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Effective biodecolorization potential of surface modified lignocellulosic industrial waste biomass

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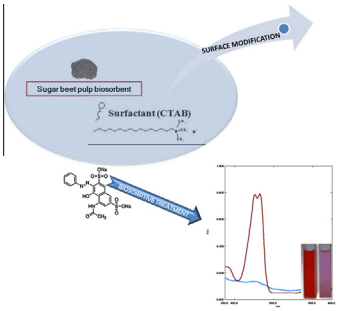
HIGHLIGHTS

- Surfactant modified biosorbent showed excellent removal performance for AR1.
- Maximum AR1 biosorption was observed at acidic conditions.
- Modified biosorbent was successfully used for AR1 biosorption from real wastewater.
- Electrostatic interaction and complexation were main mechanisms.

GRAPHICAL ABSTRACT



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ABSTRACT

The biosorption ability of sugar-beet pulp was improved by modifying with quaternary ammonium-salt for examination of its potential application in decolorization process from wastewater. Decolorization conditions were investigated as functions of different experimental parameters such as initial pH, biosorbent amount, time and dye concentration. At the optimum pH (2.0) the biosorption reached to an equilibrium within relatively short time (30 min) and was followed by the pseudo-second-order kinetic model. Langmuir isotherm better fitted the equilibrium data with the maximum monolayer biosorption capacity of 98.32 mg g^{-1}. AR1 biosorption performance of quaternary ammonium-salt modified sugar-beet pulp (QAMSBP) was also investigated in the mix solutions containing RB49 and AY17 dyes at different concentrations (1, 50 and 100 mg L^{-1}) and the biosorption potential of QAMSBP did not change at 1 and 50 mg L^{-1} of other dyes. Obtained results demonstrated that AR1 biosorption onto QAMSBP could also be successfully applied to real wastewater in continuous system. IR analysis revealed the complexation is one of the important mechanisms involved in AR1 biosorption. All the results indicated that QAMSBP was a potential biosorbent for toxic dye removal from wastewaters.

1. Introduction

Organic and/or inorganic contaminants in natural water sources lead to important environmental pollution. In this context, great efforts have been made to develop effective and economically feasible treatment methods for the protection of the quality of limited fresh water sources in the world.

Among the organic pollutants, synthetic dyes are widely used in textile and some other industries. Colored effluents released into environment not only lead to visual pollution in the water bodies but also cause hazardous effects on living systems. Especially, toxic and carcinogenic aromatic amine compounds are occurred by the reductive cleavage of azo groups in the chemical structure of dyes. Therefore, colored wastewaters must be adequately treated before being discharged into aquatic environment [1].

Biosorption is a biomass-based water treatment technology and it can be defined as the remove ability of biomaterials for organic

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or inorganic water pollutants through effective physico-chemical sequestration mechanisms. This technology seems to be promising candidate for the treatment of colored effluents with the advantages of cost-effectiveness, no hazardous by-product generation and good regeneration potential of biosorbent [2].

Various biomaterials including plant, fungi, bacteria and yeasts have shown good dye removal performance from contaminated waters [3,4]. In recent years, numerous approaches have been made for the improvement of the biosorption potential of biomaterials by various modifications such as pretreatment and immobilization [5,6]. Particularly, remarkable results have been reported for removal of different pollutants by using surfactant treated biomasses [7,8]. The choice of an industrial waste as biomass is an ideal approach for the process economy and continuous supply of the biomass in the large scale biosorption applications [9]. In this work, sugar beet pulp (SBP) was employed as raw biomass source to prepare a modified dye remover because of its sorption potential towards some dye molecules reported in recent years [10–12] and its good response to surfactant modification [13]. The main components of the polysaccharide composition of sugar beet pulp are pectin, cellulose microfibrils and hemicelluloses. This product used as feed for ruminants has some disadvantages such as lower feed value and high drying cost. Hence, the researches for alternative uses of SBP are focused on the attractive options [14] such as bioethanol production [15].

The present investigation reports the biosorption characteristics of Acid Red 1 (AR1) dye on a cationic quaternary ammonium salt (Cetrimonium bromide) treated sugar beet pulp (QAMSBP). The optimization results of batch and continuous mode of applications were presented. Biosorption of AR1 onto QAMSBP was evaluated by modeling of experimental data. Surface morphology of the biosorbent and AR1 biosorption mechanism were characterized using zeta potential measurements, IR and SEM techniques. Practical application potential of QAMSBP was also successfully evaluated at real wastewater conditions.

