

www.elsevier.com/locate/cej

Sorption of malachite green by a novel sorbent, dead leaves of plane tree: Equilibrium and kinetic modeling

Oualid Hamdaoui [a,*], Fethi Saoudi [a], Mahdi Chiha [a], Emmanuel Naffrechoux [b]

[a] *Department of Process Engineering, Faculty of Engineering, University of Annaba, P.O. Box 12, 23000 Annaba, Algeria*
[b] *Laboratoire de Chimie Moléculaire et Environnement, Polytech'Savoie, Université de Savoie,*
73376 Le Bourget du Lac Cedex, France

Received 26 July 2006; received in revised form 10 October 2007; accepted 19 December 2007

Abstract

In the present study, the dead leaves of plane tree (*Platanus vulgaris*) were investigated as a novel biosorbent of dyes taking aqueous malachite green solutions as a model system. Kinetic data and sorption equilibrium isotherms were carried out in batch process. The effect of different experimental conditions such as contact time, sorbent dose, initial concentration of dye, agitation speed, ionic strength, and temperature on the kinetics of malachite green removal was studied. Modeling of kinetic results shows that sorption process is best described by the type 1 expression of the pseudo-second order model. The sorption rate constant, the sorption equilibrium capacity, and the initial sorption rate were functions of the sorbent dose, the initial concentration, the temperature, and the ionic strength. The agitation speed showed a limited influence on the removal kinetics. The activation energy of the sorption process was also calculated. The malachite green uptake process was found to be controlled by pore diffusion. The average intraparticle diffusion coefficient (D/d^2) was calculated and found to be $6.03 \times 10^{-4}\ \text{min}^{-1}$. Equilibrium isotherm data could be well described by both the Langmuir and Freundlich models, but the Langmuir expression fits the equilibrium data better. The five Langmuir linear equations were discussed. The effect of temperature on the sorption isotherms of dye has been also studied and the thermodynamic parameters ΔG°, ΔH°, and ΔS° were determined.

Keywords: Sorption; Malachite green; Plane tree leaves; Kinetics; Isotherm; Modeling

1. Introduction

Dye pollutants from various industries are an important source of environmental contaminations. Most industries use dyes and pigments to color their products, which include textile, tannery, food, paper and pulp, printing, carpet, and mineral processing industries. Perhaps dyes are the serious polluters of our environment as far as color pollution is concerned. Color is a visible pollutant and the presence of even very minute amount of coloring substance makes it undesirable due to its appearance. The effluents from dye manufacturing and consuming industries are highly colored coupled with high chemical and biochemical oxygen demands (COD and BOD) and suspended solids. Discharge of such effluents imparts color to receiving streams and affects its aesthetic value. The dyes are, generally, stable to light, oxidizing agents and heat, and their presence in wastewaters offers considerable resistance to their biodegradation, and thus upsetting aquatic life [1]. Color affects the nature of water and inhibits the sunlight penetration into the stream and reduces photosynthetic activity [2]. Some of the dyes are carcinogenic and mutagenic [2].

The removal of color from dye-bearing effluents is one of the major problems due to the difficulty in treating such wastewaters by conventional treatment methods. The most commonly used methods for color removal are physical or chemical processes. All these methods have different color removal capabilities, capital costs, and operating rates. Liquid phase adsorption processes have been shown to be highly efficient for removal of dyes from industrial wastewater. Granular activated carbon (GAC) is the most-popular adsorbent, which has been used with great success. However, GAC is expensive and its regeneration and reuse makes it more costly. Sorption process becomes economic, if the sorbent is inexpensive and does not require any expensive pre-treatment. Thus, there is a continuous search for alternate low-cost sorbent material to replace high cost activated carbon for water and wastewater treatment. The use of biomaterials

---

* Corresponding author. Tel.: +213 71 59 85 09; fax: +213 38 87 65 60.
E-mail address: ohamdaoui@yahoo.fr (O. Hamdaoui).

1385-8947/$ – see front matter © 2007 Elsevier B.V. All rights reserved.
doi:10.1016/j.cej.2007.12.018

Nomenclature

A_0	temperature independent factor in the Arrhenius equation ($\mathrm{g\,mg^{-1}\,min^{-1}}$)
b	Langmuir constant related to the free energy of sorption ($\mathrm{L\,mg^{-1}}$)
BOD	biochemical oxygen demand
C	final dye concentration at any time t ($\mathrm{mg\,L^{-1}}$)
C_e	equilibrium concentration of the dye in the bulk solution ($\mathrm{mg\,L^{-1}}$)
C_0	initial dye concentration ($\mathrm{mg\,L^{-1}}$)
COD	chemical oxygen demand
d	the diameter of sorbent (cm)
D	the intraparticle diffusion coefficient ($\mathrm{cm^2\,min^{-1}}$)
E_a	activation energy of sorption ($\mathrm{kJ\,mol^{-1}}$)
GAC	granular activated carbon
ΔG°	Gibb's free energy change ($\mathrm{kJ\,mol^{-1}}$)
h	initial sorption rate ($\mathrm{mg\,g^{-1}\,min^{-1}}$)
ΔH°	enthalpy change ($\mathrm{kJ\,mol^{-1}}$)
K_F	Freundlich constant indicative of the relative sorption capacity ($\mathrm{mg^{1-1/n}\,L^{1/n}\,g^{-1}}$)
K_1	Lagergren pseudo-first order rate constant ($\mathrm{min^{-1}}$)
K_2	pseudo-second order rate constant ($\mathrm{g\,mg^{-1}\,min^{-1}}$)
n	Freundlich constant indicative of the intensity of the sorption
q	amount of dye sorbed at any time t ($\mathrm{mg\,g^{-1}}$)
q_e	amount of dye sorbed at equilibrium ($\mathrm{mg\,g^{-1}}$)
q_m	maximum sorption capacity in the Langmuir model ($\mathrm{mg\,g^{-1}}$)
R_g	gas constant ($8.314\,\mathrm{J\,mol^{-1}\,K^{-1}}$)
R_L	dimensionless separation factor of Hall
R^2	coefficient of determination
ΔS°	entropy change ($\mathrm{J\,mol^{-1}\,K^{-1}}$)
t	time (min)
T	solution temperature (K, °C)
V	volume of solution (L)
W	sorbent weight (g)
Greek letter	
α	initial sorption rate ($\mathrm{mg\,g^{-1}\,min^{-1}}$)
β	constant related to the extent of surface coverage and activation energy for chemisorption ($\mathrm{g\,mg^{-1}}$)

as sorbents for the treatment of wastewaters will provide as a potential alternate to the conventional treatment. Consequently, many investigators have studied the feasibility of using low-cost substances for the removal of various dyes and pollutants from wastewaters [3]. The plane tree regularly sheds its leaves during autumn, which become waste. These leaves can be put to good use as a sorbent for removal of color from industrial and other effluents. In the present work, plane tree leaves, a waste biomaterial, has been used as a sorbent for the removal of dyes from aqueous solutions. Additionally, the use of plane tree leaves as low-cost sorbent for the removal of dyes from water, to our knowledge, has not been investigated.

Malachite green is most widely used for coloring purpose, amongst all other dyes of its category, which is selected as a model compound in order to evaluate the capacity of plane tree leaves for the removal of dye malachite green from its aqueous solutions. It has wider applications that include coloring paper, coloring leather products, dyeing cotton, wool, silk, and jute and also used in distilleries [4,5]. The dye under consideration is an important water-soluble dye belonging to triphenylmethane family. In the aquaculture, commercial fish hatchery and animal husbandry it also acts as an antifungal, anti-bacterial, and anti-parasitical therapeutic agent, while for humans it is used as antiseptic and fungicidal [6–8]. Its oral consumption is carcinogenic and that is why it is applied on the external wounds and ulcers [9]. The available toxicological information reveals that in the tissues of fish and mice malachite green easily reduces to persistable leuco-malachite green [5,6], which acts as a tumor promoter. This dye may enter into the food chain and could possibly cause carcinogenic, mutagenic, and teratogenic effects on humans [10,11]. Thus, the detection of malachite green in fishes, animal milk, and other foodstuff, destined for human consumption, alarm the health hazards against human being [7,12]. Studies also confirm that the products formed after degradation of malachite green are also not safe and have carcinogenic potential [13,14].

