Adsorptive removal of textile reactive dye using *Posidonia oceanica* (L.) fibrous biomass

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ABSTRACT: The Mediterranean seagrass *Posidonia oceanica* (L.) leaf sheaths were used as low cost, available and renewable biological adsorbent for the removal of reactive textile dye from aqueous solutions. Batch experiments were carried out for sorption kinetics and isotherms. Operating variables studied were temperature, pH and chemical pre-treatment. Biosorption capacity seems to be enhanced by increasing the temperature. Maximum colour removal was observed at pH 5. Pre-treating fibres with H_3PO_4 and HNO_3 solutions increased the adsorption efficiency up to 80 %. Experimental sorption kinetic data were fitted to both Lagergren first-order and pseudo-second-order models and the data were found to follow first-order equation for raw fibres and pseudo-second-order for pre-treated ones. Equilibrium data were well represented by the Freundlich isotherm model for all tested adsorption systems. Besides, the thermodynamic study has showed that the dye adsorption phenomenon onto *P. oceanica* biomass was favourable, endothermic and spontaneous.

Key words: *Biosorption, posidonia seagrass, reactive dye, chemical treatments, modeling*

INTRODUCTION

Several biological, physical and chemical methods have been used for the treatment of industrial textile wastewater including microbial biodegradation, membrane filtration, oxidation and ozonation (Forgacs, *et al.,* 2004). However, many of these technologies are cost prohibitive, especially when applied for treating large waste streams. Consequently, adsorption techniques seem to have the most potential for future use in industrial wastewater treatment Babel and Opiso, 2007) because of their proven efficiency in the removal of organic and mineral pollutants and for economic considerations (Robinson, *et al.,* 2002a, Garg, *et al.,* 2003, Abdel-Ghani, *et al.*, 2007). The most widely used adsorbent for this purpose is activated carbon, but its overlying coast (McKay, *et al.,* 1987, Low, *et al.,* 1995) has led to search for cheaper alternative materials such as orange and banana peels (Annadurai, *et al.,* 2002), neem leafs (Bhattacharyya, *et al.,* 2003), agricultural residues (Robinson, *et al.,* 2002b) and peanut hull (Gong, *et al.,* 2005). The main objective of the present study was to develop a low cost and efficient wastewater treatment technology by studying the capacities of a

marine lignocellulosic material, *Posidonia oceanica* leaf sheaths for adsorptive removal of a reactive textile dye: C.I. Reactive Red 228. The kinetic and equilibrium data of sorption studies were processed to understand the sorption mechanism of the dye molecule onto *P. oceanica* fibres.

MATERIALS AND METHODS

Adsorbent and adsorbate preparation

P. oceanica leaf sheaths (PLS) were collected from Chott-Meriem bay (Eastern coast of Tunisia). The fibres are manually separated, washed with generous amounts of distilled water to remove the surface-adhered particles and then dried in an oven at 40 °C for 48 h to a constant weight. Two kind of chemical treatments were then performed: 0.2 M nitric acid (PLS-HNO_3) and 0.2 M phosphoric acid (PLS-H_3PO_4) in one hand and 4°CHL sodium hypochlorite (PLS-NaOCl) and 30 % (v/v) hydrogen peroxide (PLS-H_2O_2) for a bleaching process in the other hand. For the chemical treatment, a constant mass of 1 g of dried raw PLS was treated with 200 mL of the appropriate solution for 6 hours at 25°C. A Ciba Geigi textile Azo dye has been experimented in this study: C.I. Reactive Red 228 (R.

Red). Stock solutions were prepared by dissolving accurately weighed amount of dye in distilled water to give a concentration of 1000 mg/L and diluting when necessary. Initial pH was adjusted by addition of dilute HCl or NaOH solutions.

