The effect of impurities on metal biosorption

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Industrial effluents contaminated with heavy metals contain various kinds of compounds that can be considered as “impurities” in the metal-removal process. These could be light metal ions, surfactants and chelating agents and that may significantly affect the performance of the biosorption process. In this study the effect of NaCl, as a model impurity, on the uptake of chromium(VI) and vanadium(V) was experimentally investigated and mathematically modeled. Increasing concentrations of NaCl suppressed the uptake of both metals. The extended Langmuir model was used to describe the experimental results. The impurities, Na^+ and Cl^- in this study, were considered as a single “fictitious” component. The model was successfully used for prediction and simulation of biosorption isotherm under different conditions of biosorption.

1. INTRODUCTION

Biosorption of metals has been demonstrated as a feasible and very cost-effective alternative for detoxification of effluents generated by several key industrial sectors [1-3]. While synthetic pure metal-bearing solutions have been used for laboratory biosorption studies, actual industrial wastewaters contain different types of impurities which may tend to significantly affect the performance of biosorption [4]. The type of these impurities is likely to differ depending on the type of effluent considered for treatment by biosorption. Among such impurities, light ions exist in most industrial effluents and tend to affect the metal biosorption to a different degree [5-9].

In order to predict the biosorption performance with actual wastewater and to facilitate the design and/or optimization of the biosorption process for meeting the metal discharge regulations, computer simulation based on a suitable process model provides an essential tool. Otherwise, separate experiments would have to be carried out for each different wastewater in order to obtain process design and/or operating parameters. Until now, ionic impurities have been generalized as ionic strength in some models [6-7]. However, it is not easy to measure the ionic strength in the actual wastewater because of its complex ionic composition.

Recent adsorption research on activated carbon proposed the fictitious component approach which has been successfully used for modeling the effect of unknown impurities on the adsorption performance [10,11]. In this approach various kinds of impurities could be considered lumped together and their effect approximated as that of one fictitious component. Similarly, the fictitious component approach can be proposed for dealing with metal biosorption in the impurity-containing solution, which represents a novelty in the field.

The purpose of the present work is to assess the possibility of applying the fictitious component approach to the metal biosorption system. In this study, NaCl was used as a model impurity affecting biosorption of chromium(VI) and vanadium(V) onto crab-shell material. The fictitious component approach was coupled with the extended Langmuir model to assist in the prediction of the biosorption performance in the impurity-containing solution.

2. MATERIALS AND METHODS

2.1. Biosorbent

Waste crab-shells (*Ucides cordatus cordatus*) were obtained sundried from Paraiba, Piaui, Brazil. They were crushed and sieved (6-16 mesh) giving 1-3.35 mm particles subsequently washed with 0.2 N HCl (6 hrs) to remove $CaCO_3$ and rinsed with distilled water until the final pH stabilized at pH 3. The residual material was air-dried and represented approximately 52% of dry raw crab shells. It mainly contained chitin complexed with small amounts of protein, and pigments. This treatment also removed various ions naturally embedded in the crab shell material.

2.2. Biosorption experiments [12]

Biosorption isotherm were obtained in batch equilibrium experiments. Different amounts of NaCl were added to the metal solutions prepared using analytical grade CrO_3 and Na_2VO_4. Approximately 40 mg of acid-washed crab shell material was contacted for 24 h with 20 ml of the metal solution in flasks, the suspension shaken at 150 rpm at room temperature. The solution pH was adjusted during sorption experiments to pH 2.0 (for chromium) and pH 2.5 (for vanadium) with concentrated NaOH and HCl. The equilibrium final metal concentration was analyzed by a sequential inductively-coupled plasma (ICP) atomic emission spectrometer (Thermo Jarrell Ash, Trace Scan).

2.3. Parameter estimation

Parameters of the model were estimated using the Marquardt-Levenberg nonlinear regression algorithm [13]. The software Mathematica (Version 4.0, Wolfram Research, USA) was used for the nonlinear regression [14].

3. RESULTS AND DISCUSSION

3.1. Model description

Ionic impurities in this study were represented as one lumped fictitious ionic component interfering with metal biosorption. In other words, the solution containing the heavy metal and impurities was simplified into a binary system composed of one primary-interest metal (component 1) and one fictitious ionic component (component 2).

