Desalination and Water Treatment
www.deswater.com
doi: 10.1080/19443994.2014.928235

55 (2015) 1956–1965
August

The use of a forest waste biomass, cone of *Pinus brutia* for the removal of an anionic azo dye Congo red from aqueous medium

Abdallah Bouguettoucha[a,*], Derradji Chebli[a], Tahar Mekhalef[b], Amine Noui[a], Abdeltif Amrane[c,d]

[a]*Faculté de Technologie, Département de Génie des Procédés, Université SETIF-1, Elbez, Sétif 19000, Algeria, Tel./Fax: +213 36 92 51 21; emails: abd_bouguettoucha@yahoo.fr (A. Bouguettoucha), derradji_chebli@yahoo.fr (D. Chebli), noui_hicheme@live.fr (A. Noui)*
[b]*Département de Chimie, Université de Skikda, Skikda, Algeria, Tel. +213 6 67 56 34 01; email: smekhalif@yahoo.fr*
[c]*Ecole Nationale Supérieure de Chimie de Rennes, Université de Rennes 1, CNRS, UMR 6226, Avenue du Général Leclerc, CS 50837, 35708 Rennes Cedex 7, France, Tel. +33 0 2 23 23 81 55; email: abdeltif.amrane@univ-rennes1.fr*
[d]*Université européenne de Bretagne, Bd Laënnec, Rennes 35000, France*

Received 25 October 2013; Accepted 22 May 2014

ABSTRACT

Cone biomass of *Pinus brutia*, a novel low-cost adsorbent prepared from forest waste has been utilized as an adsorbent for the removal of Congo red (CR) dye from an aqueous solution. The adsorbate concentration, pH, time, and temperature were examined in batch tests. Maximum biosorption capacity was 102.8 mg/g, showing that cone biomass of *P. brutia* was more efficient than most of the other adsorbents. Experimental data were analyzed by Langmuir, Freundlich, and Sips adsorption isotherms models and showed that the adsorption process followed a Sips model. Pseudo-first-order, pseudo-second-order, and intraparticle diffusion models were used to fit experimental data, showing that the adsorption of CR could be described by a pseudo-second-order equation and that intraparticle diffusion was not the only rate-limiting mechanism for the biosorption of CR. Thermodynamic parameters such as ΔG^o, ΔH^o, and ΔS^o were also evaluated and it was found that the sorption process was feasible, spontaneous, and endothermic in nature. These results indicated that cone biomass of *P. brutia* is promising as a low-cost alternative compared to other commercial adsorbents for the removal of dyes from wastewater.

Keywords: Biosorption; Azo dye; Wastewater treatment; Isotherm models; Kinetics; Thermodynamic parameters

1. Introduction

Textile industries rank first in the usage of dyes when compared to other industries like food, paper, cosmetics, and carpet industries. Effluents of these industries may therefore contain undesired quantities of these pollutants and need to be treated. It is reported that there are around 100,000 commercially available dyes with a production of over 7×10^5 metric tons per year. Dyeing industry effluents constitute one of the most problematic wastewaters to be treated, not only for their high chemical and biological oxygen demands, suspended solids, and content in toxic

---

*Corresponding author.

compounds but also for color, causing an esthetic pollution, since a very small amount of dye in water is highly visible [1]. Dyes may significantly affect photosynthetic activity in aquatic life. The presence of coloring material in water system also reduces light penetration and photosynthetic activity due to their content in aromatics, metals, chlorides, etc. Therefore, the treatment of aquatic systems contaminated with dyes and improvement of water quality are important topics in the field of environmental technologies [1–3].

Many physical, chemical, and biological methods have been developed to remove dyes, such as coagulation/flocculation, electroflocculation, advanced oxidation, ozonation, membrane filtration, liquid–liquid extraction, electrochemical destruction, ion-exchange, and irradiation [4–7]. However, all these processes have their own limitations; they can appear expensive and not adaptable to a wide range of dye wastewaters [8]. Adsorption is a very effective separation technique and now it is considered to be more efficient than other techniques for water treatment in terms of investment cost, simplicity of design, ease of operation, and insensitiveness to toxic substances [5,6,9,10]. In this process, the dye species are transferred from the water effluent to a solid phase, leading to decreasing polluted water volume [11]. A commonly used adsorbent, activated carbon, has a high capacity for the removal of dyes/organics [12,13]; but some of its disadvantages are its high price and the difficulty to be regenerated inducing an increase of the wastewater treatment cost.

There is therefore an increasing demand for other adsorbents, especially made up of inexpensive material and locally available to allow adsorption processes to become economically viable. Biosorption has emerged as an alternative eco-friendly technology to dye removal from aqueous solutions. This technology has several advantages, such as simplicity of design, ease of operation, insensitivity to toxic substances, and complete removal of pollutants [1,6,14]. Biosorption refers to the ability of certain biomaterials to bind and concentrate toxic pollutants from even the most dilute aqueous solutions [1]. In the case of dyes removal, many biosorbents have been reported in the literature, such as chitosan [15], fungi [16,17], algae [14,18], bacteria [19–21], and *Stipa tonacissima* fibers [22].

CR is a water-soluble azo dye, which is widely used in the textile, paper manufacturing, printing, pharmaceutical, and food industries, as well as in research laboratories. It is an anionic dye which is known to cause an allergic reaction and can be metabolized to benzidine, a human carcinogen [23,24]. Therefore, an increasing interest has been focused on the removing of such dye from wastewater. There are several natural adsorbents including clay minerals that have been used for the removal of anionic dyes including CR from aqueous solutions; they have been recently reviewed by Abd El-Latif et al. [6] and Salleh et al. [25].

Cone biomass of *Pinus brutia* is a waste and almost readily available biosorbent. The mature cones are sessile or shortly stalkless, not reflected to the base of the branch, perpendicular or upright on the twig, dark brown in color. Their shape is conical or oval, 5 × 11 × 4, 5 cm dimensions. For more details see the paper of Nahal [26].

