Kinetic and equilibrium studies of methylene blue biosorption by *Posidonia oceanica* (L.) fibres

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Abstract

Batch biosorption experiments were carried out for the removal of methylene blue, a basic dye, from aqueous solution using raw *Posidonia oceanica* (L.) fibres, a marine lignocellulosic biomass. A series of assays were undertaken to assess the effect of the system variables, i.e. contact time, solution pH, biosorbent dosage and initial dye concentration. The results had showed that biosorption capacity was optimal using 6–9 solution pH range and by increasing the biosorbent concentration up to 1 g/L. The biosorption kinetics were analyzed using irreversible-first-order, reversible-first-order and pseudo-second-order and the sorption data were very well described by the pseudo-second-order model for the entire adsorption time with squared correlation coefficients equal to unity for all experimented initial dye concentrations. Besides, equilibrium data were very well represented by both Langmuir and Redlich–Peterson isotherm models followed by Freundlich, which confirm the monolayer coverage of methylene blue molecules onto *P. oceanica* fibres.
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Keywords: Biosorption; Basic dye; Biofibres; Isotherms; Kinetics; Modelling

1. Introduction

Many industries often use synthetic dyes to colour their products including textile dyeing and colouring paper and wool. Over 7×10^5 tons of these dyes are produced annually worldwide. It is estimated that 10–15% of these chemical compounds are discharged into waste streams by the textile industry. Some dyestuffs, among them methylene blue, are not strongly hazardous, but an acute exposure could make them harmful to fish and other aquatic organisms [1]. Furthermore, their presence in aquatic systems, even at low concentrations, is highly visible, reduces light penetration and has a derogatory effect on photosynthesis [2]. Therefore, decolourisation of dye-containing effluent is becoming an obligation both environmentally and for water re-use.

Previously, several research works had been performed to search for efficient and low-cost materials to remove methylene blue and other basic dyes from aqueous solution, including rice husk [3], beech sawdust [4], agro-industry wastes [5] and activated carbon from date pits [6].

The main focus of this study was to evaluate the biosorption aptitude of a novel, low cost, and renewable biomass, *Posidonia oceanica* fibres for the removal of methylene blue as a model compound for basic dyes. The effects of pH, contact time, initial dye concentration and biomass dosage on the biosorption capacity were investigated. Moreover, kinetic and equilibrium models were used to fit experimental data.

2. Materials and methods

2.1. Biomass and dye solution preparation

The seagrass, *P. oceanica,* is an endemic marine magnoliophyta present in the Mediterranean Sea. The adsorbant used in this study was the fibrous basal part of the leafs, namely leaf sheaths. This biomass was collected from Chott-Meriam 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

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Nomenclature

A_R	Redlich–Peterson isotherm constant $(\text{L/mg})^\beta$
C_e	equilibrium concentration of methylene blue in the solution (mg/L)
C_0	initial concentration of methylene blue in the solution (mg/L)
k	equilibrium rate constant for the reversible kinetic model $(=k_1/k_{-1})$
k_I	rate constant of first-order kinetic model (min^{-1})
k_{II}	rate constant of pseudo-second-order kinetic model (g/mg min)
k_1	forward reaction rate constant
k_{-1}	reverse reaction rate constant
K_F	Freundlich isotherm constant $[(\text{mg/g}) (\text{L/mg})^{(1-n/n)}]$
K_L	Langmuir isotherm constant (L/mg)
K_R	Redlich–Peterson isotherm constant (L/g)
M	mass of *P. oceanica* fibres (g)
n	Freundlich exponent related to adsorption intensity
q_e	calculated amount of methylene blue adsorbed per unit of biomass (mg/g)
Q	amount of methylene blue adsorbed per unit of biomass at time t (mg/g)
Q_e	experimental amount of methylene blue adsorbed per unit of biomass (mg/g)
Q^o	Langmuir monolayer adsorption capacity (mg/g)
R^2	squared regression correlation coefficient
t	time (min)
V	solution volume (L)
X	methylene blue concentration in the solid phase

Greek letter

β	Redlich–Peterson exponent

48 h to a constant weight. The dried biomass was stored in the desiccator for further use.

Methylene blue has been used in this study as a model molecule for basic dyes. Stock solutions were prepared by dissolving accurately weighed samples of dye in distilled water to give a concentration of 1000 mg/L and diluting when necessary. Initial pH was adjusted by adding dilute solutions of HCl or NaOH.

