Journal of Saudi Chemical Society (2017) **21**, S1–S6

King Saud University

Journal of Saudi Chemical Society

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ORIGINAL ARTICLE

Biosorption of reactive red 2 using positively charged *Metapenaeus monoceros* shells

E. Thiyagarajan, P. Saravanan, S. Shiyamala devi, P. Saranya, N. Nagendra Gandhi, S. Renganathan *

Department of Chemical Engineering, A. C. College of Technology, Anna University, Chennai 600 025, India

Received 17 February 2012; accepted 18 May 2013
Available online 31 May 2013

KEYWORDS

Reactive red 2;
Biosorption;
Biopolymer;
Metapenaeus monoceros shell;
Equilibrium kinetics

Abstract *Metapenaeus monoceros* shell used for the removal of reactive red 2 from an aqueous solution was studied by batch biosorption system. The maximum dye uptake capacity was examined at biosorbent dosage, different pH, contact time and initial dye concentration. From the study the maximum dye uptake capacity was obtained as 166 mg/g at an optimal condition of 0.1 g/L of biosorbent dosage, pH value of 2 and initial dye concentration of 100 mg/L. When compared to the Langmuir isotherm model, the equilibrium data were fitted well with the Freundlich isotherm model. The kinetic data were fitted well with the pseudo second order rate equation when compared to the pseudo first order rate equation. The biosorbent characteristics were observed by SEM and FTIR analyses.

1. Introduction

Due to the increase in industrial activity, the discharge of large quantities of organic pollutants into the receiving waters has been causing pollution. Synthetic dyes are a group of organic pollutants that are extensively used in textile industries. The colored effluents damage the aesthetic quality of water and reduce light penetration and photosynthesis and also some of the dyes are toxic or mutagenic, carcinogenic and allergenic. Hence decolorization of the dye-bearing effluents is of great importance (Chia-Pin and Foster, 2003). The traditional physical or chemical decolorization methods including flocculation using chemicals, coagulation using chemicals, irradiation, ion exchange, precipitation using chemicals, ozonation and adsorption using activated carbon or a combination of these methods have been used for dye removal from wastewaters (Churchley, 1994).

However application of these methods is restricted due to some limitations such as cost involved for separation, development of hazardous derivative, high energy requirement and limited adaptability to a wide range of effluents. The use of biological materials as sorbents for the treatment of colored effluents appeared as a potential alternative process to the conventional method. Currently, numerous studies have focused on the dye biosorption, in the decolorization process (Chen et al., 2003). Compounds such as chitin, chitosan, protein and other biopolymeric components present on the biological material provide active binding sites for dye molecules and

* Corresponding author. Mobile: +91 9941613532.
E-mail address: rengsah@rediffmail.com (S. Renganathan).
Peer review under responsibility of King Saud University.

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http://dx.doi.org/10.1016/j.jscs.2013.05.004

biosorption processes based on interactions between the dyes and binding sites in a manner of surface biosorption, ion exchange operation, complexation, chelation using chemicals and microprecipitation using precipitating agent. Currently research is focused on finding optimal biopolymeric biosorbent and reaction conditions in order to develop optimal processes enabling decolorization of large volumes of waters (Pairat, 2002).

The sorption of dyes using biopolymers such as chitin and chitosan is one of the reported emerging biosorption methods for the removal of dyes, even at low concentration. Chitin and chitosan are easily obtainable, renewable and eco-friendly degradable biological resources (Chia-Pin and Foster, 2003). Chitin is a naturally available mucopolysaccharide. It has originated from various natural sources such as insects, crustaceans, annelids, molluscs and fungi. Usually, chitin and chitosan are economically obtained from crustaceans (crab, krill, and crayfish) because a huge quantity of crustacean's exoskeleton is obtainable as a derivative of food processing industries. The worldwide yearly crustacean shell generation has been projected to be 1.2×10^6 tons, and the recovery of chitin and protein from this waste is an additional income (Aksu and Tezer, 2005). From this literature survey the chitosan-based biosorbents are considered to be an efficient material and have an extremely high affinity for many classes of dyes. They are also adaptable materials. This flexibility permits the sorbent to be used in various forms such as, flake-types, gels, bead-types and fibers (Mishra and Tripathy, 1993). The conventional and salable source of chitin and chitosan is from shells of crab, *Metapenaeus monoceros* and krill that are wastes from the processing of marine food products. This product is produced from the chitin by chemical treatment to remove N-acetyl groups as acetic acid (Roussy and Viraraghavan, 2001). Chitosan is a polymer compound with multiple glucosamine sugar groups. It is a cationic (positively charged) polymer.

