



## Novel tannin-based adsorbent in removing cationic dye (Methylene Blue) from aqueous solution. Kinetics and equilibrium studies

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### ABSTRACT

Natural tannin-based adsorbent has been prepared on the basis of the gelification of *Quebracho* bark extract. The resulting product, *Quebracho Tannin Gel* (QTG) was tested as cationic dye adsorbent with Methylene Blue (MB). Kinetics of adsorption process were studied out and a period of 15 days was determined for reaching equilibrium. The influences of pH and temperature were evaluated. As pH or temperature raise  $q$  capacity of QTG increases. Theoretical modelization of dye-QTG adsorption was carried out by multiparametric adjustment according to Langmuir's hypothesis. Values of the  $k_{t1}$ ,  $k_{t2}$  and activation energies were calculated.

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### 1. Introduction

Textile industry involving dye production and usage is one of the largest in the world, and the implications to economic and social conditions in many countries are very important [1]. There are a number of dye substances that may differ attending to various factors such as fiber class, colour or industrial process. Almost all of them could be highly polluting if released into the environment.

Over 50,000 tonnes of dye, containing hazardous substances which can damage aquatic and vegetal life, are discharged via effluent into the environment annually [2]. Researchers have been working on ways of removing dyes from wastewater for many years researchers. Therefore, different procedures have been developed: adsorption onto materials such activated carbon [3,4] or waste products [5,6], physical and chemical degradation [7,8] in addition to a large number of other techniques: Fenton's oxidation, electrocoagulation [9], ozonization. . . [10,11].

Dyes may be classified into several different groups, according to their usage in dyestuff. Regarding to this fact, there are acid, basic, disperse, direct . . . dyes (family names that have to do with when and how dyes are used). Regarding, on the other hand, to their chemical structure, lots of compounds are included as dye.

Industrial pollution involving dyes leads to coloured water that can destroy environmental equilibrium. Many dyes are toxic and even carcinogenic. Although some of them are used in pharmaceutical production, large exposure to them can cause several harmful effects. Methylene Blue (MB) (structure showed in Fig. 1), which is the one selected in the current investigation, can cause increased heart rate, vomiting, shock, cyanosis, jaundice and many other dangerous injuries [12].

The remediation of several pollution problems is a target of many researchers nowadays. Technical ways of solving environmental concerns and menaces such as the dumping of surfactants, dyes, pharmaceuticals and other hazards are available long time ago, but making them cheaper and sustainable is still a challenge. Natural raw materials are a possible source of low-cost adsorbents that could provide a successful solution [13–15].

Under *tannins* denomination there are lots of chemical families. Tannins have been used traditionally for animal skins process, but it is possible to find several products that are distributed as flocculants. Tannins come from vegetal secondary metabolites [16]: bark, fruits, leaves. . . Tannin-rich barks come from trees such as *Acacia*, *Castanea* or *Schinopsis*. However, it is not needed to search for

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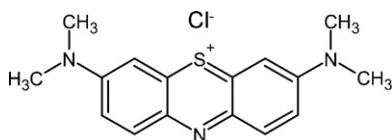


Fig. 1. Chemical structure of Methylene Blue.

tropical species: *Quercus ilex*, *suber* or *robur* have also tannin-rich bark.

Many few authors have investigated about tannins water treatment capacity, although their ability in removing heavy metals is well demonstrated [17]. Zhan and Zhao [18] tried to remove lead from water by using an adsorbent, tannin-based gel. Process of metal removal is improved by tannin gelification. In the same sense, there are other works ([19,20] and recently [21]).

Palma et al. [22] used tannins extracted *in situ* from *Pinus radiata* bark in order to polymerize a solid which is used in heavy metals removal. Bark itself was combined with a tannin solid into adsorption columns.

The specific removal of heavy metals and several kinetics studies have been developed recently by Sengil and Özacar [23] by using tannin resin from valonia. The results showed very interesting conclusions, and tannin resin seems to be a novel adsorbent that may be used in remediation and recovery of wastes. Other authors have researched in the same sense [24,25]

*Schinopsis balansae*, commonly known as *Quebracho*, is a tree that comes from South America. It was considered the first source of tannins until *Acacia mearnsii* de Wild replaced it because its high percentual tannin content and its relatively easy reproduction procedure. However, *Quebracho* is an important feedstock for tannin production [26]. Its content in tannins has been thoroughly determined [27].

Tannins from *Quebracho* have been thoroughly characterized by several researchers [28]. About *Quebracho* composition it can be said that is mainly based on combinations of resorcinol, catechol and pyrogallol building blocks [29]. In fact, *Quebracho* tannins have been used in resin synthesis and its usage in biosorption of Pb(II) [30].

The main aim of this paper is to investigate this novel adsorbent that have been thoroughly tested in metal removal in the new field of cationic dyes removal. Firstly, we have focused our research activity in kinetics of QTG–MB adsorption. Then, we have developed a theoretical modelization of QTG–MB adsorption equilibrium taking into account MB concentration in bulk solution, according to Langmuir equation.

## 2. Materials and methods

The reagents and the procedures we have used in this investigation are referred below.

### 2.1. Buffered solution

All assays were done in a pH-stable medium. A pH 7-buffered solution was prepared by mixing 1.2 g of  $\text{NaH}_2\text{PO}_4$  and 0.885 g of  $\text{Na}_2\text{HPO}_4$  in 1-L flask. Assays with different pH were carried out by adjusting this buffered solution to the specific pH by using HCl 0.5 M and NaOH 0.5 M. All reagents were supplied by PANREAC in analytical purity grade.

