http://dx.doi.org/10.5935/0103-5053.20160046

J. Braz. Chem. Soc., Vol. 27, No. 9, 1667-1678, 2016.
Printed in Brazil - ©2016 Sociedade Brasileira de Química
0103 - 5053 $6.00+0.00

Article

A Kinetic, Equilibrium, and Thermodynamic Study on the Biosorption of Tl^+ and Cd^{2+} by *Eichhornia crassipes* Roots Using Carbon Paste Electrode

Carolina Martínez-Sánchez,[a] Luz M. Torres-Rodríguez*,[a] and Ramón F. García-de la Cruz[b]

[a]Laboratorio de Electroquímica and [b]Laboratorio de Bioquímica Vegetal, Centro de Investigación y Estudios de Posgrado (CIEP), Facultad de Ciencias Químicas, Universidad Autónoma de San Luis Potosí, Avenida Manuel Nava No. 6, Zona Universitaria, C.P. 78210, San Luis Potosí-S.L.P., México

In this work, *Eichhornia crassipes* roots were used as a modifier for carbon paste electrode in a biosorption study of thallium (Tl^+) and cadmium (Cd^{2+}) ions. The ions were accumulated on modified electrode surfaces at open circuit potential and analyzed by square wave anodic stripping voltammetry. Before the biosorption study, the effect of ratio of biomass and binder in uptake metal was evaluated. The biosorption study shows that adsorption of ions was dependent on pH. The kinetic study showed that, for both ions, experimental data were well described by the pseudo-second order model ($R^2 > 0.99$) and the equilibrium was better described by the Langmuir model. The value of dimensionless equilibrium parameter (R_L) obtained in the equilibrium study showed that *Eichhornia crassipes* can be considered an effective biomaterial for Tl^+ and Cd^{2+} removal from an aqueous solution. The thermodynamic parameters calculated, enthalpy ($\Delta H°$), entropy ($\Delta S°$) and Gibbs energy ($\Delta G°$), indicated that the biosorption process was spontaneous and endothermic.

Keywords: modified carbon paste electrode, *Eichhornia crassipes*, biosorption, thallium, cadmium

Introduction

Heavy metal pollution is one of the most serious environmental problems today. This is because the heavy metals are released into the environment by industries such as electroplating, mining, and metallurgy. Heavy metals also occur in the environment due to the use of rodenticides, insecticides, dyes, and the like.[1] Cadmium (Cd^{2+}) and thallium (Tl^+) are two heavy metals present in natural waters.

Cd^{2+} is one of the most toxic heavy metals associated with considerable environmental and occupational concern because it combines with protein sulfhydryl groups and restrains the enzyme activity in human beings. Long-term exposure to Cd^{2+} can cause anemia, hypertension, muscular cramping, osteoporosis, and renal damage.[2] On the other hand, thallium is present in the environment in low concentrations and in natural waters as Tl^+. Because the solubility of thallium compounds is high, the Tl^+ is easily transported throughout aquatic systems and is more toxic than many other metal ions, such as Cd^{2+}. Thallium ions can damage the heart, lungs, liver, and nervous system; therefore, removing thallium compounds from water and aqueous solutions, as well as controlling their impact on the environment, is very important.[3,4] There are different methods to remove these heavy metals,[4-6] for example, the biosorption. This removal technology uses biological materials for binding and concentration of the pollutant from an aqueous solution. Biomass of non-living *Eichhornia crassipes* (water hyacinth) is a good option for biosorption. In fact, this free-floating aquatic plant features vegetative reproduction and a vigorous growth rate. A typical biomass from land plants is composed of 30-50% cellulose, 20-40% hemicellulose, and 15-30% lignin.[7] In addition, this plant has a high tolerance to pollution and is regarded as an economic adsorbent.[7] The biomass of *Eichhornia crassipes* has been used largely for removal of Cd^{2+},[8-11] and other ions such as Pb^{2+},[12] Cu^{2+},[13] and Zn^{2+}.[12] In contrast, the biosorption of Tl^+ by *Eichhornia crassipes* has not been studied previously. There are only some works that have studied the elimination of Tl^+ by biomass such as *Ulmus carpinifolia*,[14] modified sugar beet pulp,[15] *Aspergillus niger*,[16] and eucalyptus leaves.[17]

Generally, kinetic, equilibrium and thermodynamic studies of biosorption have been performed by contacting the biomass with the ion solution (batch procedure) and

---

*e-mail: luzmaria@uaslp.mx

periodically sampling them for later analysis. In earlier works, our work team has proposed the use of carbon paste electrodes modified with biomass.[18,19] With this method the electrode modified with biomass is exposed to a solution containing the ion studied, and the ion fixed to the electrode through biomass is analyzed by electrochemical techniques. This methodology has the advantage of requiring a small quantity of biomass and reagents moreover the time used for experiments is considerably smaller than the batch studies. However, the uptake of ion for the biomass is carried out on a surface, and the charge or the current are used as a measure of uptake. As a consequence, the constant obtained from empirical models cannot be interpreted by habitual form.

Hence, this work proposed the use of modified carbon paste electrodes for studied the removal of Tl^+ by *Eichhornia crassipes* roots. In order to compare the uptake of a monovalent and divalent ion, a parallel study for Cd^{2+} was realized under the same conditions.

Experimental

Reagents

All reagents were of analytical grade, and obtained from Sigma Aldrich (St. Louis, MO. USA). The graphite powder and mineral oil were purchased from Alfa Aesar (Haverhill, MA, USA). The solutions 0.01 mol L^{-1} of Tl_2CO_3 and $Cd(NO_3)_2$ were prepared and used to perform dilutions for the purpose of obtaining the working solutions. The sodium perchlorate ($NaClO_4$, 0.1 mol L^{-1}) was used as a supporting electrolyte. All solutions were prepared with deionized water (18.6 MΩ cm).

Instruments

The voltammetric measurements were performed while employing the modified carbon paste electrode (MCPE) with *Eichhornia crassipes* roots as a working electrode having a surface area of 0.193 cm^2, an Ag|AgCl|NaCl 3.0 mol L^{-1} and platinum wire were used as electrode reference and as counter electrode, respectively.

To perform the electrochemical studies, potentiostat/galvanostat BASi EC epsilon was used and controlled by the BASi Epsilon-EC software version 1.31.65 NT (Bioanalytical Systems Inc., West Lafayette, IN, USA).

To control the temperature, a heating bath Lauda Eco Silver (Lauda-Brinkmann, LP, Delran, NJ, USA) was used. The MCPEs (modified carbon paste electrodes) were exposed to a cell that contained the working solutions.

Electrochemical impedance spectroscopy measurements were performed with a potentiostat/galvanostat Autolab PGSTAT302N (Metrohm Autolab BV, Utrecht, The Netherlands). Measures were performed using the same three electrode-cell setup described previously. Parameters of the electrical equivalent circuits were obtained via the Zview 2 program.

A Metrohm pHmeter (Metrohm Autolab BV, Utrecht, The Netherlands) was used to adjust the pH of the solutions.

Treatment of *Eichhornia crassipes* roots

Eichhornia crassipes plants, obtained from Dam San José in the municipality of San Luis Potosí (San Luis Potosí, Mexico) were transported to the greenhouse at the Faculty of Chemical Sciences of Universidad Autónoma de San Luis Potosí and grown there. The roots of the *Eichhornia crassipes* were first washed with running water, and then with deionized water. After, the roots were separated from the rest of the plant. These roots were frozen and subjected to a drying process in a freeze vacuum pump model 7522900 (Labconco, Kansas City, MO, USA) at –48 °C for 16 h. The roots were then pulverized in an analytical mill Cole-Parmer (London, UK) and stored in bottles at room temperature.

