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Equilibrium study of the binary mixture of cadmium–zinc ions biosorption by the *Sargassum filipendula* species using adsorption isotherms models and neural network

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Abstract

In this work, experiments have been carried out in the batch reactor to obtain equilibrium data of the individual biosorption and the mixture of cadmium and zinc ions by the biomass of the *Sargassum filipendula* species pre-treated with 0.5 mol/L calcium chloride. The experiments have been performed for the chosen temperature of 30 °C and operational conditions such as constant agitation and pH 5.0. Six adsorption isotherms models of the Langmuir type have been tested to represent the equilibrium data of the binary system. The artificial neural nets technique was used to fit the equilibrium experimental data. Different types of the net architecture have been tested varying the neurons number of the entrance and the hidden layer. The equilibrium concentrations of the fluid phase were used as input variables and the equilibrium concentrations of the biosorbent were used as output variable. The obtained simulation results have shown that the applied technique of artificial neural network has better adjusted the equilibrium data of the binary system when compared with the conventional biosorption isotherm models.

Keywords: Biosorption; Neural network; Isotherm; Multi-component

1. Introduction

The pollution, because of the heavy metal presence, is an ambient problem of world-wide interest. The heavy metals such as cadmium and zinc are, among others, the common pollutants found in the industrial effluents. Even in low concentrations, these metals are toxic for diverse organisms including human beings. The majority of salts heavy metals are soluble in water and consequently it cannot be separate for conventional physical processes of separation [1]. Some treatment technologies such as precipitation, ionic exchange and adsorption have been applied for metallic ions removal in aqueous solution. However, a promising technological proposal for the metal removal is the use of living and death biomass capable to remove metallic ions from aqueous solution in low concentrations. The industrial potential of the biosorption depends on the many factors, such as biosorption capacity, efficiency and selectivity an easiness of the metal recovery and, mainly, equivalence with performance and cost of traditional processes. The investigation of biosorbent performance is made for the purposes of the industrial application of biosorption and corresponding equipment design. This analysis is normally carried out through equilibrium studies on the system of interest [2].

The studies of metal removal by biosorption have been focused in the following areas: binding mechanisms, equilibrium study of batch sorption, effect of the acidity on the equilibrium study, influence of the biosorbent shape (entire, particulate) on the metal removal, biomass physical–chemical treatment to confer greater mechanics resistance of the biosorbent and study of removal in columns. It should be notice that little emphasis has been given to the study of multi-component system. However, the majority of the industrial effluents contain more than one metallic species, therefore, it is necessary to study the multi-component systems in relation to an industrial application of the biosorption process.

Following these thoughts is essential to study the effect of the presence of another metal species in solution because they will be able to compete for the active sites of a biosorbent and to

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Nomenclature

a_j	Freundlich mono-component isotherm constant
b_j	Langmuir isotherm constant (L/mequiv.)
C_j	concentration in the fluid phase (mequiv./L)
C_j^0	initial concentration in the fluid phase (mequiv./L)
C_j^*	concentration at equilibrium in the fluid phase (mmol/L)
k_1, k_2, K	multi-component Langmuir-type constants
n_j	Freundlich mono-component isotherm constant
m_s	dry mass of biosorbent (g)
q_m	Langmuir constant related to the capacity of adsorption (mequiv./g)
q_j^*	concentration at equilibrium in the biosorbent (mequiv./L)
V	solution volume (L)

Greek letters

$\alpha_{12}, \alpha_{21}, \alpha_{11}, \alpha_{12}, \alpha_{21}, \alpha_{22}$	Freundlich binary isotherm constant

Subscripts

J	metal species

interfere with the capacity of biosorption of the metallic species of interest [3,4].

In multi-component system, the biosorption of the metallic ion not only depends on the biomass surface properties and physical–chemical parameters of a solution such as: pH, temperature, initial metallic ion concentration and biomass concentration, but also depends on the metallic ion number in solution that compete for the active sites and metal concentration [5,6].

The ability of different *Sargassum* species to remove metallic ions has been studied by many researchers where its high potential as biosorbents has been confirmed by authors [7–12]. However, the simultaneous biosorption of mixture of metallic ions was not extensively investigated.

The applications of mathematical models to describe the biosorption process can give a quantitative its evaluation as well as will help to optimize its operational conditions.

1.1. Mono-component system

Despite the identification of the ion exchange as being the main mechanism of ions removal by a biosorbent, the treatment has been generally used to represent the equilibrium data like in the adsorption isotherms form that have appropriately represented the equilibrium of these systems. For the adsorption isotherms, the equilibrium relation is established only between the chemical species in the fluid phase; therefore, the chemical species liberated by biosorbent did not influence the concentration of adsorbed components.

The evaluation of the biosorbent performance normally is made by applying the isotherms analysis obtained from the equilibrium study of ions sorption in batch assays. The Langmuir and Freundlich isotherms are used to represent the individual metallic ions adsorption.

The mathematical expression that represents the Langmuir isotherm can be written as follows:

$$q_j^* = \frac{q_m b_j C_j^*}{1 + b_j C_j^*} \tag{1}$$

where q_m and b_j are Langmuir isotherm constants. These constants have a physical meaning and b_j parameter represents the ratio between sorption and desorption rates. Therefore, the high b_j values indicate high affinity of the ion for the site of the adsorbent material, while the q_m parameter represents the total number of available sites of the biosorbent. When $b_j C_j^* \gg 1$, the isotherm is very favorable; however, if $b_j C_j^* < 1$ the isotherm is quasi linear.

A Freundlich isotherm in an empirical model can be represented as follows:

$$q_j^* = a_j (C_j^*)^n \tag{2}$$

where a_j and n are the Freundlich isotherm constants.

The Freundlich isotherm does not predict the sorbent saturation. Thus, the model allows the existence of an infinite superficial covering. The Freundlich isotherm frequently is used to model the limited segments of experimental data [13].

1.2. Binary isotherms

Usually, the industrial effluent present a mixture of ions which compete between itself for the active biosorbents sites, that is important for a determination of the ions selectivity in the solution by the biosorbent material.

The multi-component Langmuir model was the most frequently used to fit the binary biosorption data. The mathematical expression that represents the model of the Langmuir isotherm for a binary mixture can be written as follows:

$$q_1^* = \frac{q_m C_1^* b_1}{1 + b_1 C_1^* + b_2 C_2^*} \tag{3}$$

where q_m, b_1 and b_2 are the binary Langmuir isotherm constants.

Chong and Volesky [14] and Sanchez et al. [15] have applied a model originally developed by Bailey and Ollis [16] to represent the binary data of biosorption equilibrium. The original model was developed to describe the non-competitive inhibition during enzymatic kinetic studies. This model is represented by Eq. (4):

$$q_1^* = \frac{q_m C_1 b_1 [1 + (K/b_1) C_2^*]}{1 + b_1 C_1^* + b_2 C_2^* + 2K C_1^* C_2^*} \tag{4}$$

where q_m, b_1, b_2 and K are model constants.

Chong and Volesky [14] and Sanchez et al. [15] have been used modified models of the Langmuir isotherm to represent the biosorption equilibrium data in binary mixtures. These models have been developed through the incorporation of the new parameters to the original model of the Langmuir isotherm (Eq. (1)).