2. Materials and methods

2.1. Dye type and procurement

Reactive red 2 dye was obtained from the Department of Textile Technology, Anna University. These dyes are based on Dichlorotriazene. They are extremely reactive, in need of mild fixing conditions and are mainly used for exhaust dyeing. This dye of analytical grade and their molecular structure is shown in Fig. 1.

2.2. Preparation of Metapenaeus monoceros shell powder and dye solution

M. monoceros shells obtained from the local fish market were washed with deionized water until free of dirt particles. The washed biosorbent was dried in an oven at 70 °C for 48 h, crushed with ball mill and sieved to obtain particle size varying from 0.212 to 0.180 mm and then soaked in hexane for the removal of carotene present in the *M. monoceros* shell. 1 g of dye was dissolved in 100 ml of distilled water as the stock dye solution (10,000 mg/L). The experimental dye solution concentrations varying from 20 to 100 mg/L were obtained by diluting the dye stock solution.

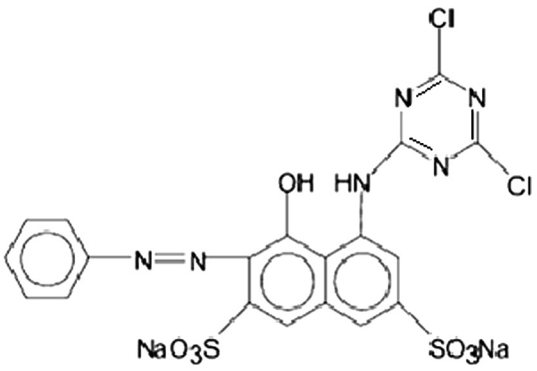

Figure 1 Chemical structure of reactive red 2.

2.3. Study of biosorbent dosage

100 mL of reactive red-2 solution of 30 mg/L concentration was equally dispersed into five conical flasks and added with different sorbent dosages (0.1–0.6 g/L) of biosorbent. These flasks were kept in a rotary shaker at 180 rpm. Samples were withdrawn for every 15 min and the aliquots were centrifuged at 12,000 rpm for 10 min. The supernatant was separated and the absorbance was determined using UV-spectrophotometer (Hitachi, U3210, Japan) at a maximum wavelength of 540 nm.

2.4. Study of pH

The initial pH value of the solution is an important factor which must be considered during sorption research work (Aksu and Tezer, 2005). The influence of pH on the removal of dye was analyzed over the pH range of 2–7. In this study 100 mL of dye solution of 30 mg/L concentration was taken and adjusted to different pH (2–7). The pH was adjusted using diluted NaOH and HCl solutions. Dried biomass of 0.1 g was added to the dye solution. The samples were withdrawn for every 15 min and centrifuged for separation at 12,000 rpm for 10 min. Using UV-spectrophotometer, the absorbance of the supernatant solution was analyzed.

2.5. Study of initial dye concentration

The initial dye concentration varying from 20 to 100 mg/L was used for finding out the dye uptake capacity. 0.1 g of *M. monoceros* shell biomass particles was added in 100 mL of dye solution with different concentrations at optimum pH and kept in rotary shaker at 180 rpm. Samples were withdrawn for different time intervals (0, 15, 30, 60, 90, 120, 150, 180 and 240 min) and then the uptake capacity was analyzed.