Determination of pH_{zpc}

To determine the pH of zero point charge (pH_{zpc}), this study followed the methodology reported by Leyva *et al.*,[20] for which 0.1 g of acidulated root in 20 mL of a solution of 0.01 mol L^{-1} KCl-0.004 mol L^{-1} KOH were added. The suspension was stirred for 48 h and, after that time, it was titrated with the addition of 0.1 mL of 0.1 mol L^{-1} HCl to register the pH of the solution after each addition. Also, the assessment of a solution of 0.01 mol L^{-1} KCl-0.004 mol L^{-1} KOH was performed under the same conditions but without the root. The point where the titration curves (with and without the root) intersect is the pH_{zpc} because the pH of the solution with and without the root is the same, which means that the root has no charge; so that is the value of extrapolating the intersection of both lines is pH_{zpc}.

Preparation of modified carbon paste electrodes

Three carbon paste electrodes were prepared by mixing 0.43 g of nujol, 0.50 g of graphite powder and 0.07 g of lyophilized *Eichhornia crassipes* root. The paste that formed was placed in an insulin syringe and contact was made through a copper wire. The electrode's surfaces were renewed after each experiment by removing a small amount of the paste and polishing the surfaces with sandpaper. A control electrode without the root was prepared by mixing 0.60 g of graphite powder and 0.40 g of nujol.

Characterization of MPECs by impedance

Impedance spectra were recorded with electrodes in a $NaClO_4$ solution for the purpose of characterizing the modified electrodes. The initial frequency used was 10 kHz, and the final frequency used was 10 mHz, with 10 points *per* decade. The alternating current amplitude was 10 mV under open circuit potential conditions.

Electrochemical experiments

To study the uptake of metal by electrochemistry, experiments were carried out in both controlled temperature and room temperature. MCPEs were submerged in ion solutions unstirred during a selected time at open circuit. After this, the electrode was rinsed with water and transferred to a solution containing only support electrolyte ($NaClO_4$ 0.1 mol L^{-1}). Square wave anodic stripping voltammetry (SWASV) experiments were carried out, and a deposition potential (E_{dep}) of –0.75 V was applied during 120 s for Cd^{2+}, while for Tl^+ E_{dep} was –0.8 V and was applied for 60 s. These conditions were obtained in earlier works for Cd^{2+},[19] and obtained experimentally for Tl^+. For both ions, a square wave with a frequency of 10 Hz, amplitude of 0.02 V, and potential step size of 0.004 V was applied at a range of –1.2 to 0.2 V. All experiments were performed in triplicate, and the standard deviation was calculated.

To study the effects of pH, MCPEs were exposed to a single metal ion solution concentration of 1.0 mmol L^{-1} of Tl^+ and Cd^{2+} ions for 15 min. The pH of the solutions changed within a range of 2.6 to 9.7. Solutions of different pH were obtained by addition of 0.1 mol L^{-1} HCl and/or NaOH 0.1 mol L^{-1}. After exposure, the MCPEs were rinsed and transferred to the working cell that contained only the supporting electrolyte.

To perform the kinetic and equilibrium study, in the preconcentration step, the MCPEs were exposed to ion solutions of different concentrations (0.1 to 6.0 mmol L^{-1}) for different times (1, 2, 3, 4, 5, 7, 10, 15, 20 and 30 min) while maintaining the temperature constant. After exposure, the MCPEs were transferred to the working cell, and the response was obtained via SWASV, as mentioned previously.

Data treatment

In this work, the metal adsorption was correlated to current (I) measured in an electrochemical experiment. The surface under the current-potential (time) curve represents the electroactive coverage Γ (mol cm^{-2}), and the amount of heavy metal immobilized in the surface electrode is given by equation 1:

$$\Gamma = \frac{Q}{nFA} \tag{1}$$

where Q is the charge, A is the surface of the electrode, n is the number of electrons transferred, and F the Faraday constant. Note that if the number of moles is Q/nF and Q = It, then electroactive coverage (equation 1) can be expressed by (equation 2):

$$\Gamma = \frac{It}{nFA} \tag{2}$$

In this expression, the current and the electroactive coverage are proportional. The electrochemical response was obtained via the technique of SWASV. This technique has two stages. In the first, the ion accumulated in the surface of the electrode is reduced by application of a potential during a certain time. In the second, the metal formed is stripping. The reactions carried out during this stage are:

$$Tl^0 \rightarrow T^+ + e^- \tag{3}$$

$$Cd^0 \rightarrow Cd^{2+} + 2e^- \tag{4}$$

In consequence, n is one and two for Tl^+ and Cd^{2+}, respectively. To compare adsorption of both ions, it was considered that the surface of the electrode and the scan rate (time) of equation 2 are the same for both ions, but n is different. As a consequence, the current measured was divided between n. The value of the current used and reported in voltammograms was corrected by subtraction of the capacitive current of the current measured. The value of the current used in the graphs was the average of three measures.

Results and Discussion

Selection of composition of MCPEs for adsorption studies

In the first part of the study, we determined the optimal proportions for preparing the carbon paste modified with the root. First, the effect of the proportion of the root was analyzed. For this, MCPEs were prepared with different percentages of root (1, 3, 5, 7 and 10%), while the proportion of nujol was maintained at a constant of 43% and the percentage of graphite was adjusted to reach the necessary 100%. The MCPEs were exposed to a single metal ion solution of Tl^+ and then were transferred to the working cell, and the voltammetric response was obtained. Figure 1 shows the response of Tl^+, and a peak can be observed in the center at –0.79 V, which is characteristic of this metal. The I, which is proportional to uptake metal, increased when the amount of root in the electrode increased. This shows that when there are more root, there are a large number of sites for metal uptake and a higher adsorption.

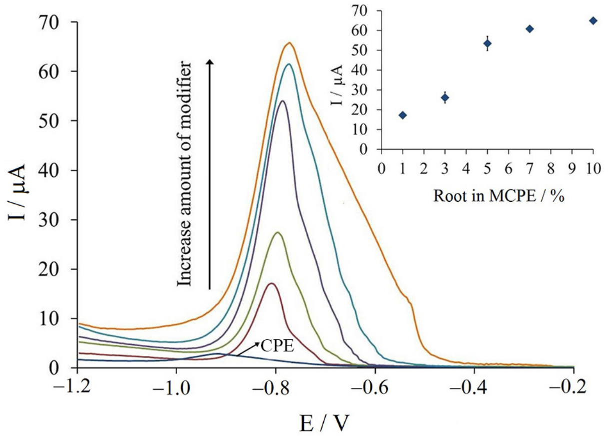

Figure 1. Square wave anodic stripping voltammetry (SWASV) response of 0.1 mmol L^{-1} of Tl^+ using different percentages of *Eichhornia crassipes* roots (1, 3, 5, 7, and 10%) in a modified carbon paste electrode. The accumulation time was 20 min at open circuit potential; supporting electrolyte was $NaClO_4$ 0.1 mol L^{-1}. Inset corresponds to the curve of peak current *vs.* percentage of root in the modified carbon paste electrode (MCPE). CPE: Unmodified electrode.

However, the amount of metal that accumulated in the 10% modified electrode was very similar to that in the 7% modified electrode with *Eichhornia crassipes* roots (Figure 1). In this proportion, the electrode surface probably is fully covered by the roots. Based on these results, we chose to modify the electrode with a ratio of 7% roots, since a lesser amount of biomass is required to modify the electrode.

The accumulation of ion in an unmodified electrode (CPE) also was studied. The same procedure was repeated, and the curve obtained did not present response of Tl^+ (Figure 1). This showed that the ions are not immobilized in the carbon paste, and are accumulated only on the roots.

