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Valorization of an agricultural waste, *Stipa tenassicima* fibers, by biosorption of an anionic azo dye, Congo red

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ABSTRACT

The removal of Congo red dye (CR) from aqueous solutions using a novel low-cost biological adsorbent, *Stipa tenassicima* fibers, has been investigated in this paper. Batch experiments were conducted to examine the effect of the main parameters, such as the initial CR concentration, the pH, and the temperature on the sorption of the dye. Maximum adsorption removal was observed at pH 4 and biosorption capacity of *S. tenassicima* was enhanced by increasing the temperature. Rate constants of pseudo-first order, pseudo-second order, and intraparticle diffusion coefficient were calculated to analyze the dynamic of the sorption process; they showed that sorption kinetics followed an intraparticle diffusion model, while the two straight lines describing experimental data indicated that intraparticle diffusion was the limiting step for biosorption. Among the tested isotherm models, the Sips isotherm was found to be the most relevant to describe CR sorption onto *S. tenassicima* fibers. Thermodynamic parameters, such as changes in standard free energy, enthalpy, and entropy, were also evaluated and the results suggested that the sorption reaction was spontaneous and endothermic in nature. The potential of *S. tenassicima* fibers, an easily available and low-cost material, to be used as an alternative biosorbent material for the removal of a dye, CR, from aqueous solutions was therefore confirmed.

Keywords: Sorption; *Stipa tenassicima*; Isotherm models; Kinetics; Thermodynamic parameters

1. Introduction

Synthetic dyestuffs are a group of organic pollutants, which are extensively used in textile, cosmetic, plastic, paper and pulp, printing, iron-steel, coke, petroleum, pesticide, paint, solvent, food, wood preserving chemicals, and pharmaceutical industries [1]. 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

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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 compounds but also for their color, causing an esthetic pollution, since a very small amount of dye in water is highly visible [2]. 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 the presence of aromatics, metals, chlorides, etc. Therefore, the treatment of dye-contaminated aquatic systems and improvement of water quality are important topics in the field of environmental technologies [1,3,4].

The synthetic origin and complex aromatic structures of dyes make them stable and difficult to be biodegraded [5,6]. Dyes are classified as anionic (direct, acid, and reactive dyes), cationic (basic dyes), and nonionic (disperse dyes). The chromophores in anonic and nonionic dyes mostly consist of azo groups or anthraquinone types. Anthraquinone-based dyes are more resistant to degradation due to their fused aromatic structures [7]. 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 [8–11]. However, all these processes have their own limitations; they are highly expensive and not adaptable to a wide range of dye wastewaters [7]. Adsorption is a very effective separation technique and now it is considered to be superior to other techniques for water treatment in terms of investment cost, simplicity of design, ease of operation, and insensitiveness to toxic substances [9,10,12,13]. In this process, the dye species are transferred from the water effluent to a solid phase, leading to the decrease in the volume of polluted effluent [14]. A commonly used adsorbent, activated carbon has a high capacity for the removal of dyes/organics [15,16]; but some of its disadvantages are its high price and the difficulty to be regenerated resulting in an increase of the wastewater treatment cost.

There is therefore a 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 remove dyes 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 [1,10,17]. Biosorption refers to the ability of certain biomaterials to bind and concentrate on 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 [18], fungi [19,20], algae [17,21], and bacteria [4,22,23].

Congo red (CR) is a water-soluble azo dye, which is widely used in the textile, paper manufacturing, printing, pharmaceutical, food industries, as well as in research laboratories. It is an anionic dye which has been known to cause an allergic reaction and to be metabolized to benzidine, a human carcinogen [24,25]. Therefore, an increasing interest has been focused on removing such dyes from wastewater. There are several natural adsorbents including clay minerals that have been used for the removal of anionic dyes such as CR from aqueous solutions, which have been recently reviewed by [2,10,26].