### 2.2. QTG preparation

QTG was prepared according to Nakano et al. [19]. 5 g of *Quebracho* bark extract (supplied by TANAC, Brazil) were dissolved

in 32 mL of NaOH (PANREAC)  $0.125 \text{ mol L}^{-1}$  and 30 mL of distilled water at 353 K. When mixture was homogeneous, 2 mL of formaldehyde (SIGMA) 37% (v/v) were added and reaction was kept at the same temperature for 8 h until polymerization was considered completed. Then, the apparent gummy product was lead to complete evaporation of water remain and dried in oven ( $65^\circ\text{C}$ ) overnight. After gelation, QTG was crushed and sieved to produced 38–53  $\mu\text{m}$  diameter particles. They were washed successively with distilled water and  $\text{HNO}_3$   $0.1 \text{ mol L}^{-1}$  (PANREAC) to remove unreacted formaldehyde. Finally, QTG was dried again in oven. Differences are found between this preparation way and the description made by Yurtsever and Sengil [30], mainly concerning the amount of formaldehyde (10 mL instead of 2 mL).

For characterizing *Quebracho* tannin before and after gelification, FTIR spectra were recorded on a Thermo-Nicolet FTIR 300 spectrophotometer. A sample of *Quebracho* extract and QTG were dried at  $60^\circ\text{C}$  and stored under vacuum. Potassium bromide disk was prepared by mixing 1 mg of tannin with 250 mg of KBr (Merck, spectrometry grade) at  $10,000 \text{ kg cm}^{-2}$  pressure for 5 min under vacuum. The spectra were recorded from  $4000$  to  $400 \text{ cm}^{-1}$ .

The spectra of both samples are shown in Fig. 2. Wide bands in the range of  $3600$ – $3100 \text{ cm}^{-1}$  correspond to –OH bridging groups in all systems and are attributed to O–H stretching (phenolic or alcoholic group) and to water molecules hydrogen bonded with –OH groups. The small peaks in the region of  $2950$ – $2850 \text{ cm}^{-1}$  are associated with the methylene (– $\text{CH}_2$ –) bridges. Also, stretching vibrations of C–H groups in the aromatic rings give absorption bands in this region. The absorption bands between  $1620$  and  $1450 \text{ cm}^{-1}$  are characteristic of the elongation of the aromatic –C=C– bonds. The deformation vibration of the C–C bonds in the phenolic group absorbs in the region of  $1500$ – $1400 \text{ cm}^{-1}$ . The peak at  $1390$ – $1370 \text{ cm}^{-1}$  is associated with the O–H deformation vibration of phenolic or alcoholic group. The peaks in the region  $1280$ – $1210 \text{ cm}^{-1}$  are associated with the –CO stretchings of the aromatic ring and the methylene ether bridges formed by reaction with formaldehyde. The peaks at  $1160$ – $975 \text{ cm}^{-1}$  are due to asymmetrical C–O–C stretching and C–H deformation. The deformation vibrations of the C–H bond in the aromatic rings give absorption bands in the range of  $835$ – $650 \text{ cm}^{-1}$ .

### 2.3. General dye removal assay

A Methylene Blue (SIGMA)  $1000 \text{ mg L}^{-1}$  solution was prepared by adding 0.250 g in 250 mL. Different volumes of this initial solution were put into 100 mL-flask, and a fixed quantity of QTG was added (20 mg). Magnetic stirring was applied for 15 days in a magnetic multistirrer (SELECTA), until equilibrium was achieved. Kinetics are studied by collecting samples at regular periods of time. Then, a sample was taken and it was centrifuged. Photometric analysis was carried out in a 1-cm glass cell. The maximum absorbance wavelength was 665 nm and a linear relationship of absorbance versus dye concentration was determined at this wavelength. An HELIOS UV/vis spectrophotometer was used for photometric measures.

### 2.4. Mathematical and statistical procedures

Linear data adjustment were carried out by using *Origin v. 7.0 for Windows*. Non-linear multiparametric data adjustment was carried out by using *SPSS 15.0.1 for Windows*.

## 3. Results and discussion

This investigation may be divided into two big parts: kinetics and equilibrium studies. We have also researched on variables