Selection of the amount and type of binder for preparing MCPEs

After determining that the optimal amount of root to modify the electrode was 7%, we proceeded to test the effect of the amount and nature of the binder. Tests were conducted with varied proportions of nujol in the MCPEs between 40 and 52%, while maintaining the ratio of the root at 7% and proportions of graphite necessary to reach 100%. MCPEs cannot be elaborated with proportions of nujol lower than 40% because the paste acquires a very stiff consistency and cannot be manipulated. The MCPEs were exposed to the Tl^+ solution, and the metal uptake was then analyzed by SWASV (Figure 2a). The maximum current, or the maximum accumulation of heavy metal, was obtained at ratios of 40 and 43% of nujol. However, the consistency of the paste electrode prepared at 40% nujol was very stiff, and this texture made the experiments difficult because the electrode is pulverized easily. The current decreased considerably when the nujol ratio was 50%, and no voltammetric response was obtained by modifying the MCPE with 52% of nujol (inset Figure 2a).

Diminution of adsorption with an increase of nujol can be due to the nujol has increased electrical and

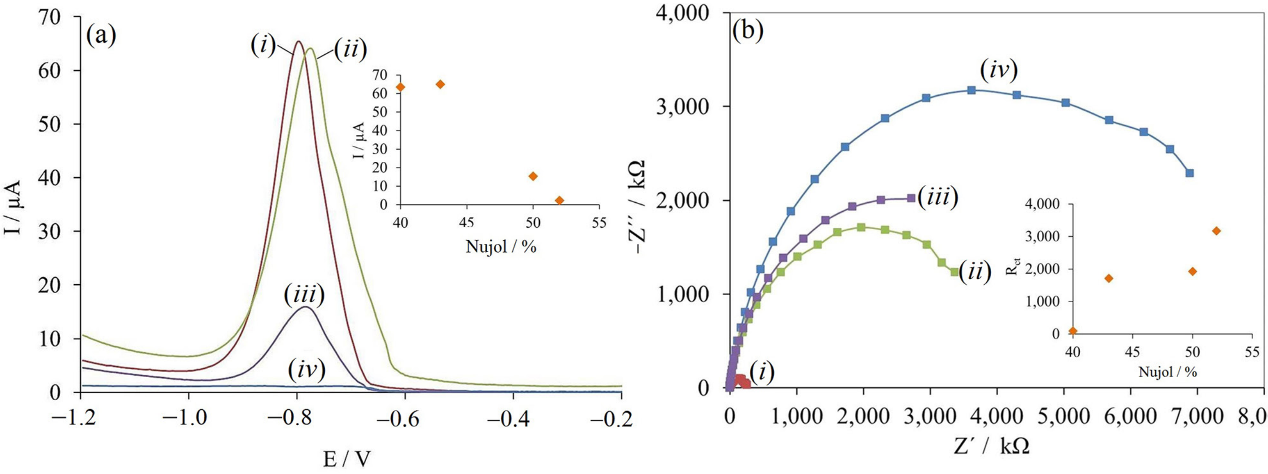

Figure 2. (a) Voltammograms obtained in $NaClO_4$ from modified carbon paste electrode (MCPE) with 7% of root after being exposed for 15 min to a solution of 0.1 mmol L^{-1} of Tl_2CO_3 and prepared with the following proportions of nujol: (*i*) 40%; (*ii*) 43%; (*iii*) 50%; and (*iv*) 52%; inset corresponds to the curve of peak current (I) *vs.* percentage of nujol; (b) Nyquist plot of MCPE prepared with the same proportion of (a); inset corresponds to the charge transfer resistance (R_{ct}) *vs.* percentage of nujol in the MCPE.

diffusional resistance of the electrode.[21] On the other hand, the number of ions accumulated also can be diminished because the nujol is hydrophobic, therefore increasing the hydrophobicity of the electrode surface.

In order to determine how the conductivity of MCPEs changes with the binder, electrochemical impedance tests were carried out. The Nyquist diagram in Figure 2b shows that the experimental data form a semicircle and the diameter of the circle changes with the proportion of nujol. In fact, as the paste contains a lower proportion of nujol, the diameter of the semicircle related to the electrochemical process decreases, suggesting that as the amount of nujol decreases, the charge transfer resistance (R_{ct}) is minor (inset Figure 2b). These results are congruent with the results obtained by SWASV for the study of accumulation of Tl^+ in which the response of accumulated metal in the MCPEs decreased with the amount of nujol.

Finally, to determine the effect of hydrophobicity, MCPE was prepared using the ionic liquid (IL) 1-butyl-3-methylimidazolium hexafluorophosphate ($BMI{\cdot}PF_6$) as a binder (MCPE IL). This binder was chosen because it is highly hydrophobic but is a good ionic conductor. Figure 3 shows the voltammetric response of MCPE IL after exposure to a solution of Tl^+.

It was observed that the response featured much noise and a capacitive current; therefore, the peak was less defined than that obtained with the MCPE prepared with nujol (Figure 3). These results indicate that a greater number of the Tl^+ ions interacted with the electrode prepared with nujol. This may have occurred because the $BMI{\cdot}PF_6$ is more dense and viscous than nujol, which makes the Tl^+ ion diffusion difficult. The results suggest that the MCPEs prepared with 43% nujol are the best choice for use in the study of adsorption of Tl^+ and Cd^{2+} ions.

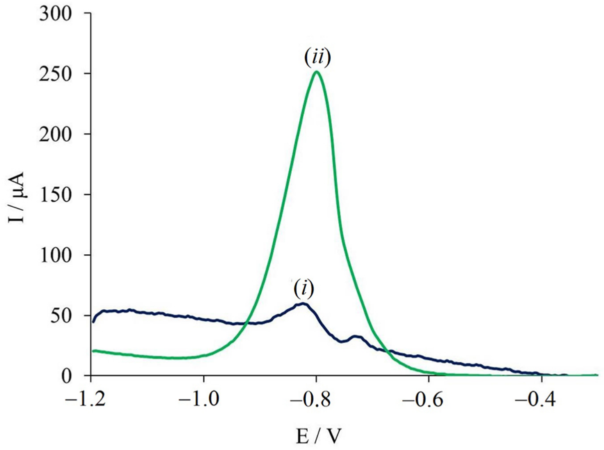

Figure 3. Voltammograms obtained in $NaClO_4$ from (*i*) modified carbon paste electrode (MCPE) with *Eichhornia crassipes* roots prepared using the ionic liquid (IL) 1-butyl-3-methylimidazolium hexafluorophosphate ($BMI{\cdot}PF_6$) as a binder (MCPE IL); and (*ii*) MCPE after being exposed for 15 min to a solution of 1.0 mmol L^{-1} of Tl_2CO_3.

Effect of pH in uptake of Tl^+ and Cd^{2+} by *Eichhornia crassipes* roots

Once the preparation of MCPEs was optimized, the study of bioaccumulation was carried out. First, the effect of pH was analyzed because it is one of the most important factors influencing the efficiency of the adsorption of metal ions in biomass; pH is able to change the surface properties of the biosorbent and the form which the metal ions can exist in the solution. The electrodes were exposed to the solutions with different pH values, and then their response was obtained in $NaClO_4$. The results of accumulation are illustrated in Figure 4.