Batch adsorption experiments

Adsorption experiments were carried out by agitating 5 g of PLS with 250 mL of dye solution for the desired concentration and pH in a horizontal shaker at 100 rpm for the time required to reach the equilibrium state (48 h). Studies were conducted at 25 °C ± 2 using a temperature-controlled water bath. Dye concentration was estimated spectrophotometrically at the wavelength corresponding to maximum absorbance, 540 nm, using a CamSpec M330 spectrophotometer. The samples were taken from the shaker at predetermined time intervals and the dye solution was filtered through a 0.45 μm membrane ûlter and then analyzed. The amount of dye adsorbed onto PLS, q_e(mg/g), was calculated as follows:

$$q_e = (Ci - Ce)\frac{V}{W} \qquad (1)$$

where Ci and Ce are the initial and equilibrium time solution concentrations of the dye (mg/L), respectively, V the volume of the solution (L) and W the weight of the dry PLS used (g). Each experiment was performed twice at least under identical conditions.

RESULTS

Effect of temperature

The data of dye adsorption onto raw PLS at different temperatures indicates a change in the dye removal efficiency. This effect is shown in Fig. 1. The increase in the equilibrium sorption capacity of the R. Red dye,

for the two concentrations investigated, indicates that a high temperature favours dye removal. Indeed, by increasing the temperature of the reaction from 15 to 60 °C, the equilibrium capacity of the dye increased from 1.092 to 1.824 mg/g for the concentration of 50 mg/L and 2.631 to 3.497 mg/g for 100 mg/L. Consequently, it is clear that adsorption equilibrium is a thermo-dependent process. This effect may be due to the fact that at higher temperatures, an increase in the movement of the solute occurs. Similar results are mentioned by other researchers (Chakraborty, *et al.,* 2005).

Effect of pH solution

The initial pH value of the solution is an important factor which must be considered during sorption studies (Aksu, 2005). The effect of pH on the amount of dye removal was analyzed over the pH range from 2 to 10 and the results are presented in Fig. 2. As shown, the maximum biosorption capacity was reached at pH 5 with 1.938 and 4.121 mg/g, respectively for 50 and 100 mg/L concentration. This trend might be explained by the fact that we deal with an Azo-based reactive dye combining different types of reactive groups. The pH 5 might correspond to the rate of dissociation of this dye with maximum ionisation of the molecule. Furthermore, in such pH, the PLS combines both negatively and positively charged cells surface, which enhance the electrostatic attraction between anionic and cationic species of both sorbate and adsorbate. Moreover, inhibition of the dye sorption onto raw PLS at low acidic and high basic pH ranges may be attributed to the increase of hydroxyl and hydrogen ions leading to formation of aqua complexes thereby retarding the dye sorption (Mohan, *et al.,* 2002).
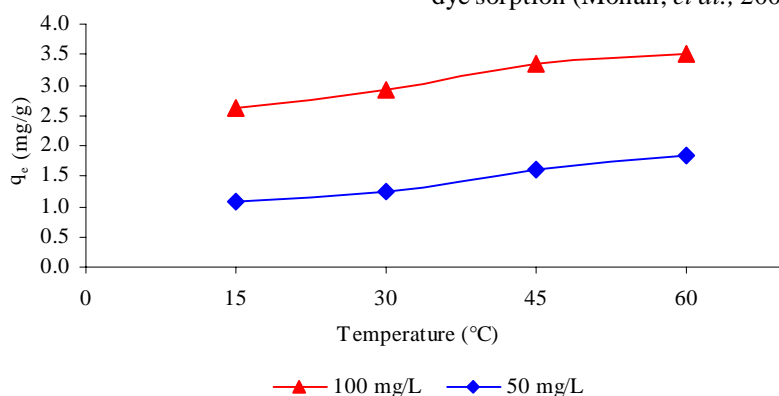

Fig. 1: Influence of temperature on the biosorption equilibrium capacity onto raw PLS