The aim of the present investigation is to study the removal of malachite green, a cationic dye, from aqueous solutions by the dead leaves of plane tree. Kinetic data and sorption equilibrium isotherms are carried out in batch process. The effect of different experimental conditions such as contact time, initial concentration of dye cations, agitation speed, particle size, biosorbent mass, temperature and ionic strength on the removal kinetics is studied. Equilibrium isotherm and kinetic data are analyzed and modeled using different models. The obtained results may contribute to a better understanding of the sorption phenomena at the liquid/solid interface.

2. Materials and methods

2.1. Sorbent

The dead leaves of plane tree (*Platanus vulgaris*) used in the present study was collected in autumn 2005 from the Scientific Campus of Savoie Technolac, University of Savoie, Le Bourget du Lac, France. The collected leaves were washed with permuted water several times to remove dirt particles and water-soluble materials. The washing process was continued till the wash water contained no color. The washed materials were then completely dried in an oven at 50 °C for 3 days. The dried leaves were then cut into small pieces, crushed, and sieved to eliminate fine particles (<0.5 mm). The obtained material was washed repeatedly with UHQ water (Elga elgastat 18.2 MΩ) until the wash water contained no color and its electric conductivity and UV absorbance were equal to zero and the pH remains constant. Finally, the obtained material was then dried in an air circulating oven at 50 °C for 7 days and stored in a desiccator until use.

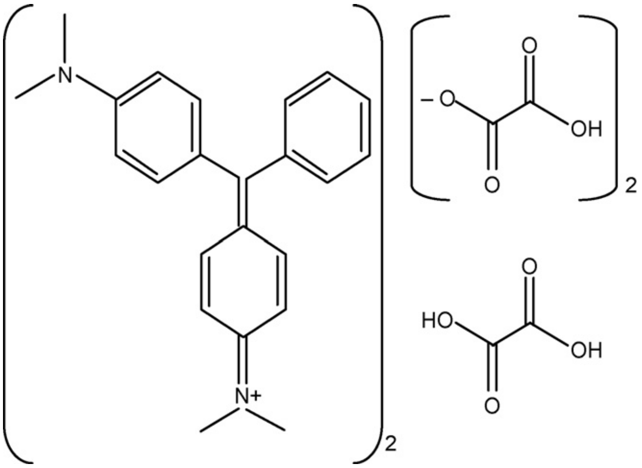

Fig. 1. Chemical structure of malachite green (oxalate salt).

2.2. Sorbate and chemicals

A cationic basic dye (C.I. 42000; Basic Green 4), malachite green oxalate salt (molecular formula $C_{52}H_{56}N_4O_{12}$, FW 929), was obtained from Merck and used without further purification. This dye was chosen as a model compound of triarylmethane dyes. Fig. 1 displays the structure of this dye.

Malachite green solutions were prepared by dissolving requisite amount of the dye in UHQ water before each experiment. All other reagents used were of analytical grade.

2.3. Sorption kinetics

For kinetic studies, the batch technique was used because of its simplicity. For dye removal kinetic experiments, 0.25 g of plane tree leaves was contacted with 100 mL malachite green solutions in a sealed flask agitated vigorously by a magnetic stirrer using a water bath maintained at a constant temperature of 25 °C. The stirring speed was kept constant at 400 rpm. At predetermined intervals of time, solutions were analyzed for the final concentration of malachite green by using a UV–vis spectrophotometer (Hewlett Packard 8453) set at a wavelength of 618 nm, maximum absorbance. The wavelength resolution and the bandwidth were, respectively, 1 and 0.5 nm. The calibration plot was constructed and repeated five times during the period of measurements. The linearization of this plot usually provided determination coefficient close to 0.999. For each measurement, a volume of 0.5 mL was pipetted and, after the determination of absorbance, this volume was returned in the flask containing the suspension. In all cases, the working pH (about 5.2–5.5) was that of the solution and was not controlled.

The influence of various parameters such as sorbent dose, initial concentration of dye, agitation speed, ionic strength, and temperature on the kinetics of malachite green sorption was studied. The effect of pH on the sorption capacity was not carried out since addition of acid or alkali caused the color of the sorbate to change significantly.

The dye uptake q (mg g^{-1}) was determined as follows:

$$q = \frac{(C_0 - C)V}{W} \tag{1}$$

where C_0 and C are the initial and final dye concentrations (mg L^{-1}), respectively, V is the volume of solution (L), and W is the sorbent weight (g).

All the experiments were carried out in triplicate and the mean values are presented.

2.4. Sorption isotherm

For the sorption isotherms, 0.05 g of plane tree leaves was equilibrated separately with 50 mL solutions containing different malachite green concentrations (50–500 mg L^{-1}). The contact time was determined by kinetic tests using the same conditions. The temperatures examined were 25, 35, and 45 °C. The suspensions were agitated with a constant speed of 400 rpm for 24 h. Then, the suspensions were decanted and the solutions were analyzed for malachite green concentrations using UV–vis spectrophotometer. All experiments were conducted in triplicate, and sometimes repeated again and the mean values have been reported.

2.5. Sorption kinetic models

2.5.1. Pseudo-first order equation

A simple kinetic analysis of sorption can be performed with a pseudo-first order equation as suggested by Lagergren [15]

$$\frac{dq}{dt} = K_1(q_e - q) \tag{2}$$

where K_1 (min^{-1}) is the rate constant of the pseudo-first order sorption, q_e (mg g^{-1}) is the amount of dye sorbed on the sorbent surface at equilibrium, and q (mg g^{-1}) is the amount of dye sorbed at any time t (min).

Eq. (2) above can be integrated to the following form by applying the boundary conditions $q = 0$ at $t = 0$

$$\ln\left(\frac{q_e - q}{q_e}\right) = -K_1 t \tag{3}$$

This rate expression is known as the Lagergren pseudo-first order equation. The value of K_1 can be determined by the slope of linear plots of $\ln[(q_e - q)/q_e]$ versus t.

2.5.2. Pseudo-second order equation

An expression of the pseudo-second order rate based on the solid capacity has been presented by Blanchard et al. [16]

$$\frac{dq}{dt} = K_2(q_e - q)^2 \tag{4}$$

where K_2 is the pseudo-second order rate constant (g mg^{-1} min^{-1}), q_e is the amount of dye sorbed at equilibrium (mg g^{-1}), and q is the amount of dye cation on the surface of the sorbent at any time t (mg g^{-1}).

Table 1
Linear forms of the pseudo-second order kinetic model

Type	Linear form	Plot	Parameters
Type 1	$\frac{t}{q} = \frac{1}{K_2 q_e^2} + \frac{1}{q_e} t$	t/q vs. t	$q_e = 1/\text{slope}$; $K_2 = \text{slope}^2/\text{intercept}$; $h = 1/\text{intercept}$
Type 2	$\frac{1}{q} = \frac{1}{q_e} + \frac{1}{K_2 q_e^2} \frac{1}{t}$	$1/q$ vs. $1/t$	$q_e = 1/\text{intercept}$; $K_2 = \text{intercept}^2/\text{slope}$; $h = 1/\text{slope}$
Type 3	$q = q_e - \frac{1}{K_2 q_e} \frac{q}{t}$	q vs. q/t	$q_e = \text{intercept}$; $K_2 = -1/(\text{slope} \times \text{intercept})$; $h = -\text{intercept}/\text{slope}$
Type 4	$\frac{q}{t} = K_2 q_e^2 - K_2 q_e q$	q/t vs. q	$q_e = -\text{intercept}/\text{slope}$; $K_2 = \text{slope}^2/\text{intercept}$; $h = \text{intercept}$
Type 5	$\frac{1}{t} = -K_2 q_e + K_2 q_e^2 \frac{1}{q}$	$1/t$ vs. $1/q$	$q_e = -\text{slope}/\text{intercept}$; $K_2 = \text{intercept}^2/\text{slope}$; $h = \text{slope}$
Type 6	$\frac{1}{q_e - q} = \frac{1}{q_e} + K_2 t$	$1/(q_e - q)$ vs. t	$q_e = 1/\text{intercept}$; $K_2 = \text{slope}$; $h = \text{slope}/\text{intercept}^2$

Integrating Eq. (4), considering that $q = 0$ when $t = 0$ and that $q = q$ when $t = t$, results in the expression

$$\frac{1}{q_e - q} = \frac{1}{q_e} + K_2 t \tag{5}$$

which is the integrated equation for pseudo-second order.

