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Phenomenological mathematical modeling of heavy metal biosorption in fixed-bed columns

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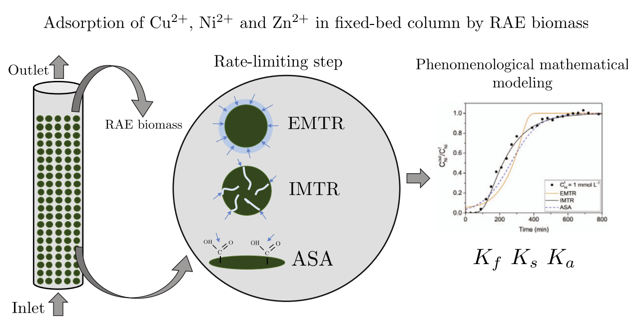
HIGHLIGHTS

- Phenomenological biosorption modeling was successfully applied.
- Dynamics and equilibrium were evaluated.
- The biomass efficiently removed Cu(II), Ni(II) and Zn(II) ions.
- The phenomenological model was validated in different experimental conditions.
- The process is rate limited by the internal mass transfer resistance.

GRAPHICAL ABSTRACT



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ABSTRACT

A phenomenological mathematical modeling has been applied in order to describe the dynamic behavior of the biosorption of heavy metals in fixed-bed columns. The mathematical model hereby proposed was evaluated on experimental breakthrough curves of the ions Cu(II), Ni(II) and Zn(II) in monocomponent systems using the residue of alginate extraction from *Sargassum filipendula* as biosorbent. Some authors have studied mathematical models to describe the biosorption of heavy metals, however, in most cases, they have fitted the models to the experimental data without evaluating the prediction capacity of the model in different operational conditions. This capacity is inherent of phenomenological models. Therefore, in addition to the breakthrough curves used to obtain the kinetic parameters of the models, an extra set of breakthrough curves has been studied outside the range evaluated for the fitted parameters in order to validate the model. The equilibrium data for the three studied ions was adequately represented by the Langmuir isotherm. The quantity of Ni(II) removed was very similar to the quantity related to the Zn(II) removal and the removal of Cu(II) ions was far superior than the other ions. The high values for the breakthrough time obtained for the Cu(II) ions represent a high removal efficiency and affinity with the biomass. The mathematical model was able to predict the dynamic behavior of removal for the three investigated ions, indicating that the internal mass transfer resistance is the rate limiting-step. The validation of the model demonstrated the prediction capacity in the different evaluated conditions, characterizing it as a useful tool when analyzing and designing heavy metal biosorption processes in fixed-bed columns.

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1. Introduction

It is well known that the contamination of the water bodies with heavy metal ions is a global concern due to the high toxicity, non-biodegradability and accumulation in the human body [1]. Heavy metals have different chemical and physical properties and, similarly, each metal has its specific toxicological effects. In general, the contamination caused by heavy metals can have different effects in the human body such as: cardiovascular, respiratory, endocrine, immunologic and problems related to the reproductive system [2].

There are several available technologies that are used to remove heavy metals from industrial wastewater such as: chemical precipitation [3], coagulation and flocculation [4], biological treatments [5] and membranes [6]. The chemical precipitation is the most used process, showing good results when used to remove heavy metal ions in high concentrations [7]. The conventional treatment processes, usually effective when removing great quantities of contaminants, become expensive or inefficient when the objective is to remove the pollutants until a trace level is reached, established by environmental legislations [8]. Consequently, it is necessary to apply a complementary process able to bring the heavy metal concentration to a level that is in agreement with the environmental regulations.

The adsorption process is consolidated as one of the most efficient technologies applied when removing contaminants to trace levels, providing a treated effluent of high quality [9]. For this process, in addition to a high removal capability, it is indispensable to have a low cost material as adsorbent. Low cost adsorbents are considered the ones that require a little or no processing and are found in abundance in the environment, being by-products or residues of industrial processes [10].

