ELSEVIER

Journal of Hazardous Materials B139 (2007) 280–285

Journal of Hazardous Materials

www.elsevier.com/locate/jhazmat

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

Mohamed Chaker Ncibi [a,b,*], Borhane Mahjoub [a,b], Mongi Seffen [b]

[a] *Laboratory of Chemistry, Horticultural High School, B.P. 47 Chott Meriem, Sousse 4042, Tunisia*
[b] *Applied Chemistry and Environment Research Unit, EPAM Sousse 4000, Tunisia*

Received 2 April 2006; received in revised form 8 June 2006; accepted 10 June 2006
Available online 15 June 2006

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.

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

* Corresponding author. Tel.: +216 73348546; fax: +216 73348691.
E-mail address: ncibi_mc@yahoo.com (M.C. Ncibi).

0304-3894/$ – see front matter © 2006 Elsevier B.V. All rights reserved.
doi:10.1016/j.jhazmat.2006.06.029

Nomenclature

A_R	Redlich–Peterson isotherm constant $(L/mg)^{\beta}$
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 $[(mg/g)\,(L/mg)^{(1-n/n)}]$
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 ± 2 °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:

$$Q_e = [(C_0 - C_e) \times V/M]\,(mg/g) \quad (1)$$

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

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

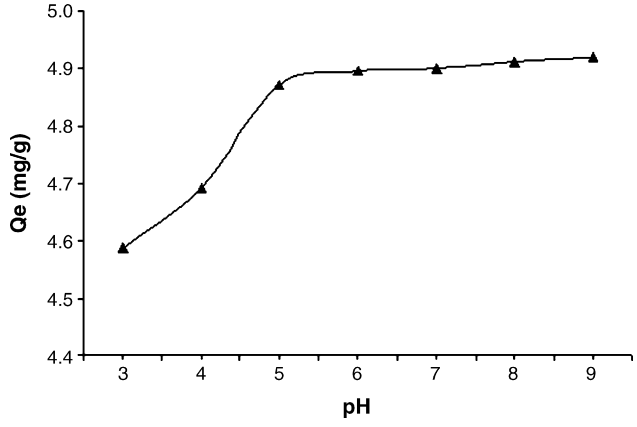

Fig. 1. Effect of pH on the biosorption capacity of methylene blue (biomass concentration = 10 g/L, dye concentration = 50 mg/L, temperature = 30 ± 2 °C).