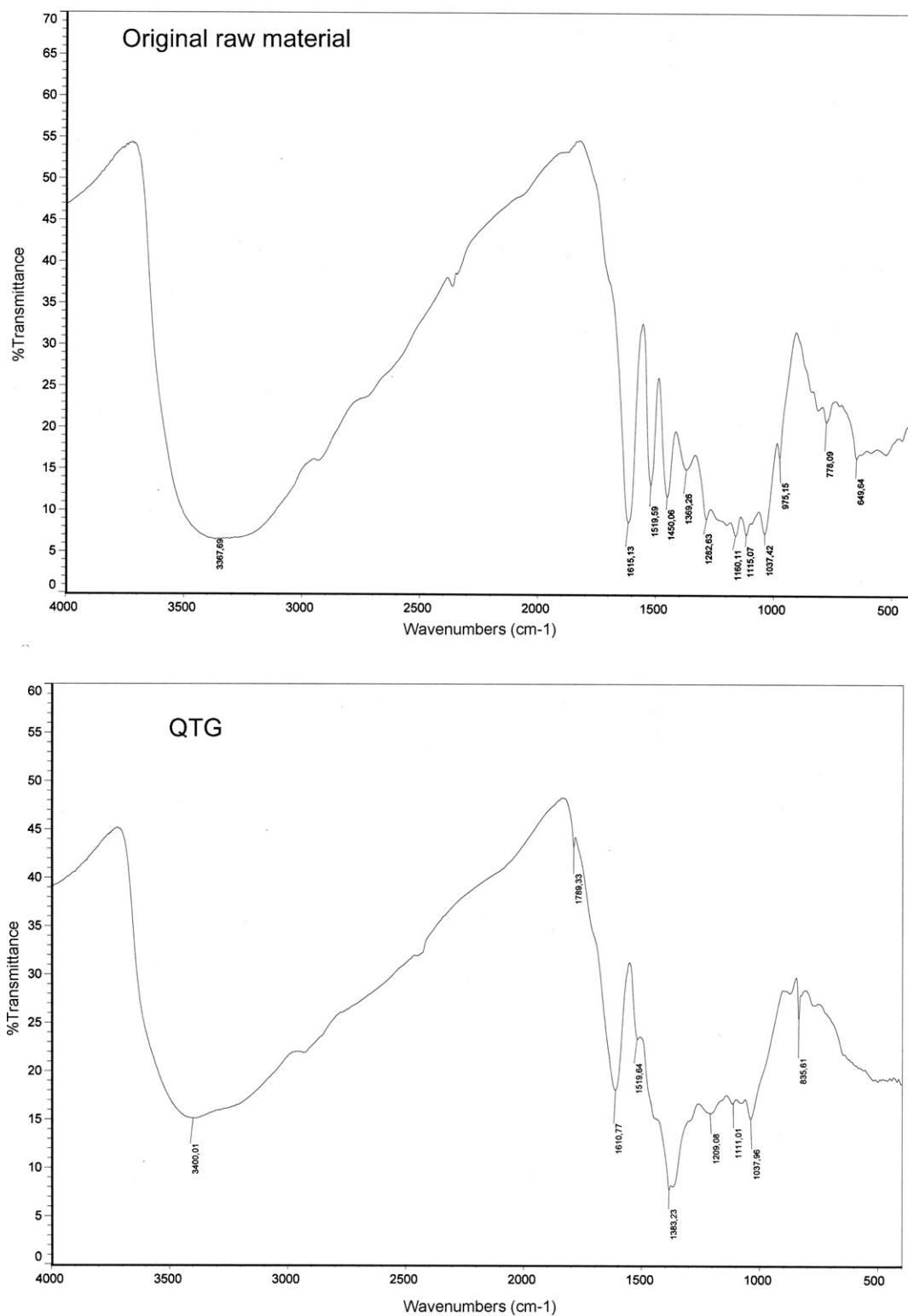


Fig. 2. FTIR spectra of raw and gelified *Quebracho* tannin.

influence and theoretical modelization. We present these results in the following sections.

### 3.1. Kinetics of dye removal

As a first step in the research process, a kinetic study was carried out. A series of assays was performed with a

fixed initial dye concentration (IDC) ( $100 \text{ mg L}^{-1}$ ) and with different proportions of QTG and MB (mmol per g of adsorbent). Fig. 3 reports the decreasing concentration of dye in six experiments with 1.5, 1.8, 2.2, 2.5, 2.8 and  $3.7 \text{ mmol g}^{-1}$ . A rather rapid dye removal is achieved in the first 150 h, although complete equilibrium dye concentration is reached at 350 h.

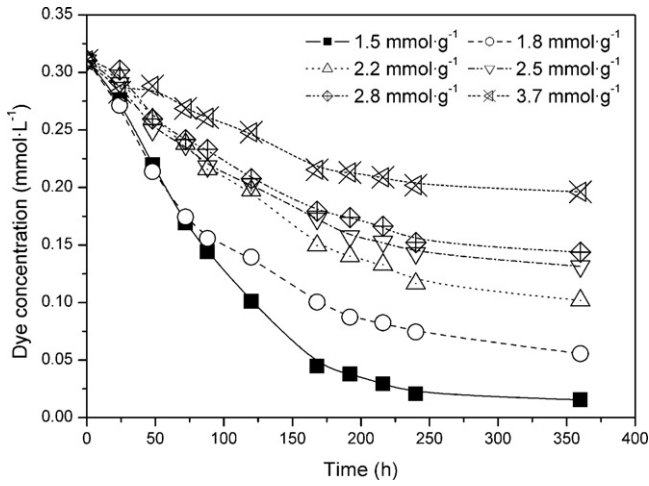


Fig. 3. Kinetics of dye removal.

Firstly, adsorption capacity ( $q$ ) has been determined, defined as:

$$q = \frac{(C_0 - C_t) \cdot V}{W} \quad (1)$$

where  $C_0$  is initial dye concentration ( $\text{mmol L}^{-1}$ ),  $C_t$  is equilibrium dye concentration in bulk solution ( $\text{mmol L}^{-1}$ ),  $V$  is the volume of solution (L), and  $W$  is adsorbent mass (g).

For the kinetic of adsorption process three theoretical models have been considered: Lagergren first order [31]; Ho second order [32] and Elovich model [33].

### 3.1.1. First order: Lagergren model

The Lagergren equation (2) is one of the most widely used adsorption rate equations for the adsorption of solute from a liquid solution. The modified first order kinetic model of Lagergren may be represented by the following equation:

$$\frac{dq}{dt} = k_l \cdot (q_e - q) \quad (2)$$

where  $q$  is the adsorption capacity defined according to Eq. (1) ( $\text{mmol of dye (g of QTG)}^{-1}$ );  $k_l$  is the first order Lagergren constant ( $\text{h}^{-1}$ );  $q_e$  is the equilibrium  $q$  capacity ( $\text{mmol of dye (g of QTG)}^{-1}$ ); and  $t$  is the contact time (h).

Integrating this equation with the boundary conditions  $t = 0$  to  $t = t$  and consequently  $q = 0$  to  $q = q$ , gives (3):

$$q = q_e - q_e \cdot e^{-k_l \cdot t} \quad (3)$$

which can be used in a non-linear adjustment in order to determine  $q_e$  and  $k_l$ .

### 3.1.2. Second order: Ho model

The second order kinetic model is expressed as (4):