Stipa tenassicima covers vast areas of the Algerian highlands. This plant serves in particular to produce high quality papers and has also some ecological interest, since it is involved in fighting against erosion in arid regions. However, and to our knowledge, no work has been reported regarding its use for dye adsorption. This research may be therefore helpful to develop an alternative technology for its use. In the present study, *S. tenassicima* has been used as an adsorbent for the removal of CR from aqueous solutions. The purpose is to optimize the management of this important waste as a biosorbent. The main focus of this study was to evaluate the effects of the main operating parameters, namely pH and temperature on the biosorption capacity of CR onto this raw lignocellulosic material. Various isotherm models namely Freundlich [27], Langmuir [28], and Dubinin–Radushkevich (D–R) [29] were applied to fit equilibrium biosorption data. Furthermore, the thermodynamic parameters (ΔG, ΔH, and ΔS) were also determined. The biosorption experimental data were analyzed by means of the pseudo-second-order and intraparticle diffusion models.

2. Materials and methods

2.1. Preparation of the biosorbent

S. tenassicima fibers were collected from arid regions (south of Algeria). The fibers were manually separated, washed with distilled water to remove the surface-adhered particles, and then dried in an oven at 40°C for 48 h to a constant weight. The dried biomass was stored in a desiccator for further use.

2.2. Preparation of dye solution and determination of dye concentrations

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^{-1} and was obtained from Sigma Aldrich with 99.99% purity. A stock solution of 500 mg/L was prepared by dissolving an appropriate amount (500 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 the 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℃. The SP-8,001 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 of a given amount of adsorbent in 50 ml of dye solutions of a known concentration in a series of 250 ml conical flasks were carried out.

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

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

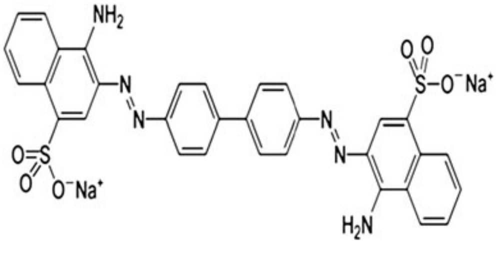

Fig. 1. Molecular structure of CR.

And dye removal efficiency, i.e. % of adsorption was calculated as:

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

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 *S. tenassicima* fiber.

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 capacity of the adsorbent. To analyze *S. tenassicima* interaction with CR, experimental data points were fitted to the Langmuir and Freundlich empirical models which are the most frequently used two- and three-parameter equations in the literature describing the nonlinear equilibrium between the pollutant adsorbed on the cells (Q_e) and the pollutant in solution (C_e) at a constant temperature.

The Langmuir isotherm model assumes uniform energies of adsorption onto the adsorbent surfaces. 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 [28] 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 is the equilibrium dye concentration in solution (mg/L); Q_m is the monolayer capacity of the adsorbent (mg/g); and K_L is the Langmuir constant. A nonlinear fit was performed by means of the Origin Software in order to obtain the Langmuir model parameters. The parameter statistic "adjusted R^2" were 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 [27]:

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

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

The Sips isotherm is a combination of the Langmuir and Freundlich isotherms [30]:

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

where Q_m is the maximum monolayer biosorption (mg/g), ks is the Sips constant solution ($\mathrm{L\,mg^{-1}}$), and m is 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, Elovich equation, and intraparticle diffusion models were 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. (3):

$$\log(Q_e - Q_t) = \log Q_e - \frac{k_1 t}{2.303} \tag{6}$$

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, and 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 $\log(Q_e - Q_t)$ 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 [31]. This model is given by Eq. (4):

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

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

2.4.3. The Elovich equation

The linear form of Elovich equation is given by Eq. (5):

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

where α is the initial adsorption rate constant (mg/(g min)) and the parameter β is related to the extent of surface coverage and activation energy for chemisorption (g/mg). The values of α and β can be calculated from the plot of Q_t against ln(t).