3. Results and discussion

3.1. Effect of biosorbent dosage

The sorbent dosage was varied from 0.1 to 0.6 g in a fixed volume of 100 mL with 30 mg/L initial concentration of dye. The equilibrium dye uptake capacity for each biosorbent dosage is shown in Fig. 2. From Fig. 2 the equilibrium dye uptake decreases with an increase in biosorbent dosage. This may be

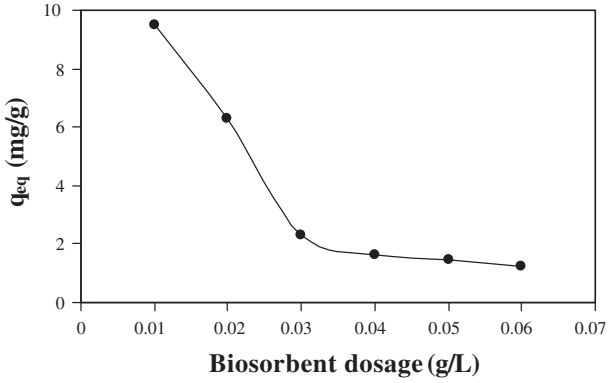

Figure 2 Effect of biosorbent dosage on the equilibrium dye uptake capacity of *Metapenaeus monoceros* shells biomass for reactive red 2 dye (initial dye concentration = 30 mg/L, temperature = 30 °C, agitation rate = 180 rpm).

due to a decrease in solute transfer rate onto the adsorbent surface. In addition the amount of adsorbent gets split with increasing adsorbent dosage (Renganathan et al., 2008). A similar type of result was previously reported by Kalpana et al. (2011) for the removal of Basic Violet 1 using *Calotropis gigantea* biomass.

3.2. Effect of pH

The influence of pH for the maximum dye uptake capacity was observed for the pH range 2–7. The effect of pH on biosorption using *M. monoceros* shell biomass for reactive red 2 dye is shown in Fig. 3. The maximum dye uptake capacity was found to be lower pH value of 2. This may be due to electrostatic attraction between positively charged biosorbent and negatively charged dye anion (Renganathan et al., 2008). A similar trend was previously reported by Naveen et al. (2011) for the removal of reactive red 120 using *Hydrilla verticillata*.

3.3. Effect of initial dye concentration

Effect of initial dye concentration on biosorption of reactive red 2 using *M. monoceros* shell biomass is shown in Fig. 4.

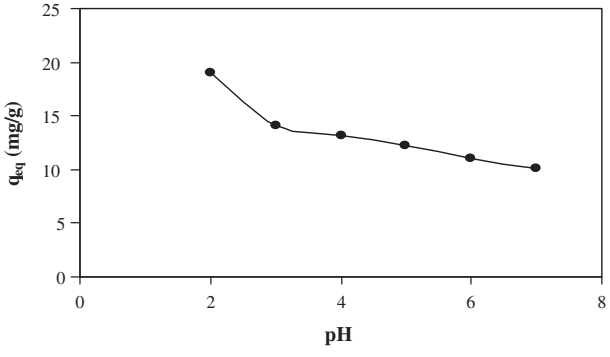

Figure 3 Effect of pH on the equilibrium dye uptake capacity of *Metapenaeus monoceros* shells biomass for reactive red 2 dye (initial dye concentration = 30 mg/L, temperature = 30 °C, agitation rate = 180 rpm, sorbent dosage = 0.1 g/L).

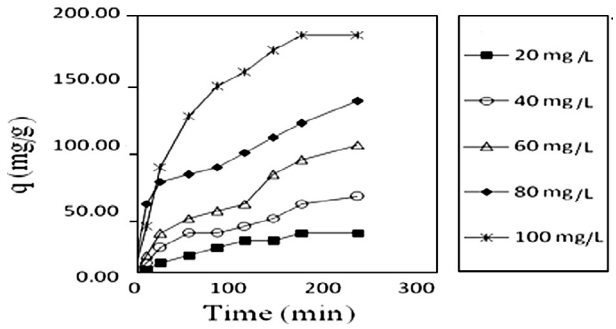

Figure 4 Effect of initial dye concentration on the uptake capacity of *Metapenaeus monoceros* shells biomass for reactive red 2 (temperature = 30 °C, agitation rate = 180 rpm, sorbent dosage = 0.1 g /L, pH = 2).