There are only few studies dealing with such biosorbent; *Pinus sylvestris* have been used to remove chromium (VI) [27] and reactive red dye [28] from aqueous solutions. The removal of copper (II) from aqueous solutions by pine cone powder as biosorbent has also been reported by Ofomaja et al. [29]. Pine cone has also been used as efficient adsorbent in the removal of textile dye [30] and phosphate ions [31]. *Pinus* species has also been used for the removal of phenol [32].

In this study, local and widely available cone biomass, *P. brutia*, was therefore tested as an adsorbent for the removal of dye from aqueous solutions; and an anionic dye, CR, was selected for this purpose since cone biomass, *Pinus radiata*, was previously promisingly tested for its removal [2]. The management of this important waste as a biosorbent was optimized. Improving the knowledge regarding the interactions of CR with Cone biomass of *P. brutia* and to examine the adsorption mechanism of CR on this adsorbent was also the purpose of this paper.

2. Materials and methods

2.1. Preparation of the biosorbent

Cones biomass of *P. brutia* was used in this investigation. Cones were collected from forest (Ain Oulmene, North-East of Algeria). They were washed with distilled water to remove the surface-adhered particle and were dried at 80˚C for 24 h to a constant weight; ground in a mortar to a very fine powder and stored in a desiccator for further use.

2.2. Dye preparation and determination

CR, a typical anionic dye (Fig. 1), was selected as an adsorbent. CR dye is a sodium salt, 3,3´-([1, 10-biphenyl]-4,40-diyl) bis(4-aminonaphthalene-1-sulfonic acid), namely with the following formula, $C_{32}H_{22}N_6Na_2O_6S_2$. CR has a molecular weight of 696.66 g/mol and was obtained from Sigma Aldrich with 99.99% purity. A

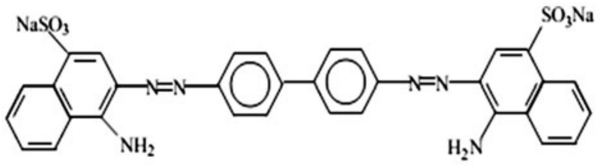

Fig. 1. Molecular structure of CR.

stock solution of 50 mg/l was prepared by dissolving an appropriate amount (50 mg) of CR in a liter of distilled water. The working solutions were prepared by dilution of the stock solution with distilled water to yield the appropriate concentrations. The pH of the solutions was adjusted by addition of either 0.1 M HCl or 0.1 M NaOH solutions, respectively. Before use, all bottles and glassware were beforehand cleaned and then rinsed with distilled water and oven-dried at 60 ˚C. A SP-8001 UV/VIS Spectrophotometer of Axiom (Germany, Shimadzu) was used to determine the residual dye concentrations in solution. After withdrawing samples at fixed time intervals and centrifugation, the supernatant was analyzed for residual CR at $\lambda_{\max}$ corresponding to the maximum adsorption for the dye solution ($\lambda_{\max} = 496$ nm). Calibration curve was plotted between absorbance and concentration of the dye solution to obtain the absorbance concentration profile.

2.3. Biosorption studies

2.3.1. Kinetic experiments

Batch experiments were performed in a series of 250 ml conical flasks containing a given amount of adsorbent in 50 ml of dye solution of a known concentration.

The amount of dye adsorbed onto cone biomass of *P. brutia* at time t, Q_t (mg/g), was calculated by means of the following mass balance relationship:

$$Q_t = \frac{(C_0 - C_t)V}{m} \tag{1}$$

and dye removal efficiency i.e. % of adsorption was calculated according to:

$$\%\text{adsorption} = \frac{(C_0 - C_t)}{C_0} \times 100 \tag{2}$$

where C_0 is the initial dye concentration (mg/l), C_t is the concentration of dye at any time t, V is the volume of solution, and m is the mass of cone biomass of *P. brutia*.

2.3.2. Equilibrium modeling

Equilibrium data, commonly known as adsorption isotherms, describe how adsorbates interact with adsorbents and hence, are critical in optimizing the use of adsorbents and provide information on the type and capacity of the adsorbent. To analyze cone biomass interaction with CR, experimental data points were fitted to the Langmuir [33], Freundlich [34], and Sips [35] empirical models, which are the most frequently used two- and three-parameter equations in the literature to describe the non-linear equilibrium between adsorbed pollutant onto the cells (Q_e) and pollutant in solution (C_e) at a constant temperature.

The Langmuir isotherm model assumes uniform adsorption energy onto the adsorbent surface. Furthermore, the Langmuir equation is based on the assumption of the existence of monolayer coverage of the adsorbate at the outer surface of the adsorbent where all sorption sites are identical. The Langmuir equation [33] is given as follows:

$$\frac{Q_e}{Q_m} = \frac{K_L C_e}{1 + K_L C_e} \tag{3}$$

where Q_e is the equilibrium dye concentration on the adsorbent (mg/g); C_e, the equilibrium dye concentration in solution (mg/l); Q_m, the monolayer capacity of the adsorbent (mg/g); and K_L is the Langmuir constant. A non-linear fit was performed by means of the Origin Software in order to obtain the Langmuir model parameters. The parameter statistic "adjusted R-square" was also determined to identify the most accurate model to describe experimental results.

The Freundlich isotherm model assumes neither homogeneous site energies nor limited levels of sorption. The Freundlich model is the earliest known empirical equation and is shown to be consistent with exponential distribution of active centers, characteristic of heterogeneous surfaces [34]:

$$Q_e = K_F C_e^{1/n} \tag{4}$$

where Q_e is the equilibrium dye concentration on the adsorbent (mg/g); C_e, the equilibrium dye concentration in solution (mg/l); K_F and $1/n$ are empirical constants indicative of sorption capacity and sorption intensity, respectively. The Freundlich parameters were obtained by performing a non-linear fit (Origin software).