2.2. Batch adsorption experiments

Adsorption experiments were carried out by shaking 0.5 g of *P. oceanica* fibres with 50 mL of dye solution (i.e. 10 g/L) for the desired dye concentration and pH. Studies were conducted at $30 \pm 2\,^\circ\text{C}$ using a thermo-regulated water bath operating at 100 rpm. Methylene blue residual concentration was estimated using the spectrophotometric technique at the wavelength of 665 nm. The samples were taken from the shaker at predetermined time intervals for kinetics and at equilibrium time for

isotherms. The dye solution was centrifuged at 5000 rpm for 2 min and then analyzed [7]. To calculate the dye removal, biosorption capacity at equilibrium time (Q_e) or biosorption removal efficiency, will be determined respectively according to the following equations:

$$Q_e = [(C_0 - C_e) \times V/M]\,(\text{mg/g}) \tag{1}$$

$$\text{biosorption removal efficiency} = (C_0 - C_e) \times 100/C_0\,(\%). \tag{2}$$

3. Results and discussions

3.1. Influence of pH

The aqueous solution pH exerts profound influence on the sorptive uptake of dyes presumably due to its impact on both the surface binding-sites of the biosorbent and the ionisation process of the dye molecule. In the present biosorption system, the effect of pH was investigated for values between 3 and 9 and the result was presented in Fig. 1. As shown, the equilibrium sorption capacity was minimum at pH 2 (4.59 mg/g) and increased up to 5, then remained nearly constant (4.91 mg/g) over the initial pH ranges of 6–9.

At lower pH, the surface charge may get positively charged, thus making (H^+) ions compete effectively with dye cations causing a decrease in the amount of dye adsorbed. At higher pH the fibres biopolymers, mainly lignin and cellulose chains, may get negatively charged, which enhances the positively charged dye cations through electrostatic forces of attraction.

3.2. Influence of initial dye concentration and contact time

The relationship between contact time and methylene blue biosorption onto raw *P. oceanica* fibres at different initial dye concentrations is presented in Fig. 2. The results show that the equilibrium states were attained at almost 10 min within the experimental concentration range. Furthermore, raising the dye concentration from 10 to 50 mg/L allows the fibres to increase their biosorption capacities from 0.42 to 4.64 mg/g, respectively
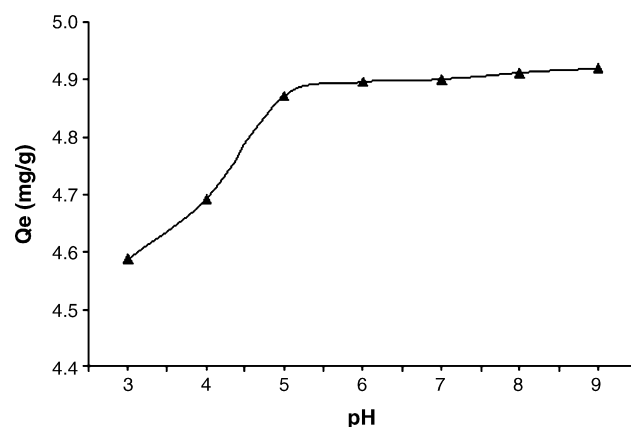

Fig. 1. Effect of pH on the biosorption capacity of methylene blue (biomass concentration = 10 g/L, dye concentration = 50 mg/L, temperature = $30 \pm 2\,^\circ\text{C}$).
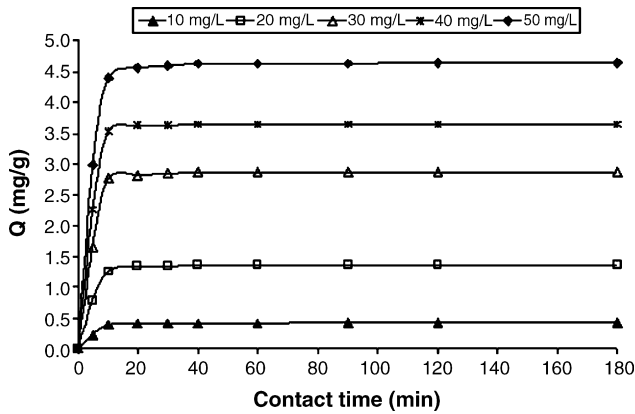
Fig. 2. Effect of contact time on biosorption amount at different initial dye concentration (biomass concentration = 10 g/L, initial solution pH 6, temperature = 30 ± 2 °C).
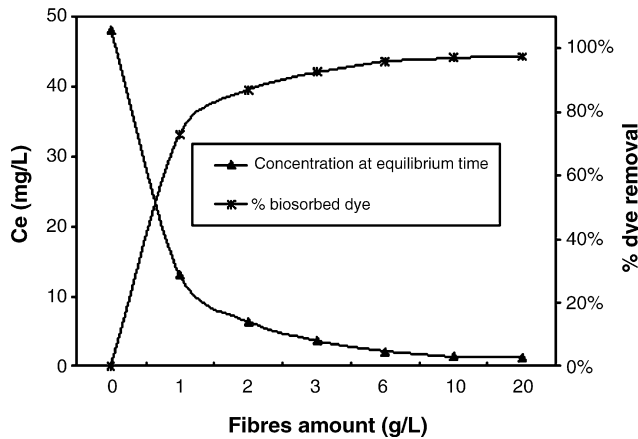

