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Simultaneous biosorption of Arsenic (III) and Arsenic (V): Application of multiple response optimizations

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ABSTRACT

In this work, simultaneous biosorption of As(III) and As(V) by *Sargassum glaucescens* was optimized using multiple response optimizations and Doehlert experimental design. The optimum condition for simultaneous biosorption of As(III) and As(V) were: biosorbent dosage 0.47 g L^{-1}, pH 5.9 and initial concentration 120.34 mg L^{-1} with maximum overall desirability of 0.94. Different isotherms were fitted to biosorption equilibrium data and the Freundlich isotherm was the most suitable model. Based on thermodynamic study, the biosorption of arsenic species onto alga was endothermic and spontaneous. Kinetic results indicated that intraparticle diffusion model was the best kinetic model. Biosorption capacity of *S. glaucescens* and other biosorbents were also compared.

1. Introduction

The toxicity and ecological effects of arsenic is related to its different chemical forms and oxidation states (Ma et al., 2014). Metabolic activities of enzymes are inhibited by arsenic and can be led to death. As(III) because of its greater cellular uptake is more toxic than As(V). For drinking waters, 10 μg/L is maximum level of arsenic (Guzman et al., 2016).

Different arsenic removal techniques have been used such as electrocoagulation/flocculation (Guzman et al., 2016), reverse osmosis (Abejón et al., 2015), and membrane distillation (Dao et al., 2016). Recently nanocomposite hydrogels (Thakur et al., 2017a, 2017b; Wróblewska-Krepsztul et al., 2018) have shown excellent performance for removal of various pollutants from water. Inefficient removal, expensive reagent, not eco-friendly, large amounts of sludge and energy consumption are disadvantages of these techniques. Biosorption is removal of pollutants by different biomasses such as algae, bacteria and agricultural wastes. Low costs, regeneration and no sludge generation are advantages of this technique. Different functional groups in the cell walls of biomass (such as OH, COOH and NH_2) interact with pollutants. Biosorption of arsenic were reported by different researchers (Banerjee et al., 2016; Iriel et al., 2015; Johansson et al., 2016; Kazi et al., 2018; Jaiswal et al., 2018). Algae as renewable natural biomass exhibit different affinities toward different metals, and are very important candidates, employed as biosorbent materials. Metal-uptake capacities of certain marine and river algae (studied for adsorption and elution of Au, Ag, and Co) are reported to be much higher than activated carbon, natural zeolite, and synthetic ion-exchange resin (Kumar et al., 2015). Also, the performance of brown algae in removal of extremely toxic metal ions is better than other algae (green and red algae). Among various brown algae, the *Sargassum* sp. seems to better perform in metal uptake. (Mata et al., 2008). *Sargassum glaucescens* belong to genus of *Sargassum* sp. and family of *Sargassaceae*.

In response surface methodology (RSM), data is obtained from experimental design; different mathematical models are fitted to the experimental results, statistical techniques used to model verification and interactions between variables and responses studied. Finding the optimal conditions for a single response is relatively simple (Witek-Krowiak et al., 2014). However, in many situations, several responses must be simultaneously optimized. In multicriteria methodology, RSM is combined with the Derringer's desirability function. This function transforms a several response variables into a single response case (desirability value), which can be optimized by univariate techniques (Grosso et al., 2014).

The objective of this work was investigation of simultaneous biosorption of As (III) and As(V) by *S. glaucescens*. Biosorption conditions (pH, biosorbent dosage and initial concentration of arsenic ions) were optimized by Doehlert design and multiple response optimizations.

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2. Materials and methods

2.1. Chemicals and biosorbent

Stock standards (1000 mg L^{-1}) of As (III) and As (V) were prepared from $Na_2HAsO_4{\cdot}7H_2O$ and As_2O_3, respectively. Brown macroalga (*Sargassum glaucescens*, Oman Sea, Chabahar, Iran) was washed twice, sun-dried, ground and sieved (size: 0.3–0.8 mm).

2.2. Biosorption

First, pH of arsenic solution [As(III) and As(V)] was adjusted by 0.1 mol L^{-1} HCl or NaOH at desired pH and then 0.045 g alga was added. Solution was stirred at room temperature. Biosorbent was separated by centrifuging and resulting solution analyzed for remaining arsenic. The biosorption efficiency and capacity of arsenic were calculated as follows:

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

$$q = (C_i - C_e)\frac{V}{W} \quad (2)$$

where C_i (mg L^{-1}) and C_f (mg L^{-1}) are the initial and final arsenic concentrations, respectively, q is biosorption capacity (mg g^{-1}), V is the volume of the arsenic solutions (mL) and W is the amount of biosorbent (g). All the experiments were performed in triplicates.

2.3. Spectrophotometric determination of As (III) and As (V)

Spectrophotometric determination of arsenic using the molybdenum blue is an inexpensive and sensitive procedure (Dhar et al., 2004; Hu et al., 2012) and also permits the speciation of arsenic. The molybdenum blue colorimetric method is very selective for As(V). After biosorption, the solution containing As(III) and As(V) divided to two aliquot. One aliquot was measured by molybdenum blue colorimetric method for As(V) (Dhar et al., 2004). Color reagent contains ascorbic acid (10.8%), ammonium molybdate (3%), antimony potassium tartrate (0.56%) and sulfuric acid (13.98%) at a ratio of 2:2:1:5. This reagent formed a blue arsenomolybdate complex (λ_{max} = 880 nm) with As(V). Total arsenic concentrations $[As]_t$ were determined similarly after oxidizing the As(III) to As(V) by reacting second aliquot with 0.25% w/v MnO_4. As (III) concentration was calculated from As(V) and total concentration of arsenic.