The Sips isotherm is a combination of the Langmuir and Freundlich isotherms [34]:

$$\frac{Q_e}{Q_m} = \frac{(ksC_e)^m}{1 + (ksC_e)^m} \tag{5}$$

where Q_m is the maximum monolayer biosorption (mg/g), ks is the Sips constant solution (L/mg), and m the exponent of the Sips model.

2.4. Kinetic modeling

The study of adsorption dynamics described the solute adsorption rate. This rate controlled the residence time of adsorption at the solid–solution interface. Several kinetic models such as pseudo-first-order, pseudo-second-order, and intraparticle diffusion models can be applied to fit experimental data.

2.4.1. Pseudo-first-order equation

The pseudo-first-order kinetic model is the first equation for the adsorption of solid/liquid system based on the adsorption capacity. The linear form of the pseudo-first-order equation is given by Eq. (6):

$$\ln (Q_e - Q_t) = \ln Q_e - k_1 t \tag{6}$$

where Q_e (mg/g) and Q_t (mg/g) refer to the amount of dye adsorbed at equilibrium and at time t (min), respectively, k_1 (1/min) is the equilibrium rate constant of pseudo-first-order equation. The rate constants are obtained from the straight line plots of ln (Q_e–Q_t) against t.

2.4.2. Pseudo-second-order equation

The pseudo-second-order model is based on the assumption of chemisorption of the adsorbate on the adsorbent [36]. This model is given by Eq. (7):

$$\frac{t}{Q_t} = \frac{1}{k_2 Q_e^2} + \frac{1}{Q_e} t \tag{7}$$

where k_2 (g/(mg min)) is the equilibrium rate constant of the pseudo-second-order equation. The straight line plot of t/Q_t against t was considered to obtain rate parameters.

2.4.3. Intraparticle diffusion model

Intraparticle diffusion model is commonly used to identify the adsorption mechanism for design purpose. According to Weber and Morris [37], for most adsorption processes, the uptake varies almost proportionately with $t^{½}$ rather than with the contact time and can be represented as follows:

$$Q_t = K_{id} t^{0.5} + C \tag{8}$$

where Q_t is the amount adsorbed at time t and $t^{0.5}$ is the square root of the time, C is the intercept, and K_{id} (mg/g min$^{0.5}$) is the rate constant of intraparticle diffusion.

2.5. Scanning electron microscopy

Scanning electron microscopy of *P. brutia* before adsorption was visualized by using Hitachi S-3000N scanning electron microscope (SEM) at 7 kV, and 100, 1,000, and 5,000 magnification.

3. Results and discussion

3.1. Influence of the pH

Fig. 2 shows the effect of pH on the adsorption of CR onto cone biomass of *P. brutia*. As shown and irrespective of the initial CR concentration (in the range 50–300 mg/l) and pH in the range 3–11, equilibrium sorption capacity was maximum at pH 4 and decreased sharply for increasing pH before remaining nearly constant in the range 7–11; experiments were not performed at more acidic pH owing to dye precipitation. The surface of cone biomass of *P. brutia* contains cellulose, hemicelluloses, and lignin, and hence contain polar functional groups in their cell walls such as alcohols, aldehydes, ketones, carboxylic, phenolic,

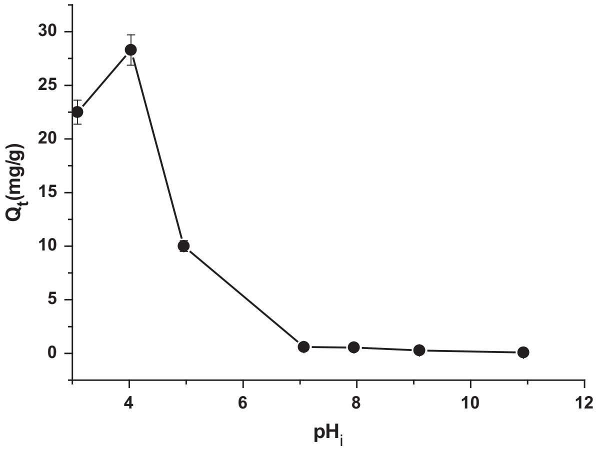

Fig. 2. Effect of pH on the biosorption capacity of CR onto cone biomass of *P. brutia* at various dye concentrations.

and other groups [9,29]. This results in a strong protonation at acidic pH, which induces an overall positive charge of the cell wall biopolymers, leading to a high attraction of an anionic dye like CR and hence, accounting for the high efficiency found at pH 4.

3.2. Effect of the temperature on dye adsorption

In order to understand the effect of temperature on the removal of CR by cone biomass of *P. brutia*, experiments were carried out at 295, 313, and 333 K, and pH 4.0. As shown in Fig. 3, the removal efficiency slightly increased with a rise in temperature from 295 to 333 K, indicating that a high temperature favored dye removal. The enhancement of the adsorption could be also due to a decrease of the thickness of the boundary layer surrounding the sorbent with the rise in temperature *t*, so that the mass transfer resistance of the adsorbate in the boundary layer decreases [38]. This may also be a result of an increase in the mobility of the dye molecule with an increase in their kinetic energy, as well as an enhanced rate of intraparticle diffusion of sorbate with the rise in temperature. It is clear that the sorption of CR on the sorbent is an endothermic process, in agreement with other findings dealing with CR removal by low-cost materials [22,24,25,39,40].

3.3. Effect of the contact time

Contact time is among the main parameters to be examined for successful implementation of biosorbents for practical application [2]. The effect of the contact time on the biosorption of CRonto cone biomass of *P. brutia* is presented in Fig. 4. CR showed a fast rate of biosorption during the first 50 min and equilibrium was achieved within 120 min. Beyond equilibrium time, the amount of biosorbed dye did not show significant change. It is therefore clear that dye removal was dependent on its initial concentration.