2.4.4. Intraparticle diffusion model

Intraparticle diffusion model is commonly used to identify the adsorption mechanism for design purpose. According to Weber and Morris [32], for most adsorption processes, the uptake varies almost proportionately with $t^{1/2}$ rather than with the contact time and can be represented as follows:

$$Q_t = K_{id} t^{0.5} + C \tag{9}$$

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} ($\mathrm{mg/g\,min^{0.5}}$) is the rate constant of intraparticle diffusion.

3. Results and discussions

3.1. Influence of pH at various initials concentrations

The effect of pH was investigated for values between 4 and 10 and the results are presented in Fig. 2. As shown and irrespective of the initial CR concentration (in the range 50–300 mg/L), equilibrium sorption capacity was maximum at pH 4 and decreased sharply for increasing pH and then remained nearly constant in the range 8–10; experiments were not performed at more acidic pH owing to dye precipitation. *S. tenassicima* fibers contain cellulose, hemicelluloses, and lignin in their cell walls, and hence contain some polar functional groups on their surface, such as alcohols, aldehydes, ketones, carboxylic, phenolic, and other groups [12,33]. This leads

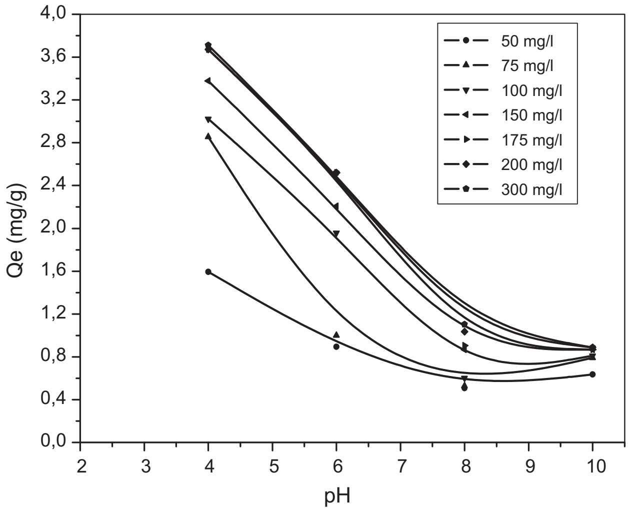

Fig. 2. Effect of pH on the biosorption capacity of CR onto *S. tenassicima* fibers at various dye concentrations (biomass concentration = 0.3 g/L and temperature = 25 ± 1 ℃).

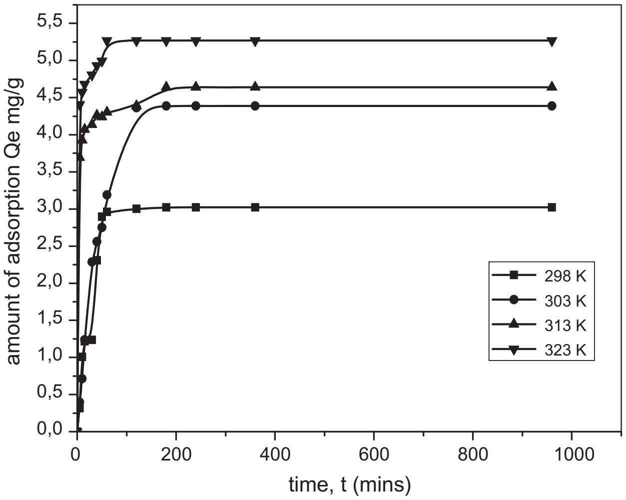

Fig. 3. Effect of contact time on the biosorption capacity of CR onto *S. tenassicima* fibers at various temperatures (biomass concentration = 0,3 g/L, CR concentration = 100 mg/L, and pH = 4).

to 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. When the pH of the suspension is higher than the pHpzc (5.3), the surface of *S. tenassicima* fibers is negatively charged, lowering the electrostatic attraction between the sulfonate groups and the negative adsorption site of the adsorbent of *S. tenassicima* fibers. On the other hand, when the pH of the suspension is lower than the pHpzc, the surface of *S. tenassicima* fibers biomass is positively charged leading to a high electrostatic attraction.