Eq. (5) was previously reported by Blanchard et al. [16] for the exchange reaction of divalent metallic ions onto NH_4^+ ions fixed onto zeolite particles. This equation can be linearized to six different linear forms as shown in Table 1. A type 1 expression as shown in Table 1 was previously reported by Ho [17,18]. This is the most used linearized form for the pseudo-second order equation.

The initial sorption rate h ($\text{mg g}^{-1} \text{min}^{-1}$) is given by the following equation

$$h = K_2 \cdot q_e^2 \tag{6}$$

2.5.3. *Elovich equation*

The Elovich equation is given as follows [19]

$$\frac{dq}{dt} = \alpha\, e^{-\beta q} \tag{7}$$

The integration of the rate equation with the same boundary conditions as the pseudo-first and pseudo-second order equations becomes the Elovich equation.

$$q = \frac{1}{\beta} \ln(\alpha\beta) + \frac{1}{\beta} \ln t \tag{8}$$

where α is the initial sorption rate ($\text{mg g}^{-1} \text{min}^{-1}$), and the parameter β is related to the extent of surface coverage and activation energy for chemisorption (g mg^{-1}).

2.6. *Sorption equilibrium isotherm models*

2.6.1. *Langmuir model*

The Langmuir model assumes uniform energies of adsorption onto the surface and no transmigration of adsorbate in the plane of the surface. The Langmuir equation may be written as

$$q_e = \frac{q_m b C_e}{1 + b C_e} \tag{9}$$

where q_e is the amount of solute sorbed per unit weight of sorbent (mg g^{-1}), C_e is the equilibrium concentration of the solute in the bulk solution (mg L^{-1}), q_m is the monolayer sorption capacity (mg g^{-1}), and b (L mg^{-1}) is the constant related to the free energy of sorption.

Eq. (9) can be linearized to five different linear forms as shown in Table 2.

2.6.2. *Freundlich model*

The Freundlich equation can be written as

$$q_e = K_F \cdot C_e^{1/n} \tag{10}$$

where q_e is the amount of solute adsorbed per unit weight of adsorbent (mg g^{-1}), C_e is the equilibrium concentration of solute in the bulk solution (mg L^{-1}), K_F is a constant indicative of the relative adsorption capacity of the adsorbent ($\text{mg}^{1-1/n} \text{L}^{1/n} \text{g}^{-1}$), and n is a constant indicative of the intensity of the adsorption. The Freundlich expression is an exponential equation and therefore, assumes that as the adsorbate concentration increases, the concentration of adsorbate on the adsorbent surface also increases. The linear form of the Freundlich isotherm is shown in Table 2.

3. Results and discussion

3.1. *Kinetics*

Information on the kinetics of solute uptake is required for selecting optimum operating conditions for full-scale batch process. The effect of different experimental conditions such as contact time, sorbent mass, dye initial concentration, agitation speed, ionic strength, and temperature on the kinetics of malachite green removal was investigated.

Table 2
Freundlich and Langmuir isotherms and their linear forms

Isotherm		Linear form	Plot
Freundlich	$q_e = K_F \cdot C_e^{1/n}$	$\ln q_e = \ln K_F + \frac{1}{n} \ln C_e$	$\ln q_e$ vs. $\ln C_e$
Langmuir-1	$q_e = \frac{q_m b C_e}{1 + b C_e}$	$\frac{1}{q_e} = \frac{1}{b q_m} \frac{1}{C_e} + \frac{1}{q_m}$	$1/q_e$ vs. $1/C_e$
Langmuir-2		$\frac{C_e}{q_e} = \frac{1}{q_m} C_e + \frac{1}{q_m b}$	C_e/q_e vs. C_e
Langmuir-3		$q_e = -\frac{1}{b} \frac{q_e}{C_e} + q_m$	q_e vs. q_e/C_e
Langmuir-4		$\frac{q_e}{C_e} = -b q_e + b q_m$	q_e/C_e vs. q_e
Langmuir-5		$\frac{1}{C_e} = b q_m \frac{1}{q_e} - b$	$1/C_e$ vs. $1/q_e$

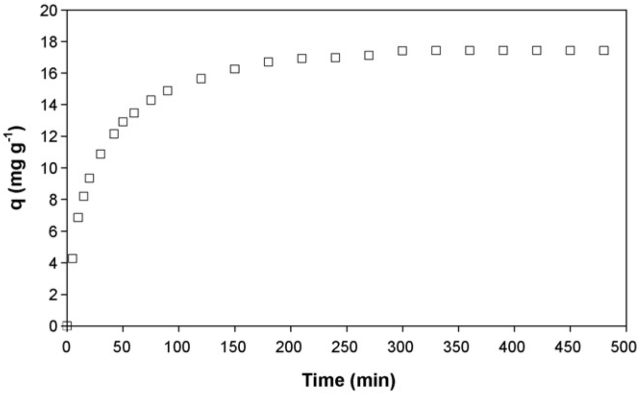

Fig. 2. Sorption kinetics of malachite green by the dead leaves of plane tree (100 mL, 50 mg L^{-1}, 0.25 g, 400 rpm).

3.1.1. *Effect of contact time*

The contact time between the dye molecules and the sorbent is of significant importance in the wastewater treatment by sorption. The effect of contact time on the sorption of malachite green was studied for an initial dye concentration of 50 mg L^{-1}, a sorbent mass of 0.25 g, a solution volume of 100 mL, an agitation speed of 400 rpm, and a temperature of 25 °C. The effect of contact time on the removal of dye by the studied sorbent is shown in Fig. 2. The obtained results reveal that the uptake of sorbate species is fast at the initial stage of the contact period (90 min), and thereafter, it becomes slower near the equilibrium. In between these two stages of the uptake, the rate of sorption is found to be nearly constant. This is obvious from the fact that a large number of vacant surface sites are available for sorption during the initial stage, and after a lapse of time, the remaining vacant surface sites are difficult to be occupied due to repulsive forces between the solute molecules on the solid and bulk phases. The contact time necessary to reach equilibrium is about 300 min. At this point, the sorbed amount of dye by plane tree leaves is in a state of dynamic equilibrium with the amount of the dye desorbing from the sorbent. Additionally, the curve of contact time is single, smooth, and continuous leading to equilibrium. This curve indicates the possible monolayer coverage of dye on the surface of plane tree leaves.

The experimental kinetic results for the sorption of malachite green by the leaves of plane tree were fitted to the pseudo-first order kinetic expression, the six linearized forms of the pseudo-second order model, and the Elovich expression. The pseudo-first order kinetic constant (min^{-1}) based on pseudo-first order kinetics can be obtained from the plot of $\ln[(q_e - q)/q_e]$ versus t. The way to obtain the pseudo-second order kinetic model constant K_2 (g mg^{-1} min^{-1}), the amount of malachite green sorbed at equilibrium q_e (mg g^{-1}), and the initial sorption rate h (mg g^{-1} min^{-1}) are explained in Table 1. The initial sorption rate α (mg g^{-1} min^{-1}) and the parameter β (g mg^{-1}) of the Elovich equation can be determined from the plot of q versus $\ln t$. Linear plots of $\ln[(q_e - q)/q_e]$ versus t, t/q versus t, and q versus $\ln t$ are shown in Fig. 3. The calculated kinetic constants and the values of determination coefficients were shown in Table 3.

For Lagergren pseudo-first order equation, the lower coefficient of determination value (Table 3) suggests that it is inappropriate to use this equation to represent the sorption of malachite green by the dead leaves of plane tree.

