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ORIGINAL ARTICLE

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

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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

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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.

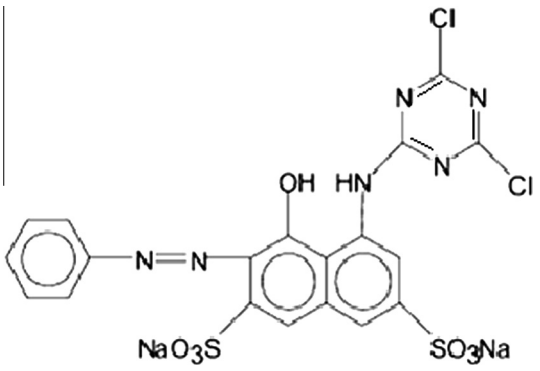

Figure 1 Chemical structure of reactive red 2.

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

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