Fig. 3. Effect of biosorbent dosage on the removal of methylene blue (initial dye concentration = 50 mg/L, initial solution pH 6, temperature = 30 ± 2 °C).

at a temperature of 30 ± 2 °C. Hence, to ensure equilibrium, the isotherms experiments were left for 3 h. A similar trend was also observed for methylene blue adsorption onto giant duckweed [8] and sewage sludge [9].

3.3. Influence of biosorbent amount

The effect of biosorbent dosage on the removal of methylene blue was investigated at 50 mg/L dye concentration. A range of 0.05–1.0 g of *P. oceanica* fibres were mixed with 50 mL of the dye solution (i.e. 1–20 g/L). The result, displayed in Fig. 3, shows that an increase in the biomass quantity causes a decrease in the residual methylene blue concentration at equilibrium time and consequently an increase in the biosorption removal efficiency. Indeed, the biosorption removal efficiency
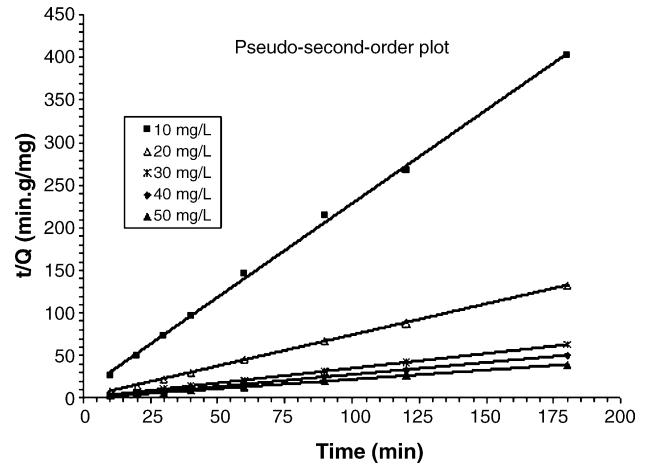

Fig. 4. Pseudo-second-order kinetic plots at different initial dye concentration (biomass concentration = 10 g/L, solution pH 6, temperature = 30 ± 2 °C).

values increased from 73% to 97%, as the biomass dose was increased from 1 to 20 g/L. Such a trend is mainly attributed to an increase in the sorptive surface area and the availability of more adsorption sites. Quite similar tendency was reported for methylene blue adsorption onto fly ash [10].

3.4. Adsorption kinetic modelling

In order to predict the mechanism involved during of the present biosorption process, three kinetic models were used to fit the experimental data, namely, Irreversible first-order, reversible first-order and pseudo-second-order models. The best-fit model was selected based on both linear regression correlation coefficient (R^2) and the calculated q_e values. The mathematical equations of these models are illustrated in Table 1.

In most studied adsorption systems, the irreversible first-order equation of Lagergren does not fit well over the entire adsorption period and is generally applicable over the first 20–30 min of the sorption process [11–13]. The reversible first-order model is derived on the assumption that the rate of the forward reaction (adsorption) and reverse rate (desorption) constants are equal to the equilibrium reaction rate constant. Thus, the net rate of reaction can be expressed in terms of the forward rate constants k_1 and the equilibrium rate constant k. The pseudo-second-order model is also based on the biosorption capacity of the solid phase but contrary to the previous models it predicts the "chemisorption" behaviour over the whole time adsorption [14].