It can be observed that the peaks are localized at ca. −0.8 V for Tl^+ and −0.6 V for Cd^{2+}. The ion adsorption, or the current, is dependent on pH in the range studied (between 2 and 8). The amount of adsorbed ions increases

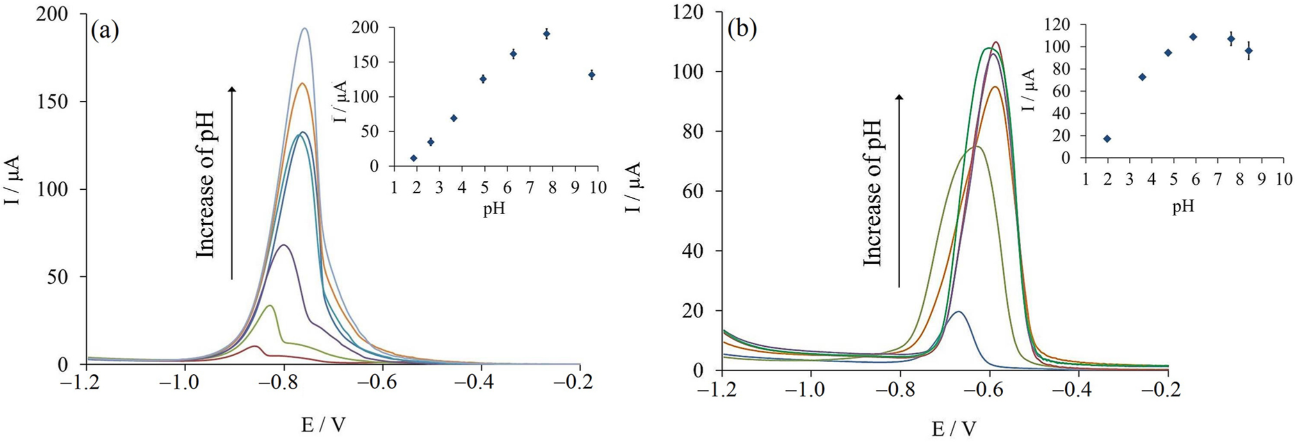

Figure 4. Voltammograms of modified carbon paste electrode (MCPE) with *Eichhornia crassipes* roots exposed to 2.0 mmol L^{-1} of (a) Tl^+; and (b) Cd^{2+} solutions of different pH values. Supporting electrolyte was $NaClO_4$ 0.1 mol L^{-1}. Insets correspond to the curve of peak current (I) evolution *vs.* pH.

with increasing pH, between 2 and 6, in contrast with pH higher than 8, for which the adsorption diminishes. This behavior can be explained for the composition of *Eichhornia crassipes* roots. Recent work has determined through infrared spectroscopy and potentiometric titration that the groups present in the roots of *Eichhornia crassipes* are alcohols, carboxylic acids, amines, sulfonates and esters.[18] This means that the root has acid sites where the metallic ions can be adsorbed, and that the accumulation of ions in the roots is dependent on pH. It can be observed that the adsorption is significant after pH = 2; this can be related with the pH_{zpc}. pH_{zpc} calculated for *Eichhornia crassipes* root was 2.3; then for a high pH_{zpc}, the acid groups present in the root are primarily in dissociated form. As a consequence, the acid groups present a negative charge, which is adequate for the accumulation of ions. When pH increases, the dissociated groups increase and the adsorption increase. However, when the pH is higher than 8, the adsorption diminishes, which may be due to an excess of OH^- interacting with the ions in the bulk solution. It is noteworthy that in this pH range both Tl^+ and Cd^{2+} are held in ionic form. The evolution of uptake with pH was similar for Tl^+ and Cd^{2+}; this likely shows that both ions should be fixed to the root through the same acid groups. On the other hand, the values of the current were higher for Tl^+ than Cd^{2+}; thus we can deduce that the Tl^+ is accumulated in greater amount than Cd^{2+}; probably because as Tl^+ is monovalent, for each divalent acid site it can be accumulated two unity of Tl^+, while only a Cd^{2+} unit can be accumulated in a divalent site.

Effect of ionic strength in uptake of Tl^+ and Cd^{2+} by *Eichhornia crassipes* roots

On the other hand, wastewater normally contains a certain amount of electrolytes with a variety of ionic species. The presence of salt or co-ions in the solution can affect the adsorption of metal ions.[22] To determine the effect of ionic strength on the accumulation of Tl^+, MCPEs were exposed for 15 min to solutions of Tl^+ prepared in $NaClO_4$ 0.1, 0.01 and 0.001 mol L^{-1}. After, the voltammetric response was obtained. The value of I obtained, which is proportional to the amount of accumulated metal, were 166, 175, and 207 µA for $NaClO_4$ 0.1, 0.01 and 0.001 mol L^{-1}, respectively. These results indicate that the amount of Tl^+ accumulated decreases with the ionic strength, possibly because the Na^+ ions compete with Tl^+ for the active sites of the root, so that the more concentrated the electrolyte, the lower its adsorption. The same trend was observed in the case of Cd^{2+}.

Kinetic study

The amount of ion accumulated was studied as a function of time, and the curves obtained are shown in Figure 5. As the exposure time increases, the peaks broaden and the current increases, indicating that the amount of accumulated metal increases; the increment is more evident in the first minutes. For both ions, after 10 min, the I remains virtually constant, which indicates that, although the electrode is exposed for longer durations, the number of ions that accumulate are practically the same. This also indicates that equilibrium is attained, and the time necessary to reach equilibrium is the same for both ions. I is greater for Tl^+ than Cd^{2+}, which means that Tl^+ adsorption is higher than Cd^{2+}.

The evolution of ion accumulation over time can be due to the fact that the root surface of *Eichhornia crassipes* initially has more unoccupied active sites, offering easy interaction; therefore, in the first min, the concentration gradient of the ions between the solid-liquid interface

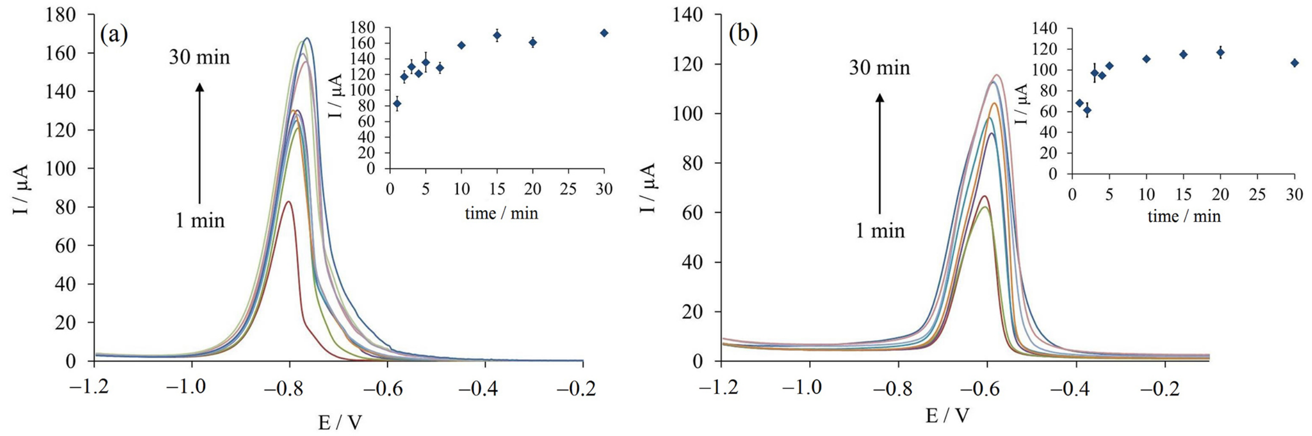

Figure 5. Voltammograms of modified carbon paste electrode (MCPE) with *Eichhornia crassipes* roots obtained at different times to 0.9 mmol L^{-1} concentration of (a) Tl^+; and (b) Cd^{2+} at 308 K. Supporting electrolyte was $NaClO_4$ 0.1 mol L^{-1}. Insets correspond to the curve of peak current (I) evolution *vs.* time.

is large enough to allow the ion to exceed the resistance between liquid and solid phases, during which, in the first 10 min, adsorption is rapid. As time passes, the active sites are occupied until saturate, and the concentration gradient of the ions between the solid-liquid interfaces decreases so that the equilibrium is reached,[23] as observed for 10 min in the inset of Figure 5, which shows the current for each exposure times.