From the Table 3, it was observed that the rate constant, the sorbed amount at equilibrium, and the initial sorption rate values obtained from the six linear forms of pseudo-second order expressions were different. It is clear that transformations of non-linear pseudo-second order kinetic model to linear forms implicitly alter their error structure and may also violate the error variance and normality assumptions of standard least-squares method [20,21]. The extremely higher coefficient of determination value for type 1 expression suggests that the pseudo-second order kinetic expression is the optimum kinetic expression to represent the uptake of malachite green by plane tree leaves. Additionally, a type 1 pseudo-second order expression predicts reasonably the theoretical q_e value. The lower determination

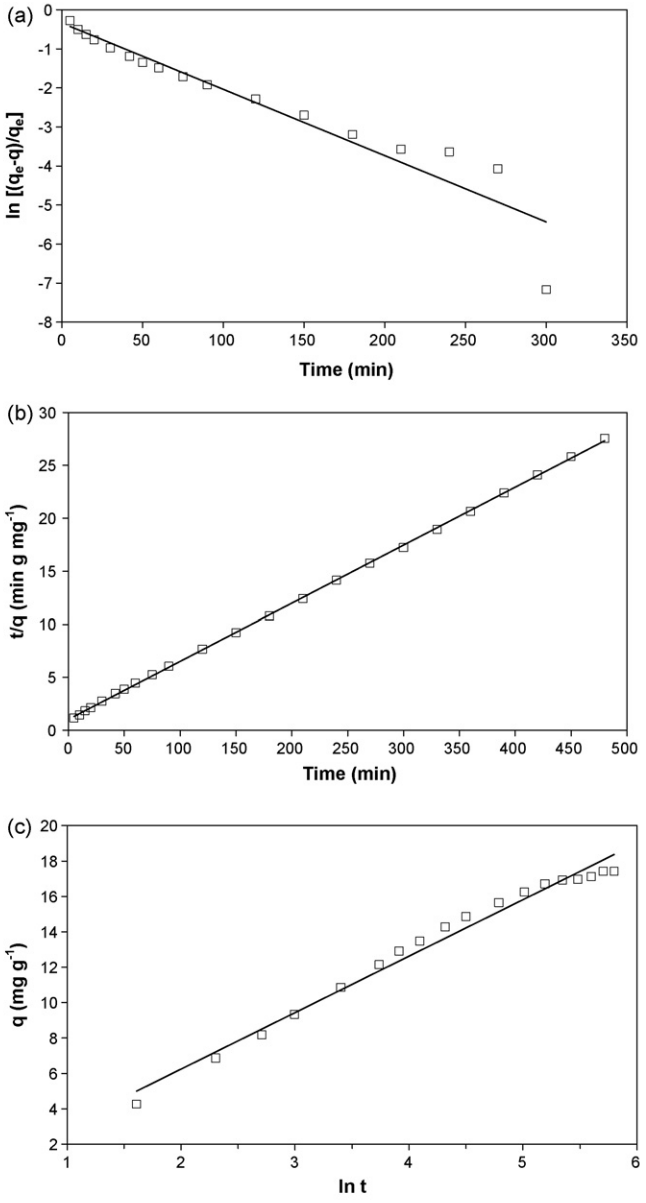

Fig. 3. Modeling of sorption kinetics by different models: (a) pseudo-first order (Lagergren), (b) pseudo-second order (Ho), and (c) Elovich.

Table 3
Parameters of the kinetic models

Model	Type	Parameters			
Lagergren	–	$K_1 = 0.017\,\text{min}^{-1}$		$R^2 = 0.904$	
Pseudo-second order	1	$K_2 = 2.91 \times 10^{-3}\,\text{g mg}^{-1}\,\text{min}^{-1}$	$q_e = 18.25\,\text{mg g}^{-1}$	$h = 0.969\,\text{mg g}^{-1}\,\text{min}^{-1}$	$R^2 = 1$
	2	$K_2 = 3.55 \times 10^{-3}\,\text{g mg}^{-1}\,\text{min}^{-1}$	$q_e = 17.64\,\text{mg g}^{-1}$	$h = 1.104\,\text{mg g}^{-1}\,\text{min}^{-1}$	$R^2 = 0.996$
	3	$K_2 = 3.24 \times 10^{-3}\,\text{g mg}^{-1}\,\text{min}^{-1}$	$q_e = 17.96\,\text{mg g}^{-1}$	$h = 1.046\,\text{mg g}^{-1}\,\text{min}^{-1}$	$R^2 = 0.984$
	4	$K_2 = 3.18 \times 10^{-3}\,\text{g mg}^{-1}\,\text{min}^{-1}$	$q_e = 18.03\,\text{mg g}^{-1}$	$h = 1.033\,\text{mg g}^{-1}\,\text{min}^{-1}$	$R^2 = 0.984$
	5	$K_2 = 3.52 \times 10^{-3}\,\text{g mg}^{-1}\,\text{min}^{-1}$	$q_e = 17.67\,\text{mg g}^{-1}$	$h = 1.099\,\text{mg g}^{-1}\,\text{min}^{-1}$	$R^2 = 0.996$
	6	$K_2 = 10.4 \times 10^{-3}\,\text{g mg}^{-1}\,\text{min}^{-1}$	$q_e = -4.44\,\text{mg g}^{-1}$	$h = 0.205\,\text{mg g}^{-1}\,\text{min}^{-1}$	$R^2 = 0.894$
Elovich	–	$\alpha = 3.068\,\text{mg g}^{-1}\,\text{min}^{-1}$	$\beta = 0.313\,\text{g mg}^{-1}$		$R^2 = 0.983$

coefficient value for type 6 pseudo-second order expression suggests that it is not appropriate to use this type of linearization. The theoretical amount sorbed at equilibrium value determined using this expression (type 6) is negative that is experimentally and practically impossible. The initial sorption rate calculated using the type 6 expression is unacceptable since it is very different from those calculated using the five other linear expressions.

The values of Elovich parameters are presented in Table 3. The determination coefficient indicates that Elovich equation describes the sorption kinetics of malachite green by plane tree leaves, but the type 1 expression of the pseudo-second order kinetic model fits the kinetic data better.

Among the tested models, the best fit of the experimental kinetic data is obtained by using the type 1 expression of the pseudo-second order kinetic model because the highest coefficient of determination is calculated from the fitted equation.

3.1.2. *Effect of sorbent dose*

The effect of biosorbent concentration on the amount of color sorbed was obtained by agitating 100 mL of dye solution of concentration 50 mg L^{-1} with 0.25, 0.35, 0.5, 0.75, and 1 g of plane tree leaves at constant temperature (25 °C) and constant stirring speed of 400 rpm. The effect of sorbent dosages on the sorption of malachite green is shown in Fig. 4. The removal of dye cations increases with sorbent dosage. This may be attributed to increased sorbent surface area and availability of more sorption sites resulting from the increased dose of the sorbent. But the amount of dye sorbed per unit mass of sorbent decreases with an increase in sorbent dose. At higher plane tree leaves to solute concentration ratios, there is a very fast superficial sorption onto the sorbent surface that produces a lower solute concentration in the solution than when the biomaterial to solute concentration ratio is lower. This is because a fixed mass of leaves can only sorb a certain amount of dye. Therefore, the higher the sorbent dosage is, the larger the volume of effluent that a fixed mass of plane tree leaves can purify is. The decrease in the amount of malachite green sorbed with increasing sorbent mass is due to the split in the flux or the concentration gradient between solute concentrations in the solution and on the sorbent surface. From Fig. 4, it can also be seen that the sorbent dosage has an influence on the contact time necessary to reach equilibrium. For the smallest chitin dosage (0.25 g/100 mL) equilibrium was reached after about 300 min, while for the higher sorbent dosage (1 g/100 mL) equilibrium was attained after 90 min. Thus, the necessary time to reach equilibrium decreased with an increase of sorbent dosage. The higher the sorbent dosage, the lower the time necessary to reach equilibrium is. This is due to the availability of sorption sites for higher sorbent dosage.