From Fig. 4 the dye uptake capacity was found to increase with an increase in initial dye concentration. This may be due to concentration gradient acting as a driving force for binding of dye onto biosorbent (Renganathan et al., 2008). The maximum dye uptake capacity was found to be higher in dye concentration. The maximum uptake capacity for the removal of reactive red 2 *Nymphaea rubra* was previously reported as 66 mg/g (Renganathan et al., 2009). However in the present study the maximum uptake capacity was found to be 303 mg/g. *M. monoceros* shell biomass is comparable with other low cost biosorbents.

3.4. Equilibrium modeling

Analysis of the result obtained from the equilibrium isotherm studies is fundamental to evaluate the affinity of a sorbent for a particular sorbate. Equilibrium studies were described by a sorption isotherm characterized by certain constants whose values expressed the surface properties and affinity of the sorbent. The monolayer coverage of the sorbate on a sorbent surface at constant temperature is represented by the Langmuir isotherm. The Langmuir isotherm expression is presented by,

$$q_{eq} = \frac{Q^{\circ} b C_{eq}}{1 + b C_{eq}} \quad (1)$$

where q_{eq} (mg/g) and C_{eq} (mg/L) are the quantity of dye adsorbed per unit weight of biosorbent and unadsorbed dye concentration in solution at equilibrium, respectively. Q° (mg/g) is the maximum quantity of dye adsorbed per unit weight of biosorbent to form a complete monolayer on the surface and b (L/mg) is the constant related to the affinity of the binding spot (Low et al., 1995).

Freundlich adsorption isotherm equation explains about the adsorption onto a heterogeneous surface and is given by,

$$q_{eq} = K_F C_{eq}^{1/n} \quad (2)$$

where K_F and n are Freundlich adsorption isotherm constants, receivable from the plots of $\ln q_{eq}$ versus $\ln c_{eq.}$ K_F and n indicate adsorption capacity and adsorption intensity, respectively. From (Table 1), it was observed that the Freundlich isotherm model exhibited a better fit to the equilibrium data when compared to the Langmuir isotherm model analyzed. The best fit of the model for equilibrium data was determined based on

Table 1 Langmuir and Freundlich isotherm constants and correlation coefficients for the sorption of reactive red 2 using *Metapenaeus monoceros* shell biomass.

Parameters	Isotherm constant values for the biosorption using *Metapenaeus monoceros shell* biomass
Langmuir adsorption isotherm	
$Q°$ (mg/g)	303.03
b (L/mg)	0.1153
R^2	0.848
Freundlich adsorption isotherm	
K_F (mg/g)	69.3
n	1.95
R^2	0.961

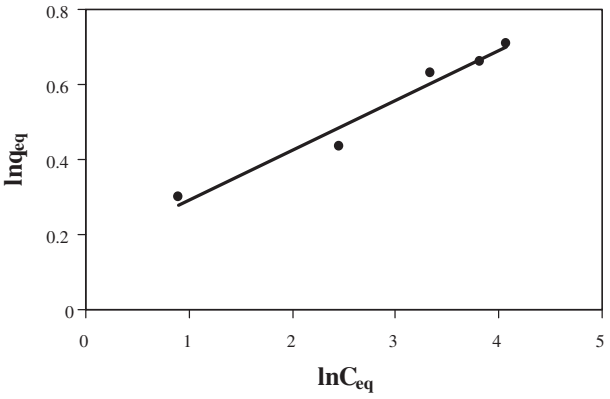

Figure 5 Plots for the Freundlich isotherm for the *Metapenaeus monoceros* shell biomass for reactive red-2 dye at different initial dye concentrations (sorbent Dosage = 0.1 g/L; pH = 2; temperature = 30 °C; agitation rate = 180 rpm).

the coefficient of determination R^2 and the plot is shown in (Fig. 5).

3.5. Kinetic modeling

The biosorption mechanism and potential rate controlling steps have been investigated by using the Pseudo first-order and Pseudo second-order kinetics models.