There are various kinds of empirical models capable of describing the sorption behavior of a binary system, such as extended forms of Langmuir [15], Freundlich [16], and Sips models [17]. In this study the extended Langmuir model was used due to its simplicity. For single metal sorption, the mathematical representation of the Langmuir model is

$$q_1 = \frac{q_1^0 b_1 C_1}{1 + b_1 C_1} \tag{1}$$

where q_1 is the metal uptake (mmol g^{-1}) at the equilibrium solution concentration of metal (C_1, mmol l^{-1}), q_1^0 represents the maximum uptake (mmol g^{-1}) and b_1 is the sorption energy (l mmol^{-1}).

For the binary system, the model can be extended as follows:

$$q_1 = \frac{q_1^0 b_1 C_1}{1 + b_1 C_1 + b_2 C_2} \tag{2}$$

$$q_1 = \frac{q_2^0 b_2 C_2}{1 + b_1 C_1 + b_2 C_2} \tag{3}$$

where subscripts 1 and 2 represent the primary-interest metal (here, chromium or vanadium) and the fictitious ionic component, respectively.

q_1 and q_2 are the uptakes of the metal and of the fictitious component, respectively, in the binary system.

q_1 q_1^0 and q_2^0 and b_1 and b_2 represent the maximum uptake and the biosorption energy of the metal and fictitious component, respectively, in the single component system.

Table 1. The estimated parameters for the extended Langmuir model.

	Metal (Component 1)	Impurity (Component 2)
Chromium(VI) biosorption	$q_1^0 = 0.80$ mmol g^{-1} $b_1 = 0.42$ l mmol^{-1}	$q_2^0 = 1.92 \times 10^{-9}$ mmol g^{-1} $b_2 = 1.81$ l mmol^{-1} $C_{2i} = 14.4$ mmol l^{-1}
Vanadium(V) biosorption	$q_1^0 = 1.03$ mmol g^{-1} $b_1 = 0.55$ l mmol^{-1}	$q_2^0 = 3.60 \times 10^{-9}$ mmol g^{-1} $b_2 = 0.73$ l mmol^{-1} $C_{2i} = 9.45$ mmol l^{-1}

3.2. Parameter estimation

Once the sorption isotherms of the metal and of the fictitious component in their respective single component systems are found, the metal uptake in the binary system can be straightforwardly calculated according to the extended Lamgmuir model. The metal isotherm can easily be obtained from common batch equilibrium experiments and it shown in Fig. 1. The values of parameters q_1^0 and b_1 were determined and are summarized in Table 1. However, since the fictitious component is a hypothetical one affecting the metal biosorption, it is not possible to obtain its sorption isotherm directly by the experimental method.

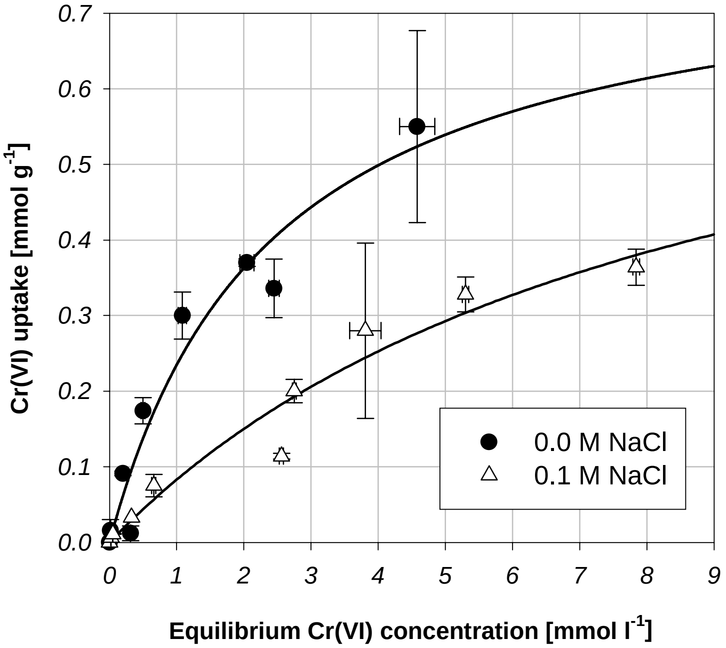

Figure 1. The uptake of chromium(VI) by crab shells at pH 2.0 in the single chromium(VI) system and in the binary system composed of chromium(VI) and impurities (NaCl). The data points and error bars are the average values and standard deviations (n = 2 – 4), the lines were produced using the model.

