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On the utilization of a lignocellulosic waste as an excellent dye remover: Modification, characterization and mechanism analysis

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HIGHLIGHTS

- CTAB modified SMSBP has excellent biosorption performance for RR2 removal.
- The removal process followed Langmuir isotherm and pseudo-second-order kinetics.
- RR2 biosorption by SMSBP endothermically occurred.
- Biosorption mechanism, desorption and usability in real conditions were explored.

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ABSTRACT

Biosorption potential of sugar beet pulp was significantly improved via grafting by quaternary ammonium salt. Initial pH, biosorbent dosage, contact time, temperature and flow rate were investigated as design parameters. A higher biosorption yield, shorter period of equilibrium time and lower amount of biosorbent were recorded as the main characteristics for batch mode decolorization. The pseudo-second-order model better fitted the kinetic data while Langmuir isotherm model is found to be best represent the biosorption equilibrium. Thermodynamic findings indicated that the nature of Reactive Red 2 (RR2) biosorption is endothermic and spontaneous. The modified sugar beet pulp was also successfully used in dynamic flow mode removal of RR2. Recovery of biosorbed RR2 from the modified biomaterial was investigated in alkaline solutions and good values were observed. IR, SEM, AFM, EDX, potentiometric titration and zeta potential studies were used to characterize the biosorbent structure in addition to real sample application of modified biomaterial.

1. Introduction

Pollution of the water sources by organic and inorganic contaminants is a major concern in many industrialized countries. The removal of these from aquatic environment by ecofriendly technologies is one of the important issues in the field of water treatment because of their possible toxic and hazardous effects. In recent years, the use of biosorption process for the treatment of effluents is receiving more attention.

Biosorption potential of a biomaterial is based on the interactions between contaminants and hydroxyl, carboxyl, phosphoryl and other charged groups localized on the cell wall structure of the organisms composed of macromolecules such as heteropolysaccharides, proteins and lipids. Adsorption, complexation, and chelatation and ion exchange can play a role in the biosorption mechanisms [1,2]. Recently, utilization of different types of biosorbents derived from fungi, yeast, algae, bacteria, chitosan and lignocellulosic materials in pollutant removal process has been extensively reviewed by several researchers [3–5]. Among the commonly available sorbents, biomasses obtained as industrial by-products have been shown more convenient in practical applications due to their low- or no-costs, easy handling and good biosorption performances. Hence, the use of these biomaterials for water treatment has received much more attention in recent years. Various industrial by-products or wastes such as crab shells [6], *Streptoverticillium cinnamoneum* [7], olive pomace [8,9], olive stone [10], *Citrus sinensis* [11], *Pleurotus mutilus* [12], *Capsicum annuum* seeds [13], sugarcane bagasse [14], *Phaseolus vulgaris* [15] and beer yeast [16] have been successfully applied for the removal of organic and inorganic contaminants.

Sugar beet pulp, a lignocellulosic by-product of the sugar refining industry is produced annually in large quantities. Cellulose, hemicelluloses and pectin are the main constituents of its polysaccharide content. The pectin substances and hemicelluloses hinder the utilization of this by product in the paper production. The typical end-use of this by-product was in animal feed manufacture

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[17,18] apart from some specific alternative uses such as matrix in bioethanol production [19], supplemental substrate [20] source of pectin [21] and cellulose microfibrils [18]. Besides, although some reports are available in the literature concerning the heavy metal removal ability of the sugar beet pulp [22–24], a limited number of studies have so far been focused on the use of this by-product for decolorization of dye contaminated waters [25–27].

In the present communication, decolorization potential of sugar beet pulp was significantly improved by a chemical modification. Cetil trimethylammonium bromide (CTAB) was used as modification agent and high biosorption yields were obtained by small amounts of modified biosorbent. Design parameters in batch and continuous modes were investigated. Modeling and characterization studies were also conducted in addition to regeneration and application studies.

2. Experimental

2.1. Biosorption studies

2.1.1. Biosorbent modification and dye solutions

The sugar beet pulp was obtained from the Sugar factory in Eskişehir, Turkey. It was washed repeatedly with deionized water and left to dry in an oven at 60 °C. The dried solid waste was grounded in a laboratory mill and <212 μm particle size was selected for biosorption and modification studies.

The powdered pulp sample (4.0 g) was treated with 250 mL of (%1 (w/v)) CTAB solutions. After magnetically stirring at 200 rpm for 24 h, surfactant modified sugar beet pulp (SMSBP) was separated from mixture by filtration. SMSBP was repeatedly washed with deionized water until free from bromide ions and then, dried again at 60 °C.

