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KINETIC MODELING OF THE BIOSORPTION OF Cd^{2+} IONS FROM AQUEOUS SOLUTIONS ONTO *Eichhornia crassipes* ROOTS USING POTENTIOMETRY: LOW-COST ALTERNATIVE TO CONVENTIONAL METHODS

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This work presents the use of potentiometric measurements for kinetic studies of biosorption of Cd^{2+} ions from aqueous solutions on *Eichhornia crassipes* roots. The open circuit potential of the Cd/Cd^{2+} electrode of the first kind was measured during the bioadsorption process. The amount of Cd^{2+} ions accumulated was determined in real time. The data were fit to different models, with the pseudo-second-order model proving to be the best in describing the data. The advantages and limitations of the methodology proposed relative to the traditional method are discussed.

Keywords: biosorption; potentiometry; kinetics.

INTRODUCTION

Presently, there is a growing interest on the use of biosorption for the elimination of toxic heavy metal ions from industry wastewater.[1,2] These studies are principally focused on equilibrium and kinetic properties.[2] Despite the many works that have modeled the biosorption kinetics, the methodology usually used to obtain the data to compare with the kinetic models has remained unchanged: samples are withdrawn from a suspension of a macroscopic amount of sorbent in a heavy metal aqueous solution at different times and filtered; the metal ion concentration in solution is usually determined by optical methods.[3,4] This analytical routine has the following disadvantages: it requires a large amount of biosorbent and generates a significant volume of waste, which contributes considerably to environmental pollution. In addition, several steps are needed to obtain the final result. An alternative to this methodology that is used for kinetic studies is the use of ion-selective electrodes.[5,6] This technique allows many experimental data points to be collected without removing solution aliquots. Nevertheless, the amount of biosorbent and the solution volume required for the experiment are significant, and only a limited number of selective electrodes are available, which limits the number of metallic ions that can be studied with these electrodes. It is also possible to determine the concentration of metallic ions in real time during their bioaccumulation by measuring the open circuit potential (OCP) of a metal, M, in equilibrium with its ion, M^{z+}, where $z+$ is the charge of the ion.[7] However, to our knowledge, this technique has not been used in biosorption studies despite the following advantages: the need for only very small amount of solution and sorbent, real-time measurements, and the use of easily accessible and low-cost equipment. Therefore, the goal of this work is to use potentiometric measurements to study the effect of the initial concentration of Cd^{2+} ions on their bioaccumulation kinetics. The selected biosorbent was *Eichhornia crassipes* (water hyacinth) roots because the biomass of this plant has shown promising potential for the removal of cadmium ions from aqueous media.[3,4,8–10]

EXPERIMENTAL

Collection and treatment of plant samples

Eichhornia crassipes plants were obtained from Tenanguillo in the municipality of Tabasco, Zacatecas, México, which were transported to the greenhouse at the Faculty of Chemical Sciences of UASLP and grown there. The roots were first washed with running water and then with deionized water. Excess water was eliminated from the roots using an absorbent paper, following which, the roots were separated from the aerial part of the plant and frozen. The frozen roots were subjected to drying in a freeze dryer with a LabCom 7522900 vacuum pump to −48 °C for 16 h. Once dried, the roots were pulverized in a Cole-Parmer analytic mill and stored in bottles at room temperature.

Apparatus and reagents

Analytical reagent-grade chemicals were used without further purification. All solutions were prepared with deionized water (18 MΩ cm). The solutions were purged with pure nitrogen before conducting the electrochemical experiments, and the nitrogen flow was directed over the solution surface during the measurement.

Potentiometric measurement

A $5 \times 0.4 \times 0.2$ cm^3 Cd commercial foil (99.999%, Alfa-Aesar) was used as the working electrode and an Ag/AgCl (3 mol dm^{-3} NaCl) electrode (BAS) as the reference electrode. The OCP was measured with both a BAS 100 W potentiostat and a digital multimeter (UNI-T). First, the working electrode was polished using sandpaper. Next, it was rinsed thoroughly with deionized water and sonicated in an ultrasonic bath for 10 min. The cadmium electrode was placed in a cell containing 2.5 mL of different stirred deoxygenated solutions of $Cd(NO_3)_2.4H_2O$ in 0.1 M $NaClO_4$. The OCP was determined before, during, and after the addition of 20 mg of roots. In order to maintain a constant ionic strength, $NaClO_4$ was added to the solution; however, it is possible to perform the experiment without using a support electrolyte.

