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Biosorption of copper(II) ions on *Enteromorpha prolifera*: Application of response surface methodology (RSM)

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ABSTRACT

In this study, the biosorption of copper(II) ions on *Enteromorpha prolifera*, a green seaweed, was investigated in a batch system. The effects of operating parameters such as initial pH, temperature, initial metal ion concentration and biosorbent concentration on the copper(II) biosorption were analysed using response surface methodology (RSM). The proposed quadratic model for central composite design (CCD) fitted very well to the experimental data that it could be used to navigate the design space according to ANOVA results. The optimum biosorption conditions were determined as initial pH 4.0, temperature 25 °C, biosorbent concentration 1.2 g/L and initial copper(II) ion concentration 200 mg/L. The Langmuir and Freundlich isotherm models were applied to the equilibrium data at different temperatures and initial pH values. The maximum monolayer coverage capacity of *E. prolifera* for copper(II) ions was found to be 57.14 mg/g at 25 °C and initial pH 4.0 indicating that the optimum biosorption temperature and initial pH. The external and intraparticle diffusion models were also applied to biosorption data of copper(II) ions with *E. prolifera* and it was found that both the external diffusion as well as intraparticle diffusion contribute to the actual biosorption process. The pseudo-second order kinetic model described the copper(II) biosorption process with a good fitting. The thermodynamics of copper(II) biosorption on *E. prolifera* indicated its spontaneous and exothermic nature.

1. Introduction

Copper(II) is known to be one of the heavy metals most toxic to living organisms and it is one of the more widespread heavy metal contaminants of the environment [1]. For example, continued inhalation of copper-containing sprays is linked with an increase in lung cancer among exposed workers [2]. The World Health Organization (WHO) recommended a maximum acceptable concentration of copper(II) in drinking water of 1.5 mg/L. It is essential that potable waters be given some treatment to remove copper before domestic supply [3]. The potential sources of copper in industrial effluents include metal cleaning and plating baths, pulp, paper board mills, wood pulp production, the fertilizer industry, etc [4]. The conventional methods of copper(II) removal from wastewaters are precipitation, ion-exchange, electrolysis, adsorption, etc. These methods require high capital and operating costs, and may result in large volumes of solid wastes. In addition, there are also limitations concerning their use, especially for treating a large volume of dilute metal concentrations [5]. Therefore, there is a growing interest in the search of low-cost, easily available and environment friendly biological materials suitable for the efficient removal of heavy metal ions [6].

Biosorption is an alternative technology to remove heavy metals from dilute aqueous solutions using inactive and dead biomass [7]. Biosorption uses cheaper materials such as biosorbents and biosorptive process is generally rapid and is suitable for the extraction of metal ions from large volumes of water [5]. Biosorption is either metabolism, such as physical or chemical adsorption onto the cell wall, or metabolism related, such as transport, internal compartmentalization, and extra cellular precipitation by metabolites [8]. The physico-chemical phenomenon of metal biosorption, based on adsorption, ion-exchange, complexation and/or microprecipitation, is relatively rapid and can be reversible. Therefore, the biosorption is a process separation and can be explained with the adsorption principles. The characteristics of the adsorption behaviour is generally understood in terms of both equilibrium and adsorption kinetics.

Recent investigations by various groups have shown that selected species of seaweeds possess impressive adsorption capacities for a range of heavy metal ions and dye anions but no information are available for copper(II) ions from aqueous solutions by inactivated *Enteromorpha prolifera*, a green seaweed, in the

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Nomenclature

A	cross-sectional area of metal ion (m^2)
$C_{ad,eq}$	the amount of copper(II) ion (mg) biosorbed on the biosorbent per L of the solution at equilibrium (mg/L)
C_{eq}	metal ion concentration remaining in solution at equilibrium (mg/L)
C_0	initial metal ion concentration (mg/L)
D	effective diffusivity of solutes within the particle
e_i	error in the model, $i = 1–4$
ΔG	free energy change (kJ/mol)
ΔH	enthalpy change (kJ/mol)
k_2	pseudo-second order rate constant (g/mg min)
K_a	constant related to the affinity of the binding sites (L/mg)
K_F	adsorption capacity
K_i	intraparticle rate constant (mg/g $min^{1/2}$)
M	molecular weight of metal
n_F	adsorption intensity
n	number of experiments
N	Avogadro number
p	number of model parameters
q_{eq}	the amount of biosorbed metal per unit weight of biosorbent at equilibrium (mg/g)
$q_{eq,exp}$	experimental amount of biosorbed metal per unit weight of biosorbent at equilibrium (mg/g)
$q_{eq,cal}$	calculated amount of biosorbed metal per unit weight of biosorbent at equilibrium (mg/g) from the pseudo-second order kinetic model
q_{max}	maximum monolayer coverage capacity of biosorbent (mg/g)
q_f	amount of biosorbed metal on the surface of the biosorbent at the end of biosorption (mg/g)
R	the universal gas constant, 8.314 (J/mol K)
R^2	correlation coefficient
R^2_{adj}	adjusted correlation coefficient
S	specific surface area (m^2/g biosorbent)
ΔS	entropy change (kJ/mol K)
T	absolute temperature (K)
t	time (min)
X_0	biosorbent concentration (g/L)
x_i	independent variable, $i = 1–4$
y_i	response, $i = 1–4$