These experimental results were fitted to the pseudo-second order model, which linearized equation is as follows (equation 5):

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \tag{5}$$

where t is the exposure time (min), and q_e (mg g^{-1}) and q_t (mg g^{-1}) are the amounts of solute adsorbed at equilibrium and at time t, respectively. From the slope and intercept of the graph t/q_t *vs.* t were obtained q_e and k_2, respectively.[24]

Equation 5 can be written in terms of the current since the experimental data are obtained in terms of I, which is proportional to q (equation 6):

$$\frac{t}{I_t} = \frac{1}{k_2 I_e^2} + \frac{1}{I_e} t \tag{6}$$

where I_e (μA) and I_t (μA) are the equilibrium current and at time t, respectively. Figure 6 illustrates the graph of t/I_t *vs.* t for a concentration of 2.0 mmol L^{-1}. It can be observed that experimental data of Tl^+ and Cd^{2+} present a good linear fit; this observation is confirmed by the correlation coefficient being higher than 0.99, which indicates a good fit for this model and then the adsorption kinetics is of pseudo-second order. This result coincides with the studies in batch processes, which determined that the kinetic of adsorption of Cd^{2+} on *Eichhornia crassipes* follows the pseudo-second order model.[8-11] As this kinetic model assumes that the chemisorption is the limiting step in the adsorption process, the limiting step in this case is probably the interaction between Tl^+ and Cd^{2+} ions and the functional groups of the root.

From the slope and the intercept of graphs in Figure 6, I_e and k_2 were obtained and the initial velocity (h) was obtained from $h = k_2 q_e^2$. Values are presented in Table 1 and I_e, calculated from equation 6, is similar to the experimental value ($I_{e(exp)}$); this indicates a good fit for the pseudo-second order model.

It can be observed that h is higher for Tl^+; therefore the monovalent ion interacts more quickly with the functional groups of the cell wall. The fact that the kinetic constants are higher for Tl^+ than Cd^{2+} may occur because the radius

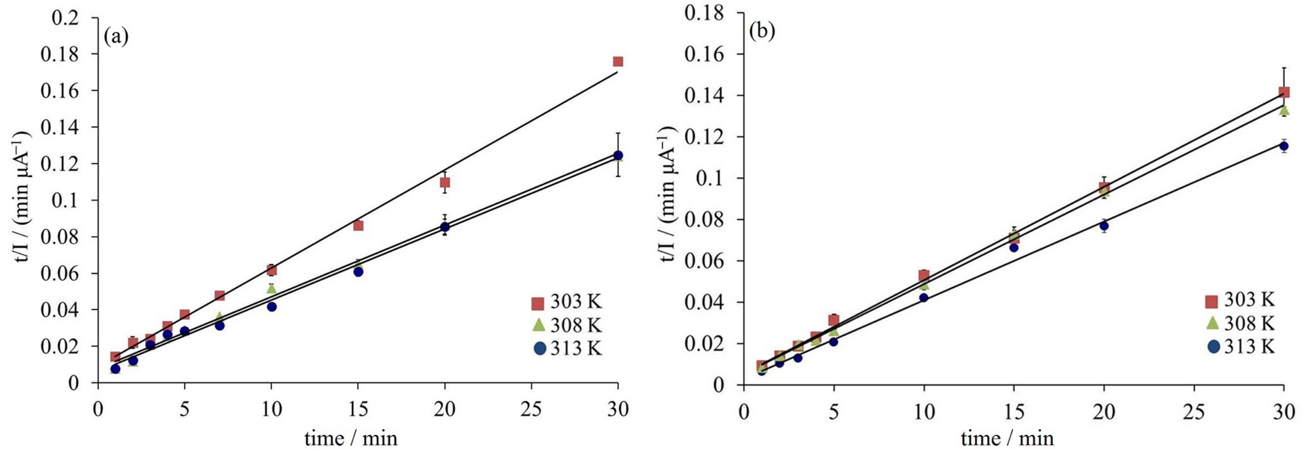

Figure 6. Pseudo-second order plots for (a) Tl^+; and (b) Cd^{2+} adsorbed on *Eichhornia crassipes* root at three different temperatures (2.0 mmol L^{-1} concentration).

Table 1. Kinetic parameters for adsorption of Tl^+ and Cd^{2+} on *Eichhornia crassipes* roots at three different temperatures, starting from a solution of 2.0 mmol L^{-1}

Ion	Temperature / K	h / (μA min^{-1})	k_2 / (μA^{-1} min^{-1})	I_e / μA	$I_{e(exp)}$ / μA	R_w	R^2
Tl^+	303	111.6	0.0032	186.07	182	0.053	0.996
	308	128.07	0.0019	254.96	232	0.064	0.995
	313	162.47	0.0025	256.04	246	0.050	0.993
Cd^{2+}	303	87.19	0.0069	111.68	105	0.041	0.999
	308	94.45	0.0071	115.48	107	0.039	0.999
	313	170.93	0.0098	131.49	130	0.025	0.995

h: Initial velocity; I_e: equilibrium current; $I_{e(exp)}$: experimental current value; k_2: pseudo-second order constant; R_w: approaching equilibrium factor; R^2: correlation coefficient.

of the hydrated ion of Cd^{2+} (4.25 Å) is larger than that of Tl^+ (3.3 Å), that is why the Tl^+ mobilizes easier through the pores of the root, which has diameter of 176.30 Å.[18] On the other hand, I_e was higher for Tl^+ than Cd^{2+}, meaning that *Eichhornia crassipes* root can accumulate more quantity of Tl^+ than Cd^{2+}. As Cd^{2+} and Tl^+ follow the pseudo-second order model, it is very probably that a chemical reaction should be carried out between a functional group of the plant and the ions. The difference between both probably is that the stoichiometry of reaction of Cd^{2+} and the functional group should be 1:1, and for Tl^+ 1:2; therefore, Tl^+ is accumulated in more quantity than Cd^{2+}.

Once the kinetic behavior to a fix temperature was defined, an analysis was carried out for different temperatures. As can be seen in Figure 6 and Table 1, the data agreed well with the pseudo-second order model for all temperatures. For all temperatures studied, the adsorption was faster for Tl^+ than Cd^{2+}, and the root accumulated more Tl^+ than Cd^{2+}. In relation to the evolution of adsorption kinetics and temperature, values of Table 1 show that the initial velocity constant, h, increases as the temperature increases. The increment in the initial rate is due to the following factors. First, there is an increase in the ions kinetic energy because there is an increase in the mobility of the ions, which interact quickly with the functional groups of the root. Second, as the temperature increases, the viscosity of the ion solution decreases, which facilitates the movement of ions.[25] Finally, another factor may be that increasing temperature can cause swelling within the internal structure of the root, allowing the ions to penetrate more easily, as Ho *et al.*[26] pointed out in the case of the adsorption of heavy metals in ferns.

From the kinetic constant of Table 1, the approaching equilibrium factor (R_w) was calculated for all studied temperatures. R_w indicates whether equilibrium is reached; when $R_w = 1$, the equilibrium is not approaching. The characteristic adsorption curve is called approaching equilibrium, in the range $1 > R_w > 0.1$; well approaching pseudo equilibrium in the range $0.1 > R_w > 0.01$; and drastically approaching equilibrium when $R_w < 0.01$. The value is obtained using the following equation:[27]

$$R_W = \frac{1}{1 + k_2 q_e t_{ref}} \quad (7)$$

It is written in current terms as:

$$R_W = \frac{1}{1 + k_2 I_e t_{ref}} \quad (8)$$

where t_{ref} is the longest operation time used in kinetic experiments, I_e is the equilibrium current and k_2 is the pseudo-second order constant, both calculating from equation 6. R_w values obtained for Tl^+ varied from 0.053 to 0.050, while for Cd^{2+}, adsorption fluctuated between 0.041 and 0.025. These results establish that the equilibrium for adsorption of both ions is well approaching in all temperatures. On the other hand, R_w decreases with increasing temperature. This behavior indicates that the increase in temperature facilitates equilibrium.