(Solid/Liquid ratio = 5 g/250 mL, pH = 5, contact time = 48 h, agitation rate = 100 rpm)
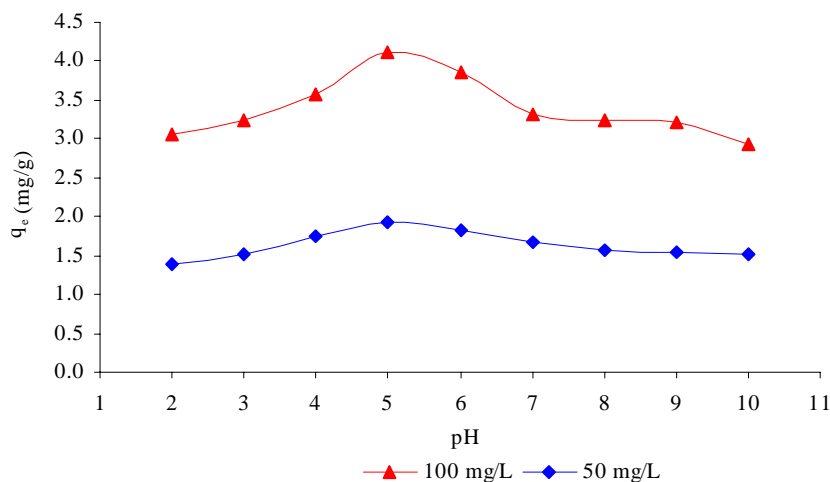
Fig. 2: Influence of pH on the biosorption equilibrium capacity onto raw PLS
(Solid/Liquid ratio = 5 g/250 mL, temperature = 25±2 °C, contact time = 48 h, agitation rate = 100 rpm)
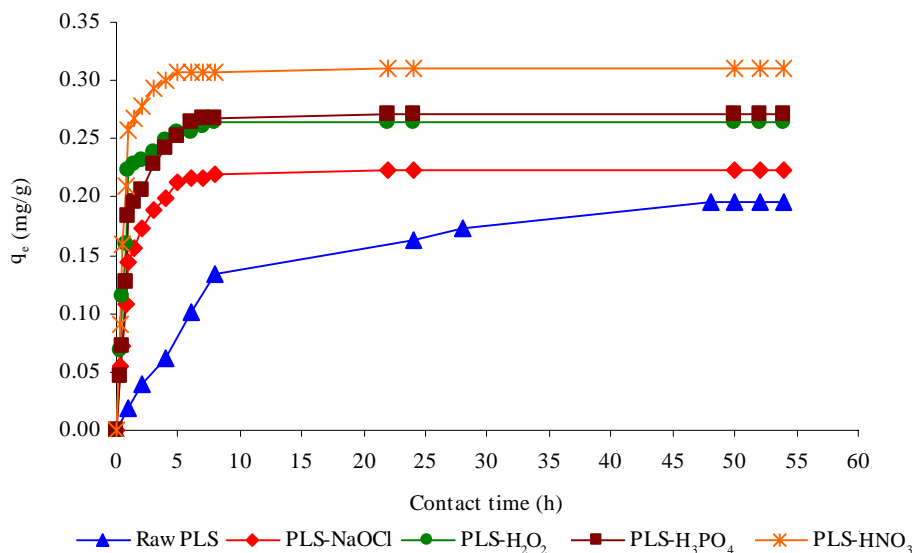

Fig. 3: Biosorption kinetics of R. red onto pretreated PLS
(Solid/Liquid ratio = 5 g/250 mL, Ci = 10 mg/L, pH = 5, temperature = 25±2 °C, agitation rate = 100 rpm)

Effect of chemical pre-treatment

Fig. 3 shows that all chemical treatment had enhanced the biosorption equilibrium capacity compared with the raw PLS. Indeed, for an initial dye concentration equal to 10 mg/L, PLS-HNO$_3$ had the highest removal amount (0.310 mg/g). PLS-H$_3$PO$_4$, PLS-H$_2$O$_2$ and PLS-NaOCl had also showed an increase in dye uptake with 0.271, 0.265 and 0.222 mg/g, respectively. In addition, the equilibrium was reached within 10 h for all pre-treated PLS, against 48 h for the raw PLS. In the case of PLS treated with acidic solutions, it seems that the negative charges on

the hydrolysed R. red dye molecules were electrostatically attracted by the positive charge on the surface of PLS- HNO$_3$ and PLS-H$_3$PO$_4$, which was increased by the excess of H$^+$ ions in the solution (Kumar, *et al.,* 2002). Therefore, such results suggest that the present biosorption phenomenon might be via a chemiosorption mechanism. In other hand, the increase of the dye uptake using bleached PLS is probably due to the hydrolysis of the natural pigments (mainly phycoxanthines) which are chemically similar to synthetic

dyes, generating therefore new active sorptive sites. The enhancement of the dye adsorption capacity through chemical treatment of the biomass was also reported by Inthorn, *et al.* (2004) and Gong, *et al.* (2005).