The pseudo first order rate expression of Lagergren, 1898 is

$$\frac{dq}{dt} = k_{1,ad}(q_{eq} - q) \tag{3}$$

where q is the amount of dye adsorbed on the biosorbent at time t and $k_{1,ad}$ (min^{-1}) is the rate constant for pseudo first order biosorption. The integral form of Eq. (3) is

$$\log(q_{eq} - q) = \log q_{eq} - \frac{k_{1,ad}}{2.303}t \tag{4}$$

A linear fit of log (q_{eq}–q) versus t shows the applicability of kinetics model. From the slope and intercept, the Pseudo first-order rate constant ($k_{1,ad}$) and q_{eq} values were determined and shown in (Table 2). The coefficient of determination of the pseudo first-order kinetic model obtained for the sorption of dye using *M. monoceros* shell biomass was determined from the plot.

Expression for the pseudo second order kinetic model (Ho and McKay, 1999) is

$$\frac{dq}{dt} = k_{2,ad}(q_{eq} - q)^2 \tag{5}$$

where $k_{2,ad}$ (g/mg min) is the rate constant of the Pseudo second-order kinetic model expression. The integrated linear form of expression (5) is

$$\frac{t}{q} = \frac{1}{k_{2,ad}q_{eq^2}}\frac{1}{q_{eq}}t \tag{6}$$

If the experiment data fit the plot of t/q versus t as linear relationship, the pseudo second-order rate kinetic model is valid. From Eq. (6), t/q was plotted against t for different initial dye concentrations. The pseudo second order biosorption rate constant ($k_{2,ad}$) and q_{eq} values were determined from the slope and intercept of the plot.

The kinetic data were analyzed using linearized form of the Pseudo second-order kinetic model at different initial dye concentrations. The equilibrium dye uptake capacity was found to increase with an increase in initial dye concentration. The q_{eq} calculated values were found to be very closer to q_{eq} experimental values in the case of second order kinetics when compared to first order kinetics. From the analysis, it was observed that the kinetic data fit very well with the Pseudo second-order rate equation when compared to Pseudo first-order rate equation. In view of the values of coefficient of determination (R^2) in Table 2, the Pseudo second-order kinetics model exhibited better fit when compared to the Pseudo first-order kinetics model.

3.6. Fourier transform infrared analysis (FTIR)

The FTIR spectroscopic analysis is shown in Fig. 6. Fig. 6 showed a strong band at 3422 cm^{-1} and indicative of N-H of the primary amine groups (Renganathan et al., 2008). The

Table 2 The pseudo first-order and pseudo second-order rate constants, calculated and experimental q_{eq} values for the biosorption of for reactive red-2 dye using *Metapenaeus monoceros* shell biomass.

Concentration (mg/L)	Pseudo-first order			Pseudo-second order		
	K_{1ad} (min^{-1})	$q_{eq,cal}$ (mg/g)	R^2	K_{2ad} (g/mg min)	$q_{eq,cal}$ (mg/g)	R^2
20	2.303	87.4614	0.892	10.3	105	0.985
40	2.462	92.8016	0.931	28.7	112.85	0.979
60	2.641	97.8777	0.922	39.94	125.85	0.996
80	3.044	99.0881	0.93	56.63	146.66	0.988
100	3.21	102.055	0.926	72.51	166	0.999