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RESULTS AND DISCUSSION

Potentiometric measurement

The OCP of a metal, M, in equilibrium with its ion, M^{z+}, can be used to determine the concentration of metal ions in real time during their bioaccumulation.[7] This test involves immersing the studied metal in a solution containing its ion, nonliving biomass, and a reference electrode. It is important to establish equilibrium between the metal and its ions for an accurate measurement; the metal must be very stable so that during the experiments it does not form metal oxides or other compounds on the surface of the metallic electrode, which can disrupt the results. Cadmium has been shown to exhibit a large hydrogen overpotential and a small corrosion rate in deoxygenated solutions at neutral pH.[11] In addition, it has been reported to be suitable for use as an electrode of the first kind.[12] After verifying the suitability of cadmium as an electrode of the first kind, the kinetics of accumulation of Cd^{2+} ions by *Eichhornia crassipes* roots was studied by following the OCP during bioaccumulation. The cell, in which an Ag/AgCl/NaCl (3 M) reference electrode was used, can be represented as follows:

$$\mathrm{Ag} \mid \mathrm{AgCl} \mid \mathrm{NaCl}\ (3\ \mathrm{M}) \parallel \mathrm{Cd}^{2+} \mid \mathrm{Cd}$$

Using the equation $E_{\text{cell}} = \text{OCP} = E_{\text{right}} - E_{\text{left}}$, the cell potential can be written in the following form:

$$E_{cell} = \text{OCP} = E_{M^{z+}/M} - E_{ref} \quad (1),$$

where $E_{M^{z+}/M}$ can be obtained from the Nernst equation:

$$E_{M^{z+}/M} = E^0 + \frac{0.0591}{n}\log a_{Cd^{2+}} \quad (2)$$

where E^0 is the standard potential; n is the number of electrons per molecule oxidized or reduced; a_{Cd2+} represents the activity of Cd^{2+} ions in mol L^{-1}; 0.0591 is the value of RTF^{-1} at 25 °C (298 K), multiplied by 2.303 to convert the expression from natural log to log base 10; and R, F, and T are the gas constant, Faraday constant, and absolute temperature, respectively.

For a low concentration of Cd^{2+} ions, the activity of cadmium can be replaced by its concentration ($[Cd^{2+}]$). Considering that $n = 2$ for this case and substituting equation (2) into equation (1), the OCP measure at a given time can be expressed as follows:

$$\text{OCP} = E^0 + 0.02955\log[\text{Cd}^{2+}] - E_{ref} \quad (3)$$

Here, one can clearly see that a decrease in the metal ion concentration reduces the OCP.

The experiment was initiated by measuring the OCP of Cd/Cd^{2+} with respect to an Ag/AgCl electrode. The OCP was measured using a potentiostat, and measurements were recorded every 0.2 s. Because the roots aggregated in solution, a perturbation was observed initially (Figure 1); however, equilibrium was reached after several seconds. For the purpose of modeling, the time at which equilibrium was reached was reconsidered to be the initial time. After equilibration, a continuous decrease in OCP was observed, which could be attributed to a decrease in the concentration of Cd^{2+} ions in solution due to their adsorption by the roots. As indicated in equation (3), a reduction in the $[Cd^{2+}]$ in solution was associated with a decrease in OCP.