It is important to note that the results obtained in this part of the work for Cd^{2+} adsorption coincides with the studies in batch processes, which determined that the kinetic of adsorption of Cd^{2+} on the whole plant of *Eichhornia crassipes*[9-11] and on the roots[8] follow the pseudo-second order model. In addition, R_w values are similar to those calculated from data of earlier works for adsorption of Cd^{2+} in *Eichhornia crassipes* by batch procedure.[28]

Equilibrium study

The analysis of the experimental data by adjusting the pseudo-adsorption isotherms is important in determining the model that describes the adsorption step. The Freundlich and Langmuir models were applied to the data (I_e used was obtained in kinetic experiments using equation 6 for each concentration) obtained at three temperatures studied.

The Langmuir isotherm assumes monolayer adsorption onto a surface containing a finite number of uniform adsorption sites without the migration of adsorbed molecules on the surface; through this model, we obtain the Langmuir constant (k_L), which shows the affinity of the biomass by the metal ion and q_{max} represents the maximum amount of metal that can accumulate in the biosorbent.[29] The equation of this model in its linearized form is as follows:

$$\frac{[M^{z+}]}{q_e} = \frac{1}{k_L q_{max}} + \frac{[M^{z+}]}{q_{max}} \quad (9)$$

where q_e is the amount of metal adsorbed at equilibrium (mg g^{-1}), $[M^{z+}]$ is the concentration of the metal in the bulk solution (mg L^{-1}), q_{max} is the maximum adsorption capacity (mg g^{-1}), and k_L is the constant related to the affinity of the binding sites (L mg^{-1}). Langmuir constants, q_{max} and k_L can be obtained by the slope and intercept from the graph $[M^{z+}]/q_e$ *vs.* $[M^{z+}]$. This equation can be written in terms of the current, as follows:

$$\frac{[M^{z+}]}{I_e} = \frac{1}{k_L I_{max}} + \frac{[M^{z+}]}{I_{max}} \quad (10)$$

where I_e is the equilibrium current for each concentration and it was obtained from equation 6 and I_{max} is the maximum current measured due to the ions adsorbed.

The Freundlich model relates the concentration of the adsorbed metal on the surface of a biosorbent with the metal concentration in the solution that is in contact. It is based on the surface of the biosorbent as heterogeneous, such that the active sites have affinities or different energies; this means that sites with higher affinity or energy are filled first with a more powerful bond than the sites with lower levels of energy.[29] Its equation, in linearized form, can be written as follows:

$$\log q_e = \log k_F + \frac{1}{n}\log[M^+] \tag{11}$$

where q_e is the amount of adsorbed metal at equilibrium (mg g^{-1}), $[M^+]$ is the concentration of the metal ion in the solution, and k_F and n are Freundlich constants related to the capacity and to the adsorption intensity, respectively. Thus, from the slope and intercept of the graph $\log q_e$ *vs.* $\log[M^+]$, the constants values of n and k_F, respectively, are obtained. Equation 11 can be written in terms of the current, as follows:

$$\ln I_e = \ln k_F + \frac{1}{n}\ln[M^+] \tag{12}$$

The data were adjusted to the Langmuir and Freundlich models, and we can observe that these are better adjusted to the Langmuir model (Figures 7a and 8). The values of Langmuir and Freundlich constants were calculated, and the results, presented in Table 2, illustrate that the data are better adjusted to the Langmuir model, according to the correlation coefficients for different temperatures. This indicates that probably the adsorption is carried out by forming a monolayer of metal. It is noted that k_L increases with increases in temperature. These values obtained with MCPE are the same order as those reported in the literature for accumulation of Cd^{2+} in *Eichhornia crassipes*, which were obtained from batch processes.[8]

The essential characteristics of the Langmuir isotherm parameters can be used to predict the affinity between the sorbate and sorbent using the separation factor or dimensionless equilibrium parameter, R_L, expressed as in the following equation:[30]

$$R_L = \frac{1}{(1 + k_L C_0)} \tag{13}$$

where k_L is the Langmuir constant and C_0 is the initial concentration of Tl^+ or Cd^{2+}. The value of the separation parameter R_L provides important information about the nature of adsorption: if $R_L = 0$ is irreversible; if $0 < R_L < 1$ is favorable; if $R_L = 1$ is linear; and if $R_L > 1$ is unfavorable. Figure 7b shows the values of R_L for Tl^+ and Cd^{2+} at different concentrations. The values of the dimensionless parameter R_L calculated for studied ions are between 0 and 1, which indicates that the adsorption of Tl^+ and Cd^{2+} in the roots of *Eichhornia crassipes* is favorable at all concentrations studied.

On the other hand, n calculated *per* Freundlich model increases from 2.67 to 3.98 for Tl^+ and from 2.38 to 6.05 for Cd^{2+} in the range of temperatures studied, where n indicates the intensity of the adsorption. If the value of n is less than 1, it is considered poor adsorption; if the value found is between 1 and 2, the adsorption is moderately difficult; and if it is between 2 and 10, adsorption is considered good.[31]

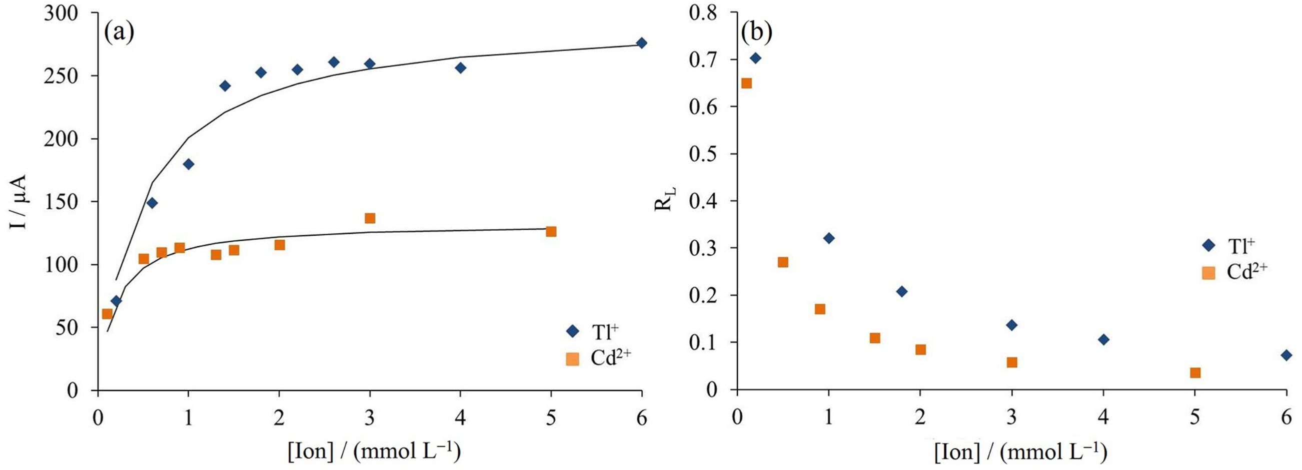

Figure 7. (a) Adsorption pseudo-isotherms of Tl^+ and Cd^{2+} on *Eichhornia crassipes* roots at 308 K. The lines correspond to the fit of the data to the Langmuir model; (b) dimensionless equilibrium parameter (R_L) values of Tl^+ and Cd^{2+} for adsorption on *Eichhornia crassipes* roots at different concentrations.