$$\frac{dq}{dt} = k_h \cdot (q_e - q)^2 \quad (4)$$

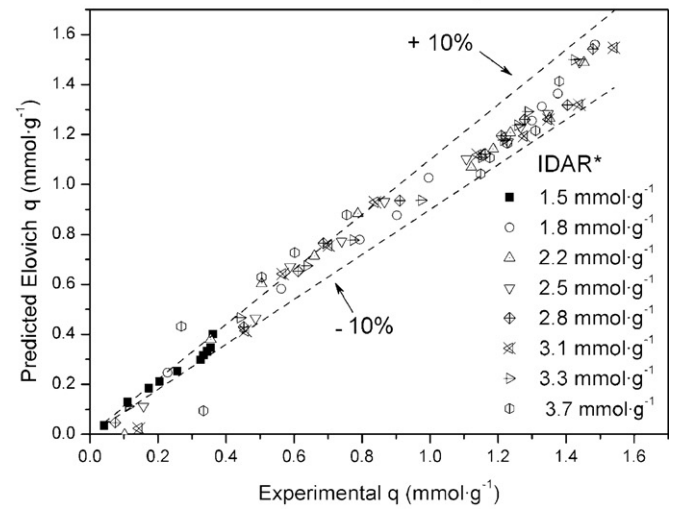
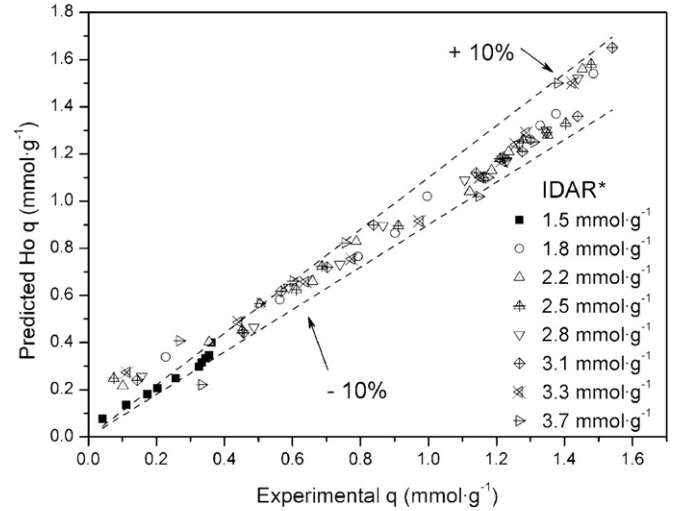
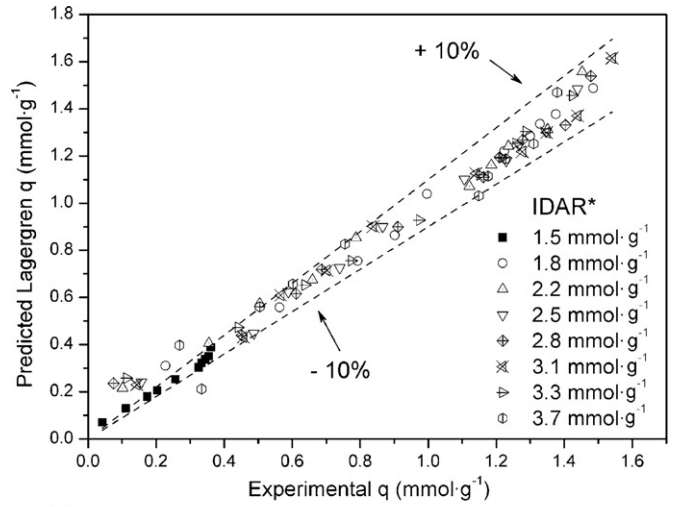
Rearranging the variables and taking into account similar boundary conditions as in Eq. (2), second order model can be represented by the Eq. (5):

$$q = \frac{t}{(1/h) + (t/q_e)} \quad (5)$$

where  $h$  is the initial adsorption rate, defined as Eq. (6)

$$h = k_h \cdot q_e^2 \quad (6)$$

and  $k_h$  is the second order constant ( $\text{g mmol}^{-1} \text{h}^{-1}$ ).



\* Initial Dye-Adsorbent Ratio

Fig. 4. Kinetic data adjustment.

### 3.1.3. Elovich model

The Elovich model is presented by the following equation (7):

$$q = \frac{1}{\beta_E} \cdot \ln(\alpha_E \cdot \beta_E) + \frac{1}{\beta_E} \cdot \ln t \quad (7)$$

**Table 1**

Theoretical kinetic models parameter. Units in text.

Lagergren									
Initial dye mmol g <sup>-1</sup>	1.5	1.8	2.2	2.5	2.8	3.1	3.3	3.7	Average <sup>a</sup>
$k_l$	$7.88 \times 10^{-3}$	$9.36 \times 10^{-3}$	$5.20 \times 10^{-3}$	$6.70 \times 10^{-3}$	$6.11 \times 10^{-3}$	$5.44 \times 10^{-3}$	$7.53 \times 10^{-3}$	$5.55 \times 10^{-3}$	$6.70 \times 10^{-3}$
$q_e$	$4.13 \times 10^{-1}$	$1.54 \times 10^{-1}$	1.84	1.63	1.73	1.88	1.56	1.70	
$r^2$	0.98	0.99	0.98	0.99	0.98	0.98	0.98	0.95	0.98
Linear regression $r^2$	0.99	0.99	0.96	0.97	0.96	0.96	0.99	0.93	0.97
Ho									
Initial dye mmol g <sup>-1</sup>	1.5	1.8	2.2	2.5	2.8	3.1	3.3	3.7	
$h$	$3.6 \times 10^{-3}$	$1.69 \times 10^{-2}$	$9.80 \times 10^{-3}$	$1.21 \times 10^{-2}$	$1.15 \times 10^{-2}$	$1.10 \times 10^{-2}$	$1.30 \times 10^{-2}$	$1.01 \times 10^{-2}$	
$q_e$	$5.74 \times 10^{-1}$	2.06	2.80	2.34	2.56	2.83	2.20	2.56	
$k_h$	$1.11 \times 10^4$	$3.95 \times 10^3$	$1.24 \times 10^3$	$2.19 \times 10^3$	$1.74 \times 10^3$	$1.36 \times 10^3$	$2.67 \times 10^3$	$1.53 \times 10^3$	
$r^2$	0.96	0.98	0.97	0.98	0.97	0.97	0.97	0.94	0.97
Linear regression $r^2$	0.93	0.99	0.89	0.97	0.96	0.94	0.98	0.86	0.94
Elovich									
Initial dye mmol g <sup>-1</sup>	1.5	1.8	2.2	2.5	2.8	3.1	3.3	3.7	
$\alpha_E$	$7.32 \times 10^{-3}$	$3.36 \times 10^{-2}$	$2.29 \times 10^{-2}$	$2.64 \times 10^{-2}$	$2.51 \times 10^{-2}$	$2.45 \times 10^{-2}$	$2.66 \times 10^{-2}$	$2.46 \times 10^{-2}$	
$\beta_E$	7.40	2.06	1.82	1.97	1.81	1.78	1.95	2.05	2.60
$r^2$	0.98	0.99	0.97	0.98	0.98	0.97	0.99	0.90	0.97
Linear regression $r^2$	0.97	0.99	0.97	0.98	0.98	0.97	0.99	0.90	0.97

<sup>a</sup> When appropriate.

where  $\alpha_E$  is the initial adsorption rate (mmol g<sup>-1</sup> h<sup>-1</sup>) and  $\beta_E$  is the desorption constant (g mmol<sup>-1</sup>).