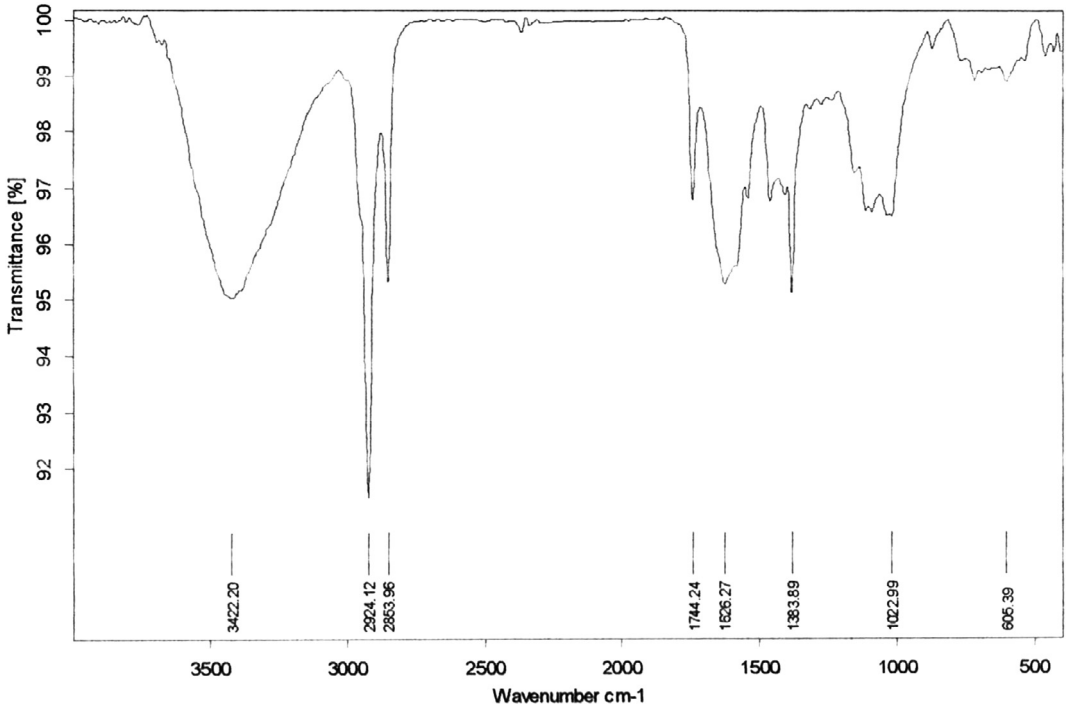

Figure 6 FTIR spectra of *Metapenaeus monoceros* shell biomass.

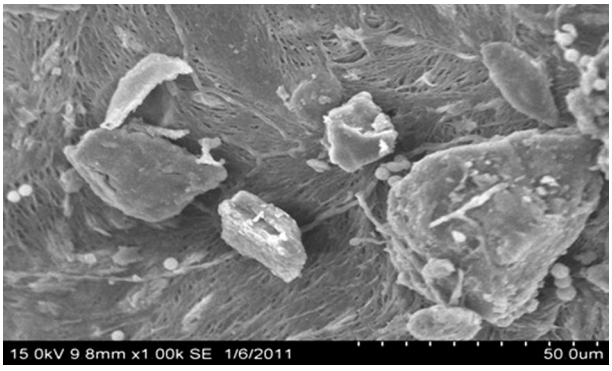

Figure 7 Scanning electron microscope (SEM) image of *Metapenaeus monoceros* shell biomass.

spectrum showed the peaks at 2927, 2853 cm^{-1}, representing the carboxyl groups. The carboxyl groups were likely to have been responsible for reactive red dye bonding. As the pH is less than five, the positive sites increase further. These positively charged groups of the biomass are likely to have more binding with negatively charged anionic dye molecule (Won et al., 2006; Low et al., 1995). So it is to be noted that the FTIR spectrum of the *M. monoceros* shell biomass supports the presence of the amino group.

3.7. SEM imaging

A scanning electron microscope (SEM) is a powerful microscope that uses electrons to form an image of *M. monoceros* shell biomass object. SEM provides a greater magnification of field. SEM is also used to analyze complex and three-dimensional objects to remain sharp. The surface morphology of the *M. monoceros* shell sorbent was exemplified by the scanning electron micrograph (Fig. 7). The fiber like structure on the surface of biomass was observed. This fiber surface property should be considered as a factor for providing an increase in the uptake capacity of dye solution (Renganathan et al., 2009).

4. Conclusion

Batch experiment was conducted to study the effect of sorbent dosage, initial dye solution pH and initial dye concentration. The equilibrium data were found to be fitted very well with the Freundlich adsorption isotherm model with higher coefficient of determination when compared to the Langmuir adsorption isotherm model. The kinetic data fit very well with the pseudo second-order rate equation when compared to pseudo first-order rate equation. The adsorbent prepared from *M. monoceros* shell was found to be one among the effective adsorbents for the removal of reactive dyes from waste water.

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