The metal ion content in solution at each time point was evaluated by calculating the difference between the initial (OCP-1) and final (OCP-2) OCP values:

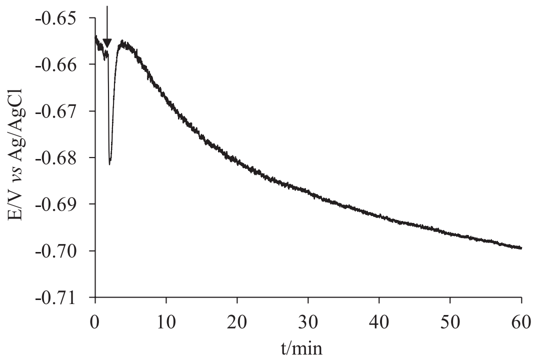

Figure 1. *OCP before, during and after the addition of* Eichhornia crassipes *root powder for a Cd electrode immersed in solution 1 x 10^{-4} M of $Cd(NO_3)_2$ in $NaClO_4$ (0.1 M). The arrow indicates root powder addition*

$$\text{OCP}-1 = E^0 + 0.02955\log[\text{Cd}^{2+}]_1 - E_{ref} \quad (4)$$

$$\text{OCP}-2 = E^0 + 0.02955\log[\text{Cd}^{2+}]_2 - E_{ref} \quad (5)$$

Because E_{ref} and E^0 are constant for a given measurement, the difference is given by the following equations:

$$\begin{aligned}\Delta\text{OCP} &= (\text{OCP}-1) - (\text{OCP}-2)\\ \Delta\text{OCP} &= 0.02955\log[\text{Cd}^{2+}]_1 - 0.02955\log[\text{Cd}^{2+}]_2\end{aligned} \quad (6)$$

$$\text{or} \quad \Delta\text{OCP} = 0.02955\log\frac{[\text{Cd}^{2+}]_1}{[\text{Cd}^{2+}]_2} \quad (7)$$

Knowledge of the initial metal ion concentration prior to the addition of roots helps determine the metal ion concentration at any other point in time according to the following equation:

$$[\text{Cd}^{2+}]_2 = [\text{Cd}^{2+}]_1 10^{\frac{-\Delta\text{OCP}}{0.02955}} \quad (8)$$

The cadmium ion content adsorbed onto per gram of *Eichhornia crassipes* roots within a given time (q_t) was calculated according to the following relation:

$$q_t = \frac{\left([\text{Cd}^{2+}]_1 - [\text{Cd}^{2+}]_2\right)V\ 112.40}{\text{root mass}} \times 1000 \quad (9)$$

where 112.40 corresponds to the molar mass of cadmium in g mol^{-1}, V is the solution volume in liters, the root mass is given in grams, and the result obtained is multiplied by 1000 to convert the cadmium mass from grams to milligrams. The values of q_t were calculated from the potentiometric measurements to obtain the curve shown in Figure 2a. The amount of cadmium adsorbed increased rapidly during the first few minutes, and the adsorption rate asymptotically approached a limiting value toward the end of the process. This trend indicated that the removal of Cd^{2+} ions was rapid during the initial few minutes, following which, the elimination proceeded at a slower rate until equilibrium was reached. This behavior is analogous to that reported for other biosorption processes.[4–7] The final removal percentage after 50 min was 96.42%, indicating that the greater part of cadmium is taken up by the roots. Similar percentages were obtained for the other concentrations studied.