Sorption kinetic modelling

For evaluating the adsorption kinetics of R. Red dye, Lagergren ûrst-order and pseudo second order models were used to ût the experimental data. The first order equation is:

$$\log (q_e - q) = \log q_e - \frac{K_{ad}}{2.303} t \qquad (2)$$

where q_e and q (both in mg/g) are the amounts of adsorbed dye respectively at equilibrium time and at time t. K_{ad} (h^{-1}) is the rate constant of first order model. From the slopes and intercepts of plots of $\log (q_e - q)$ versus t obtained for the biosorption of R. Red by PLS-HNO$_3$, PLS-NaOCl and raw PLS (Fig. 4), the first order rate constant K_{ad} and the calculated q_e (q_{ecal}) values were determined, respectively (Table 1). The correlation coefficients for the first-order kinetic model obtained at all studied PLS were low, except for the raw biomass with 99.09 %. However, in the same, the theoretical q_{ecal} did not give acceptable values even for the raw PLS. Therefore, these studied biosorption systems were not considered as a first order reaction, and its applicability is just over the initial 20 min of the sorption process involving raw PLS. This time-limited application of the

Lagergren model was previously mentioned in the scientific literature by Namasivayam, *et al.* (1996) and Aksu and Donmez (2003). In the order hand, the pseudo-second-order model is also based on the biosorption capacity of the solid phase. But, contrary to the previous model it predicts the sorption behaviour over the whole time adsorption (Ho and McKay, 1999a). The pseudo second order equation is expressed as:

$$\frac{t}{q} = \frac{1}{K_2 . q_e{}^2} + \frac{t}{q_e} \qquad (3)$$

where K_2 is the rate constant of second-order model (g/mg.h). When the second-order kinetic is applicable, the plot of t/q against t should give a linear relationship (Fig. 5), from which K_2 and q_{ecal} can be determined respectively from the intercept and slope of the plot. The results are given in Table 1. The second-order model shows satisfactory fit with the experimental data related to the biosorption onto treated PLS with high correlation coefficients (99.9 %). Moreover, as shown in Table 1, the calculat q_e are quite similar to the experimental values. However; for the case of raw PLS, the second-order model did not correlates well based on both low correlation coefficient and unacceptable value of the q_{ecal}. Hence, as the pseudo-second order kinetic model provide the best correlation of the experimental data using treated biomass, chemical reaction might be considered as the rate-controlling step in the studied adsorption systems (Ho and McKay, 1999b).
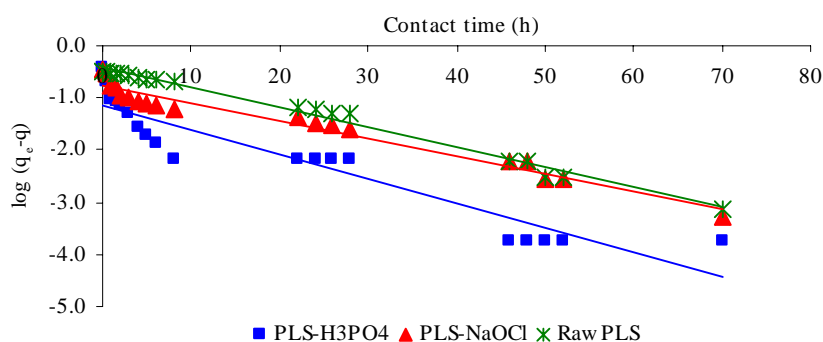

Fig. 4: Linearized lagergren first-order kinetic model for R. red uptake by raw and treated PLS
(Solid/Liquid ratio = 5 g/250 mL, Ci = 10 mg/L, pH = 5, temperature = 25±2 °C)

Table 1: Adsorption rate constants calculated from Lagergren first order and pseudo secondorder kinetic models