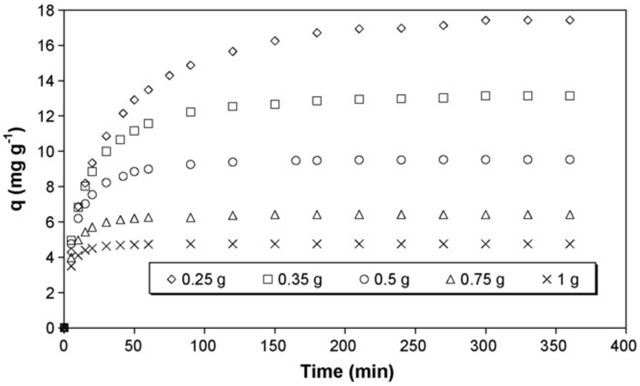

Fig. 4. Effect of sorbent dose on the sorption of malachite green by the dead leaves of plane tree.

The experimental kinetic data were fitted to the pseudo-first order kinetic expression, the six linearized forms of the pseudo-second order equation and the Elovich expression. The sorption of malchite green by the leaves of plane tree was found to be well represented by the type 1 expression of the pseudo-second order kinetic equation (Table 4). The obtained coefficient of determination is extremely high (equal to unity) for all sorbent dosages. Increasing the dose of plane tree leaves enhanced the initial sorption rate and the rate constant. However, the theoretical amount sorbed at equilibrium decreased with sorbent mass.

3.1.3. *Effect of malachite green initial concentration*

In all experiments, the temperature was maintained at 25 °C and the agitation speed maintained at 400 rpm. Fig. 5 illustrates the sorption of malachite green for different initial dye concentrations for a sorbent dose of 0.25 g as a function of contact time. The data also showed that the initial dye concentrations influenced the contact time necessary to reach equilibrium and that the sorption capacity increased for the higher initial dye concentrations. This is a result of the increase in the driving force the concentration gradient, as an increase in the initial dye ion concentrations. The initial rate of sorption was greater for higher initial malachite green concentration, because the resistance to the dye uptake decreased as the mass transfer driving force

Table 4
Pseudo-second order (type 1) kinetic parameters obtained for different experimental conditions

Parameters	K_2 (g mg^{-1} min^{-1})	q_e (mg g^{-1})	h (mg g^{-1} min^{-1})	R^2
Sorbent dosage (g/100 mL)				
0.25	0.00291	18.25	0.97	1
0.35	0.00738	13.53	1.35	1
0.5	0.02081	9.69	1.95	1
0.75	0.06272	6.47	2.63	1
1	0.21483	4.77	4.89	1
Initial concentration (mg L^{-1})				
5	0.09927	1.86	0.34	1
10	0.05582	3.82	0.82	1
20	0.01265	7.84	0.78	1
30	0.00488	11.75	0.67	1
40	0.00331	15.29	0.77	1
50	0.00271	18.25	0.97	1
Stirring speed (rpm)				
0	0.00073	12.17	0.11	0.962
100	0.00241	18.32	0.81	1
200	0.00323	18.25	1.08	1
400	0.00271	18.25	0.97	1
800	0.00244	18.42	0.83	1
Ionic strength (g/100 mL)				
0	0.00291	18.25	0.97	1
0.25	0.00202	16.84	0.57	1
2	0.0014	15.31	0.33	0.997
Temperature (°C)				
25	0.00291	18.25	0.97	1
35	0.00307	18.8	1.09	1
45	0.00349	19.31	1.3	1

increased. When initial dye concentration was increased from 5 to 50 mg L^{-1}, the equilibrium sorption capacity increased from 1.83 to 17.42 mg g^{-1}. The necessary time to reach equilibrium is variable according to the initial concentration of dye: about 120 min for $C_0 = 5$ and 10 mg L^{-1}, 180 min for $C_0 = 20$ mg L^{-1}, 240 min for 30 mg L^{-1}, 270 for 40 mg L^{-1}, and 300 min for 50 mg L^{-1}.

The kinetic of dye biosorption by the leaves of plane tree were analyzed using pseudo-first order equation, the six linear expressions of the pseudo-second order kinetic model and the Elovich relation. The kinetics of malachite green sorption by the biosorbent follows the pseudo-second order rate expression of type 1. The obtained kinetic parameters are regrouped in Table 4. The values of the rate constant decrease with increasing initial dye concentrations. The values of determination coefficient are extremely high (equal to unity) for all initial dye concentrations. The values of equilibrium sorption capacity increase from 1.86 to 18.25 mg g^{-1} with increasing initial dye concentration. These values are in agreement with experimental data as to be in the effect of sorbent dose. However, there was no clear trend for changes in the initial sorption rate when initial dye concentrations were changed in this study.

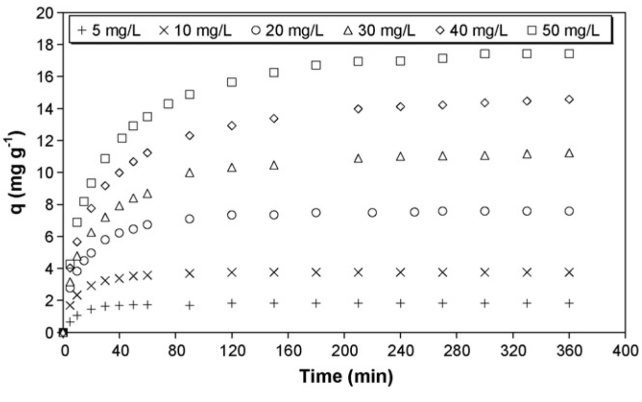

Fig. 5. Effect of initial concentration of dye on the sorption of malachite green by the dead leaves of plane tree.

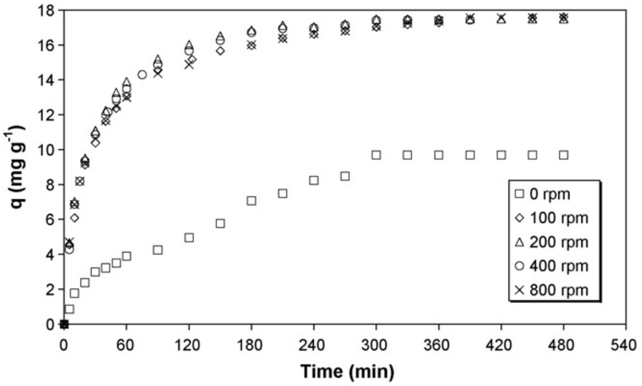

Fig. 6. Effect of agitation speed on the sorption of malachite green by the leaves of plane tree.

3.1.4. Effect of agitation speed

In all the experiments in which the effect of agitation speed was studied, the sorbent dose, initial dye concentration, and solution temperature were 0.25 g, 50 mg L^{-1}, and 25 °C, respectively. Fig. 6 shows the sorption of malachite green by the leaves of plane tree at different agitation speeds raging from 0 (without agitation) to 800 rpm. The obtained results show that there is no effect of the agitation speeds between 100 and 800 rpm. These agitation speeds assure a good diffusion of dye cations toward biosorbent particles. For the experiment conducted without agitation, it is noticed a significant reduction of the equilibrium sorption capacity. The amount of dye sorption increases with the increase of the stirring speed from 0 to 100 rpm. When increasing the stirring speed, the diffusion rate of dye ions from the bulk liquid to the liquid boundary layer surrounding sorbent particles became higher because of an enhancement of turbulence and a decrease of the thickness of the liquid boundary layer. From Fig. 6, it can also be seen that the agitation speed has an influence on the contact time necessary to reach equilibrium. For an agitation speed of 100 rpm, the equilibrium was reached after 450 min, while for a stirring speed of 800 rpm equilibrium was achieved after 300 min.

The kinetic results were fitted to the pseudo-first order kinetic expression, the six linearized forms of the pseudo-second order equation and the Elovich expression. The sorption of malachite green by the leaves of plane tree was found to be well represented by the type 1 expression of the pseudo-second order kinetic equation (Table 4).