Greek letters

β_0, β_i and β_{ij}	linear and quadratic interaction coefficients, i and $j = 1–4$
β_L	external diffusion constant (cm/min)
η	response
σ^2	residual mean square from ANOVA table

literature. Seaweeds are a widely available source of biomass as over two million tonnes are either harvested from the oceans or cultured annually for food or phycocolloid production, especially in the Asia-Pasific region [9]. Seaweeds are suitable for human and animal feed, as well as for fertilizer, fungicides, herbicides, and phycocolloids (alginate, carrageenan and agar) [10]. The green algae genus *Enteromorpha* has great potential for commercial exploitation because of its abundant and varied chemical composition, and quality and concentration of basic nutrients for other living organisms [10]. Aguilera-Morales et al. were reported that the main constituents in *Enteromorpha* spp. were minerals, protein and ether extract and hemicellulose was dominant in the cellular wall of algae [10]. *Enteromorpha* spp. contains 9–14% protein, 2–3.6% ether extract, 32–36% ash, polyunsaturated fatty acids n-3 and n-4:10.4 and 10.9/100 g of total fatty acids, respectively [11]. Christ et al. reported that cell wall of *E. prolifera* was rich in sulphated polysaccarides which are strong ion-exchangers [12].

The design and efficient operation of adsorption processes require equilibrium data for use in kinetic and mass transfer models. These models can then be used to predict the performance of the adsorption contact processes under a range of operating conditions [13]. The purpose of this study was to investigate the biosorption characteristics of copper(II) ions on *E. prolifera*. The effects of operating parameters such as initial pH, temperature, initial metal ion and biosorbent concentrations on the biosorption of copper(II) ions on *E. prolifera* were analysed using RSM. In this study, response surface design was selected because it provides a reasonable distribution of data points throughout the region of interest, allows model adequacy including lack of fit, allows designs of higher order to be built up sequentially, provides an internal estimate of error. Response surface designs also do not require a large number of runs and do not require too many levels of the independent variables [14,15].

2. Materials and methods

2.1. Preparation of biosorbent solution

E. prolifera, a kind of green seaweed collected from Mediterranean cost in Mersin, Turkey was used as a biosorbent. For the biosorption studies, the harvested fresh cells were rinsed with tap water, washed several times with distilled water and then inactivated in an oven at 105 °C for 24 h. After that, a given amount (10 g) of inactivated dried *E. prolifera* was suspended in 1 L double-distilled water, homogenizing in a commercial blender (Waring). Necessary dilutions were made from the stock biosorbent solution to prepare solutions in the range of concentrations 0.5–2.0 g/L.

2.2. Copper(II) solution

A stock solution of copper(II) (1.0 g/L) was prepared by dissolving weighed amount of $CuCl_2$ in 1 L of distilled water. Necessary dilutions were made from the stock solution to prepare solutions in the range of concentrations 25–300 mg/L. The initial pH of each solution was adjusted to the required value with concentrated and diluted HCl and NaOH solutions before mixing the biosorbent suspension.

2.3. Batch biosorption studies

Batch biosorption experiments were conducted in 250 mL Erlenmeyer flasks containing 100 mL of biosorption solution. The biosorbent solution (10 mL), except for the studies of biosorbent concentration effect, was mixed with 90 mL of the desired initial copper(II) concentration and initial pH in Erlenmeyer flasks. The flasks were agitated on a shaker at constant temperature for 2 h ample time for biosorption equilibrium. Samples were taken before mixing the biosorbent suspension and copper bearing solution, then at pre-determined time intervals for the residual copper(II) concentration in the solution. Samples were filtered by using Whatman # 1 filter paper and the copper(II) ion concentration remaining in supernatant was analysed. Experiments were repeated for different initial pH, initial copper(II) concentration, temperature and biosorbent concentration values.