The application of these three models have been carried out by a non-linear adjustment and results are presented in Fig. 4. As it can be appreciated, the three of them fit reasonably well to the experimental situations, so regression coefficient  $r^2$  may be considered in order to discriminate the goodness of each data fit. Table 1 refers these data of parameters and  $r^2$ .

The validity of the different models can be checked by each linearized plot, which is possible in the three cases. Linearized expressions of Eqs. (3), (5) and (7), as well as the corresponding linear plot may be found in supplementary data.

According to  $r^2$  values of each model, the three models explain rather well the adsorption process, as  $r^2$  values are over 0.97. With little differences, Lagergren model gives a 0.98 regression coefficient. Due to its simplicity and to the goodness of the linear correlation, not only the non-linear regression, this hypothesis may be assumed as the best theoretical model in this adsorption case. Similar phenomena have been reported in MB adsorption on other natural products [34].

Bearing in mind these kinetic data, further experiments were carried out for the duration of 15 days in total to guarantee the chemical equilibrium was achieved.

### 3.2. pH influence

Previous studies have shown that pH has an important role in the adsorption process [35,36]. Because of this fact, several assays with different pH values have been carried out, varying the pH between 4 and 10, with an IDC of 0.320 mmol L<sup>-1</sup> and with fixed amount of 0.125 mg L<sup>-1</sup> of QTG. Fig. 5 shows the experimental results as a percentage of dye removal versus pH. As it is reported, decreasing pH values leads to a dramatic loss of efficiency.  $q$  values also report the same behaviour.

pH is one of the most important variables controlling the adsorption of MB onto QTG. The removal of dye increased with pH change of solution from 4 to 10. The pH of the solution affects the surface charge of the adsorbent as well as the degree of ionization of the dye. Change of pH affects the adsorptive process through dissociation of functional groups (phenolic, carboxylic, alcoholic, etc.) on the adsorbent surface active sites. This subsequently leads to a shift in kinetics and equilibrium characteristics of adsorption process. As the pH increases, it is usually expected that the cationic dye adsorption also increases due to increasing of the negative surface

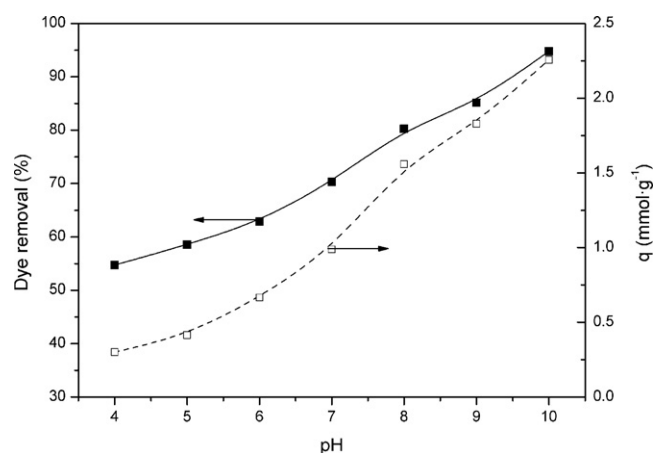
charge of adsorbents. With increasing pH values the adsorption of MB on tannin gel tends to increase, which can be explained by the electrostatic interaction of cationic dye species with the negatively charged adsorbent surface.

Although the loss of effectivity in low values was acute, pH range must be observed to be wide and this parameter can be easily fit into the operating values that are, in every case, more flexible than those reported in other investigations [37], where pH is more influential and changes along the assay.

### 3.3. Temperature influence

Evaluation of temperature was carried out with the scope of testing the ability of QTG in dye removal in the case of different kinds of effluents, bearing in mind the specific circumstances of dyestuff wastes [38,39]. Data were collected at four temperatures: from 10 to 40 °C. A fixed dosage of coagulant and IDC was used, both equal to 100 mg L<sup>-1</sup> (which corresponds approximately to a ratio of 3.1 mmol of dye per g of QTG) and  $q$  capacity was determined at pH level of 7 and according to the standard assay referred in Section 2.3.

As it is reported in Fig. 6, removal efficiency is increased by raising the temperature. Several references are found in this sense, as adsorption processes are enhanced by increasing the mobility of adsorbate molecules [40]. This aspect is also observed in the equilibrium studies (Section 3.4.2).

**Fig. 5.** pH influence.



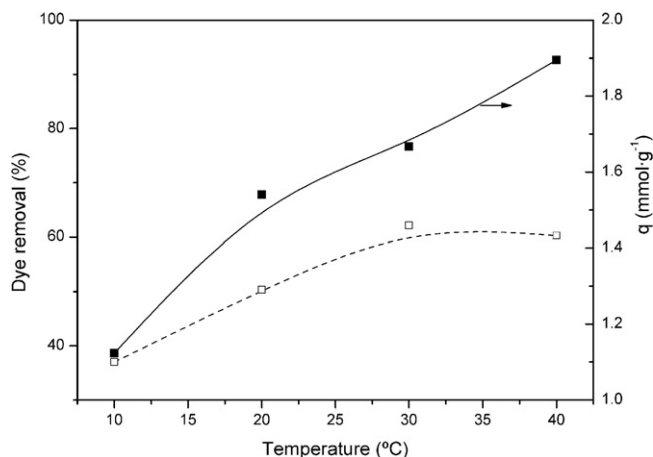


Fig. 6. Temperature influence.

### 3.4. Theoretical adsorption equilibrium modeling

In order to characterize even more the adsorption phenomenon, it is pretended to propose a theoretical model which explains the dye removal by the action of this product.