In this study, the model parameters for the fictitious component were estimated from the metal isotherm obtained in the binary system. Fig. 1, shows that the presence of NaCl as an impurity significantly reduced the chromium uptake. The decreased chromium uptake should be described by Eq. (2). Simultaneously, the fictitious component uptake should behave in accordance with Eq. (3). The mass balance of the fictitious component can be established as follows:

$$q_2 X = C_{2i} - C_2 \tag{4}$$

where C_{2i} represents the initial concentration of the fictitious component (mmol l^{-1}) and X is the concentration of biosorbent (g l^{-1}). With Eqs. (3) and (4), the equilibrium concentration of the fictitious component can be explicitly expressed as follows:

$$C_2 = \frac{b_2\left(C_{2i} - q_2^0 X\right) - \left(1 + b_1 C_1\right) + \sqrt{4 b_2 C_{2i}\left(1 + b_1 C_1\right) + \left\{1 + b_1 C_1 - b_2\left(C_{2i} - q_2^0 X\right)\right\}^2}}{2 b_2} \tag{5}$$

Combining Eqs. (2) and (5) yields q_1 as a function of C_1 containing three unknowns such as C_{2i}, q_2^0 and b_2. The unknown parameters were evaluated by regressing the resulting function to the isotherm data obtained with the impurity-containing system (Table 1). As can be seen in Fig. 1, the model could successfully describe the experimental data without any biased trends.

It should be noted here that C_{2i} is not the real concentration of impurities but the conceptual one of the fictitious component. Thus, C_{2i} can vary depending on the degree of interference of impurities present in a certain effluent. In this case, C_{2i} was estimated to be 14.37 mM on the basis of 1 M NaCl which indicated that the effective concentration of the fictitious component interfering with the chromium uptake could be as much as 1.4% of the actual concentration of NaCl. Additionally, q_2^0 was evaluated to be negligible when compared with q_1^0. This was in accordance with the previous finding indicating that the affinity of sodium ion toward the biosorbent was very weak [1].

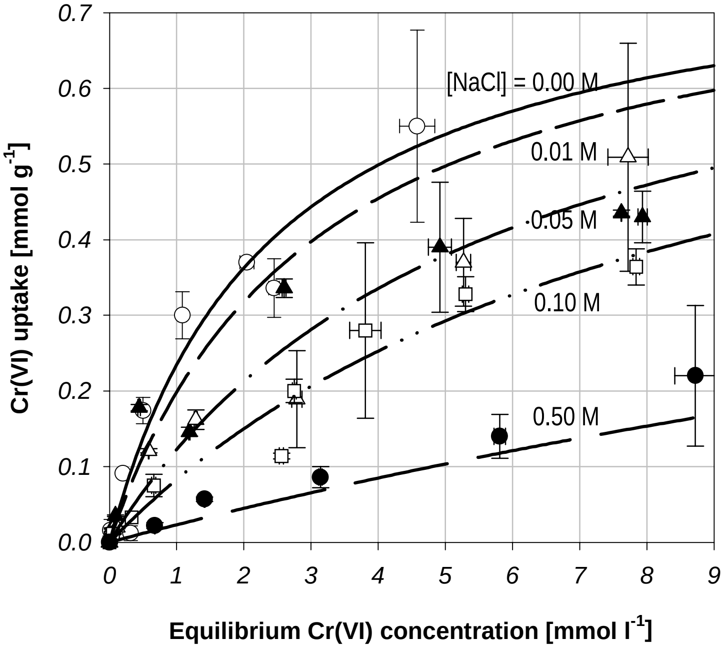

Figure 2. The comparison between the experimental data and model-predicted results for the chromium(VI) uptake by the crab-shell material at pH 2.0. The initial concentrations of NaCl were 0.00M (○), 0.01M (▲), 0.05M (△), 0.10M (□), and 0.50 M (●). The data points and error bars are the average value and standard deviations (n = 2 – 4), the lines were produced using the model.