3.2 Effect of the temperature on dye adsorption

Various textile dye effluents are produced at relatively high temperatures, which can be therefore an important factor for a real application of *S. tenassicima* fiber. Temperature is an indicator for the adsorption nature; whether it is an exothermic or endothermic process [14]. The effect of temperature on dye sorption equilibrium was investigated in the temperature range 25–50℃ and the corresponding results are displayed in Fig. 3. As shown, CR adsorption was enhanced with increasing the temperature up to 50℃, indicating that a high temperature favored dye removal. This may be due to an increase of both the mobility of the dye molecules and the number of active sites available for adsorption with increasing temperatures [26,34,14]. The enhancement of the adsorption could be also due to a decrease in the thickness of the boundary layer surrounding the sorbent with temperature, so that the mass transfer resistance of the adsorbate in the boundary layer decreases [35]. 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. Similar behavior for CR adsorption at various temperatures on organo-attapulgite [25], on agricultural solid waste [26], on hectoritel [36], and on Posidonia oceanica fibers [37] has also been reported.

3.3 Isotherm analysis

In order to optimize the design of an adsorption system, it is important to establish the most appropriate correlation for the equilibrium curve. An accurate mathematical description of equilibrium adsorption capacity is indispensable for reliable prediction of adsorption parameters and quantitative comparison of adsorption behavior for different adsorbent systems (or for varied experimental conditions) within any given system. The effect of temperature on the equilibrium isotherm of CR biosorption is shown in Fig. 4(a)–(c). However, we can note that the effect of temperature is not significant between 303 and 313 K.

Several equilibrium adsorption isotherm models are available, and the most common ones are the mono-layer adsorption developed by Langmuir [28], the multi-layer adsorption of Freundlich [27], and the Sips isotherm Milonjic [30]. Experimental data at