#### 3.4.1. Langmuir model

Langmuir adsorption model has been considered in the present work. It assumes that the molecules striking the surface have a given probability of adsorbing. Molecules already adsorbed similarly have a given probability of desorbing. At equilibrium, equal numbers of molecules desorb and adsorb at any time. The probabilities are related to the strength of the interaction between the adsorbent surface and the adsorbate [41]. That is the physical meaning of the Eq. (8):

$$q = k_{l1} \frac{C_l}{1 + k_{l2} \cdot C_l} \quad (8)$$

where  $k_{l1}$  is the first Langmuir adsorption constant ( $L[g \text{ of adsorbent}]^{-1}$ ) and  $k_{l2}$  is the second Langmuir adsorption constant ( $L[mmol \text{ of dye}]^{-1}$ ).

The linear form of Langmuir model can be expressed by Eq. (9):

$$\frac{C_l}{q} = \frac{1}{k_{l1}} + \frac{k_{l2}}{k_{l1}} \cdot C_l \quad (9)$$

By combining data series of previous sections it is possible to look for a theoretical model that fits rather well to experimental data.

For each temperature, Eq. (9) has been applied to experimental data. Linear correlations have been achieved, as expressed in Fig. 7. As it is showed, in the studied interval of 283–313 K four linear expressions are found, so Langmuir model fits with an average  $r^2$  of 0.99.

#### 3.4.2. Multiparametric adjustment

By generalizing Langmuir hypothesis, temperature can be included in the modelization by considering Langmuir constants according to Arrhenius expressions. That assumes that  $k_{l1}$  and  $k_{l2}$  may have the following form:

$$k = k_0 \cdot \exp\left(-\frac{E}{R \cdot T}\right) \quad (10)$$

where  $k_0$  is the basic constant, whose units are equal to  $k$ ,  $E$  is the activation energy ( $J \text{ mol}^{-1}$ ),  $R$  is the universal constant for perfect gases,  $8.314 (J \text{ (mol K)}^{-1})$  and  $T$  is the temperature of the adsorption process (K).

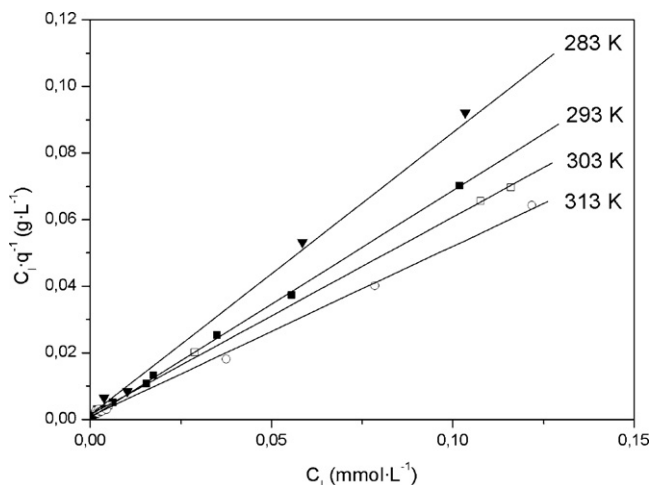


Fig. 7. Linear adjustments of equilibrium studies.

The inclusion of definition (10) into Langmuir expression (Eq. (8)) leads to the expression (11):

$$q = \frac{k_{01} \cdot \exp\left(-\frac{E_1}{R \cdot T}\right) \cdot C_l}{1 + k_{02} \cdot \exp\left(-\frac{E_2}{R \cdot T}\right) \cdot C_l} \quad (11)$$

The adequacy of the multiparametric adjustment is given by a specific  $r^2$ , which is equal to 0.86. It stands near to the average value of  $r^2$  in the case of non-linear individual adjustments for each temperature (0.84). Both non-linear procedures gives a more accurate idea of the goodness of the model, while linear regression checks the adequacy of Langmuir's hypothesis in this adsorption process. In addition, multiparametric adjustment gives us two more data: activation energies. According to the mathematical results, the first of these parameters ( $E_1$ ), which corresponds to adsorption energy (while  $E_2$  corresponds to desorption energy) is equal to  $9973.4 J \text{ mol}^{-1}$ .  $E_2$  is equal to zero, so desorption process is not temperature-depending. In every case, the values of each  $k$  belongs to similar magnitude order, as it can be appreciated according to the adjustment of experimental to predicted data (Fig. 8).

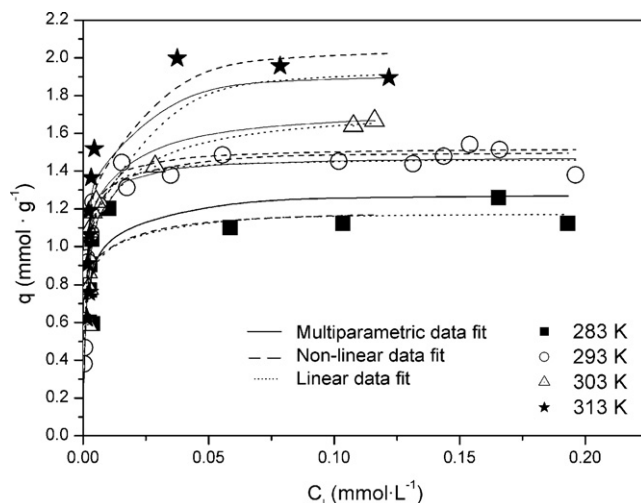


Fig. 8. Data fit of multiparametric, non-linear and linear adjustments of Langmuir equation.

**Table 2**

Comparison of the maximum capacity adsorption of MB onto adsorbents from different sources.