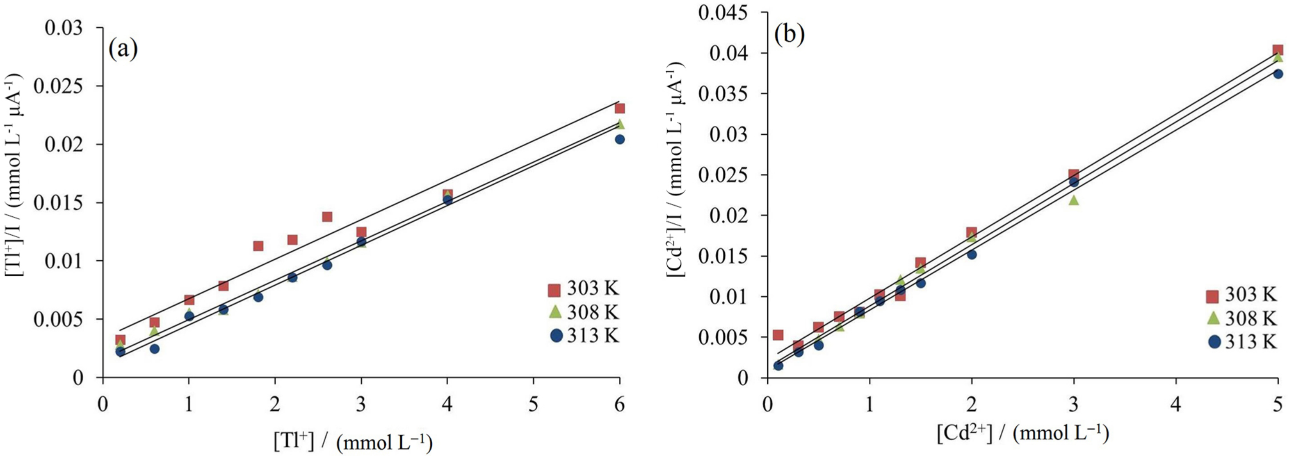

Figure 8. Langmuir pseudo-isotherms plots for biosorption of (a) Tl^+; and (b) Cd^{2+} on *Eichhornia crassipes* roots at three different temperatures (2.0 mmol L^{-1} concentration).

Table 2. Langmuir (k_L) and Freundlich (k_F) constants obtained at different temperatures for adsorption of Tl^+ and Cd^{2+} on *Eichhornia crassipes* roots

Ion	Temperature / K	Langmuir			Freundlich		
		k_L / (L mmol^{-1})	I_{max} / µA	R^2	k_F / µA	n	R^2
Tl^+	303	1.00	295.35	0.988	137.60	2.67	0.913
	308	2.11	295.83	0.998	170.60	2.95	0.802
	313	3.13	292.60	0.996	195.96	3.98	0.674
Cd^{2+}	303	3.34	132.18	0.991	91.02	2.38	0.717
	308	5.40	133.24	0.993	104.96	5.07	0.848
	313	7.65	135.30	0.998	112.99	6.05	0.779

I_{max}: maximum current measured due to the ions adsorbed; n: Freundlich constant related to the adsorption intensity; R^2: correlation coefficient.

Based on our results, therefore, the adsorption of both ions is considered good at the three temperatures studied, which coincides with the results obtained with R_L parameter; in addition, according to the n values, increase in temperature increases the adsorption intensity.

As shown in Table 2, the association constants, k_L, and n values calculated are greater for Cd^{2+} than for Tl^+ at each of the studied temperatures, indicating that the interactions between the divalent ion and the functional groups root are more intense compared to those of the monovalent ion. The probable cause for this is that Cd^{2+} has a greater electronegativity value (1.7) than Tl^+ (1.62). Although Cd^{2+} interacts more strongly with the active sites of the root, I_{max} is greater for Tl^+; for example, at 308 K, I_{max} is 295.83 µA, while for Cd^{2+}, it is 133.24 µA (Figure 7a). This result may be due to the hydrated ion radius, as mentioned earlier: the radius of Cd^{2+} is 5 Å, and the radius of the Tl^+ is 3.3 Å, that is why Tl^+ has easier access to the active sites of the roots and interacts with them in greater quantities.

It has been reported that for the adsorption of Ag^+ and Cd^{2+} in various biomaterials, such as *Chlorella vulgaris*, *Scenedesmus quadricauda*,[32] *Aspergillus niger*, *Mucor rouxii*,[33] and *Sphaerotilus natans*,[34] the monovalent ion is adsorbed in greater quantities compared to the divalent ion, which coincides with the results obtained in this study while using modified electrodes. According to the results obtained in this work, Tl^+ is adsorbed in greater amounts than Cd^{2+}; therefore, *Eichhornia crassipes* can be considered an effective adsorbent for removal of Tl^+ ions from aqueous solutions.

Thermodynamic study

The thermodynamic study provides information on the nature of the adsorption process. The parameters to determine are the changes in the Gibbs energy (ΔG°), in enthalpy (ΔH°), and in entropy (ΔS°). The change in ΔG° indicates the spontaneity of a chemical reaction. Reactions occur spontaneously if ΔG° at a given temperature is negative. The change in Gibbs free energy is given by equation 14:

$$\Delta G^\circ = -RT\ln k_L \quad (14)$$

where R is the universal gas constant and T is the absolute temperature, in Kelvin. The equilibrium constant, k_L, obtained from the Langmuir model, can be expressed in terms of the change in enthalpy of adsorption and in entropy, as a function of temperature. k_L and the relationship between temperature is given by the Van't Hoff equation:[35]

$$\ln k_L = \frac{-\Delta H^o}{RT} + \frac{\Delta S^o}{R} \quad (15)$$

ΔH° and ΔS° can be determined from the slope and intercept of the graph of $\ln k_L$ *vs.* 1/T (Figure 9).

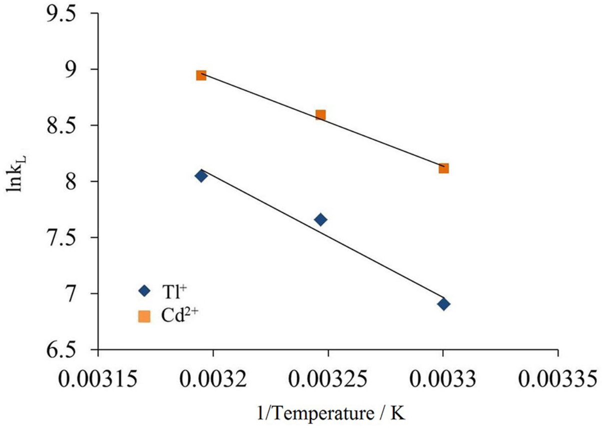

Figure 9. $\ln k_L$ *vs.* 1/temperature plot for estimation of thermodynamic parameters for the adsorption of Tl^+ and Cd^{2+} on *Eichhornia crassipes* roots. k_L: Langmuir constant.

The thermodynamic parameters obtained are shown in Table 3. The negative values of ΔG° indicate that the adsorption process of Tl^+ and Cd^{2+} ions on the *Eichhornia crassipes* roots was spontaneous.

The ΔH° calculated is 90.22 and 65.41 kJ mol^{-1} for Tl^+ and Cd^{2+}, respectively. The positive values indicate that the process is endothermic; so the adsorption is improved with increasing temperature.