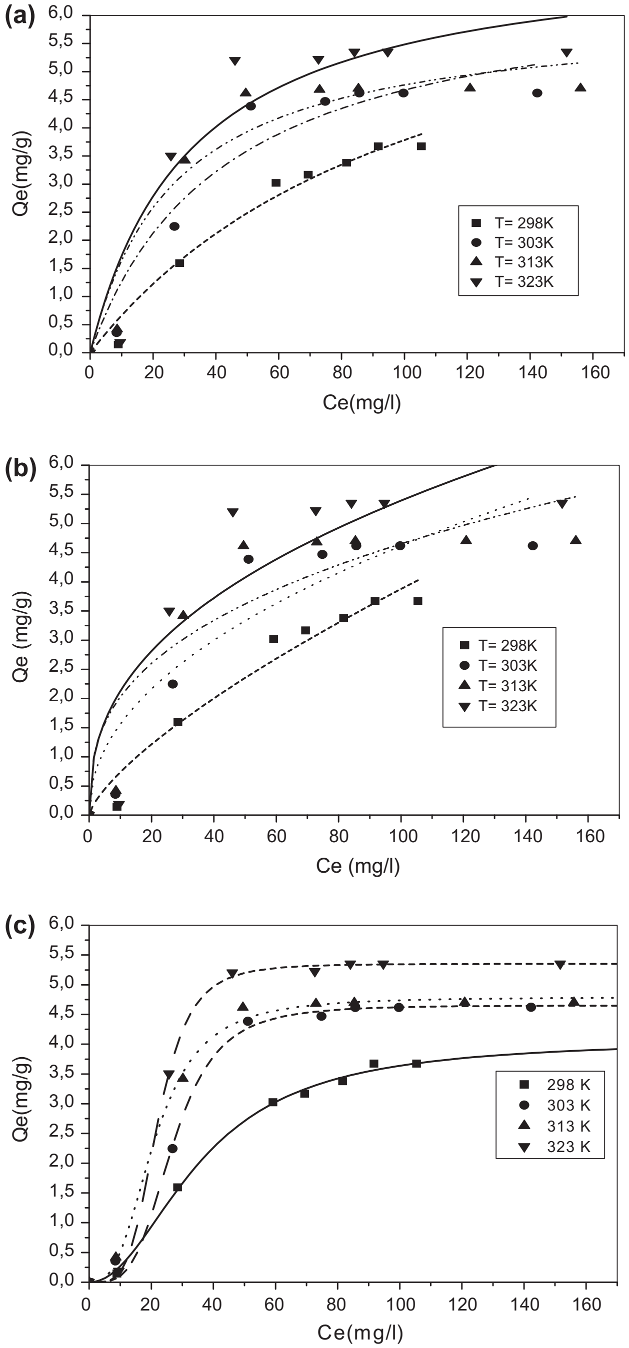

Fig. 4. Experimental (symbols) and calculated isotherm data (lines) for CR adsorption onto *S. tenassicima* fibers at various temperatures (biomass concentration = 0.3 g/L and initial pH 4). (a) Langmuir; (b) Freundlich; (c) Sips.

various temperature of CR on the *S. tenassicima* were fitted to the isotherm models using origin software and the graphical representations of these models are presented in Fig. 4(a)–(c). All parameter values of the considered parameters, as well as the R^2 values, are collected in Table 1.

Table 1
Langmuir, Freundlich, and Sips constants for the biosorption of CR onto *S. tenassicima* at various temperatures

Isotherm	T (K)	298	303	313	323
Langmuir	Q_m (mg/g)	7.93	6.67	6.04	7.24
	$K_L \times 10^2$ (L mg^{-1})	0.91	2.33	3.72	3.11
	R^2	*0.98*	*0.94*	*0.92*	*0.89*
	n	1.39	2.12	2.78	2.47
Freundlich	K_F (mg/g) (L mg^{-1})$^{1/n}$	0.14	0.53	0.88	0.84
	R^2	*0.96*	*0.87*	*0.82*	*0.80*
	Q_m (mg/g)	4.07	4.65	4.79	5.35
Sips	$ks \times 10^2$ (L mg^{-1})	2.8	3.7	4.7	4.5
	m	2.07	3.79	2.87	4.29
	R^2	*0.997*	*0.994*	*0.996*	*0.999*

Experimental data yielded excellent fits and based on their R^2 values showed the following order: Sips > Langmuir > Freundlich. Table 1 indicate a heterogeneous biosorption process and a multiple biosorption sites on the *S. tenassicima* fibers. The higher values of m from the Sips model (Table 1) confirmed that CR sorption onto *S. tenassicima* occurred by the formation of a multilayer. In summary, experimental data for adsorption equilibrium of the considered azo dye were most accurately fitted by the Sips model if compared to Langmuir and Freundlich models. The maximum biosorption capacities (Q_m) obtained from the Sips model were 5.35 mg/g at 323 K, namely close to the experimental ones. The comparison of maximum adsorption capacity of some dyes onto various adsorbents is presented in Table 2. It should be observed that even if the biosorbent is a smooth fiber, its adsorption capacity appeared similar to those of other adsorbents, including activated carbon.

3.4. Biosorption kinetics

The prediction of batch adsorption kinetics is necessary for the design of industrial adsorption columns. The nature of the adsorption process

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

Adsorbents	Q_m (mg/g)	Reference
Cashew nut shell	5.18	[38]
Activated carbon (LR)	1.88	[39]
Coir pith	6.70	[40]
Kolin	5.44	[41]
S. tenassicima fiber	3.7–5.35	This work

depends on physical and chemical characteristics of the adsorbent system, as well as the system conditions. In the present study, the applicability of the pseudo-first-order [42], pseudo-second-order [43], the Elovich, and the intraparticle diffusion [32] models has been tested for CR adsorption onto *S. tenassicima* fibers. Biosorption kinetics appeared to be accurately fitted by the pseudo-second-order and the Weber–Morris models (Table 3), while the pseudo-first-order and the Elovich models (result not shown) did not results in an accurate description of experimental data, since they yielded correlation coefficients (R^2) below 0.90 (Table 3).

