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Removal of basic yellow dye from aqueous solution by sorption on green alga *Caulerpa scalpelliformis*

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Abstract

Dynamic batch experiments were carried out for the biosorption of basic yellow dye on to the green macroalgae *Caulerpa scalpelliformis*. The factors affecting the sorption process such as the initial concentration of the dye and pH of the solution, the adsorbent dosage and the time of contact were studied. The sorption kinetics followed pseudo-second order kinetic model. The *Caulerpa* species exhibited a maximum uptake of 27 mg of dye per gram of seaweed. The Boyd's plot confirmed the external mass transfer as the rate-limiting step. The average effective diffusion coefficient was found to be 2.47×10^{-4} cm^2/s. Sorption equilibrium studies demonstrated that the biosorption followed Freundlich isotherm model, which implies a heterogeneous sorption phenomenon. Various thermodynamic parameters such as enthalpy of sorption ΔH°, free energy change ΔG° and entropy ΔS° were estimated. The negative value of ΔH° and negative values of ΔG° show the sorption process is exothermic and spontaneous. The negative value of entropy ΔS° shows the decreased randomness at the solid–liquid interface during the sorption of dyes onto green seaweed.

Keywords: Basic yellow dye; Biosorption; Diffusion coefficient; Equilibrium isotherm; Green seaweed; Macroalgae

1. Introduction

Pollution control is one of the prime concerns of society today. Untreated or partially treated wastewaters and industrial effluents into natural ecosystems pose a serious problem to the environment. Among the industrial wastewaters, the removal of color from dye bearing effluents is one of the major problems due to the difficulty in treating such wastewaters by conventional treatment methods. This is because synthetic dyes have a complex aromatic molecular structure, which makes them more stable and difficult to biodegrade [1]. Although number of processes like flocculation, chemical coagulation, precipitation, ozonation and adsorption has been employed for the treatment of dye bearing wastewaters, they possess inherent limitations such as high cost, formation of hazardous by-products and intensive energy requirements [2]. Biological processes such as bioaccumulation and biodegradation have been proposed as having potential application in removal of dyes from dye bearing wastewater [3,4].

Biosorption passive uptake of pollutants from aqueous solutions by the use of non-growing or non-living microbial mass, thus allowing the recovery or environmentally acceptable disposal of the pollutants, could also be considered [5–8]. The main attractions of biosorption are high selectivity and efficiency, cost effectiveness and good removal performance. Raw materials, which are either abundant or wastes from other industrial operations, can be used as biosorbents, presenting performances often comparable with those of ion exchange resins. The use of dead cells in biosorption is most advantageous for wastewater treatment in that, the dead organisms are not affected by toxic wastes, do not require a continuous supply of nutrients and can be regenerated and reused for many cycles. Dead cells may be stored or used for extended periods at room temperature without putrefaction. Biological materials such as chitin, chitosan, peat, yeasts, fungi or bacterial biomass are used as chelating and complexing sorbents in order to concentrate and remove dyes from solutions [9–14]. However, these low cost adsorbents have generally low adsorption capacities, leading to utilization of large amounts of adsorbents.

Algae have been found to be potential, suitable biosorbent because of their fast and easy growth and their wide availability. The special surface properties of algae, bacteria and fungi

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enable them to adsorb different kinds of metallic and organic pollutants from solutions. Algal cell wall offers a host of functional groups including amino, carboxyl, sulfate, phosphate and imidazoles associated with polysaccharides alginic acid and proteins for binding various pollutants [15]. Different micro/macroalgal species have been proved to be effective biosorbent for the treatment of wastewater. But almost all the studies have been focused only on the removal of metal cations from wastewaters [16,17]. Even though thousands of algal species are known, only a few of them have been investigated for their organic pollution control ability and subsequent use for wastewater treatment. In the present investigation, the biomass of green seaweed has been used as a biosorbent and its capacity to remove basic dye (cationic dye) has been evaluated.