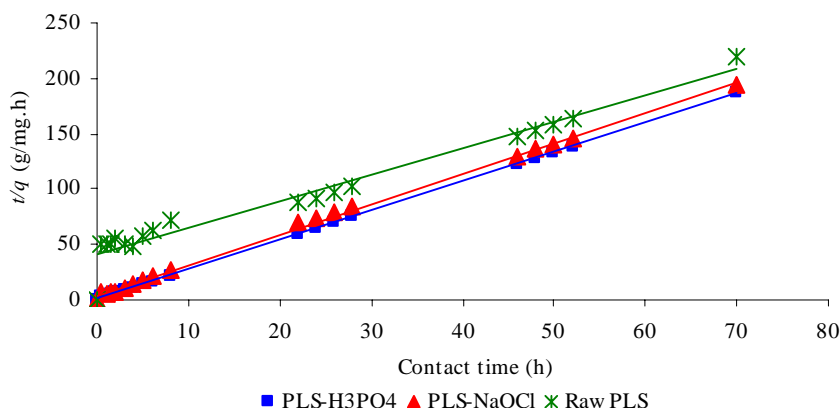|		Lagergren first-order model			Pseudo-second-order model		
	$q_{e\ exp}$ (mg/g)	K_{ad} (h^{-1})	q_{ecal} (mg/g)	R^2	K_2 x 10^{-2} (g/mg.h)	$q_{e\ cal}$ (mg/g)	R^2
Raw PLS	0.320	0.0875	0.348	0.990	0.79	0.418	0.953
PLS-H$_3$PO$_4$	0.376	0.1004	0.307	0.876	35.43	0.377	0.999
PLS-NaOCl	0.359	0.0783	0.467	0.967	8.74	0.364	0.999

Fig. 5: Linearized pseudo second order kinetic model for R. red uptake by raw and treated PLS
(Solid/Liquid ratio = 5 g/250 mL, Ci = 10 mg/L, pH = 5, temperature = 25±2 °C)

Sorption equilibrium modelling

The adsorption curves were applied to both Langmuir and Freundlich equations. The linearized form of the Langmuir isotherm equation is represented as:

$$\frac{Ce}{q_e} = \frac{1}{K_L \cdot q^0} + \frac{Ce}{q^0} \qquad (4)$$

where q_e (mg/g) is the amount adsorbed per unit mass of biosorbent corresponding to complete coverage of the adsorptive sites, Ce (mg/L) is the equilibrium concentration of dye in solution, q^0 (mg/g) is the monolayer sorption capacity of the biomass and the Langmuir constant K_L (L/mg) is the sorption energy. A plot of Ce/q_e versus Ce would give q^0 and K_L from the slope and intercept, respectively. The linearized form of the Freundlich isotherm equation is given by:

$$\log q_e = \log K_F + \frac{1}{n} \log Ce \qquad (5)$$

where KF ((mg/g)*(L/mg)^n) is the Freundlich constant and n the constant related to adsorption intensity. A plot of $ln\ q_e$ against $ln\ Ce$ would give the value of n and K_F, from the slope and the intercept, respectively. The results of both Langmuir and Freundlich adsorption constants at different pH values were shown in Table 2. Fig. 6 shows the fitted equilibrium data for both isotherm models. The low correlation coefficient related to the Langmuir isotherm showed that this model is not suitable to describe the adsorption equilibrium, except for pH 5 (R² = 96.8 %) which probably predicts the monolayer coverage of R. Red onto raw PLS. In the other hand, the Freundlich

isotherms generate a satisfactory fit to experimental data for all tested pH with high correlation values (99.2-99.5 %). Moreover, it is apparent that value of the constant, n obtained indicates favourable adsorption, as it lies between 1 and 10. On the other hand, in order to situate our novel biosorbent among those used to remove synthetic Azo dyes from aqueous solutions, a comparison based on both Langmuir saturation capacity q^0 and Freundlich adsorption intensity n was made.