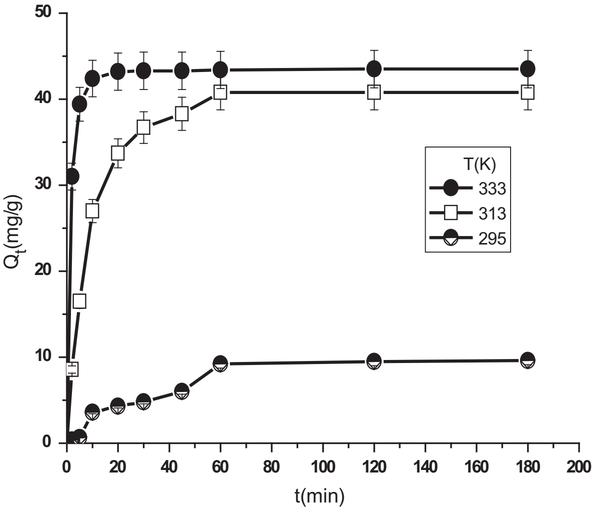

Fig. 3. Effect of the temperature on the removal of CR by cone biomass of *P. brutia* (pH 4).

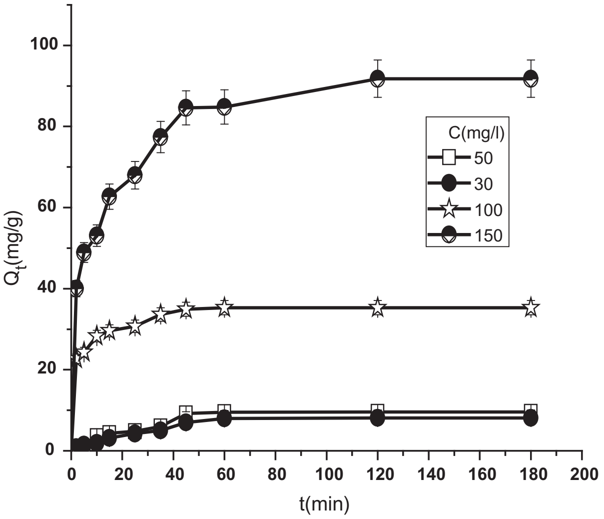

Fig. 4. Effect of contact time on the biosorption capacity of CR onto cone biomass of *P. brutia* at various concentrations ($T = 22 \pm 2$°C, pH 4).

3.4. Isotherm analysis

Within any given system, an accurate mathematical description of equilibrium adsorption capacity is essential for reliable prediction of adsorption parameters and quantitative comparison of adsorption behavior for different adsorbent systems (or for varied experimental conditions). In order to optimize the design of an adsorption system, it is important to establish the most appropriate correlation describing the equilibrium curve. Several equilibrium adsorption isotherm models are available, and the most common ones are the mono-layer adsorption developed by Langmuir [33], the multi-layer adsorption of Freundlich [34], and the Sips isotherm [35]. Experimental data of CR on the cone biomass of *P. brutia* were fitted to the isotherm models using Origin software and the graphical representations of these models are presented in Fig. 5. All of the constants, as well as the R^2 values resulting from the non-linear fitting of experimental data, are collected in Table 1.

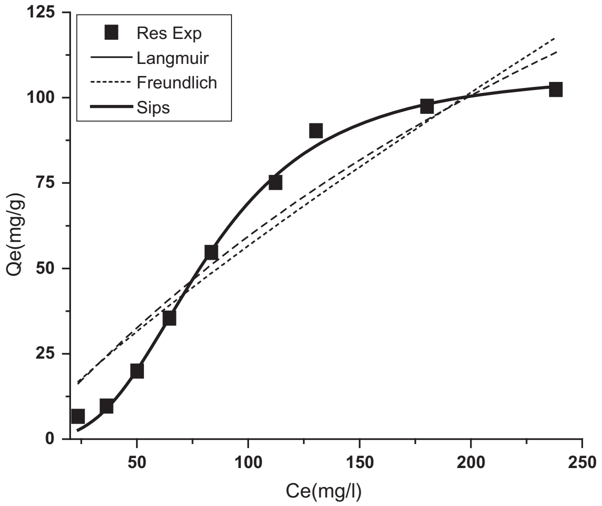

Fig. 5. Experimental (symbols) and calculated isotherm data (lines) for CR adsorption onto cone biomass of *P. brutia* at various concentrations ($T = 22 \pm 2$°C, pH 4), Langmuir; Freundlich; and Sips models.

Table 1
Langmuir, Freundlich, and Sips constants for the biosorption of CR onto cone biomass of *P. brutia* ($T = 22 \pm 2$°C, pH 4)

Langmuir	Q_m (mg/g)	329.6
	K_L (L/mg) × 10^3	2.2
	R^2	*0.91*
Freundlich	n_F	1.2
	$1/n_F$	0.83
	K_F (mg/g) $(\mathrm{L/mg})^{1/n}$	1.17
	R^2	*0.89*
Sips	Q_m (mg/g)	107.65
	K_{LF} (L/mg)	0.012
	m_{LF}	2.96
	R^2	*0.996*

Table 2
Comparison of maximum adsorption (Q_m) of CR onto various adsorbents

Adsorbents	Q_m (mg/g)	Refs.
Cashew nut shell	5.18	[41]
Activated carbon (LR)	1.88	[42]
Coir pith	6.70	[43]
Kolin	5.44	[44]
S. tonacissima fiber	3.7–5.35	[22]
Cone pine	40.19	[2]
Tamarind fruit shell	10.48	[45]
NaBentonite	35.84	[8]
Chitosan hydrobeads	92.59	[46]
Cone biomass of *P. brutia*	*102.80*	This work
Activated carbon	52–189	[47]

The Sips model appeared to be the most accurate to represent experimental equilibrium data. The maximum biosorption capacity (Q_m) obtained from the Sips model was 107.65 mg/g, namely close to that found experimentally. The comparison of maximum adsorption capacity of some dyes onto various adsorbents is displayed in Table 2, showing that cone biomass of *P. brutia* was more efficient than most of the other adsorbents; its maximum adsorption capacity appeared in the range of values given for the most used class of adsorbents, activated carbon.