Kinetic modeling

Intraparticle diffusion

The effects of intraparticle diffusion on the adsorption process

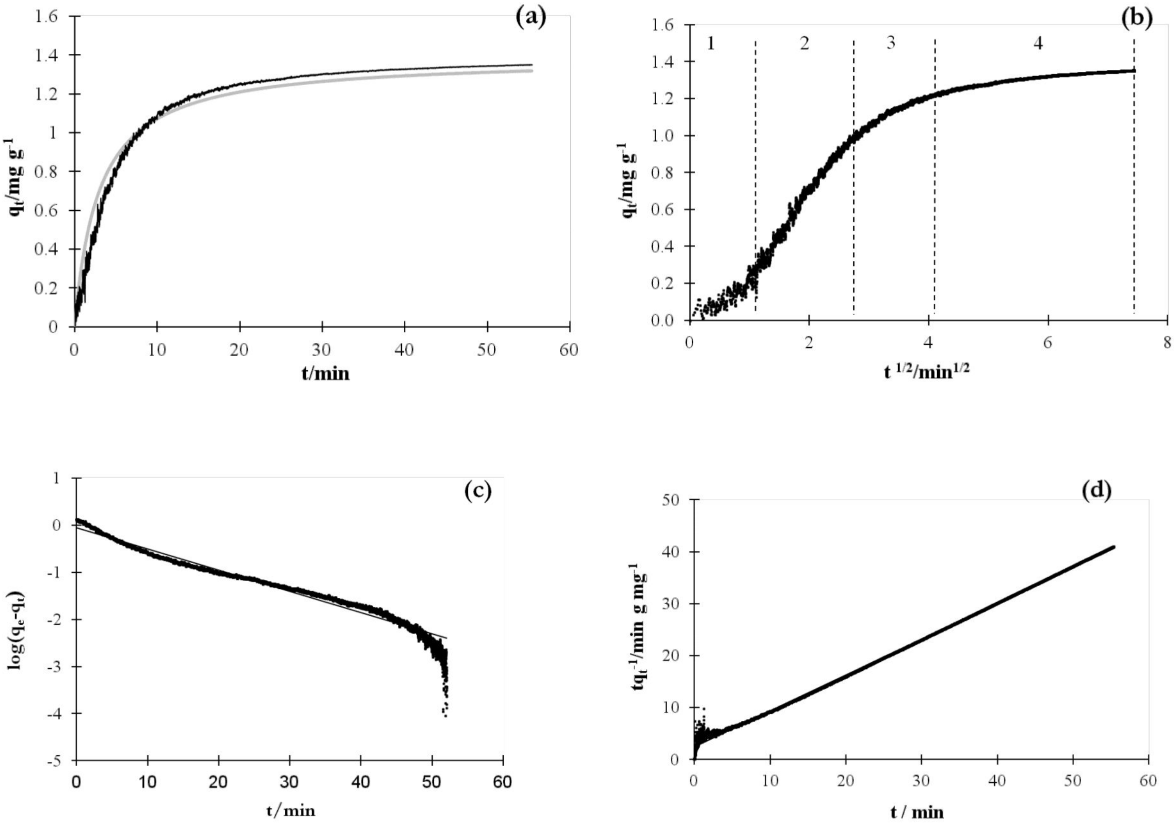

Figure 2. *Plots of data from Figure 1: (a) effect of contact time on the uptakes of Cd by Eichhornia crassipes, experimental data (—) and calculated data (—) using equation (16), (b) intraparticle diffusion plot, and (c) the linearized pseudo-first- and (d) pseudo-second-order biosorption*

were investigated by fitting the experimental data to the following equation:[13]

$$q_t = K_i t^{1/2} + C \qquad (10)$$

where q_t is the amount of adsorbate bound per unit of adsorbent mass at time t, K_i is the intraparticle diffusion rate constant, and C is a constant that indicates the boundary layer thickness. Higher values for the intercept indicate stronger boundary layer effects. When the intraparticle diffusion was the rate limiting step, q varied linearly with $t^{1/2}$ and K_i could be estimated from the slope of the line. The curve obtained here included four separate regions (Figure 2b): an initial curved region (1) followed by two linear regions (2 and 3), and then a plateau (4). Several authors[14–16] have reported similar behavior and attributed the different regions of the curve to the sequential stages of solute mass transfer to the adsorbent.

In region (1), film diffusion from the bulk solution to the sorbent surface constituted the main process. Region (2) was attributed to the movement of metal ions across the external liquid film boundary layer to the adsorbent external surface. Migration of metal ions through the pores of the sorbent by intraparticle diffusion was attributed to region (3), and adsorption at the internal binding sites was associated with region (4). Because region 3 was associated with diffusion, the values of K_i and C were calculated from the data obtained from this region of the curve, and the results for different initial concentrations of Cd^{2+} ions are given in Table 1. Both these parameters were found to depend on the initial concentration. In fact, K_i and C increased as the initial cadmium concentration increased, most likely because higher metal concentrations, as a result of the larger concentration gradient between the particle superficial film and the internal pore solution, led to faster intraparticle diffusion.