Adsorbent	Origin	$q_{\max}$ (mg g <sup>-1</sup> )	Reference
Activated carbon	Sunflower oil cake	15.8 (25 °C)	[38]
	<i>Salsola vermiculata</i> (desert plant)	130 (24 °C)	[39]
	Commercial (Merck)	140 (20 °C)	[42]
	Bamboo	143 (30 °C)	[36]
	Ground nut shell	165 (30 °C)	[36]
	Coconut shell	278 (30 °C)	[36]
	Rice husk	343 (30 °C)	[36]
	<i>Vetiveria zizanioides</i> (vetiver roots)	423 (25 °C)	[13]
	Coconut husk	435 (30 °C)	[3]
	Straw	472 (30 °C)	[36]
	<i>Passiflora edulis</i> (yellow passion fruit peel)	2.17 (25 °C)	[15]
	Biomass	<i>Azadirachta indica</i> (neem leaf powder)	8.76 (27 °C)
Hazelnut shell		56.9 (30 °C)	[34]
<i>Picea abies</i> (spruce wood)		58.8 (20 °C)	[35]
Tea waste		85.2 (25 °C)	[12]
<i>Schinopsis balansae</i> (Quebracho tannin)		483 (20 °C)	This work

### 3.5. Comparison with other similar materials

QTG seems to be a very interesting agent in the removal of cationic dyes as it is demonstrated above. Several references have been researched in order to analyse how relevant the capability of QTG is in this task. Table 2 lists the comparison of maximum monolayer adsorption capacity of MB using various adsorbents of different origins. The adsorbent prepared in this work from *Quebracho* tannin extract had a very large adsorption capacity of 483 mg g<sup>-1</sup> if compared to some data obtained from the literature. The highest adsorption capacity of QTG could be due to numerous functional groups present in its structure (phenolic, carboxylic, alcoholic, ether, aromatic rings, etc.)

## 4. Conclusions

This investigation has the following conclusions:

- *Quebracho* tannin is a good candidate to be gelificated in a formaldehyde-sodium hydroxide process. QTG so obtained presents a very interesting adsorbent capacity for cationic dye removal.
- Kinetics of this adsorption process may be correlated according to Lagergren, Ho or Elovich hypotheses.  $r^2$  values are over 0.97 in every case.
- Increasing pH raises  $q$ , inside a range of 4–10 pH values, maybe due to the fact higher pH values make the dye appear in a higher cationic degree. pH also affects to surface phenomena so electrostatic interactions are enhanced.
- Temperature enhances the adsorption process, so its increase leads  $q$  to raise, surely due to the increasing of the molecular mobility.
- Langmuir hypothesis is adequate to explain adsorption equilibrium process. Linear and non-linear adjustment gives the values of different parameters, such as activation energies and Langmuir constants.

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## Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jhazmat.2009.09.008.

## Appendix B. Supplementary data

## References

- [1] P. Sikka, Strategies for technology development in India, *Technovation* 11 (7) (1991) 445–452.
- [2] D. Brown, Effects of colorants in the aquatic environment, *Ecotoxicol. Environ. Saf.* 13 (2) (1987) 139–147.
- [3] I.A.W. Tan, A.L. Ahmad, B.H. Hameed, Adsorption of basic dye on high-surface-area activated carbon prepared from coconut husk: equilibrium, kinetic and thermodynamic studies, *J. Hazard. Mater.* 154 (1–3) (2008) 337–346.
- [4] R. Sanghi, B. Bhattacharya, Review on decolorisation of aqueous dye solutions by low cost adsorbents, *Color. Technol.* 118 (5) (2002) 256–269.
- [5] A. Mittal, L. Krishnan, V.K. Gupta, Removal and recovery of malachite green from wastewater using an agricultural waste material, de-oiled soya, *Sep. Purif. Technol.* 43 (2) (2005) 125–133.
- [6] E. Malkoc, Y. Nuhoglu, Potential of tea factory waste for chromium(VI) removal from aqueous solutions: thermodynamic and kinetic studies, *Sep. Purif. Technol.* 54 (3) (2007) 291–298.
- [7] S.K.A. Solmaz, A. Birgül, G.E. Üstün, T. Yonar, Colour and COD removal from textile effluent by coagulation and advanced oxidation processes, *Color. Technol.* 122 (2) (2006) 102–109.
- [8] T. Yonar, G.K. Yonar, K. Kestioglu, N. Azbar, Decolorisation of textile effluent using homogeneous photochemical oxidation processes, *Color. Technol.* 121 (5) (2005) 258–264.
- [9] N. Daneshvar, H. Ashassi-Sorkhabi, A. Tizpar, Decolorization of orange II by electrocoagulation method, *Sep. Purif. Technol.* 31 (2) (2003) 153–162.
- [10] K. Schliephake, D.E. Mainwaring, G.T. Loneragan, I.K. Jones, W.L. Baker, Transformation and degradation of the disazo dye Chicago Sky Blue by a purified laccase from *Pycnoporus cinnabarinus*, *Enzyme Microb. Technol.* 27 (1–2) (2000) 100–107.
- [11] S. Papic, N. Koprivanac, A.L. Bozic, Removal of reactive dyes from wastewater using Fe(III) coagulant, *Color. Technol.* 116 (11) (2000) 352–358.
- [12] M.T. Uddin, M.A. Islam, S. Mahmud, M. Rukanuzzaman, Adsorptive removal of methylene blue by tea waste, *J. Hazard. Mater.* 164 (1) (2009) 53–60.
- [13] S. Altenor, B. Carene, E. Emmanuel, J. Lambert, J.J. Ehrhardt, S. Gaspard, Adsorption studies of methylene blue and phenol onto vetiver roots activated carbon prepared by chemical activation, *J. Hazard. Mater.* 165 (1–3) (2009) 1029–1039.
- [14] A. Demirbas, Heavy metal adsorption onto agro-based waste materials: a review, *J. Hazard. Mater.* 157 (2–3) (2008) 220–229.
- [15] F.A. Pavan, A.C. Mazzocato, Y. Gushikem, Removal of methylene blue dye from aqueous solutions by adsorption using yellow passion fruit peel as adsorbent, *Bioresour. Technol.* 99 (8) (2008) 3162–3165.
- [16] P. Schofield, D.M. Mbugua, A.N. Pell, Analysis of condensed tannins: a review, *Anim. Feed Sci. Technol.* 91 (1) (2001) 21–40.
- [17] Y. Satoshi, N. Fumiaki, Effects of the hydroxylation patterns and degrees of polymerization of condensed tannins on their metal-chelating capacity, *J. Wood Chem. Technol.* 18 (2) (2008) 193–205.
- [18] X.-M. Zhan, X. Zhao, Mechanism of lead adsorption from aqueous solutions using an adsorbent synthesized from natural condensed tannin, *Water Res.* 37 (16) (2003) 3905–3912.
- [19] Y. Nakano, K. Takeshita, T. Tsutsumi, Adsorption mechanism of hexavalent chromium by redox within condensed-tannin gel, *Water Res.* 35 (2) (2001) 496–500.
- [20] Y.-H. Kim, Y. Nakano, Adsorption mechanism of palladium by redox within condensed-tannin gel, *Water Res.* 39 (7) (2005) 1324–1330.
- [21] G. Tondi, C.W. Oo, A. Pizzi, M.F. Thevenon, Metal absorption of tannin-based rigid foams, *Ind. Crop. Prod.* 29 (2/3) (2004) 336–340.
- [22] G. Palma, J. Freer, J. Baeza, Removal of metal ions by modified *Pinus radiata* bark and tannins from water solutions, *Water Res.* 37 (20) (2003) 4974–4980.
- [23] I.A. Sengil, M. Özacar, Competitive biosorption of Pb<sup>2+</sup>, Cu<sup>2+</sup> and Zn<sup>2+</sup> ions from aqueous solutions onto valonia tannin resin, *J. Hazard. Mater.* 166 (2–3) (2009) 1488–1494.
- [24] G. Vázquez, G. Antorrena, J. González, M.D. Doval, Adsorption of heavy metal ions by chemically modified *Pinus pinaster* bark, *Bioresour. Technol.* 48 (3) (1994) 251–255.
- [25] G. Vázquez, J. González-Álvarez, S. Freire, M. López-Lorenzo, G. Antorrena, Removal of cadmium and mercury ions from aqueous solution by sorption on treated *Pinus pinaster* bark: kinetics and isotherms, *Bioresour. Technol.* 82 (3) (2002) 247–251.
- [26] A. Pizzi, Tannins: major sources, properties and applications, in: A. Gandini, M.N. Balgacem (Eds.), *Monomers, Polymers and Composites from Renewable Sources*, Elsevier, Amsterdam, 2005.

