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Shrimp shell as an efficient bioadsorbent for Acid Blue 25 dye removal from aqueous solution

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ABSTRACT

This study focused on kinetics, equilibrium and thermodynamics of Acid Blue 25 (AB25) dye biosorption from aqueous solution using the shell of *Penaeus indicus* shrimp as a biosorbent. Optimum sorption conditions were identified by varying solution pH, biomass dosage, initial dye concentration, contact time, salinity and ionic strength. Equilibrium data were well fitted by the Temkin, Freundlich and Langmuir isotherm models, while the pseudo-second order model best described kinetics. Thermodynamic data showed that AB25 dye biosorption onto shrimp shell was a feasible, spontaneous and exothermic one. The biosorption capacity increased with decreasing the sorbent particle size and with the addition of salts (NaCl, $MgSO_4$, KNO_3 and KH_2PO_4). The high sorption capacity of *P. indicus* shell obtained in this study suggests its use as an effective, low-cost biosorbent for the removal of acid dyes from wastewaters.

1. Introduction

Water is one of the prime necessities for sustenance of life, but the increased industrial and agricultural activities in the past has resulted in the pollution of natural water resources around the world. Today, one of the most important global concerns is to save the planet and to make the future of mankind safe by saving natural water resources [1].

Dyes, which are responsible for generating colored wastewater, are considered the most undesirable pollutants in addition to bases, acids, toxic inorganic and organic dissolved solids [2]. Dyes are synthetic aromatic water-soluble dispersible organic colorants, which are widely used in various industries such as the textile, tannery, food, paper and pulp, printing, carpet and mineral processing ones. Wastewaters containing dye molecules are difficult to treat, since the dyes are recalcitrant pollutants, resistant to aerobic digestion, and stable when exposed to oxidizing agents [3]. The release of dye effluents into natural water resources might have a significant environmental impact on aquatic lives. Preventing the sunlight penetration into the stream, they are in fact able to reduce both photosynthetic activity and dissolution of oxygen. Some dyes can also cause cancer and gene mutation [4].

Coagulation, flocculation, ion exchange, membrane separation and oxidation processes have been widely used to decolorize wastewaters. In general, physical and chemical methods for remediation of colored effluents are often very expensive and do not always effective [5]. Therefore, the development of new economically acceptable and environmentally friendly decolorization methods is of great industrial concern.

Among several dye removal techniques, adsorption is an efficient one to remove different kinds of dyes from water and wastewater. This process is simple to design, easy to operate, cost effective, eco-friendly and insensitive to toxic substances, and usually utilizes low-cost adsorbents such as fly ash, bottom ash, zeolite, rice hull, peanut hull, orange peel and bacterial cells.

Much attention has recently been paid in seeking cheap, locally available and effective biosorbent materials such as biopolymers [6], which can be obtained in large quantities and do not have any environmental impact. Furthermore, a major point is that natural polymers are reproducible and inexhaustible materials. Special attention has been given to natural amino polymers such as chitin and chitosan. Chitin the second-most abundant polysaccharide

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after cellulose in nature [7], having high adsorption capacity associated with the presence of –OH and *N*-acetyl groups [8].

The chromophores in anionic and non-ionic dyes mostly consist of anthraquinone or azo groups. Due to fused aromatic rings, anthraquinone-based dyes are particularly resistant to degradation, and their persistence in wastewaters is growing at the present time. Acid Blue 25 (AB25) is an anthraquinone dye that is widely used in wool, nylon, silk, paper, ink, detergent, wood, fur, cosmetics and biological stain [9].

The aim of this study was to investigate the use of *Penaeus indicus* chitin shell, obtained from shrimp processing waste, as biosorbent for the removal of AB25 dye from aqueous solution. To this purpose, the effects of various parameters such as solution pH, biomass dosage, initial dye concentration, contact time, temperature, salinity and ionic strength on the uptake capacity of this biosorbent were investigated in terms of equilibrium isotherms, kinetics and thermodynamics.

2. Experimental

2.1. Dye solution

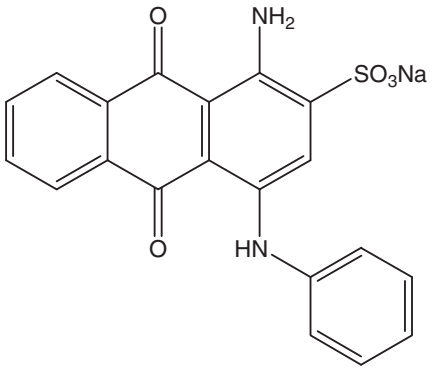
The target dye used in the present study as a sorbate was Acid Blue 25 (purity >95%), an anthraquinone compound with molecular formula $C_{20}H_{13}N_2NaO_5S$ and molecular weight of 416.38 g/mol. It was provided as a dark blue powder by Alvan Sabet Corporation (Hamedan, Iran). Other characteristics of this dye are given in Table 1.