Thermodynamic studies

In order to qualify the present adsorptive removal process, thermodynamic factors including the Gibbs free energy change of adsorption, "G° (kJ/mol), the enthalpy change of adsorption, "H° (kJ/mol) and the entropy change of adsorption; "S° (J/mol/K) were calculated using the following equations (6-8).

$$Kd = \frac{q_e}{Ce} \qquad (6)$$

$$\Delta G^0 = -RT \cdot Ln(Kd) \qquad (7)$$

$$Ln(Kd) = \frac{\Delta H^0}{RT} + \frac{\Delta S^0}{R} \qquad (8)$$

where Kd is the adsorption distribution coefficient, R is the universal gas constant (8.314 KJ/mol/K) and T is the absolute temperature (K). The experimented temperature range was from 15 to 60°C. The Gibbs free energy indicates the degree of spontaneity of the sorption process and the higher negative value reflects more energetically favourable sorption. ("H°) and ("G°) values, recorded in Table 4, were obtained from the slope and intercept of a plot of $Ln\ Kd$ against $1/T$.

Table 2: Langmuir and Freundlich isotherms constants related to the biosorption of R. red onto raw PLS at different pH solution

|	Langmuir constants			Freundlich constants		
	$q°$	K_L	R^2	K_F	n	R^2
pH 3	16.67	0.01	0.598	0.13	1.13	0.995
pH 5	5.74	0.07	0.968	0.53	1.65	0.992
pH 7	16.75	0.01	0.604	0.11	1.12	0.995

Table 3: Comparison of adsorption isotherm characteristics between *P. oceanica* fibres and other studied sorbents for textile Azo dye removal

Sorbents	Textile dyes	pH	T (°C)	Langmuir $q°$ (mg/g)	Freundlich n	References
Posidonia oceanica	Reactive red 228	5	30	5.74	1.65	This study
Orange peel	Procion orange	5.2	29	1.33	2.07	Namasivayam, *et al.,* 1996
Apple pomace	5 Reactive dyes	7.2	20	2.79	0.51	Robinson, *et al.,* 2002a
Activated sludge	Reactive blue 2	2	25	NA	1.16	Aksu, 2001
Pichia carsonii	Reactive blue 19	3	28	5	NA	Polman and Breckenridge, 1996
Kluyveromyces marxianus	Cibacron orange	3	25	8.5	NA	Bustard, *et al.,* 1998
Rice husk	Bismarck brown	NA	27	84.4	1.95	(Kumar and Sivanesan, 2005
Pseudomonas luteola	Reactive violet 2	3	28	96.4	NA	Hu, 1996

NA: Not available

Table 4: Thermodynamic parameters for adsorption of R. red onto *P. oceanica* fibres

$\triangle G°$ (kJ/mol)				$\triangle H°$	$\triangle S°$
15 °C	30 °C	45 °C	60 °C	(kcal/J)	(J/mol/K)
-7.08	-6.88	-6.30	-5.69	67.34	-129.81
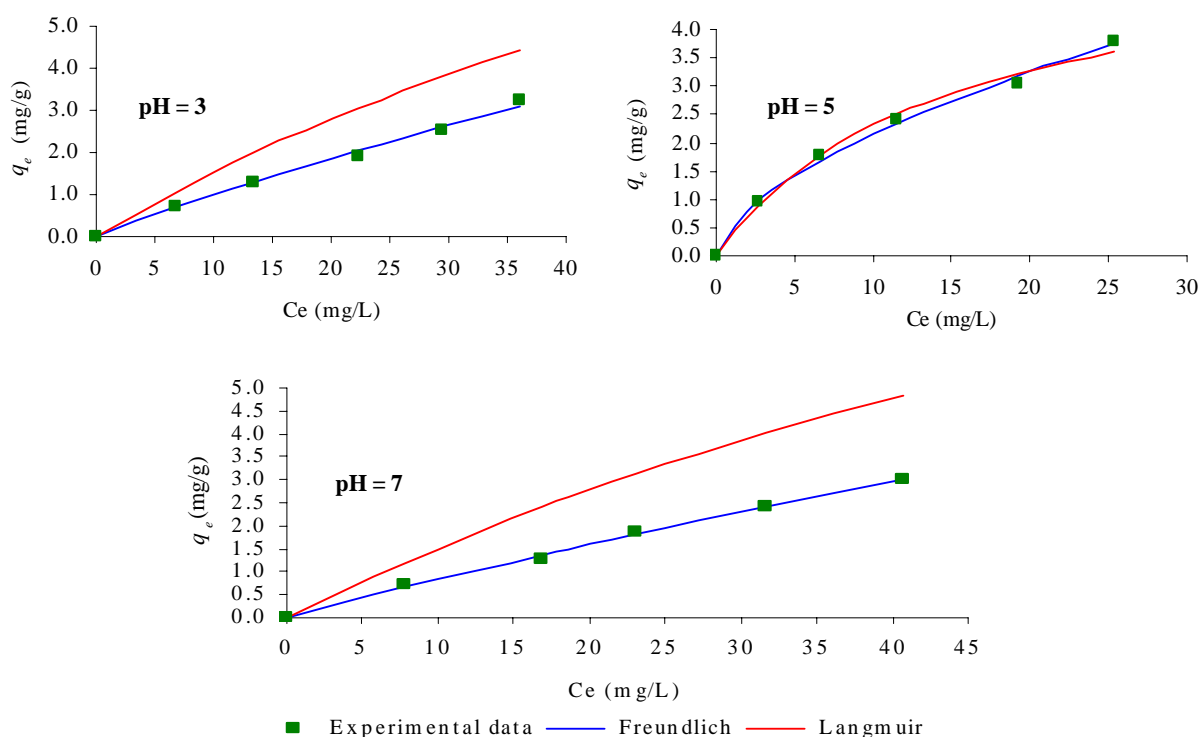
Fig. 6: Adsorption isotherms modelling of R. red on raw PLS at different pH
(Solid/Liquid ratio = 5 g/250 mL, contact time = 48 h, temperature = 25±2 °C, agitation rate = 100 rpm)