3.5. Biosorption kinetics

The prediction of batch adsorption kinetics is necessary for the design of industrial adsorption columns. The nature of the adsorption process depends on physical and chemical characteristics of the adsorbent and on the system conditions. In the present study, the applicability of the pseudo-first-order [48], the pseudo-second-order [36], and the intraparticle diffusion [37] models have been tested for CR adsorption onto cone biomass of *P. brutia*. Biosorption kinetics appeared to be accurately fitted by pseudo-second-order and intraparticle diffusion models (Table 3), while pseudo-first-order (results not shown) did not results in an accurate description of experimental data, since it yield to correlation coefficients (R^2) below 0.95 (Table 3).

In addition to the high R^2 values (>0.99 for all the tested conditions), the Q_e values estimated from the pseudo-second-order kinetic model were also in agreement with experimental data (Table 3) for all tested dye concentrations (Fig. 6). The results suggested that boundary layer resistance was not the rate-limiting step since dye biosorption followed pseudo-second-order kinetics [49].

The effect of intraparticle diffusion resistance on adsorption was evaluated by intraparticle diffusion model to identify the adsorption mechanism [50] as expressed in Eq. (8). A plot of q against $t^{0.5}$ should give a linear line whose slope is K_{id} (Fig. 7), whose values are listed in Table 3. The plot of Q_t vs. $t^{0.5}$ was linear within a certain extent but not linear over the whole time range; it can be separated into two or more linear regions. The first straight portion could be attributed to macropore diffusion (Step 1), namely the transport of dye molecules from the bulk solution to the surface of the adsorbent, and the second linear portion could be attributed to micropore diffusion (Step 2), namely the binding of the dye molecules on the active sites of biosorption. From the above results, it is clear that intraparticle diffusion was not the only

Table 3
Kinetics parameters for CR biosorption onto cone biomass of *P. brutia* at different concentrations ($T = 22 \pm 2$°C, pH 4)

Kinetic models	Parameters	30 (mg/g)	50 (mg/g)	100 (mg/g)	150 (mg/g)
	Q_{exp} (mg/g)	8.1	9.6	35.3	91.8
Pseudo-first-order	$Qe_{1\ cal}$ (mg/g)	7.38	9.81	14.60	57.43
	k_1 (1/min)	0.038	0.031	0.063	0.053
	R_1^2	*0.94*	*0.952*	*0.954*	*0.950*
Pseudo-second-order	$Qe_{2\ cal}$ (mg/g)	9.67	11.03	35.85	95.4
	$K_2 \times 10^3$ (g/mg min)	3.79	4.29	13.1	1.57
	R_2^2	*0.997*	*0.983*	*0.999*	*0.998*
Intraparticle diffusion					
Step 1	K_{id} (mg/g min$^{0.5}$)	1.09	2.02	2.29	8.18
	C (mg/g)	1.11	1.53	19.89	29.03
	R_{id}^2	*0.953*	*0.914*	*0.967*	*0.988*
Step 2	$K_{id} \times 10^3$ (mg/g min$^{0.5}$)	2.3	3.2	6.7	2.1
	C (mg/g)	7.87	9.37	35.3	75.75
	R_{id}^2	*0.999*	*0.999*	*0.999*	*0.999*

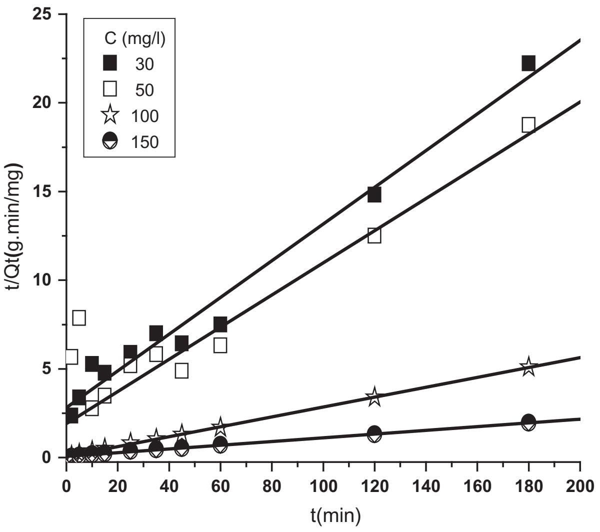

Fig. 6. Experimental (symbols) and calculated data (continuous lines) by means of pseudo-second-order kinetic model for CR biosorption onto cone biomass of *P. brutia* at various concentrations ($T = 22 \pm 2$°C, pH 4).

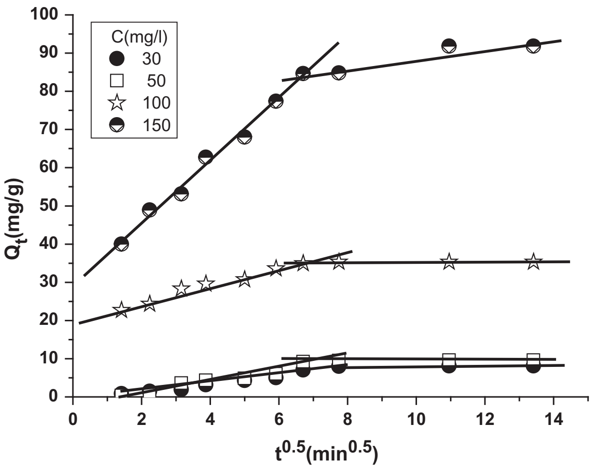

Fig. 7. Experimental (symbols) and calculated data (continuous lines) by means intraparticle diffusion model for CR biosorption cone biomass of *P. brutia* at various concentrations ($T = 22 \pm 2$°C, pH 4).

rate-limiting mechanism for the biosorption of CR onto cone biomass of *P. brutia*. Similar trend has been reported for the biosorption of CR and rhodamine B onto jute stick power [51] and CR onto *S. tonacissima* powder [22].