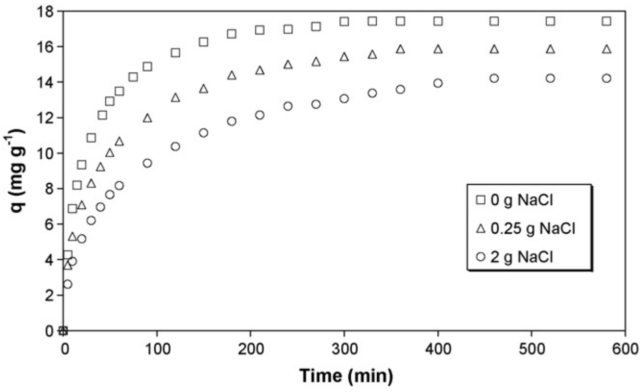

Fig. 7. Effect of ionic strength on the sorption of malachite green by the leaves of plane tree.

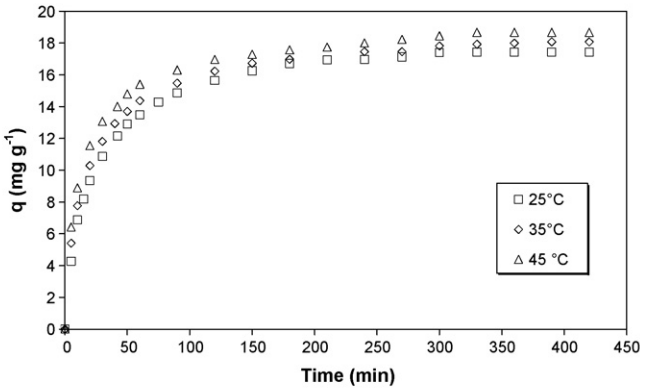

Fig. 8. Effect of temperature on the sorption of malachite green by the dead leaves of plane tree.

3.1.5. *Effect of ionic strength*

Wastewaters from textile-manufacturing or dye-producing industries contain various types of suspended solids and salts. The presence of ions leads to high ionic strength, which may significantly affect the performance of the biosorption process. Fig. 7 presents the effect of ionic strength on the uptake of dye. It was observed that the sorption potential decreased with increased concentration of NaCl in the medium. The adverse effect of ionic strength on dye uptake suggests the possibility of ion exchange mechanisms being in operation in the biosorption process. The reason for this is that, on the one hand, hydrated cations in the aqueous phase compete effectively with positively charged dye molecules for the same binding sites on the biosorbent surface. On the other hand, "ionic atmosphere" may be progressively formed around malachite green molecules with increased NaCl concentration and results in the reduction of malachite green sorption on the tested biomaterial. Another reason is the influence of the great ionic strength on the activity coefficient of dye, which reduce its transfer to the sorbent surface.

From Fig. 7, it can also be seen that the sorbent dosage has an effect on the contact time necessary to reach equilibrium. The required time to attain equilibrium is about 300 min without salt and 360 and 460 min for sodium chloride concentrations of 0.25 and 2 g/100 mL, respectively.

The experimental kinetic data were fitted to the pseudo-first order kinetic expression, the six linearized forms of the pseudo-second order equation and the Elovich expression. The sorption of malachite green by the leaves of plane tree was found to be well represented by the type 1 expression of the pseudo-second order kinetic equation. The obtained kinetic parameters are regrouped in Table 4. The values of the rate constant and initial sorption rate decrease with increasing the concentration of NaCl. The values of determination coefficient are very high ($\geq$0.997). The values of equilibrium sorption capacity decrease from 18.25 to 15.31 mg g^{-1} with increasing NaCl concentration. These values are in agreement with the experimental data.

3.1.6. *Effect of temperature*

Temperature has great effect on the sorption process. The influence of temperature on the sorption of malachite green by the leaves of plane tree was studied with a constant initial concentration of 50 mg L^{-1}, a sorbent mass of 0.25 g and an agitation speed of 400 rpm. Fig. 8 shows the effect of temperature on the sorption data as a function of contact time. The equilibrium sorption capacity increases when the temperature of dye solutions increases from 25 to 45 °C. The fact that the sorption of dye is in favor of temperature indicates that the process is endothermic.

The sorption kinetic results were fitted to the pseudo-first order kinetic expression, the six linearized forms of the pseudo-second order equation and the Elovich expression. The temperature dependence of dye sorption by the dead leaves of plane tree shows a good compliance with the type 1 expression of the pseudo-second order equation, which are reflected by extremely high coefficients of determination (Table 4). The values of the rate constant, the sorption capacity at equilibrium, and the initial sorption rate increase with increasing solution temperature.

The pseudo-second order rate constant is expressed as a function of temperature using the Arrhenius equation

$$K_2 = A_0 \exp\left(-\frac{E_a}{R_g T}\right) \tag{11}$$

where A_0 is the temperature independent factor (g mg^{-1} min^{-1}); E_a the activation energy of sorption (kJ mol^{-1}); R_g the gas constant (8.314 J mol^{-1} K^{-1}), and T is the solution temperature (K). From this equation, Arrhenius constant, A_0, is 50.96×10^{-3} g mg^{-1} min^{-1} and the activation energy of sorption E_a is 7.13 kJ mol^{-1}. The activation energy obtained is very low, and thus the sorption of malachite green by the dead leaves of plane tree may involve not only an activated process but a physical sorption.

3.2. *Equilibrium isotherms*

The sorption data for malachite green by the leaves of plane tree at different temperatures were analyzed by a regression analysis to fit the Freundlich equation and the five linearized expressions of Langmuir isotherm model. The details of these different forms of linearized Langmuir equations and the method to estimate the Langmuir constants q_m and

Table 5
Parameters of the Langmuir and Freundlich isotherms

Isotherm	T (°C)		
	25	35	45
Langmuir-1			
b (L mg^{-1}) × 10^3	55.68	70.10	90.91
q_m (mg g^{-1})	77.52	80.65	84.75
R^2	0.956	0.911	0.944
Langmuir-2			
b (L mg^{-1}) × 10^3	31.23	33.19	36.08
q_m (mg g^{-1})	85.47	91.74	97.09
R^2	0.998	0.997	0.996
ΔG° (kJ mol^{-1})	−25.46	−26.47	−27.55
Langmuir-3			
b (L mg^{-1}) × 10^3	51.31	63.36	83.93
q_m (mg g^{-1})	79.16	83.20	86.79
R^2	0.897	0.838	0.842
Langmuir-4			
b (L mg^{-1}) × 10^3	46	53.1	70.7
q_m (mg g^{-1})	80.92	86.13	89.43
R^2	0.897	0.838	0.842
Langmuir-5			
b (L mg^{-1}) × 10^3	52.6	61.9	84.4
q_m (mg g^{-1})	78.45	83.21	86.21
R^2	0.956	0.911	0.944
Freundlich			
n	4.02	3.68	4.01
K_F (mg$^{1-1/n}$ L$^{1/n}$ g^{-1})	18.68	21.76	21.92
R^2	0.991	0.996	0.995

b from these plots were explained in Table 2. Out of the five different types of linearized Langmuir isotherm equations, Langmuir-1 and Langmuir-2 are the most frequently used by several researchers because of the minimized deviations from the fitted equation resulting in the best error distribution. Values of the Langmuir constants and the Freundlich parameters are presented in Table 5 for the sorption of malachite green by the dead leaves of plane tree at 25, 35 and 45 °C. The values of the coefficient of determination obtained from Langmuir-2 expression indicate that there is strong positive evidence that the sorption of dye by the biosorbent follows the Langmuir isotherm. Fig. 9 shows the type 2 linear Langmuir equation with the experimental data for the sorption of malachite green by the leaves of plane tree at various temperatures. It seems that the isotherm obtained from Langmuir-2 expression provided a better fit to the experimental data.

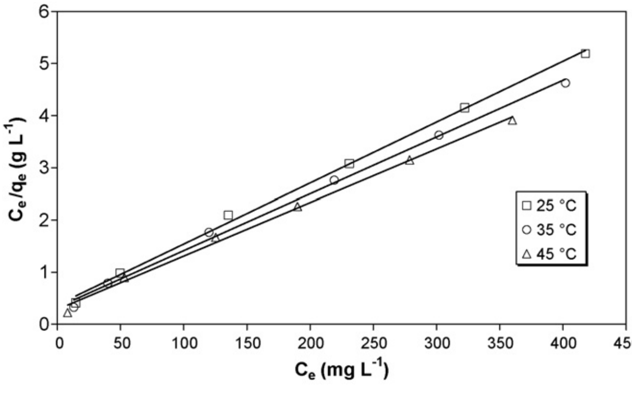

Fig. 9. Modeling of sorption isotherms of malachite green by the dead leaves of plane tree using Langmuir-1 expression.