Among the many adsorbent materials reported according to the literature, the seaweed biomass is considered one of the most promising due to its high removal capability, low cost, renewability and availability in the most part of the oceans of the planet [1]. The main component of cell wall of the brown seaweeds is the alginate biopolymer, a product with high commercial value, being used in the food, textile, pharmaceutical, cosmetic and biomedical industries [11]. The use of the alginate biopolymer in adsorption process related to the removal of heavy metals has been exhibiting a good efficacy [12]. Nevertheless, the competition with the applications reported above combined with the cost related to the extraction from the seaweeds impairs the economic viability of the process of adsorption using this material. The residue from the alginate extraction process is usually discarded, however it can still have many functional groups that are present in the seaweed such as phosphate, sulfate, amino and hydroxyl that are responsible for physical and chemical interactions between the ions in solution and the adsorbent [13]. Therefore, the application of the residue from the alginate extraction as an adsorbent is an interesting aspect to be considered from the economic point of view, once it adds value to the by-product of the process [14].

The mathematical modeling is an important tool used to understand and analyze the adsorption of heavy metals. Applied in order to identify the mechanism that controls the adsorption process, it is evaluated with the experimental data and when representing adequately the phenomenon, allows the prediction of parameters in different operational conditions, projects, optimization and process control [15–18]. Phenomenological mathematical models present as an advantage, compared to the empirical models, the possibility of identification of the mechanisms related to the mass transfer and the ability of prediction outside the evaluated range where the model parameters where obtained [17]. Some studies have been trying to represent the adsorption process through mathematical models, however, for the most part, the adsorption curves are simulated according to the parameters obtained fitting the experimental data. In this case, correlations between the fitted mass transfer coefficients and the experimental conditions can not be obtained, consequently the models are not able to validate and evaluate different process conditions [14].

In this study, the biosorption process of Cu(II), Ni(II) and Zn(II) ions in a fixed bed column and monocomponent systems has been evaluated, determining the limiting mass transfer step of the process through a phenomenological mathematical modeling approach. After determining the limiting mass transfer step, different conditions have been studied in order to confirm the prediction capability of the model and its validation.

2. Material and methods

2.1. Alginate extraction from Sargassum filipendula seaweed

The *Sargassum filipendula* seaweed used in this study was collected from the coast of northern São Paulo. After being washed with deionized water in order to remove some debris, the seaweed was dried in an oven for 24 h at 60 °C and stored in plastic recipients.

Before the extraction process, two washing steps were performed with the aim of removing phenolic compounds and clarify the biomass [19]. In the first step, the seaweed was put in contact with an aqueous solution of formaldehyde (0.4% v/v) for 30 min, biomass dose of 0.03 g L^{-1} and constant shaking of 100 rpm. Then, in the second washing step, the same procedure was performed with an aqueous solution of HCl 0.1 mol L^{-1} for 2 h.

After this procedure, the extraction was conducted according to McHugh[20]. Initially, the seaweed was put in contact with 350 mL of an aqueous solution of Na_2CO_3 (20 g L^{-1}) for 5 h and at a temperature of 60 °C. Following the extraction, the viscous mixture was vacuum filtered in order to remove the residue from the seaweed. The alginate contained in the filtered solution was then precipitated with ethanol (1:1 v/v). Gomez et al.[21] demonstrated that the extraction of alginate using ethanol can lead to a better yield and rheological properties, providing a method with a reduced numbers of extraction steps.

The residue was then washed with deionized water in order to eliminate the traces of the viscous solution that could be adhered to the surface. After that, the residue and the precipitated alginate were dried in an oven with controlled air circulation at 60 °C for 24 h.

2.2. Biomass preparation

The residue of alginate extraction (RAE) from the *Sargassum filipendula* seaweed, in a dose of 10 g L^{-1}, was acidified with an aqueous solution of HCl 0.1 mol L^{-1} until the stabilization of the pH at 4.0. Since the extraction process is carried out in a basic medium, and organic compounds present in the biomass can be dissolved during the process increasing the possibility of precipitation of the ions, this procedure enhanced the control of pH [22]. Then, the RAE biomass, after being filtered, was dried in an oven at 60 °C for 24 h and stored to be used in the fixed-bed column assays.

2.3. Preparation of the synthetic heavy metal solutions

The synthetic monocomponent solutions containing the Cu(II), Ni(II) and Zn(II) ions were prepared with the salts $Cu(NO_3)_2.3H_2O$, $Ni(NO_3)_2.6H_2O$ and $Zn(NO_3)_2.6H_2O$ and deionized water. The pH of the heavy metal solutions was set to a value of