3.6. SEM micrographs

It can be observed from the SEM image in Fig. 8 that the surface of the *P. brutia* biomass was heterogeneous, smooth, and porous. It is clear from this figure that *P. brutia* biomass has a large surface area for dye interaction and a great capacity for dye holding.

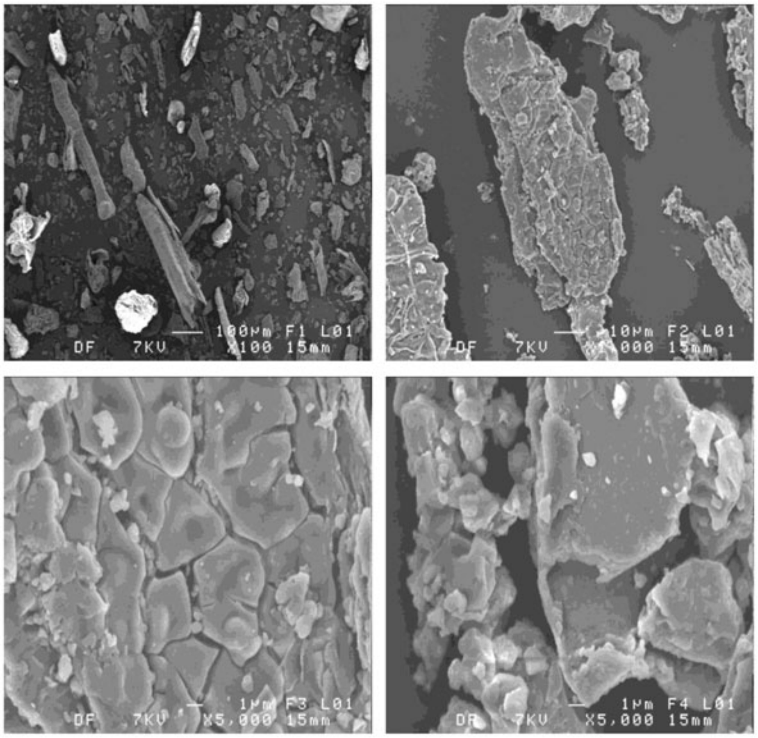

Fig. 8. Image of *P. brutia* biomass.

3.7. Thermodynamic analysis

The thermodynamic parameters reflect the feasibility and the spontaneous nature of a biosorption process. Parameters such as the free energy change (ΔG), the enthalpy change (ΔH), and the entropy change (ΔS) can be estimated using equilibrium constants varying with temperature. The free energy change of the adsorption reaction is given using Eq. (9) as reported by Milonjic [52]:

$$\Delta G^\circ = -RT \ln(\rho Kc) \tag{9}$$

where ΔG° is the free energy change (kJ mol^{-1}), R the universal gas constant (8.314 J mol^{-1} K^{-1}), T the absolute temperature (K), K_C is the thermodynamic equilibrium constant (L/g), and ρ is the water density (g/L). ΔH° and ΔS° values of the biosorption process were also calculated from the Van't Hoff Eq. (10):

$$\ln(\rho K_C) = -\frac{\Delta H}{RT} + \frac{\Delta S}{R} \tag{10}$$

ΔH and ΔS can be then deduced from the slope (ΔH/R) and the intercept (ΔS/R) of the plot of lnK_C vs. $1/T$. The calculated thermodynamic parameters are given in Table 4.

Table 4
Thermodynamic parameters for the adsorption of CR on cone biomass of *P. brutia*

Temperature (K)	ΔH^o (kJ/mol)	ΔS^o (J/mol K)	ΔG^o (kJ/mol)
293	44.61	281.0	−37.73
313			−43.35
333			−48.96

The negative values of ΔG° irrespective of the considered temperature illustrated the spontaneous nature of biosorption; the positive value of ΔH suggested its endothermic nature and the positive value of ΔS suggested an increasing randomness at the solid–solution interface during biosorption.

4. Conclusion

From the above results, adsorption dynamic analysis indicates that pseudo-second-order equation fitted accurately the adsorption of CR onto cone biomass of *P. brutia* ($R^2 > 0.99$). Intraparticle diffusion was not the only rate-limiting mechanism for the biosorption of CR onto cone biomass of *P. brutia*. The adsorption process was accurately described by the Sips model ($R^2 > 0.98$), leading to a value of the maximum adsorption capacity of CR onto cone biomass of *P. brutia* close to the experimental one, 102.80 mg/g at room temperature. Thermodynamic analysis revealed that the removal of CR was a spontaneous and endothermic process. In the light of these results it can be concluded that cone biomass of *P. brutia* is a promising low-cost adsorbent for dye removal from industrial wastewater.

References

[1] Z. Aksu, Application of biosorption for the removal of organic pollutants: A review, Process Biochem. 40 (2005) 997–1026.

[2] S. Dawood, T.K. Sen, Removal of anionic dye Congo red from aqueous solution by raw pine and acid-treated pine cone powder as adsorbent: Equilibrium, thermodynamic, kinetics, mechanism and process design, Water Res. 46 (2012) 1933–1946.