Pseudo-first order

The linear form of the pseudo-first-order equation is given as follows:

$$\log(q_e - q_t) = \log(q_e) - \frac{k_1}{2.303} t \qquad (11)$$

where q_t and q_e are the uptake capacities at t and equilibrium, respectively; k_1 is the equilibrium rate constant of pseudo-first-order adsorption; and t indicates time. The pseudo-first-order constant k_1 can be obtained from the slope of the graph of $\log(q_e - q_t)$ versus t.[17] Figure 2c shows the adjustment of the experimental data to the pseudo-first-order model; a deviation from the straight line can be noticed after 8 min of biosorption. The coefficients of correlation for this model are low, as shown in Table 1, and the values of q_e obtained from the fits ($q_{e(\mathrm{cal})}$) and from the experimental values ($q_{e(\mathrm{exp})}$) are very different. Thus, biosorption of Cd^{2+} ions onto *Eichhornia crassipes* roots does not fit a pseudo-first-order kinetic model.

Pseudo-second order

Because the data did not fit a pseudo-first-order kinetic model and the intraparticle diffusion curve was multilinear, the data were also adjusted to a pseudo-second-order equation:[18]

$$q_t = \frac{q_e^2 k_2 t}{1 + k_2 q_e t} \qquad (12)$$

or to the following linearized form:

Table 1. Parameter values calculated using the intraparticle diffusion, pseudo-first-order and pseudo-second-order kinetics models for the biosorption of Cd^{2+} by *Eichhornia crassipes* roots for different initial metal ion concentrations

Model	**Parameters**	**Different cadmium concentrations/mM**				
		1	**0.1**	**0.01**	**0.001**	**0.0001**
Intraparticle diffusion	**k_p/mg g^{-1}min$^{-1/2}$**	1.9897	0.1592	0.0133	0.0014	0.0002
	C/mg g^{-1}	4.7110	0.5813	0.0584	0.0045	0.0004
	R^2	0.9640	0.9640	0.9310	0.9636	0.9790
Pseudo first order	**$q_{e(exp)}$/mg g^{-1}**	13.1705	1.3479	0.1293	0.0121	0.0012
	$q_{e(cal)}$/mg g^{-1}	$9.862\text{x}10^{-4}$	0.8970	0.0864	$9.908\text{x}10^{-3}$	$9.33\text{x}10^{-4}$
	K_1/g mg^{-1} min^{-1}	0.101	0.104	0.0875	0.0948	0.0978
	R^2	0.8979	0.9679	0.9720	0.9487	0.9730
Pseudo second order	**$q_{e(exp)}$/mg g^{-1}**	13.1705	1.3479	0.1293	0.0121	0.0012
	$q_{e(cal)}$/mg g^{-1}	13.5685	1.4494	0.1386	0.0134	$1.3734\text{x}10^{-3}$
	h/mg g^{-1} min^{-1}	5.2994	0.4014	0.0347	0.0025	$3.1557\text{x}10^{-4}$
	k_2/g mg^{-1} min^{-1}	0.0287	0.1909	1.8063	14.1456	167.3021
	R^2	0.9995	0.9989	0.9936	0.9987	0.9996

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \tag{13}$$

where q_t and q_e are the quantities adsorbed at time t and at equilibrium, respectively, and k_2 is the rate constant of sorption. The initial sorption rate (h) was calculated using the following equation:

$$h = k_2 q_e^2 \tag{14}$$

As can be seen from Figure 2d, t/q_t varied linearly with time t. The data agreed well with the pseudo-second-order model, and the correlation coefficient for the linear plot was very good. However, the model did not fit the initial stages of the sorption process well, most likely because the roots and Cd^{2+} ions were not yet in direct contact. In fact, the diffusion model of the initial stages predicted that transport from the bulk solution to the film proceeded by diffusion through a boundary layer on the bioadsorbent. As a consequence, the pseudo-second-order model fit well once these processes had been completed, after 10 min of immersion. Similar behavior was observed for other initial concentrations of Cd^{2+} ions, and the calculated kinetic parameters are listed in Table 1. The model parameters obtained (q_e) from the fits to the equilibrium sorption data agreed well with the experimental values calculated from the equilibrium sorption measurements, indicating that pseudo-second-order kinetics provided a good description of the biosorption process. The sorption rate constant increased as the initial concentration of cadmium increased, indicating that cadmium is removed easily from a dilute aqueous solution. The coefficients obtained from a fit to a pseudo-second-order kinetic model were higher than those obtained from the intraparticle diffusion model, suggesting that a chemical reaction mechanism could be used to describe the process. The process of sorption of Cd^{2+} ions appeared to include surface chemisorption at the boundary layer between particles as well as intraparticle diffusion. The biosorption experiment was repeated using a digital multimeter, and the results were very similar to those obtained using the potentiostat. When the digital multimeter is used, the measurement is carried out each second.

Finally, it is important to note that the kinetics of accumulation of Cd^{2+} ions on *Eichhornia crassipes* roots is the same as that reported for the whole plant, using traditional methods;[3] however, the data were best described by the pseudo-second-order kinetic model.

Effect of the initial concentration of cadmium ions

One application of kinetic studies is to use the kinetic parameters to predict the evolution of the time-dependent accumulation. Using the pseudo-second-order model in Table 1, it is possible to establish a general equation that predicts the evolution of the accumulation at any time and any initial concentration of Cd^{2+} ions ($[Cd^{2+}]_0$). In fact, it is possible to obtain mathematical expressions that relate q_e and k_2 with $[Cd^{2+}]_0$ by plotting $\log[Cd^{2+}]_0$ against $\log q_e$ and $\log k_2$ against $\log[Cd^{2+}]_0$. A linear relationship between both variables implies that the slopes and intercepts express q_e and k_2 in terms of $[Cd^{2+}]_0$, as follows:

$$q_e = (1.418 \times 10^{-4})[\mathrm{Cd}^{2+}]_0^{1.0024} \tag{15}$$

$$k_2 = (5.465 \times 10^{-5})[\mathrm{Cd}^{2+}]_0^{-0.912} \tag{16}$$

Substituting values of q_e and k_2 from equations (15) and (16) into equation (12), the rate law for a pseudo-second-order reaction and the relationship between q_t, $[Cd^{2+}]_0$, and t can be represented as follows:

$$q_t = \frac{1.0988 \times 10^4 [\mathrm{Cd}^{2+}]_0^{1.0928}\ t}{1 + 0.774 [\mathrm{Cd}^{2+}]_0^{0.0904}\ t} \tag{17}$$

The theoretical and experimental lines for the roots are shown in Figure 2a for $[Cd^{2+}]_0 = 0.1$ mM; a very good agreement with the experimental data can be observed. The other initial concentrations studied exhibited similar behavior.

CONCLUSIONS

The kinetics of biosorption can be studied using potentiometric measurements, as demonstrated herein. The kinetics of Cd^{2+} biosorption on *Eichhornia crassipes* root depends on the initial concentration of the ions and can be represented by a pseudo-second-order model. To our knowledge, the use of a simple cadmium wire as the indicator electrode has not been reported previously for this type of determination; this technique leads to a substantial simplification of the experimental equipment. In addition, this methodology requires a minute amount of working solution (2.5 mL) and bioadsorbent (20 mg). However, the application of this methodology is limited by the Nernst equation. For example, the equilibrium between the metal and its ions is very important, and only some metals are stable at certain pH and in deoxygenated solutions, such as Ag, Bi, Cu, Hg, Pb, Sn, Cd, Tl, and Zn. However, these metals are heavily studied in biosorption, and the evaluated solutions often have a neutral pH. Additionally for a relatively high concentration of metallic ions, the concentration in the Nernst equation must be replaced with activities. Unfortunately, the method is not selective; thus, it is not applicable for an ion mixture, as is the case of real environmental solutions. However, biosorption in unitary systems is heavily studied and the adsorption kinetic study for real samples are not very frequent.

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