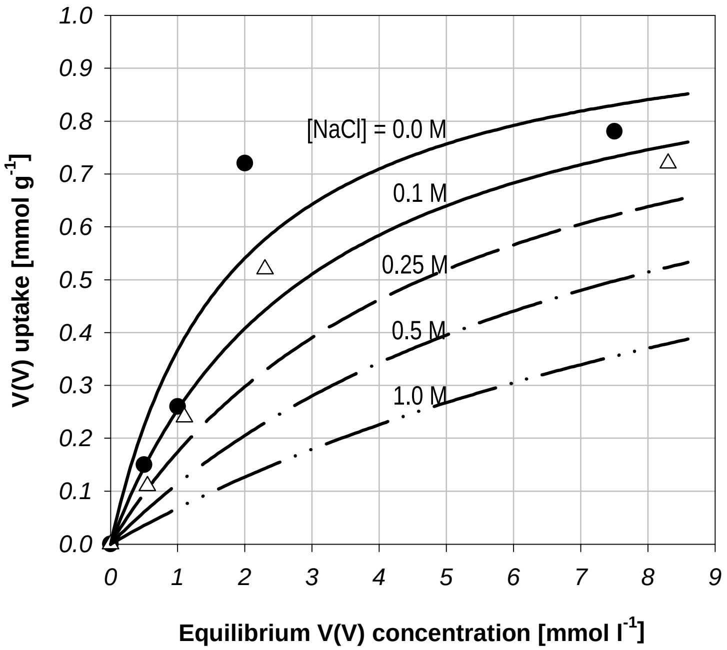

Figure 3. The vanadium(V) uptake by the crab shell material at pH 2.5. The initial NaCl concentrations of 0.0M (●) and 0.1 M (△) were used for the experiment, the lines were simulated by the model.

3.3. Discussion of Model Application

The new-concept model was applied to predict the uptake of chromium at different concentrations of the impurity. As shown in Fig. 2, the model could predict the experimental data as a whole. However, at a very low concentration of impurities (0.01 M NaCl), a significant deviation was found especially in the range of high metal concentrations (≥ 5 mM). At the moment, the reason for this could not be obviously established.

In another model application example, the uptake of vanadium(V) by the crab shell material in the presence of an impurity was predicted by using the same methodology. The model parameters for this system, summarized in Table 1, were estimated as described previously. As shown in Fig. 3, the effect of the impurity on the vanadium uptake was less significant than that observed for the chromium uptake. It was also established that the conceptual initial concentration of the impurity was 0.94 mM which is smaller than that in the case of chromium biosorption (1.4 mM). Consequently, it can be noted that the conceptual concentration of the fictitious component is a measure of the degree of interference encountered by in the biosorption process and it can vary depending upon both type of the target metal and/or impurities.

In summary, the fictitious component concept combined with the extended Langmuir model was successfully able to describe the biosorption of chromium(VI) and vanadium(V) in the presence of NaCl as an impurity. In order to validate and generalize this approach, further studies are required with other metals and various impurities and, eventually, with a broad range of actual industrial metal-bearing effluents.

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NOMENCLATURE

b_1	$\mathrm{l\ mmol^{-1}}$	Biosorption energy of the metal in the single metal system
b_2	$\mathrm{l\ mmol^{-1}}$	Biosorption energy of the fictive component in the single fictive component system
C_1	$\mathrm{mmol\ l^{-1}}$	Equilibrium concentration of the metal
C_2	$\mathrm{mmol\ l^{-1}}$	Equilibrium concentration of the fictive component
C_{2i}	$\mathrm{mmol\ l^{-1}}$	Initial concentration of the fictive component
q_1	$\mathrm{mmol\ g^{-1}}$	Uptake of the metal at equilibrium
q_2	$\mathrm{mmol\ g^{-1}}$	Uptake of the fictive component at equilibrium
q_1^0	$\mathrm{mmol\ g^{-1}}$	Maximum uptake of the metal in the single metal system
q_2^0	$\mathrm{mmol\ g^{-1}}$	Maximum uptake of the fictive component in the single fictive component system
X	$\mathrm{g\ l^{-1}}$	Concentration of biosorbent

Subscript

1	Primary-interest metal
2	Fictive component as a representative of impurities

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