2.4. Experimental design and optimization

The Doehlert design is a second-order experimental design in a spherical domain for three variables. In this design, each variable can be studied at a different number of levels. This is an advantage because some variables have constraints. Increased efficiency and reduction in experiments are advantages of Doehlert design (Nde et al., 2015; Heidarizadi and Tabaraki, 2016). In present study, biosorbent dosage [X_1], pH [X_2] and initial concentration of arsenic [X_3] were independent factors and biosorption efficiency of As(III) (Y_1) and As(V) (Y_2) were response variables. The biosorbent dosage and pH was studied at five levels. Initial concentration of arsenic species was studied at three levels. The levels of the variables were selected according to the preliminary studies. Table 1 shows the design matrix corresponding to the necessary experiments for optimization of these variables. A quadratic polynomial equation (Eq. (3)) was fitted to experimental data and terms significance were computed by analysis of variance (ANOVA):

$$Y = \beta_o + \sum_{i=1}^{3}\beta_i X_i + \sum_{i=1}^{3}\beta_{ii} X_i^2 + \sum\sum_{i=1}^{3}\beta_{ij} X_i X_j \quad (3)$$

where Y is the response, β_o, β_i, β_{ii}, and β_{ij} are the regression coefficients. MINITAB 16 software was used for response surface analysis.

In multiple response optimizations, the response was converted into corresponding desirability value (d_i) that varies from 0 (lowest) to 1 (highest desirability). In this study, higher biosorption efficiency is the desirability.

$$d_i(Y_i) = \begin{cases} 0 & \text{if} \quad Y_i(x) < Y_{\min,i} \\ \left(\frac{Y_i(x) - Y_{\min,i}}{Y_{\max,i} - Y_{\min,i}}\right)^s & \text{if} \quad Y_{\min,i} \le Y_i(x) \le Y_{\max,i} \\ 1 & \text{if} \quad Y_i(x) < Y_{\max,i} \end{cases} \quad (4)$$

Where $Y_{min,i}$ and $Y_{max,i}$ are minimum and maximum acceptable value of y_i, respectively. The exponent s is scale of desirability. The desirability function is linear, when s = 1. The individual desirability functions are then combined as the geometric mean for calculating overall desirability function (D):

$$D = d_1^{w_1}(Y_1) \times d_2^{w_2}(Y_2) \times \ldots \times d_m^{w_m}(Y_m) \quad (5)$$

where $d_i(Y_i)$ and w_i are the desirability of response Y_i and weight of various response, respectively (Liu and Tang, 2010). In this study, As (III) and As(V) biosorption efficiencies had same importance ($w_1 = w_2 = 1/2$).

2.5. Kinetic of biosorption

100 mL solutions (100 mg L^{-1}) containing As(III) and As(V) and biosorbent dosage of 0.45 g L^{-1} were used for kinetic study. Magnetic stirrer with speed of 70 rpm was used for mixing at temperature room. The pH was adjusted to 6 for As (III) and 4 for As (V) before adding the biosorbent (single component solutions). At given times, samples were taken from solutions, centrifuged and residual As(III) and As(V) concentrations in supernatant were determined. The pseudo-first-order, the pseudo-second-order and intraparticle diffusion models were fitted to kinetic data (Nekouei et al., 2015):

$$\ln(q_e - q_t) = \ln q_e - K_1 t \quad (6)$$

$$\frac{t}{q_t} = \frac{1}{K_2 q_e^2} + \frac{t}{q_e} \quad (7)$$

$$q_t = K_{dif} t^{1/2} + C \quad (8)$$

where q_e (mg g^{-1}) and q_t (mg g^{-1}) are arsenic capacity at equilibrium and time t (min), respectively; k_1 and k_2 are pseudo first and second order rate constant, respectively; K_{diff} and C are the intraparticle diffusion rate constant (mg g^{-1} $min^{-1/2}$) and constant, respectively.

2.6. Biosorption isotherms

In this study, experimental equilibrium data was fitted to the Langmuir, Freundlich and Temkin isotherms and details of each isotherm were presented elsewhere (Rangabhashiyam et al., 2014):

$$q_e = \frac{Q_0 \ K_L C_e}{1 + K_L C_e} \quad (9)$$

$$q_e = K_f C_e^{1/n} \quad (10)$$

$$q_e = \frac{RT}{B} \ln(A_T C_e) \quad (11)$$

where C_e is the equilibrium concentration of biosorbate (mg/L), q_e denotes biosorption capacity at equilibrium (mg g^{-1}), Q_0 represents the monolayer coverage capacity (mg/g) and K_L is the Langmuir isotherm constant (L/mg), K_f is the Freundlich isotherm constant ($mg^{1-(1/n)}$ $L^{1/n}$ g^{-1}), n represents the biosorption intensity, A_T is the Temkin isotherm equilibrium binding constant (L/mg), B(J/mol) is the constant related to heat of sorption ($B = \frac{RT}{b_T}$), R is the universal gas constant (8.314 J/mol K), T is the temperature (K) and b_T is the Temkin