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Optimization of C.I. Acid black 1 biosorption by *Cystoseira indica* and *Gracilaria persica* biomasses from aqueous solutions

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ABSTRACT

The aim of this study is to optimize the removal conditions of C.I. Acid black 1 (AB1) by a brown alga biomass, *Cystoseira indica*, and a red alga biomass, *Gracilaria persica*, using Box-Behnken design. The variables examined were the biomass dosage (0.5–1.5 g L^{-1}), initial AB1 concentration (10–50 mg L^{-1}), initial pH (2–6) and time (20–80 min). The determination coefficients (R^2) of predicted models were 0.9903 and 0.9955 for *C. indica* and *G. persica* biomass, respectively. These findings indicated models high validity in predicting the AB1 removal by both of biomasses. At the optimum conditions, the maximum removal efficiencies of AB1 achieved for *C. indica* and *G. persica* were 90.76 and 98.18%, respectively. These results also imply that the used brown and red algal biomasses are favorable biosorbents for the removal of AB1 from aqueous solutions.

1. Introduction

Dyes are widely used in many industrial applications including textile, leather, food processing, dyeing, cosmetics, paper, and dye manufacturing industries. Most of the synthetic dyes such as azo dyes are toxic and highly resistant to degradation owing to their chemical nature, molecular size and structure (Lu et al. 2009; Waghmode et al. 2011). Disposal of industrial effluents containing dyes in water bodies causes serious environmental problems. Therefore, there is an urgent need to develop an economic and effective way of dealing with the dyeing wastewaters. Biosorption process is a promising approach for the remediation of synthetic dyes in wastewater because of its low cost, high efficiency and eco-friendly nature (Couto 2009; Belala et al. 2011). In the recent years, for removing a wide range of dyes many low cost organisms including bacteria (Banat et al. 1996; Yang et al. 2011), fungi (Kaushik and Malik 2009; Mishra et al. 2011) and yeasts (Ertugrul et al. 2009; Phugare et al. 2010) have been tested.

The application of micro/macro algae species for removal of dye wastewater such as Acid blue 29 (Ramakrishna and Viraraghavan 1997), Basic red 22 (Allen et al. 1994) and Malachite green (Daneshvar et al. 2007; Khataee et al. 2009a, 2010) has been reported previously. Algae functional groups such as hydroxyl, carboxyl, amino and phosphate found on the algal cell surface are considered to be the responsible for separation of contaminants from water (Srinivasan and Viraraghavan 2010).

In this study *Cystoseira indica* and *Gracilaria persica* biomasses have been used for treatment of a dye solution containing C.I. Acid black 1. *Cystoseira* is one of the most widely distributed genera of the Fucales order (Phaeophyta). *C. indica* alga is Thalli 5–150 cm long, greenish to dark brown in color, grows singly or in a group of rhizomatous branches; thick, cylindrical and horizontal. Rhizomes are present parallel to the substratum. *Gracilaria* sp., belonging to Rhodophyta, Florideae, Gigartinales, Gracilariaceae, is a genus of red alga (Rhodophyta) notable for its economic importance as an agarophyte. Its cylindrical thallus is long and dark red in color (Peng et al. 2009).

To the best of our knowledge, there has been no study on the statistical optimization of experimental conditions for the biosorption of AB1 by *C. indica* and *G. persica*. Therefore, the objective of the present work was to study the effects of biomass dosage, initial AB1 concentration, initial pH and time by means of Box-Behnken Design (BBD) under response surface methodology (RSM) using Design Expert software, and the optimum conditions for removal of AB1. The main aim of this work was to compare the removal of AB1 by *C. indica* and *G. persica* at optimum conditions. The optimized removal efficiency of the biosorbents using numerical optimization methodology was also calculated.

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2. Materials and methods

2.1. Chemicals

All the chemicals used were analytical grade. The dye C.I. Acid Black 1 (purity > 85%) was supplied by Alvan Sabet Co., Iran. Its structure is depicted in Fig. 1. AB1 stock was prepared by dissolving 1000 mg AB1 in 1 L deionized water (Fig. 1). Other AB1 solutions were prepared by diluting AB1 stock to obtain different concentrations of 0.1–50 mg L^{-1}. The pH was using diluted NaOH and HCI solutions and the pH values were measured with pH meter (Metrohm, 620, Switzerland) before experiment.

2.2. Preparation of biosorbents

C. indica and *G. persica* macroalgae species were acquired from coastline and low deep water areas of Oman Sea around Chabahar, Iran. For biosorption studies, the algal biomass was washed by tap water 4–5 times, for removing its surface interfering ions and other undesired materials, such as sand particles and debris. The biomass was dried for three days in sunlight until all the moisture evaporated and then dried biomass material was washed by distilled water. Absorbents were then sun dried for a day followed by drying in an oven at 70 °C for 24 h and subsequently was ground to a fine powder. The resulting material was sieved in the size range of 106–250 μm. To make better result and reduce the error of analysis, the grounded biosorbents were washed two times with distilled water for cleaning away biomaterial of dusts resulting from grounding. Finally, algal sieved grains were dried at 70 °C for 24 h in oven and then were maintained in a desiccator for snubbing of changing weight.