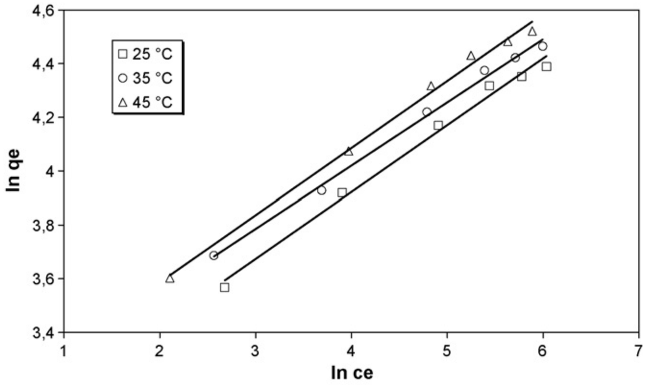

Fig. 10. Modeling of sorption isotherms of malachite green by the dead leaves of plane tree using Freundlich model.

Further, the equilibrium data were further analyzed using the linearized form of Freundlich equation using the same set experimental data, by plotting $\ln q_e$ versus $\ln C_e$ (Fig. 10). The calculated Freundlich isotherm constants and the corresponding coefficient of determination values were shown in Table 5. From Table 5, if just the linear form of Langmuir-2 is used for comparison, Langmuir-2 was more suitable for the experimental data than was the Freundlich isotherm because of the higher value of the coefficient of determination. In contrast, if using the linear form of the other Langmuir equations, the Freundlich isotherm was more suitable for the experimental data than was the Langmuir isotherm in most cases. This suggests that both the Freundlich and Langmuir-2 isotherms could be well represented the experimental sorption data of malachite green by the dead leaves of plane tree, but the Langmuir-2 expression was better.

A sorption isotherm is characterized by certain constants the values of which express the surface properties and affinity of the sorbent. The magnitude of the exponent n gives an indication of the favorability of sorption. It is generally stated that values of n in the range 2–10 represent good, 1–2 moderately difficult, and less than 1 poor adsorption characteristics [22]. The studied material is good sorbent for malachite green ($n > 3.6$). The favorable nature of sorption can be expressed in terms of dimensionless separation factor or equilibrium parameter [23]: $R_L = 1/(1 + bC_0)$, where b is the Langmuir constant and C_0 is the initial concentration of the sorbate in solution. The values of R_L indicates the type of isotherm to be irreversible ($R_L = 0$), favorable ($0 < R_L < 1$), linear ($R_L = 1$) or unfavorable ($R_L > 1$). The calculated R_L values versus initial solute concentration at three different temperatures were represented in Fig. 11. From Fig. 11, it was observed that at all temperature conditions, sorption was found to be more favorable at higher concentrations. Also the value of R_L in the range of 0–1 at all initial dye concentrations and at all the three-solution tempera-

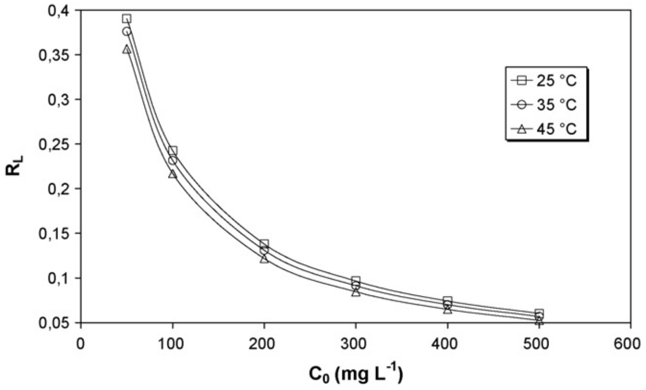

Fig. 11. Separation factors for malachite green onto dead leaves of plane tree at different temperatures.

ture conditions confirms the favorable uptake of malachite green process.

The Langmuir model makes several assumptions, such as monolayer coverage and constant adsorption energy while the Freundlich equation deals with heterogeneous surface adsorption. The applicability of both Langmuir and Freundlich isotherms to the studied system implies that both monolayer sorption and heterogeneous surface conditions exist under the used experimental conditions.

3.2.1. *Thermodynamic parameters*

In environmental engineering practice, both energy and entropy factors must be considered in order to determine what processes will occur spontaneously. Gibb's free energy change, ΔG°, is the fundamental criterion of spontaneity. Reactions occur spontaneously at a given temperature if ΔG° is a negative value. The thermodynamic parameters of ΔG°, enthalpy change, ΔH°, and entropy change, ΔS°, for the sorption processes are calculated using the following equations

$$\Delta G^\circ = -R_g T \ln b \tag{12}$$

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \tag{13}$$

where b (L mol^{-1}) is the Langmuir-2 constant, R_g the gas constant (8.314 J mol^{-1} K^{-1}), and T is the solution temperature in Kelvin (K).

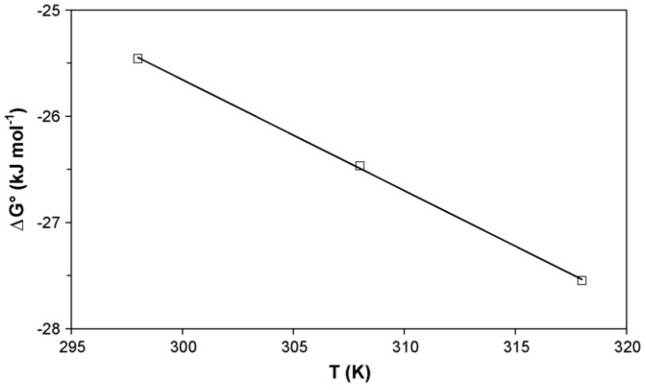

Fig. 12. Plot of Gibbs free energy change versus temperature.

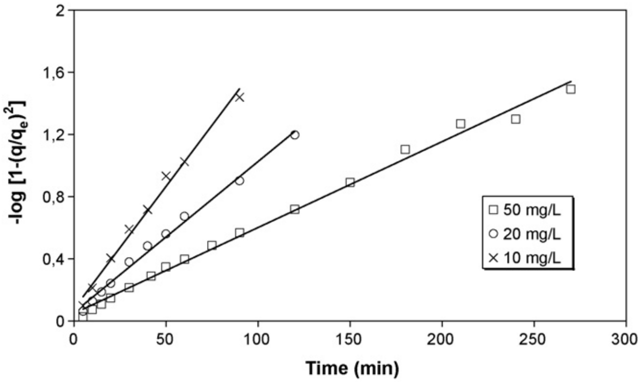

Fig. 13. Evolution of $-\log[1 - (q/q_e)^2]$ versus time for different concentrations.

A plot of ΔG° obtained using the constant b of Langmuir-2 versus temperature was found to be linear (Fig. 12). The values of ΔH° and ΔS° were, respectively, determined from the slope and intercept of the plots. The thermodynamic parameter, ΔG°, is shown in Table 5. ΔH° and ΔS° for the sorption process were calculated to be 5.7 kJ mol^{-1} and 104.5 J mol^{-1} K^{-1}, respectively. The negative value of ΔG° confirms the favorability of the process and the spontaneous nature of sorption with a high preference for malachite green to sorb onto the leaves of plane tree. The value of ΔH° was positive, indicating that the sorption process is endothermic. Finally, the positive value of ΔS° shows the increasing randomness at the solid/liquid interface during the sorption of malachite green cations onto the leaves of plane tree and an affinity of the sorbent toward the dye. The value of standard entropy change is not very large and indicates an increase due to sorption. Normally, adsorption of gases leads to a decrease in entropy due to orderly arrangement of the gas molecules on a solid surface. However, the same may not be true for the complicated system of sorption from solution onto the dead leaves of plane tree.