The plots $\log(Q_e - Q)$ versus t, $-\ln((C - C_e)/(C_0 - C_e))$ versus t and t/Q versus t (Fig. 4) should give the kinetic parameters related to irreversible first-order, reversible first-order and

Table 1
Mathematical expressions of the three used kinetic models

Kinetic model	Equation		Integrated form	
Irreversible first-order	$dq/dt = k_I(Q_e - Q)$	(3)	$\log(Q_e - Q) = \log q_e - (k_I/2.303)t$	(4)
Reversible first-order	$dc/dt = k_1 C - k_{-1} X$	(5)	$-\ln[(C - C_e)/(C_0 - C_e)] = kt$	(6)
Pseudo-second-order	$dq/dt = k_{II}(Q_e - Q)^2$	(7)	$t/Q = 1/k_{II} q_e^2 + t/q_e$	(8)

Table 2
Kinetic rate constants related to the biosorption of methylene blue onto *P. oceanica* fibres

	Initial methylene blue concentration (mg/L)				
	10	20	30	40	50
Irreversible first-order					
k_I	0.034	0.038	0.042	0.041	0.044
Calculated q_{eI}	0.461	0.342	0.452	0.406	0.564
R^2	0.826	0.715	0.741	0.686	0.771
Reversible first-order					
k	4.450	13.572	28.650	36.472	46.372
k_1	0.019	0.040	0.029	0.045	0.048
k_{-1}	0.004	0.003	0.001	0.001	0.001
R^2	0.800	0.749	0.607	0.772	0.807
Pseudo-second-order					
k_{II}	0.035	0.296	0.400	0.645	0.377
Calculated q_{eII}	0.454	1.362	2.874	3.654	4.649
R^2	0.998	1.000	1.000	1.000	1.000
Experimental Q_e	0.448	1.358	2.868	3.648	4.638

pseudo-second-order models, respectively. The results, given in Table 2, show that both irreversible and reversible first-order models data do not fall on straight lines indicating that these models were less appropriate. Besides, the calculated q_e determined from the models differs substantially from those determined experimentally, suggesting that the studied adsorption phenomenon is not a first-order reaction. In the other hand, the correlation coefficients for the peudo-second-order kinetic model are nearly equal to 1 for all investigated initial dye concentrations and the predicted values of q_e are acceptable compared to the experimental ones. This suggests that the biosorption of methylene blue onto *P. oceanica* fibres is presumably a chemisorption process involving exchange or sharing of electrons mainly between dye cations and functional groups (mainly hydroxyl and carboxyl groups) of the biomass cells [3,15,16].

3.5. Adsorption isotherm modelling

In order to optimize the design of a sorption system to remove dyes from aqueous solutions, it is important to establish the most appropriate correlation for the equilibrium curves. The isotherms data were analyzed using three of the most commonly used equilibrium models, Langmuir [17], Freundlich [18] and Redlich–Peterson [19] isotherm models (Fig. 5). The mathematical expressions are given by Eqs. (9)–(11), respectively, as follows:

$$\text{Langmuir}: \quad Q_e = (Q^o K_L C_e)/(1 + K_L C_e) \tag{9}$$

$$\text{Freundlich}: \quad Q_e = K_F C_e^{1/n} \tag{10}$$

$$\text{Redlich–Peterson}: \quad Q_e = (A_R C_e)/(1 + K_R C_e^{\beta}) \tag{11}$$

The calculated isotherm constants at 30 °C, given in Table 3, were evaluated from the linear plots represented by Eqs. (12)–(14), respectively for Langmuir, Freundlich and
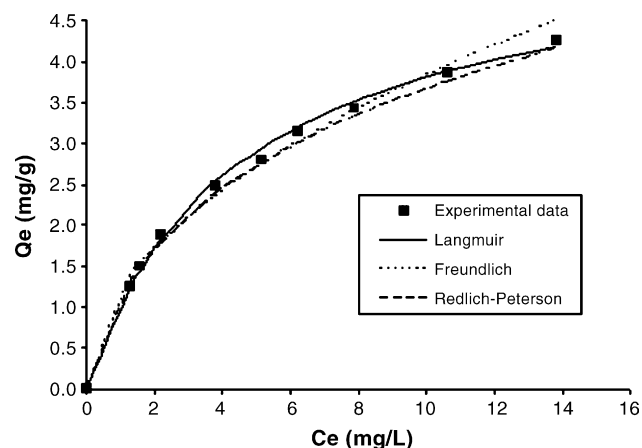
Fig. 5. Fit of the Langmuir, Freundlich and Redlich–Peterson isotherms for methylene blue biosorption (biomass concentration = 10 g/L, solution pH 6, temperature = 30 ± 2 °C).