2.3. Analytical method

The batch experiment was conducted in 100 mL Erlenmeyer flasks containing 50 mL of C.I. Acid black 1 solution. To evaluate the effects of operation and environmental factors on the efficiency of color removal, the batch experiments were carried out at different initial AB1 concentrations (10, 30 and 50 mg L^{-1}), biomass dosages (0.5, 1 and 1.5 g L^{-1}), initial pHs (2, 4 and 6) and times (20, 50 and 80 min) (Table 1). The temperature was 25 ± 2 °C along experiment and was performed under a static condition. The samples were agitated in an incubator shaker (Labcon, FSIM-SPO16, United States) at 135 rpm. All of the experiments were repeated two times. At the end of predetermined times, known flasks were removed and then their contents were filtered by 0.2 μm membrane filter (Orange Scientific, GyroDisc CA-PC, Belgium) for analysis. The quantity of remaining AB1 was determined with a spectrophotometer (Hach, DR/4000 Spectrophotometer, United States) at the maximum absorption wavelength, ($\lambda_{max} = 618$ nm) (Bekci et al. 2009; Tsaia and Chen 2010). The AB1 removal percentage in the aqueous solution by the mentioned algal biomass was computed using the following equation:

Table 1
Variables and their values.

Variables	Values		
	−1	0	+1
Biomass (g L^{-1})	0.5	1	1.5
Initial AB1 concentration (mg L^{-1})	10	30	50
Initial pH	2	4	6
Time (min)	20	50	80

$$\text{Sorption}\ (\%) = \frac{C_i - C_f}{C_i} \times 100 \quad (1)$$

where C_i and C_f are the initial and final concentrations of AB1 (mg L^{-1}) in the medium. All experimental sequences received by the Design Expert software (Version 8.0.4., Stat-Ease, Inc., Minneapolis, USA) were performed.

2.4. Experimental design

The dependency of initial AB1 concentration, pH, biomass dosage and time of sorption on the process has been previously inferred (Selvam et al. 2003; Safarikova et al. 2005). The Box–Behnken experimental design was employed to investigate the effect of operational parameters on the AB1 removal efficiency (%). 27 different combinations were constructed by Design Expert software (Version 8.0.4, Stat-Ease, Inc., Minneapolis, USA) statistical package. A second-order polynomial analysis was used to fit the quadratic model:

$$Y = \beta_0 + \beta_1 x_1 + \beta_2 x_2 + \beta_3 x_3 + \beta_4 x_4 + \beta_{12} x_1 x_2 + \beta_{13} x_1 x_3 + \beta_{14} x_1 x_4 + \beta_{23} x_2 x_3 + \beta_{24} x_2 x_4 + \beta_{34} x_3 x_4 + \beta_{11} x_1^2 + \beta_{22} x_2^2 + \beta_{33} x_3^2 + \beta_{44} x_4^2 \quad (2)$$

where Y is the measured response (AB1 removal efficiency, %); x_1, x_2, x_3, x_4 are the coded input variables; β_0 is the intercept term; β_1, β_2, β_3, β_4 are the linear coefficients showing the linear effects; β_{12}, β_{13}, β_{14}, β_{23}, β_{24}, β_{34} are the cross-product coefficients showing the interaction effects of four process variables; and β_{11}, β_{22}, β_{33}, β_{44} are the quadratic coefficients. The optimum values of the factors were obtained by solving the regression equation, analyzing the contour plot, and setting up constraints for the levels of the variables.

3. Results and discussion

3.1. Box–Behnken design model statistical analysis

The results were obtained through the Box–Behnken experimental design that was investigated when identifying the best levels of the variables (i.e. biomass dosage (0.5–1.5 g L^{-1}), initial AB1 concentration (10–50 mg L^{-1}), initial pH (2–6) and time (20–80 min)) (see Table 2). As can be seen, there was a high

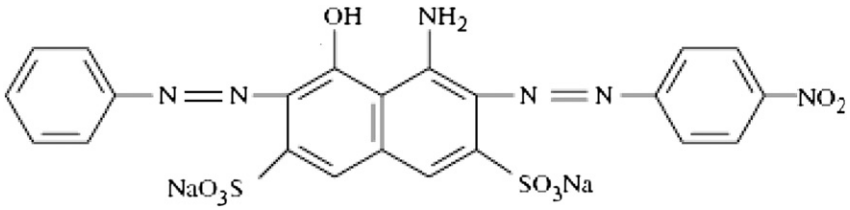

Fig. 1. Chemical structure of C.I. Acid black 1 (Color Index Number = 20,470 and $\lambda_{max} = 618$ nm).