Reactive Red 2 (RR2) was selected as model reactive textile dye. A stock solution (1000 mg L^{-1}) of RR2 was prepared by dissolving an appropriate amount of dye in deionized water. Other concentrations were freshly prepared by diluting this stock dye solution. The initial pH of the test solutions was adjusted to desired values by addition of 0.1 M HCl or 0.1 M NaOH.

2.1.2. Batch experiments

Batch biosorption experiments were conducted on a multipoint digital magnetic stirrer. 25 mL of dye solution at known concentration and a weighed amount of biomaterial were added into 100 mL glass beakers and the biosorption mixture was agitated with a stirring speed of 200 rpm. In order to design the batch biosorption conditions, experiments were performed varying the following conditions: initial pH (2.0–10.0), biosorbent amount (0.4–20 g L^{-1} for natural; 0.4–3.2 g L^{-1} for modified biosorbent), contact time (5–90 min), initial RR2 concentration (50–300 mg L^{-1}) and temperature (10, 20 and 30 °C).

2.1.3. Column experiments

Dynamic flow mode biosorption studies were performed in glass columns with 9 mm internal diameter (i.d.). A known amount of SMSBP was packed between a small portion of glass wool in the column. Dye solutions were passed through the column in downward direction. Flow rates were regulated by a peristaltic pump (Ismatec IP16). The dynamic flow mode dye removal process was optimized for the flow rate (0.5–6.0 mL min^{-1}), column i.d. (9–19 mm) and modified SMSBP amount (0.01–0.07 g). In order to identify the regeneration potential of SMSBP, desorption study was performed by passing 0.1 M NaOH solution through the column at a flow rate of 1.0 mL min^{-1}. After passing the alkaline solution, the bed was washed with deionized water and reused for the next biosorption cycle. The biosorption and desorption cycles were repeated for 4 times. The concentrations of the residual dye in the effluent samples were determined using UV–vis spectrophotometer (Shimadzu UV-2550) at maximum wavelength of dye (538.5 nm). The biosorption capacity, biosorption and desorption yields were calculated from the following relationships:

$$q_e = \frac{V(C_i - C_e)}{m} \quad (1)$$

$$\text{Biosorption yield}(\%) = \frac{(C_i - C_e)}{C_i} \times 100 \quad (2)$$

$$\text{Desorption yield}(\%) = \frac{\text{Desorbed dye concentration}}{\text{Biosorbed dye concentration}} \times 100 \quad (3)$$

where C_i and C_e are the initial and the equilibrium dye concentrations (mg L^{-1} or mol L^{-1}), respectively, V is the volume of aqueous phase (L) and m is the weight of the biosorbent (g).

2.2. Data treatment

In order to ensure the reproducibility of the results, each experiment in this study was repeated at least triplicate and the arithmetical average values from these independent experiments were used to data analysis. In figures, error bars show the standard error of the mean and the standard deviations are also given wherever necessary. Statistical treatment of the results was carried out using SPSS 15.0 for Windows.

2.3. Biomaterial characterizations

The surface charges of the natural and surfactant modified biomaterials at different pH values of 2.0–10.0 were recorded using a zeta potential analyzer (Malvern zetasizer). The surface functional groups of both biosorbents were investigated by IR analysis. Samples were prepared as KBr disks and the spectra were recorded in a Bruker Tensor 27 IR spectrophotometer in the range of 4000–400 cm^{-1}. The functional groups present on the biosorbent structure were quantitatively determined by the potentiometric (Boehm) titration method. The pH values were measured using a pH meter (WTW Inolab 720) during the titration procedure. The morphological features of the biosorbents were analyzed by scanning electron microscope (JEOL 560 LV SEM) at 20 kV and 3000× magnification. Before analysis, the samples were coated with a thin layer of gold to increase the electron conduction. For Atomic Force Microscope (AFM) analysis, biomaterial samples suspended in sterile distilled water were fixed on a thin glass plate and dried in air at room temperature (25 °C). The surface topography of biomaterials were observed by Park Systems XE-100-E AFM. The studies were carried out using non-contact imaging mode, 300 kHz frequency and 0.9 Hz scan rate in air at room temperature. The spring constant of silicon cantilever was 40 N/m.

3. Results and discussion

3.1. Batch mode biosorption studies

3.1.1. Effect of initial pH

As shown in Fig. 1a, the biosorption of RR2 on the natural biosorbent and SMSBP was significantly affected by solution pH. The maximum dye removal yields of 16.82 ± 0.43% were observed at pH 2.0 for SBP (sugar beet pulp) and 98.90 ± 0.42% at pH 3.0 for SMSBP, respectively. The good biosorption yields observed at lower pH conditions for both biosorbents can be explained by the attractive forces between dye anions and protonated biosorbent surface. The biosorption yields of the biosorbents were decreased gradually