[3] F. Denizand, S.D. Saygideger, Equilibrium, kinetic and thermodynamic studies of Acid Orange 52 dye biosorption by *Paulownia tomentosa Steud*. leaf powder as a low-cost natural biosorbent, Bioresour. Technol. 101 (2010) 5137–5143.

[4] M. Ghaedi, A. Hassanzadeh, S. Kokhdan, Multiwalled carbon nanotubes as adsorbents for the kinetic and equilibrium study of the removal of alizarin red S and morin, J. Chem. Eng. Data 56 (2011) 2511–2520.

[5] Z. Yao, L. Wang, J. Qi, Biosorption of methylene blue from aqueous solution using a bioenergy forest waste: *Xanthoceras sorbifolia* seed coat, Clean 37 (2009) 642–648.

[6] M.M. Abd El-Latif, A.M. Ibrahim, M.F. El-Kady, Adsorption equilibrium, kinetics and thermodynamics of methylene blue from aqueous solutions using biopolymer oak sawdust composite, J. Am. Sci. 6 (2010) 267–283.

[7] A. Srinivasan, T. Viraraghavan, Decolorization of dye wastewaters by biosorbents: A review, J. Environ. Manage. 91 (2010) 1915–1929.

[8] V. Vimonses, S. Lei, B. Jin, C.W.K. Chow, C. Saint, Kinetic study and equilibrium isotherm analysis of Congo red adsorption by clay materials, Chem. Eng. J. 148 (2009) 354–364.

[9] T.K. Sen, S. Afroze, H.M. Ang, Equilibrium, kinetics and mechanism of removal of methylene blue from aqueous solution by adsorption onto pine cone biomass of *pinus radiata*, Water, Air, Soil Pollut. 218 (2011) 499–515.

[10] M. Mohammad, S. Maitra, N. Ahmad, A. Bustam, T.K. Sen, B.K. Dutta, Metal ion removal from aqueous solution using physic seed hull, J. Hazard. Mater. 179 (2010) 363–372.

[11] M. Ghaedi, J. Tashkhourian, A.A. Pebdani, B. Sadeghian, F.N. Ana, Equilibrium, kinetic and thermodynamic study of removal of reactive orange 12 on platinum nanoparticle loaded on activated carbon as novel adsorbent, Korean J. Chem. Eng. 28 (2011) 2255–2261.

[12] Y.C. Sharma, Optimization of parameters for adsorption of methylene blue on a low-cost activated carbon, J. Chem. Eng. Data 55 (2010) 435–439.

[13] S. Wang, Z.H. Zhu, A. Coomes, F. Haghseresht, G.Q. Lu, The physical and surface chemical characteristics of activated carbons and the adsorption of methylene blue from wastewater, J. Colloid Interface Sci. 284 (2005) 440–446.

[14] Z. Aksu, S. Tezer, Biosorption of reactive dyes on the green alga *Chlorella vulgaris*, Process Biochem. 40 (2005) 1347–1361.

[15] G.L. Dotto, L.A.A. Pinto, Adsorption of food dyes onto chitosan: Optimization process and kinetic, Carbohydr. Polym. 84 (2011) 231–238.

[16] R. Patel, S. Suresh, Kinetic and equilibrium studies on the biosorption of reactive black 5 dye by *Aspergillus foetidus*, Bioresour. Technol. 99 (2008) 51–58.

[17] M.E. Russo, F. Di Natale, V. Prigione, V. Tigini, A. Marzocchella, G.C. Varese, Adsorption of acid dyes on fungal biomass: Equilibrium and kinetics characterization, Chem. Eng. J. 162 (2010) 537–545.

[18] A. Çelekli, F. Geyik, Artificial neural networks (ANN) approach for modeling of removal of Lanaset Red G on *Chara contraria*, Bioresour. Technol. 102 (2011) 5634–5638.

[19] Y. Yang, G. Wang, B. Wang, Z. Li, X. Jia, Q. Zhou, Y. Zhao, Biosorption of Acid Black 172 and Congo red from aqueous solution by nonviable *Penicillium* YW 01: Kinetic study, equilibrium isotherm and artificial neural network modeling, Bioresour. Technol. 102 (2011) 828–834.

[20] A. Çelekli, M. Yavuzatmaca, Predictive modeling of biomass production by *Spirulina platensis* as function of nitrate and NaCl concentrations, Bioresour. Technol. 100 (2009) 1847–1851.

[21] G.L. Dotto, E.C. Lima, L.A.A. Pinto, Biosorption of food dyes onto *Spirulina platensis* nanoparticles: Equilibrium isotherm and thermodynamic analysis, Bioresour. Technol. 103 (2012) 123–130.

[22] D. Chebli, A. Bouguettoucha, T. Mekhalif, S. Nacef, A. Amrane, Valorization of an agricultural waste, *Stipa tonacissima* fibers, by biosorption of an anionic azo-dye, Congo red, Desalin. Water Treat. (in press), doi:10.1080/19443994.2014.880154.

[23] S. Chatterjee, D.S. Lee, M.W. Lee, S.H. Woo, Enhanced adsorption of Congo red from aqueous solutions by chitosan hydrogel beads impregnated with cetyl trimethyl ammonium bromide, Bioresour. Technol. 100 (2009) 2803–2809.

[24] H. Chen, J. Zhao, Adsorption study for removal of Congo red anionic dye using organo-attapulgite, Adsorption 15 (2009) 381–389.

[25] M.A.M. Salleh, D.K. Mahmoud, W.A. Karim, A. Idris, Cationic and anionic dye adsorption by agricultural solid wastes: A comprehensive review, Desalination 280 (2011) 1–13.

[26] I. Nahal, Le pin brutia, forêt méditerranéenne (Brutia Pine, Mediterranean Forest) 2 (1983) 165–172.

