Chemical Engineering Journal 183 (2012) 68–76

Contents lists available at SciVerse ScienceDirect

Chemical Engineering Journal

journal homepage: www.elsevier.com/locate/cej

Biosorption of hexavalent chromium from aqueous solution by *Sargassum muticum* brown alga. Application of statistical design for process optimization

Yeslié González Bermúdez[a,1], Iván L. Rodríguez Rico[a,1], Eric Guibal[b,2], Mónica Calero de Hoces[c,3], María Ángeles Martín-Lara[c,*]

[a] Central University "Marta Abreu" of Las Villas, Carretera a Camajuaní Km 5 1/2, Santa Clara, Villa Clara, Cuba
[b] Ecole des Mines d'Alès, Laboratoire Génie de l'Environnement Industriel, Equipe BPCI, 6 Avènue de Clavières, F-30319 Alès Cedex, France
[c] Department of Chemical Engineering University of Granada, 18071 Granada, Spain

ARTICLE INFO

Article history:
Received 7 October 2011
Received in revised form 5 December 2011
Accepted 7 December 2011

Keywords:
Biosorption
Brown seaweed
Chromium(VI)
Statistical analysis
Sargassum muticum

ABSTRACT

In this study, an experimental design technique, the factorial design 3^3, has been used to investigate the biosorption of chromium(VI) from the aqueous solutions by the brown seaweed *Sargassum muticum*. The three factors considered were temperature, sorbent dosage and initial metal concentration at three markedly different levels. The biosorption of chromium(VI) by the algal biomass is highly pH dependent, favoring higher metal-ion removal at low pH. The *S. muticum* exhibited the higher Cr(VI) uptake capacity at pH 2. An empirical model was developed and validated applying ANOVA incorporating interaction effects of all parameters and optimized using response surface methodology. The optimization study indicates 84% as maximum removal at 50 °C, 20 mg/L of metal concentration and a sorbent dosage of 2 g/L. At these optimal conditions, kinetics and isotherm models were obtained.

The kinetics studies showed that the process of biosorption of Cr(VI) with *S. muticum* was been satisfactorily described by a process of chemical sorption of pseudo-second order. The experimental equilibrium data obtained have been analyzed using two-parameter isotherm models (Langmuir, Freundlich and Temkin). The most appropriate equation for describing the isotherm profiles was the Langmuir model.

1. Introduction

Many traditional methods are used for the elimination of the environmental pollution. Specially, the contamination of water by toxic heavy metal ions is a worldwide environmental problem. Biosorption is an alternative method suitable for the treatment of wastewater. It is characterized by low cost and high removal of metals, especially at low concentration of metal in solution. Among different biosorbents, some species of brown marine macroalgae exhibit much higher uptake values than other types of biomass, higher than activated carbon and natural zeolite, and comparable to those of synthetic ion exchange resins [1]. This is the case of the different species of Sargassum genus, which have been studied by several authors [2–4], especially Volesky and co-workers [5–7]. In this work, interest has been focused on *Sargassum muticum* because it is typically found in tropical countries and abundant in South America, and it is easily collected on beaches without any environmental damage due to its occurrence/presence in the waters of Cuba and Europe. Furthermore, *S. muticum* has been considered an invasive species in European waters, making its obliteration very important.

Chromium as a toxic heavy metal often exists in the waste streams from various industries such as mining, metal cleaning, plating, dyeing and metal processing. According to the World Health Organization (WHO) drinking water guidelines, the maximum allowable limit for total chromium is 0.05 mg/L [8]. Trivalent chromium is the most prevalent form found in natural water. Almost all the contaminant hexavalent chromium comes from human activities. Hexavalent chromium is an acute carcinogen and more mobile and toxic than trivalent chromium. Hence, hexavalent chromium is more important than trivalent chromium in water pollution control [9].

Taking into consideration the necessity to reduce the environmental negative impacts caused by the residuals contaminated with chromium(VI) and their possible repercussion in the health of the population, it becomes necessary to look for feasible economic and environmental alternatives that allow keeping the levels of these polluting agent in the permissible range.

* Corresponding author. Tel.: +34 958243311; fax: +34 958248992.
E-mail addresses: ivanl@uclv.edu.cu (Y. González Bermúdez), ivanl@uclv.edu.cu (I.L. Rodríguez Rico), Eric.Guibal@mines-ales.fr (E. Guibal), mcaleroh@ugr.es (M. Calero de Hoces), marianml@ugr.es (M.Á. Martín-Lara).
[1] Tel.: +53 42211825.
[2] Tel.: +33 0466782734; fax: +33 0466782701.
[3] Tel.: +34 958243311; fax: +34 958248992.

1385-8947/$ – see front matter © 2011 Elsevier B.V. All rights reserved.
doi:10.1016/j.cej.2011.12.022

The traditional physico-chemical processes used to eliminate heavy metals from the liquid effluents, such as chemical precipitation, electrochemical oxidation reduction, treatments, are not usually viable from the economic and energy consumption point of view, especially when the concentrations of heavy metals are low. For that reason the feasibility of the use of biosorption process to remove heavy metals from industrial effluents is investigated.