2. Experimental

2.1. Biosorbent preparation

SBP sample provided from a Sugar factory in Eskişehir was washed with deionized water. After drying at 60 °C, it was converted into modified form by treating with %1 (w/v) surfactant solution [13]. It was ground to obtain particle size of 212 μm and further used in the dye biosorption experiments.

2.2. Dye solutions

AR1 was used as target pollution for the investigation of biosorption potential of QAMSBP. It was obtained from Aldrich (Cat-N: 210633). 1000 mg L^{-1} AR1 stock solution was prepared. Working solutions at different concentrations were obtained by the dilution of this solution. 0.1 M HCl and/or 0.1 M NaOH were used for the pH adjustment of the biosorption medium.

2.3. Biosorption studies

AR1 biosorption experiments were conducted in both batch and column modes. Batch studies were carried out in beakers on a multipoint magnetic stirrer adopted with a water bath at specific temperature. Dye solutions and fixed amount of biomaterial were putted into beakers and mixed at 200 rpm. In order to choice the appropriate biosorption conditions, the initial pH values were ranged from 2.0 to 7.0 using both unmodified and modified biosorbents. Biosorption experiments were conducted with different dosages of modified (0.4–3.2 g L^{-1}) and unmodified (0.4–16 g L^{-1}) biosorbents. Biosorption kinetics was evaluated by using data obtained between 5 and 90 min at different temperatures. Initial dye concentration was ranged from 25 to 300 mg L^{-1} at 10, 20, 30, 40 and 50 °C in order to test the isotherm model appropriation for AR1 biosorption onto QAMSBP.

Continuous mode studies were carried out by pumping AR1 solutions into the glass columns. Dynamic flow conditions i.e. flow rate, biosorbent amount (bed height) and column size were optimized to reach to maximum biosorption yield for QAMSBP. A breakthrough study was also carried out to investigate the column performance of QAMSBP.

Each dye biosorption experiment in this study was repeated at least three times and the given results were the mean values of these independent experiments.

2.4. Instrumentation

At the end of all biosorption experiments, supernatants were analyzed for AR1 by spectrophotometrically. UV–visible spectrophotometer (Shimadzu UV-2550) was used to determine the dye concentration in the solutions. The pH dependent-surface charges of the biosorbents were measured using a Malvern zeta sizer. IR spectroscopic analysis of the biosorbents was carried out using a Bruker Tensor 27 IR spectrophotometer. Boehm titration method was applied to quantitatively determination of the acidic and basic functional groups on the biosorbent. A pH meter (WTW Inolab 720) was used to measure the solution pH in all experiments. The surface structure of the biosorbents was investigated by a scanning electron microscope (JEOL 560 LV SEM) at 20 kV. The BET surface area and average pore size of the biosorbents were determined from N_2 adsorption isotherm with a surface area and pore size analyzer (Quantachrome Instruments, Autosorb 1).

3. Results and discussion

3.1. Batch biosorption parameters

3.1.1. pH effect

The effect of pH on AR1 biosorption onto SBP and QAMSBP was investigated by ranging the pH of the dye solution from 2.0 to 7.0. The biosorption yields of both biosorbents as function of pH are plotted in Fig. 1a. With increasing pH, a decrease in AR1 biosorption yield of both bioorbents was observed until pH 4 ($p < 0.05$). No pH dependence was observed after this value ($p > 0.05$). The zeta potentials of the biosorbents at the same pH intervals (Fig. 1a) also showed the similar trend. The zeta potentials for SBP and QAMSBP were measured as −0.17 and +4.78 mV at pH 2.0, respectively. Similarly, modified biosorbent has more positive surface charge at all of the working pH values. The zero point charge (ZPC) for QAMSBP was determined at about pH 3. The intensive positive charge on the biosorbent surface below ZPC causes more electrostatic interaction between biosorbent surface and negatively charged dye molecules. This further results in higher biosorption yield for the modified biosorbent at these pH values. The charges of the modified biosorbent were negative above pH 3 and they varied from −15.43 to −23.15 mV while the pH was raised from 4.0 to 7.0 ($p < 0.05$). A slight reduction in the biosorption performance of QAMSBP may also be attributed to this negative charge intensity on the biosorbent surface. Therefore, the subsequent biosorption studies were conducted at pH 3.0.

3.1.2. Effect of biosorbent dosage

Fig. 1b indicated that the amount of biosorbed AR1 onto both natural and modified biosorbents increased with an increase in