[27] H. Ucun, Y.K. Bayhana, Y. Kaya, A. Cakici, O.F. Algur, Biosorption of lead (II) from aqueous solution by cone biomass of *Pinus sylvestris*, Desalination 154 (2003) 233–238.

[28] O. Aksakal, H. Ucun, Equilibrium, kinetic and thermodynamic studies of the biosorption of textile dye

(Reactive Red 195) onto *Pinus sylvestris* L, J. Hazard. Mater. 181 (2010) 666–672.

[29] A.E. Ofomaja, E.B. Naidoo, S.J. Modise, Removal of copper(II) from aqueous solution by pine and base modified pine cone powder as biosorbent, J. Hazard. Mater. 168 (2009) 909–917.

[30] N. Mahmoodi, M.B. Hayati, M. Arami, C. Lan, Adsorption of textile dyes on pine cone from colored wastewater: Kinetic, equilibrium and thermodynamic studies, Desalination 268(1) (2011) 17–125.

[31] S. Benyoucef, M. Amrani, Adsorption of phosphate ions onto low cost Aleppo pine adsorbent, Desalination 275 (2011) 231–236.

[32] G. Vazquez, R. Alonso, S. Freire, J. Gonzalez-alvarez, G. Antorrena, Uptake of phenol from aqueous solutions by adsorption in a *Pinus pinaster* bark packed bed, J. Hazard. Mater. 133 (2006) 61–67.

[33] I. Langmuir, The adsorption of gases on plane surfaces of glass, mica and platinum, J. Am. Chem. Soc. 40 (1918) 1361–1403.

[34] H.M.F. Freundlich, Ober dies adsorption in Losungen [Regarding adsorption in solution], Z. Phys. Chem. 57 (1906) 385–470.

[35] G.L. Dotto, M.L.G. Vieira, V.M. Esquerdo, L.A.A. Pinto, Equilibrium and thermodynamics of azo dyes biosorption onto *Spirulina platensis*, Braz. J. Chem. Eng. 30 (2013) 13–21.

[36] V.C. Srivastava, I.D. Mall, I.M. Mishra, Adsorption of toxic metal ions onto activated carbon, Chem. Eng. Process. 47 (2008) 1269–1280.

[37] W.J. Weber, J.C. Morris, Equilibrium and capacities for adsorption on carbon, J. Sanit. Eng. Div. ASCE 89 (1963) 31–60.

[38] Z. Aksu, A.I. Tatlı, O. Tunc, A comparative adsorption/biosorption study of Acid Blue 161: Effect of temperature on equilibrium and kinetic parameters, Chem. Eng. J. 142 (2008) 23–39.

[39] C. Xia, Y. Jing, Y. Jia, D. Yue, J. Ma, X. Yin, Adsorption properties of Congo red from aqueous solution on modified hectorite: Kinetic and thermodynamic studies, Desalination 265 (2011) 81–87.

[40] M.A. Wahab, S. Jellali, N. Jedidi, Effect of temperature and pH on the biosorption of ammonium onto *Posidonia oceanica* fibers: Equilibrium, and kinetic modeling studies, Bioresour. Technol. 101 (2010) 8606–8615.

[41] P. Senthil Kumar, S. Ramalingam, C. Senthamarai, M. Niranjanaa, P. Vijayalakshmi, S. Sivanesan, Adsorption of dye from aqueous solution by cashew nut shell: Studies on equilibrium isotherm, kinetics and thermodynamics of interactions, Desalination 261 (2010) 52–60.

[42] A. Aygün, S. Yenisoy-Karakaş, I. Duman, Production of granular activated carbon from fruit stones and nutshells and evaluation of their physical, chemical and adsorption properties, Micropor. Mesopor. Mater. 66 (2003) 189–195.

[43] C. Namasivayam, D. Kavitha, Removal of Congo red from water by adsorption onto activated carbon prepared from coir pith, an agricultural solid waste, Dyes Pigm. 54 (2002) 47–58.

[44] V.K. Gupta, A. Mittal, V. Gajbe, J. Mittal, Adsorption of basic Fuchsin using waste materials—Bottom ash and deoiled soya—as adsorbents, J. Colloid Interface Sci. 319 (2008) 30–39.

[45] M.C. Reddy, Removal of direct dye from aqueous solution with an adsorbent made from tamarind fruit shell, an agricultural solid waste, J. Sci. Ind. Res. 65 (2006) 443–446.

[46] S. Chatterjee, S. Chatterjee, B.P. Chatterjee, A.K. Guha, Adsorptive removal of Congo red, a carcinogenic textile dye by chitosan hydrobeads: Binding mechanism, equilibrium and kinetics, Colloids Surf., A 299 (2007) 146–152.

[47] L. Grabowska, G. Gryglewicz, Adsorption characteristics of Congo red on coal-based mesoporous activated carbon, Dyes Pigm. 74 (2007) 34–40.

[48] S. Lagergren, ZurTheorie der sogenannten Adsorption gelo¨ ster Stoffe [On the theory of so-called adsorption of solutes], K. Sven. Vetenskapsakad. Handl. 24 (1898) 1–39.

[49] X.J. Xiong, X.J. Meng, T.L. Zheng, Biosorption of C.I. Direct Blue 199 from aqueous solution by nonviable *Aspergillus niger*, J. Hazard. Mater. 175 (2010) 241–246.

[50] M.S. Chiou, H.Y. Li, Adsorption behavior of reactive dye in aqueous solution on chemical cross-linked chitosan beads, Chemosphere 50 (2003) 1095–1105.

[51] G.C. Panda, S.K. Das, A.K. Guha, Jute stick powder as a potential biomass for the removal of Congo red and rhodamine B from their aqueous solution, J. Hazard. Mater. 164 (2009) 374–379.

[52] S.K. Milonjic, A consideration of the correct calculation of thermodynamic parameters of adsorption, J. Serb. Chem. Soc. 72 (2007) 1363–1367.