The biosorption can be carried out by physical adsorption, ion exchange, complexation and precipitation mechanisms. In many processes of biosorption, several mechanisms can act in combination and is difficult to define it [10].

According to Fourest and Volesky, the major mechanisms responsible for the accumulation of heavy metals by biomass of bacteria, fungi and algae include ionic interactions and complex formation between metal cations and ligands contained in the structure of the biomaterials [11]. Its effectiveness to remove heavy metals depends on the biosorbent concentration, the pH of the solution, the reaction kinetics and the effluent composition. However it is necessary to investigate on the relationship between biosorption efficiency and the parameters affecting it.

The application of statistical experimental design techniques in biosorption process development can result in improved product yields, reduced process variability, closer confirmation of the output response to nominal and target requirements and reduced development time and overall costs [12,13].

The main objective of this work was to develop the potential of the marine algae *S. muticum* to remove of hexavalent chromium ions from aqueous solutions. The effect of pH, temperature, initial metal concentration and sorbent dosage was analyzed using a factorial experimental design.

The factorial experimental design methodology involves changing all variables from one experiment to the next. As the variables can influence each other and the ideal value for one of them can depend on the values of the others, the interaction between the parameters was studied and optimized using response surface methodology.

2. Materials and methods

2.1. Biomass

The *S. muticum* brown alga was collected from the north coasts of Cuba. The biomass was washed with abundant deionized water to remove the impurities and ions such as Ca^{2+} or Na^{+} that can influence the biosorption process. After that, it was dried at 60 °C and stored in desiccators. After that, the biomass was grinded and sieved into fractions <1000 μm.

2.2. Characterization test

2.2.1. Scanning electron microscopy

The surface morphology of *S. muticum* was investigated by scanning electron microscopy (SEM), Leo 1430VP, combined with a system of analysis for energy dispersive X-ray spectroscopy (EDS), Inca 350 v. 17, de Oxford instruments, to determine the chemical composition. The samples were prepared as for SEM analyses.

2.2.2. FTIR analysis

FTIR spectroscopy was used to confirm the presence of the functional groups in samples and to observe the chemical modification after chromium biosorption. Infrared spectra were recorded in the 4000–400 cm^{-1} region using a Fourier Transform infrared Spectrometer, Perkin-Elmer model Spectrum 65.

Table 1
Factorial design matrix.

Independent variable	Range and levels		
	−1	0	+1
Temperature (A, °C)	20	30	50
Metal concentration (B, mg/L)	10	30	50
Sorbent dosage (C, g/L)	0.5	1	2

2.3. Batch biosorption

The stock solution of Cr(VI) at the concentration of 1 g/L was prepared using $K_2Cr_2O_7$ and deionized water. This stock solution was used for the preparation of test solutions by dilution. The initial pH was controlled with NaOH 0.1 M and HCl 0.1 M. The biomass in amount of (0.5; 1 and 2) g/L was added to the solution in order to analyze his influence over biosorption process. Then, the suspension was maintained under agitation on a reciprocal shaker at 150 rpm for 48 h. After this time, the equilibrium pH was measured and the chromium solution was filtrated on a cellulose filter membrane (pore size 1.2 μm). Next, the filtrate was acidified with HNO_3 and analyzed by ICP-AES JY 2000 (inductively coupled plasma atomic emission spectrometry) using a Jobin Yvon Activa M (Jobin-Yvon, Longjumeau, France) in order to determine the final metal concentration.

Experiments were performed according to the matrix given in Table 1. The result was expressed as % of chromium removal, calculated as:

$$\text{Cr(VI)} \quad \text{removal} = \frac{C_0 - C_f}{C_0} \times 100 \qquad (1)$$

where C_0 and C_f are the initial and final metal concentrations, respectively.

2.4. Factorial experimental design and optimization of parameters

Factorial design is a statistical technique used to screen variables, to estimate the main effects and interaction effects of different variables, and to develop an empirical model for a given process. It is used due to its ability to gain a large amount of information from a minimum number of data points.

The first step in a factorial design test involves determination of an experimental outcome to be tested. The experimental outcome is the variable that represents a measure of process performance; this is often referred to as the response variable. Through the use of factorial design, the operating variables that influence the chromium(VI) removal can be quantified.

Temperature, metal concentration and sorbent dosage were chosen as independent variables and the percent of chromium removed as dependent output response variable. Independent variables, experimental range and levels for chromium removal are given in Table 1. A 3^3 full factorial experimental design and thus a total of 27 experiments were employed in this study. For experimental design and statistical analysis, software Statgraphics v 4.1 was used. The optimal operational variable was employed in the following experiments for modeled the biosorption isotherm and uptake kinetics.

2.5. Modeling of biosorption isotherm and uptake kinetics

In order to investigate the mechanism of biosorption and the speed at which these processes take place it is important to consider the processes of mass transfer and chemical reaction. For it, several kinetics models have been used to fit experimental data, so it is important to establish the time dependence of such