All the solutions were prepared by diluting repeatedly 1000 mg/L stock dye solution with distilled water. Standard curves with high correlation coefficients ($R^2 \geq 0.999$) were obtained measuring the absorbance of dye solutions by means of a UV/vis Spectrophotometer, model DR/4000 (Hach, Loveland, CO, USA).

2.2. Biosorbent preparation

The biosorbent was the raw chitin shell from the shrimp *P. indicus*, which was kindly provided by a sea food processing factory (Shilan Kish, Isfahan, Iran). Shells were separated from collected shrimp waste and subsequently washed with tap water several times to remove undesired particles. Washed shells were air dried for 48 h, ground in a laboratory blender and washed with distilled water to remove the remaining dust on the surface of particles. Subsequently they were dried at 70 °C for 48 h in an oven, model LDO-060E (Lab Tech, Petaluma, CA, USA), up to constant weight. Oven dried adsorbent grains were sieved through ASTM Standard sieves (53–106, 106–250 and 250–500 μm) to obtain uniform particle sizes. The powdered biosorbent was finally stored in an airtight container until use. No other chemical or physical treatments were used prior to biosorption experiments.

Table 1
General characteristics of Acid Blue 25 dye.

Chemical structure	
C.I. number	62065
C.I. name	Acid Blue 25
Class	Anthraquinone
Ionization	Acidic
λ_{max} (nm)	600

2.3. Batch experiments

Batch experiments were performed to determine the effects of various process parameters such as solution pH (2, 6.5 and 11), biosorbent dosage (0.1–0.4 g/L), initial dye concentration (50, 80 and 110 mg/L), contact time (0–60 min), temperature (283, 298 and 313 K), particle size (53–106, 106–250 and 250–500 μm), salinity (0, 0.5, 5, 10, 20 and 40 g/L) and different anions in different proportions on dye removal from aqueous solutions.

The effect of the solution pH on AB25 dye biosorption capacity was evaluated at three different pH values, namely 2, 6.5 and 11. Before experiments, the solution pH was measured by means of a pH meter and adjusted by the addition of 0.1 M HCl or 0.1 M NaOH solutions. Different biosorbent amounts in the range of 0.1–0.4 g/L were used to investigate the effect of adsorbent dosage. The effect of salinity on dye removal was investigated at different NaCl concentrations (0 to 40 g/L), while that of anions by adding 100 mg/L of KNO_3, $MgSO_4$ and KH_2PO_4 in single, binary and ternary systems. To determine the effect of biosorbent particle size on dye removal, experiments were conducted using three fractions of biosorbent sieved as earlier described. Mixtures were shaken using a platform shaker, model FSIM-SPO16 (Lab Tech, Petaluma, CA, USA) at 130 rpm and 298 K to reach equilibrium. The resulting solutions were filtered through 0.2 μm membrane filters (Orange Scientific, GyroDisc CA-PC, Braine-L'Alleud, Belgium) and analyzed quantitatively. The residual dye concentration was determined by means of the aforementioned UV/Vis spectrophotometer at the maximum absorption wavelength (λ_{max} = 600 nm) (Table 1).

The yield of AB25 dye removal (Y, %) was determined as the percentage of sorbate removed with respect to its initial amount:

$$Y(\%) = \left(\frac{c_i - c}{c_i}\right) \times 100 \quad (1)$$

where C_i and C are the concentrations of AB25 (mg/L) at the beginning of the run and that after a given time.

2.4. Biosorption equilibrium

Equilibrium experiments were carried out by using 0.1 g/L of raw *P. indicus* shell in 100 mL Erlenmeyer flasks containing 50 mL of dye solution with different initial concentrations (50–110 mg/L). Mixtures were shaken at 130 rpm at 298 K in the same shaker previously described for 60 min, which proved to be enough time to reach equilibrium.

The sorbent biosorption capacity at equilibrium, q_e (mg/g), was calculated as the difference between C_i and the AB25 dye concentration at equilibrium (C_e), both expressed in mg/L, according to the equation:

$$q_e = \frac{V(C_i - C_e)}{M} \quad (2)$$

where V is the volume of the solution (L) and M the mass of biosorbent (g).

The most common isotherm models were applied in the present study, namely the Temkin, Freundlich, Langmuir and Dubinin–Radushkevich ones.