2. Materials and methods

Beach-dried green seaweed *Caulerpa scalpelliformis* was procured from Central Salt and Marine Chemicals Research Institute (CSMCRI), Mandapam Camp, Ramnad District, India. The beach-dried seaweeds were washed with distilled water, shade dried and stored in an airtight pack at room temperature ($28 \pm 2\,^{\circ}C$). The moisture content of the dried seaweed was $5 \pm 1\%$ (w/w). The dye used in all the experiments was Sandocryl golden yellow C-2G,[1] a cationic dye, obtained from Clariant India Ltd. The synthetic dye solution was prepared by dissolving weighed amount of the dye in 1 L of distilled water. Basic dyes fall within the class of polymethine dyes. As such they are cationic polymethines; because ionization in solution they possess an overall positive charge and are therefore widely used to bind to negatively charged substrates [18]. All other reagents used were of analytical grade. Distilled water was used throughout the experiments.

2.1. Characterization of biosorbent

The acidic and ion exchange properties of the green seaweed were determined in order to study the nature and capacity of the biosorbent. The potentiometric titrations of the green seaweed were performed with 40 mL of 0.05 M KNO_3 as background electrolyte. The pH of the seaweed suspension was adjusted to ca. 2.00 with known amount of 0.127 N HCl The stirred suspension was allowed to equilibrate until the pH was stable before the titrations started. The suspension was then titrated with standard NaOH solution. The pH of the suspension was measured after titrant addition by using a pH-meter. After each addition of titrant the system was allowed to equilibrate until a stable reading was obtained. The number of carboxyl groups per gram of alga $[COOH]_{total}$ (mmol g^{-1}) was calculated by estimation of the position of inflection point (V_{eq}) in the resulting titration curve, using the following equation:

$$[COOH]_{total} = \frac{V_{eq}[NaOH]}{S} \quad (1)$$

[1] Commercial dye used for dyeing of leather. Structure and CI number of the dye are unknown.

The FT-IR spectra of untreated, pretreated, and chromium treated seaweed were obtained using the KBr disk technique. The seaweed was ground in a mortar for 5 min after drying it for a period of 2 h at 80 °C. Dilution and homogenization to 0.01% (w/w) with KBr (spectroscopic grade) were carried out with additional grinding. The disks were pressed in a hydraulic KBr press. The transmission FT-IR spectra were then recorded between 400 and 4000 cm^{-1} using a Perkin-Elmer Spectrum RX I FT-IR system.

2.2. Biosorption experiments

The effect of pH and adorbent dosage on uptake capacity of the seaweed for the dye was obtained by agitating 5 g/L of seaweed in a series of bottles, containing 50 mL of dye solution of initial concentration 150 mg/L at different solution pH ranging from 3.0 to 8.0 and with weighed amount of green seaweed ranging from 3 to 10 g/L, respectively. The effect of initial concentration of dye on the equilibrium uptake by green seaweed was estimated by contacting 5 g/L of seaweed with 50 mL of dye solution of different initial concentrations ranging from 25 to 150 mg/L. The experiments were carried out in a mechanical agitator maintained at room temperature for a period of 4 h. The concentration of the dye in the solution before and after adsorption was determined by measuring the absorbance of the solution at 438 nm using Perkin-Elmer Lambda 35 UV–vis spectrophotometer.

2.3. Adsorption kinetics and equilibrium studies

Adsorption kinetic experiments were carried out by agitating 100 ml of dye solution of known initial dye concentration with 5 g/L of seaweed at room temperature ($30 \pm 1\,^{\circ}C$) at a pH of 6.0 ± 0.1 at a constant agitation speed of 75 strokes/min. Similarly the equilibrium experiments were carried out by contacting 3–10 g/L of seaweed with 50 mL of dye solution of different initial dye concentrations (25, 50, 100 and 150 mg/L). The samples were agitated in water bath at a constant speed of 75 strokes/min for 4 h at room temperature. The concentration of the dye in the solution before and after sorption was determined using Perkin-Elmer Lambda 35 UV–vis spectrophotometer.

The amount of dye adsorbed on to the seaweed at equilibrium was calculated from the mass balance of the equation as given below:

$$q_e = (C_0 - C_e)\frac{V}{W} \quad (2)$$

where C_0 and C_e are the initial and equilibrium concentration of dye solution (mg/L), respectively, q_e is the equilibrium dye concentration on seaweed (mg/g), V the volume of the dye solution (L) and W is the mass of the seaweed used (g).

3. Results and discussion

Adsorption of basic yellow dye on to green seaweed was systematically investigated by studying the effect of various