Redlich–Peterson.

$$C_e/Q_e = 1/K_L Q^o + 1/(C_e Q^o) \tag{12}$$

$$\log Q_e = \log K_F + 1/n(\log C_e) \tag{13}$$

$$\ln[(A_R C_e/Q_e) - 1] = \beta \ln(C_e) + \ln(K_R) \tag{14}$$

The best-fit equilibrium model was determined based on the linear squared regression correlation coefficient R^2. From Table 3, it was observed that the equilibrium sorption data were very well represented by both Langmuir and Redlich–Peterson isotherms followed by the Freundlich model with high correlation coefficients of 0.997, 0.996 and 0.985, respectively. Therefore, the very high R^2 values (>0.99) showed that in addition to Langmuir isotherm, the sorption process can also be represented by the Redlich–Peterson model. Indeed, the value of β (0.74) is closer to unity than 0, which means that the isotherm is more approaching the Langmuir than the Freundlich isotherm. Hence, the best fit of equilibrium data in both Langmuir and Redlich–Peterson isotherm expressions confirm the monolayer coverage process of

Table 3
Adsorption isotherm constants for methylene blue biosorption onto *P. oceanica* fibres[a]

Langmuir	
Q^o	5.56
K_L	0.22
R^2	0.997
Freundlich	
K_F	1.20
n	1.98
R^2	0.985
Redlich–Peterson	
A_R	1.91
K_R	0.77
β	0.74
R^2	0.996

[a] The units of the isotherm constants are mentioned in the nomenclature section.

Table 4
Comparison of adsorption isotherm constants between *P. oceanica* fibres and other sorbent mentioned in the related literature

Sorbents	Langmuir constants			Freundlich constants			References
	Q^o	K_L	R^2	K_F	n	R^2	
Raw *P. oceanica* fibres	5.56	0.22	0.997	1.20	1.98	0.985	This study
Rice husk	40.5	0.13	0.984	8.62	2.76	0.968	[3]
Raw beech sawdust	9.78	1.60	0.976	6.05	1.59	0.987	[4]
Fly ash	5.57	0.54	0.996	4.38	18.2	0.882	[10]
Neem leaf powder	3.76	0.18	0.960	2.42	0.56	0.990	[22]
Coir pith activated carbon	5.78	0.93	0.973	0.85	0.71	0.867	[23]
Guava seeds activated carbon	6.50	0.67	0.508	5.26	1.05	0.988	[24]

methylene blue onto *P. oceanica* fibres. Furthermore, the value of Freundlich exponent $n = 1.98$ in the range of 1–10, indicates a favourable adsorption [20]. Also, high adsorption capacity indicates the strong electrostatic force of attraction between dye molecules and biosorbent binding-sites [21].

On the other hand, in order to situate our novel biosorbent among those used to remove methylene blue from aqueous solutions, a comparison based on both isotherms constants, Langmuir saturation capacity Q^o and Freundlich adsorption intensity n was made. The results, illustrated in Table 4, had shown that the *P. oceanica* fibres could be considered as a promising material to remove basic dyes even when compared with activated carbons prepared from biological materials [23,24]. Therefore, raw *P. oceanica* fibres seem to be competitive to other methylene blue sorbents and some optimizing treatments on this biomass might be very interesting for further studies.

4. Conclusion

Methylene blue removal from aqueous solution through biosorption onto raw *P. oceanica* fibres was investigated in the present study. The biosorption capacity was estimated as a function of initial pH, contact time at different initial dye concentrations and biosorbent dosage. The kinetic modelling study has shown that the experimental data were found to follow the pseudo-second-order model suggesting a chemisorption process. The equilibrium sorption phenomena were found to be well described by both Langmuir and Redlich–Peterson models. The comparison of the biosorption behaviour between *P. oceanica* fibres and other adsorbent materials indicated that the experimented Mediterranean biomass, showed a good biosorption capacity toward the basic dye. Besides, chemical treatments of the biomass and immobilization of some fungi or bacteria on its surface could be a promising research work to more enhance the dye removal ability of this seagrass. Studies in this subject are in progress.

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