3.3. *Sorption mechanism*

From a mechanistic viewpoint to interpret the experimental data, prediction of the rate-limiting step is an important factor to be considered in the sorption process. The sorption dynamics can be described by the following three consecutive steps: transport of the solute from bulk solution through liquid film to the sorbent exterior surface, diffusion within the pores of particle, and sorption of solute on the interior surfaces of the pores of sorbent. The last step is considered to be an equilibrium reaction. Of the three steps, 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 pore diffusion.

If the process is controlled by external resistance, the plot of ln C versus time must be linear [24]. For all the used experimental conditions, the relation was not linear and proved that the external transport was not the limiting step.

Since the sorption of malachite green by plane tree leaves did not change with the stirring speed and was not controlled by external transport, the sorption kinetics seemed to

Table 6
Intraparticle diffusion coefficient for malachite green onto plane tree leaves for different initial dye concentrations

C_0 (mg L^{-1})	$D/d^2 \times 10^4$ (min^{-1})	R^2
5	12.23	0.983
10	9.15	0.990
20	5.65	0.993
30	3.09	0.989
40	2.91	0.994
50	3.20	0.994

be controlled by the intraparticle diffusion. Therefore, the sorption data were analyzed by the Urano and Tachikawa model [25]:

$$-\log\left[1-\left(\frac{q}{q_e}\right)^2\right]=\frac{4\pi^2 D}{2.3d^2}t \qquad (14)$$

where q and q_e are the sorbed amounts (mg g^{-1}) at any time t and at equilibrium, d (cm) is the diameter of the sorbent, and D (cm^2 min^{-1}) is the intraparticle diffusion coefficient based on the concentration in solids.

Examples of the relationship between $-\log[1-(q/q_e)^2]$ and t are shown in Fig. 13. Since the relationships were linear, Eq. (14) was adequate. The calculated values of D/d^2 determined from the slope of plots are tabulated in Table 6. The average D/d^2 values were estimated to be 6.03×10^{-4} min^{-1}.

4. Conclusion

The results obtained in this study indicate that the dead leaves of plane tree can be successfully used for the removal of hazardous dye, malachite green from aqueous solutions. The batch sorption process is found dependent upon contact time, sorbent dose, initial dye concentration, ionic strength, and temperature. The agitation speed showed a restricted influence on the removal kinetics.

The kinetic data show that pseudo-second order kinetic model is obeyed better than Elovich and pseudo-first order models since second order model provide high degree of correlation with the experimental data at various experimental conditions. Among the six linear expressions of the pseudo-second order kinetic model, a type 1 expression very well represent the kinetic uptake of malachite green by the dead leaves. A type 6 expression is found to be the worse fit pseudo-second order kinetic equation. The obtained value of the activation energy is very low (7.13 kJ mol^{-1}), which indicates not only an activated process but a physical sorption. The dye uptake process was found to be controlled by intraparticle diffusion.

Langmuir-2 is the most-popular linear form which had the highest coefficient of determination compared with the other Langmuir linear equations. Both the Langmuir and the Freundlich isotherms had higher values for the coefficient of determination, but the Langmuir model is better. Thermodynamic parameters show that the sorption of malachite green by the leaves of plane tree is favorable, spontaneous in nature, and endothermic.

Thus, it can be safely concluded that the waste biomaterial, dead leaves of plane tree, can be used as excellent sorbent for the removal of dyes from wastewater.

Further experiments need to be conducted to test the dynamic sorption of malachite green in fixed bed onto the dead leaves of plane tree.

Acknowledgements

The authors gratefully acknowledge financial support from the Agence Universitaire de la Francophonie and the Ministry of Higher Education and Scientific Research of Algeria (Project No. J 0101120060043).

References

[1] Y. Wong, J. Yu, Laccase catalysed decolorisation of synthetic dyes, Water Res. 33 (1999) 3512–3520.
[2] R. Sivaraj, C. Namasivayam, K. Kadirvelu, Orange peel as an adsorbent in the removal of acid violet 17 (acid dye) from aqueous solutions, Waste Manage. 21 (2001) 105–110.
[3] Z. Aksu, Application of biosorption for the removal of organic pollutants: a review, Process Biochem. 40 (2005) 997–1026.
[4] S.D. Khattri, M.K. Singh, Colour removal from dye wastewater using sugar cane dust as an adsorbent, Adsorpt. Sci. Technol. 17 (1999) 269–282.
[5] S.J. Culp, F.A. Beland, Malachite green: a toxicological review, J. Am. College Toxicol. 15 (1996) 219–238.
[6] S.J. Culp, L.R. Blankenship, D.F. Kusewitt, D.R. Doerge, L.T. Mulligan, F.A. Beland, Toxicity and metabolism of malachite green and leucomalachite green during short-term feeding to Fischer 344 rats and B6C3F(1) mice, Chem. Biol. Interact. 122 (1999) 153–170.
[7] D.J. Alderman, Malachite green—a review, J. Fish Dis. 8 (1985) 289–298.
[8] Y. Sawa, M. Hoten, Antibacterial activity of basic dyes on the dyed acrylic fibers, Sen. I Gakkaishi 57 (2001) 153–158.
[9] R.S. Clifton-Hadley, D.J. Alderman, The effects of malachite green upon proliferative kidney-disease, J. Fish Dis. 10 (1987) 101–107.
[10] G. McKay, M.S. Otterburn, D.A. Aga, Fullers earth and fired clay as adsorbent for dye stuffs, equilibrium and rate constants, Water Air Soil Pollut. 24 (1985) 307–322.
[11] A.R. Gregory, S. Elliot, P. Kluge, Ames testing of direct black 3B parallel carcinogenecity, J. Appl. Toxicol. 1 (1991) 308–313.
[12] S.J. Srivastava, N.D. Singh, A.K. Srivastava, R. Sinha, Acute toxicity of malachite green and its effects on certain blood parameters of a catfish, *Heteropneustes Fossilis*, Aquat. Toxicol. 31 (1995) 241–247.
[13] S. Singh, M. Das, S.K. Khanna, Biodegradation of malachite green and rhodamine-b by cecal microflora of rats, Biochem. Biophys. Res. Commun. 200 (1994) 1544–1550.
[14] S. Srivastava, R. Sinha, D. Roy, Toxicological effects of malachite green, Aquat. Toxicol. 66 (2004) 319–329.
[15] S. Lagergren, Zur theorie der sogenannten adsorption gelöster stoffe, K. Sven. Vetenskapsakad. Handl. 24 (1898) 1–39.
[16] G. Blanchard, M. Maunaye, G. Martin, Removal of heavy metals from waters by means of natural zeolites, Water Res. 18 (1984) 1501–1507.
[17] Y.S. Ho, Adsorption of heavy metals from waste streams by peat, Ph.D. Thesis, University of Birmingham, Birmingham, UK, 1995.
[18] Y.S. Ho, G. McKay, The kinetics of sorption of divalent metal ions onto sphagnum moss peat, Water Res. 34 (2000) 735–742.
[19] J. Zeldowitsch, Uber den mechanismus der katalytischen oxidation von CO an MnO_2, Acta Physicochim. URSS 1 (1934) 364–449.
[20] D.G. Kinniburgh, General purpose adsorption isotherms, Environ. Sci. Technol. 20 (1986) 895–904.

[21] Y.S. Ho, C.C. Wang, Pseudo-isotherms for the sorption of cadmium ion onto tree fern, Process Biochem. 39 (2004) 759–763.
[22] R.E. Treybal, Mass-transfer operations, third edition, McGraw Hill, 1981.
[23] K.R. Hall, L.C. Eagleton, A. Acrivos, T. Vermeulen, Pore and solid diffusion kinetics in fixed bed adsorption under constant pattern conditions, Ind. Eng. Chem. Fundam. 5 (1966) 212–223.
[24] D.M. Nevskaia, A. Santianes, V. Munoz, A. Guerrero-Ruiz, Interaction of aqueous solutions of phenol with commercial activated carbons: an adsorption and kinetic study, Carbon 37 (1999) 1065–1074.
[25] K. Urano, H. Tachikawa, Process development for removal and recovery of phosphorus from wastewater by a new adsorbent. 2. Adsorption rates and breakthrough curves, Ind. Eng. Chem. Res. 30 (1991) 1897–1899.