In addition to the high R^2 values (> 0.99 for all tested conditions), the Q_e values estimated from the pseudo-second-order kinetic model were also in agreement with experimental data (Table 2) at all tested temperatures (Fig. 5). The results suggested that boundary layer resistance was not the rate-limiting step since dye biosorption followed pseudo-second-order kinetics [44].

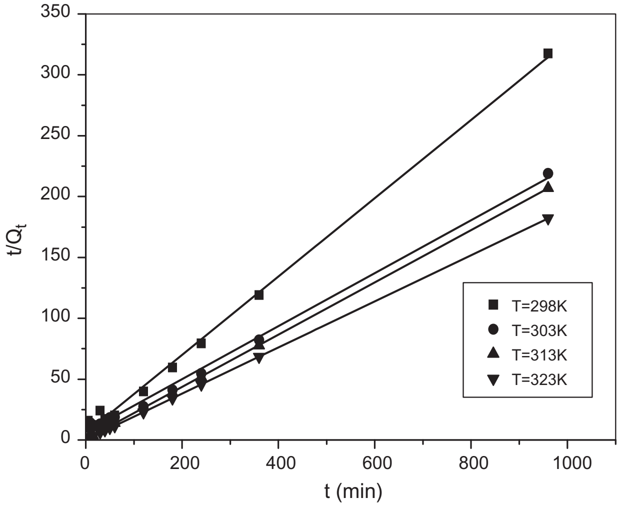

Fig. 5. Experimental (symbols) and calculated data (continuous lines) by means of pseudo-second-order kinetic model for CR biosorption onto *S. tenassicima* fibers at various temperatures.

The intraparticle diffusion model could be used to investigate the mass transfer mechanism in the dye–fiber system. The intercept gives an idea about the thickness of the boundary layer, i.e. the larger is the intercept the greater is the boundary layer effect [45]. The intraparticle diffusion plots are displayed in Fig. 6 and the parameters are summarized in Table 3. This figure showed that irrespective of the considered temperature, the intraparticle diffusion of CR within biomass occurred in two steps. 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. Intraparticle diffusion appeared therefore to be the limiting step for the biosorption of CR onto *S. tenassicima* fibers. Similar trend has been reported for the biosorption of CR and rhodamine B onto jute stick power [46]. All the intercepts calculated at 313 and 323 K were higher than those obtained at 298 and 303 K (Table 3),

Table 3
Kinetics parameters for CR biosorption onto *S. tenassicima* fibers at different temperatures

Kinetic models		Parameters	298 K	303 K	313 K	323 K
Pseudo-first-order		Q_{exp} (mg/g)	3.022	4.638	4.638	5.268
		$Q_{e1,cal}$ (mg/g)	3.129	6.837	1.109	1.704
		k_1 (1/min)	0.046	0.042	0.016	0.042
		$R_1^2 R_1{}^2$	*0.865*	*0.889*	*0.442*	*0.583*
		$Q_{e2,cal}$ (mg/g)	3.107	4.595	4.657	5.279
Pseudo-second-order		K_2 (g mg^{-1} min)	0.019	0.007	0.069	0.131
		R_2^2	*0.996*	*0.995*	*0.999*	*0.999*
		A	0.367	0.170	0.991	1.637
Elovich		B	0.847	1.234	0.230	0.297
		R_E^2	*0.848*	*0.974*	*0.953*	*0.896*
	Step 1	K_p (mg/g min$^{0.5}$)	0.30	0.46	0.07	0.116
		C (mg/g)	0.16	0.45	3.69	4.19
Intraparticle diffusion		R_P^2	*0.864*	*0.956*	*0.874*	*0.977*
	Step 2	K_p (mg/gmin$^{0.5}$)	0.0023	0.0032	0.0067	0.0021
		C (mg/g)	3.02	4.38	4.63	5.27
		R_P^2	*0.998*	*0.999*	*0.999*	*0.999*