- [27] W. Streit, D. Fengel, Purified tannins from quebracho colorado, *Phytochemistry* 36 (2) (1994) 481–484.
- [28] N. Vivas, M.F. Nonier, N. Vivas de Gaulejac, C. Absalon, A. Bertrand, M. Mirabel, Differentiation of proanthocyanidin tannins from seeds, skins and stem of grapes (*Vitis vinifera*) and heartwood of quebracho (*Schinopsis balansae*) by matrix-assisted laser desorption/ionization time-of-flight mass spectrometry and thiadidolysis/liquid chromatography/electrospray ionization mass spectrometry, *Anal. Chim. Acta* 513 (1) (2004) 247–256.
- [29] H. Pasch, A. Pizzi, K. Rode, MALDI-TOF mass spectrometry of polyflavonoid tannins, *Polymer* 42 (18) (2001) 7531–7539.
- [30] M. Yurtsever, I.A. Sengil, Biosorption of Pb(II) ions by modified quebracho tannin resin, *J. Hazard. Mater.* 163 (1) (2009) 58–64.
- [31] S. Lagergren, Zur theorie der sogenannten adsorption gelöster stoffe, *Kungliga Svenska Vetenskapsakademiens Handlingar*. Band. 24 (4) (1898) 1–39.
- [32] Y.S. Ho, G. McKay, The kinetics of sorption of basic dyes from aqueous solutions by sphagnum moss peat, *Can. J. Chem. Eng.* 76 (4) (1998) 822–827.
- [33] M.K. Aroua, S.P.P. Leong, L.Y. Teo, C.Y. Yin, W.M.A.W. Daud, Real-time determination of adsorption of lead (II) onto palm shell-based activated carbon using ion selective electrode, *Bioresour. Technol.* 99 (13) (2008) 5786–5792.
- [34] M. Dogan, H. Abak, M. Alkan, Adsorption of methylene blue onto hazelnut shell: kinetics, mechanisms and activation parameters, *J. Hazard. Mater.* 164 (1) (2009) 172–181.
- [35] P. Janos, S. Coskun, V. Pilarova, J. Rejnek, Removal of basic (methylene blue) and acid (egacid orange) dyes from waters by sorption on chemically treated wood shavings, *Bioresour. Technol.* 100 (3) (2009) 1450–1453.
- [36] N. Kannan, M.M. Sundaram, Kinetics and mechanism of removal of methylene blue by adsorption on various carbons—a comparative study, *Dyes Pigments* 51 (1) (2001) 25–40.
- [37] T.-H. Kim, C. Park, E.-B. Shin, S. Kim, Decolorization of disperse and reactive dye solutions using ferric chloride, *Desalination* 161 (1) (2004) 49–58.
- [38] S. Karagöz, T. Tay, S. Ucar, M. Erdem, Activated carbons from waste biomass by sulfuric acid activation and their use on methylene blue adsorption, *Bioresour. Technol.* 99 (14) (2008) 6214–6222.
- [39] B. Bestani, N. Benderdouche, B. Benstaali, M. Belhakem, A. Addou, Methylene blue and iodine adsorption onto an activated desert plant, *Bioresour. Technol.* 99 (17) (2008) 8441–8444.
- [40] K.G. Bhattacharyya, A. Sharma, Kinetics and thermodynamics of methylene blue adsorption on neem (*Azadirachta indica*) leaf powder, *Dyes Pigments* 65 (1) (2005) 51–59.
- [41] I. Langmuir, The constitution and fundamental properties of solids and liquids. Part I. Solids, *J. Am. Chem. Soc.* 38 (1916) 2221–2295.
- [42] S. Karaca, A. Gürses, M. Açıkyıldız, M. Ejder, Adsorption of cationic dye from aqueous solutions by activated carbon, *Micropor. Mesopor. Mater.* 115 (3) (2008) 376–382.