DISCUSSION AND CONCLUSION

In this work, the biosorption process of the reactive textile dye (C.I. Reactive Red 228) have been examined onto *Posidonia oceanica* (L.) leaf sheaths fibres. It was shown that adsorption equilibrium capacity was enhanced by raising the temperature up to 60 °C. This may be due to a relative increase in the tendency of dye molecules to escape from the liquid phase to the solid phase with increasing temperature of the solution (Ho and McKay, 2003). Besides, the highest dye removal efficiency was found at pH 5 which might correspond to the rate of dissociation of the studied dye with maximum ionisation of the molecule. Furthermore, all chemically treated PLS had showed enhancement in dye removal and they had also reached the equilibrium state quicker than raw PLS. Such tendency was related to the protonation of the biomass surface for acidic attacks and the hydrolysis of the inner pigments for bleaching treatments. On the other hand, Kinetic rate constants were determined and the data fit well with Lagergren first-order using raw PLS and pseudo second order model for treated PLS. As well, adsorption parameters for Langmuir and Freundlich isotherms were determined at different pH and the equilibrium data fit well with the Freundlich model at all experimented pH. Dealing with the comparative study, the related results (*Cf.* Table 3) revealed that the *P. oceanica* fibres could be considered as a promising biomaterial to remove textile dyes when compared to orange peels (Namasivayam, *et al.,* 1996), apple pomace (Robinson, *et al.,* 2002a), dried activated sludge (Aksu, 2001) and *Pichia carsonii* (Polman and Breckenridge, 1996). However, other sorbents have shown higher dye removal capacities among them *Kluyveromyces marxianus* (Bustard, *et al.,* 1998), rice husk (Kumar and Sivanesan, 2005) and *Pseudomonas luteola* (Hu, 1996). In addition, according to the thermodynamic analysis, the negative values of ("G°) indicate the spontaneous nature of the adsorption process for both dyes. Besides, the positive values of ("H°) indicate that the sorption process was endothermic and the negative values of ("S°) suggest the probability of favourable adsorption (Smith and Van Ness, 1987). Therefore, in addition to its phenol and methylene blue removal capacities (Ncibi, *et al.,* 2006 and 2007), the *P. oceanica* leaf sheaths could be considered as a promising material to be used as an efficient and low cost material for dye removal by biosorption. Currently, a study on the immobilization of some fungi or bacteria onto the Posidonia fibres is in progress in order to optimize the dye uptake capacity.

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