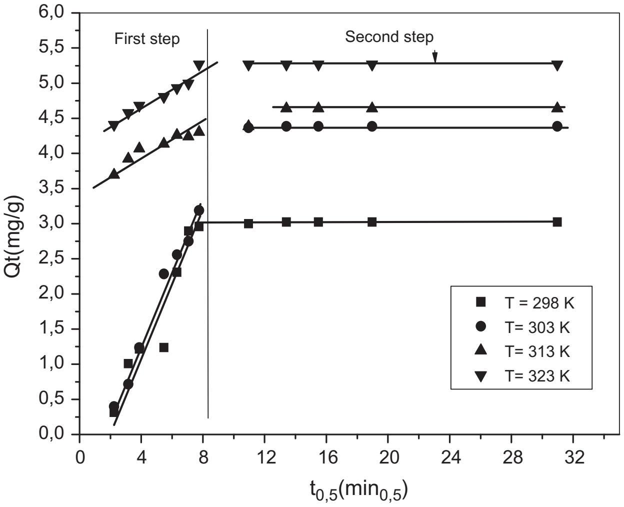

Fig. 6. Experimental (symbols) and calculated data (continuous lines) by means intraparticle diffusion model for CR biosorption onto *S. tenassicima* fibers at various temperatures.

indicating that the effect of the boundary layer on the biosorption process increased with the temperature.

3.5. 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. (10) as reported by Milonjic [30]:

$$\Delta G^\circ = -RT\ln(\rho K_c) \tag{10}$$

where ΔG° is the free energy change (kJ mol^{-1}), R is the universal gas constant (8.314 J mol^{-1} K^{-1}), T is the absolute temperature (K), K_c is the thermodynamic equilibrium constant (L g^{-1}), and ρ is the water density (g /L). ΔH° and ΔS° values of the biosorption process were also calculated from the Van't Hoff equation (11):

$$\ln(\rho K_C) = -\frac{\Delta H}{RT} + \frac{\Delta S}{R} \tag{11}$$

ΔH and ΔS can be then deduced from the slope ($\Delta H/\mathrm{R}$) and the intercept ($\Delta S/R$) of the plot of $\ln K_C$ vs. $1/T$. The calculated thermodynamic parameters are given in Table 4.

Table 4
Thermodynamic parameters for CR biosorption onto *S. tenassicima* at various temperatures

Dye CR	Temperature (K)	ΔG° (kJ mol^{-1})	ΔH° (kJ mol^{-1})	ΔS° (J mol^{-1})
	298	−9.12	10.017	64.20
	303	−9.43		
	313	−10.08		
	323	−10.72		

In general, the change of free energy for physisorption is between −20 and 0 kJ mol^{-1}. and ranges from −80 to −400 kJ mol^{-1} for chemisorption. The result obtained, about −10 kJ mol^{-1}, at different temperatures indicates that this is a spontaneous physisorption process. As shown in Fig. 3, CR adsorption was enhanced with the raise in temperature up to 50°C, indicating that a high temperature favored dye removal leading to positive value of ΔH; hence the adsorption is an endothermic process. The positive value of entropy change suggests the increased randomness at the solid–solution interface during the adsorption of CR on the biosorbent.

4. Conclusion

From the above results, experimental data were found to follow a Langmuir isotherm model. Batch studies showed that a simple model such as pseudo-second-order kinetic equation can adequately predict the adsorption of CR onto *S. tenassicima* fibers at all studied temperatures. These results imply that chemisorption mechanism may play an important role in dye adsorption. It was also observed that kinetic study revealed that intraparticle diffusion was the limiting step for biosorption. The negative values of ΔG confirmed a favorable biosorption process. In the light of these results it can be concluded that *S. tenassicima* fibers has the potential to be used as an alternative biosorbent material for the removal of CR dye from aqueous solutions due to its availability and its low cost.

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