Additionally, the magnitude of ΔH° gives information on the type of biosorption, which can be physical or chemical. ΔH° ranging from 2.1-20.9 kJ mol^{-1} corresponds to physisorption, and ranges from 20.9 to 418.4 kJ mol^{-1}, a chemisorption.[36] In our study, calculated ΔH° value of Tl^+ and Cd^{2+} ions fell into the range of chemisorption, although for Tl^+ at 303 and 308 K, the value is close to the physisorption. Based on this result, the biosorption processes of Tl^+ and Cd^{2+} ions onto *Eichhornia crassipes* roots probably occurred via chemisorption.

By the intercept of the graph of Figure 9, the ΔS° was obtained with a value of 361.28 and 283.49 J mol^{-1} K^{-1} for Tl^+ and Cd^{2+}, respectively. The positive ΔS° values suggest an increased randomness in the solution-solid interface during the adsorption process. This occurs as a result of redistribution of energy among the metal ions and the biomass. Before the adsorption, metal ions that are found near the surface of the adsorbent are more ordered than when the ions have been adsorbed. When ions are adsorbed, water molecules that were previously bound to the metal ions are released and dispersed in the solution, increasing the disorder of the system; this is the result of the increase in the entropy change.[35]

Table 3. Thermodynamic parameters obtained for the adsorption process of Tl^+ and Cd^{2+} on *Eichhornia crassipes* roots

Ion	Temperature / K	ΔG° / (kJ mol^{-1})	ΔH° / (kJ mol^{-1})	ΔS° / (J mol^{-1} K^{-1})
Tl^+	303	−17.40	90.22	361.28
	308	−19.61		
	313	−20.94		
Cd^{2+}	303	−20.44	65.41	283.49
	308	−22.01		
	313	−23.27		

ΔG°: Gibbs energy; ΔH°: enthalpy; ΔS°: entropy.

Conclusions

The results showed the following differences between the adsorption processes of monovalent and divalent ions in *Eichhornia crassipes* roots: first, the kinetic constants showed that Tl^+ adsorbs faster than Cd^{2+}, both following a pseudo-second order kinetics; second, biosorption equilibrium data were better described by the Langmuir model and showed that the monovalent ion was adsorbed in greater amounts on the *Eichhornia crassipes* roots at all temperatures used during the study; and third, the thermodynamic parameters indicate that, according to the negative ΔG° values and the positive ΔH° values, the biosorption process of Tl^+ and Cd^{2+} was spontaneous and endothermic. Additionally, the results showed that the adsorption is dependent on pH, indicating that the ions probably are accumulated in acid sites. Kinetic, equilibrium, and thermodynamic study indicated that both monovalent and divalent ions are accumulated in biomass by a similar mechanism and in the same acid sites. However, stoichiometric reaction is different for monovalent (1:2) and divalent (1:1); as a consequence, a major quantity of monovalent ion can be accumulated in biomass.

Based on the results of the present work, *Eichhornia crassipes* is an effective alternative for the removal of Tl^+ ions from an aqueous medium. According to literature, the trend in the kinetic and equilibrium adsorption of Cd^{2+} ions obtained from batch processes is similar to that obtained in this study using MCPEs; therefore, the use of MCPEs is an excellent choice for studying the biosorption processes of different metal ions.

Acknowledgments

The authors thank SEP-CONACYT (2009-133456) for their financial support. C. Martínez-Sánchez is also grateful for the CONACYT scholarship 328265/229789.

References

1. Barakat, M. A.; *Arabian J. Chem.* **2011**, *4*, 361.
2. Zhang, F.; Wang, X.; Yin, D.; Peng, B.; Tan, C.; Liu, Y.; Tan, X.; Wu, S.; *J. Environ. Manage.* **2015**, *153*, 68.
3. Galván-Arzate, S.; Santamaría, A.; *Toxicol. Lett*. **1998**, *9*, 1.
4. John-Peter, A. L.; Viraraghavam, T.; *Environ. Int.* **2005**, *31*, 493.
5. Khairy, M.; El-Safty, S. A.; Shenashen, M. A.; *TrAC, Trends Anal. Chem.* **2014**, *62*, 56.
6. Mudhoo, A.; Garg, V. K.; Wang, S.; *Environ. Chem. Lett.* **2012**, *10*, 109.
7. Sanmuga-Priya, E.; Senthamil-Selvan, P.; *Arabian J. Chem.*, *in press*, DOI: 10.1016/j.arabjc.2014.03.002.
8. Murithi, G.; Onindo, C. O.; Wambu, E. W.; Muthakia, G. K.; *BioResources* **2014**, *9*, 3613.
9. Amboga-Anzeze, D.; Mmari-Onyari, J.; Mwanza-Shiundu, P.; Gichuki, J. W.; *IOSR J. Appl. Chem.* **2014**, *7*, 29.
10. Ibrahim, H. S.; Ammar, N. S.; Soylak, M.; Ibrahim, M.; *Spectrochim. Acta, Part A* **2012**, *96*, 413.
11. Módenes, A. N.; Espinoza-Quiñones, F. R.; Borba, C. E.; Trigueros, D. E. G.; Lavarda, F. L.; Abugderah, M. M.; Kroumov, A. D.; *Water Sci. Technol.* **2011**, *64*, 1857.
12. Mahamadi, C.; Nharingo, T.; *Bioresour. Technol*. **2010**, *101*, 859.
13. Módenes, A. N.; Espinoza-Quiñones, F. R.; Trigueros, D. E. G.; Lavarda, F. L.; Colombo, A.; Mora, N. D.; *Chem. Eng. J. (Amsterdam, Neth.)* **2011**, *168*, 44.
14. Zolgharnein, J.; Asanjarani, N.; Mousavi, S. N.; *Clean: Soil, Air, Water* **2011**, *39*, 250.
15. Zolgharnein, J.; Asanjarani, N.; Shariatmanesh, T.; *Toxicol. Environ. Chem*. **2011**, *93*, 207.
16. John-Peter, A. L.; Viraraghavan, T.; *Bioresour. Technol*. **2008**, *99*, 618.
17. Khavidaki, H. D.; Aghaie, H.; *Clean: Soil, Air, Water* **2013**, *41*, 673.
18. Martínez-Sánches, C.; Torres-Rodríguez, L. M.; García-de la Cruz, R. F.; *Av. Cienc. Ing*. **2013**, *4*, 1.
19. Martínez-Sánchez, C.; Torres-Rodríguez, L. M.; Velázquez-Jiménez, L. H.; Sustaita-Martínez, J. I.; García-de la Cruz, R. F.; *Electroanalysis* **2012**, *24*, 1121.
20. Leyva, R.; Díaz, P. E.; Guerrero, R. M.; Mendoza, J.; Aragon, A.; *Rev. Soc. Quim. Mex*. **2004**, *48*, 196.
21. Kalcher, K.; Kauffmann, J. M.; Wang, J.; Svancara, I.; Vytras, K.; Neuhold, C.; Yang, Z.; *Electroanalysis* **1995**, *7*, 5.
22. Miretzky, P.; Muñoz, C.; Carrillo-Chavéz, A.; *Bioresour. Technol.* **2010**, *101*, 2637.
23. Babalola, J. O.; Overah, L. C.; Adesola, B.; Vincent, O. O.; Olatunde, A.; *J. Appl. Sci. Environ. Manage*. **2011**, *15*, 607.
24. Ho, Y. S.; Mckay, G.; *Water Res.* **2000**, *34*, 735.
25. Shroff, K. A.; Vaidya, V. K.; *Chem. Eng. J. (Amsterdam, Neth.)* **2011**, *171*, 1234.
26. Ho, Y. S.; Huang, C. T.; Huang, H. W.; *Process Biochem. (Oxford, U. K.)* **2002**, *37*, 1421.
27. Wu, F.-C.; Tseng, R.-L.; Huang, S.-C.; Juang, R.-S.; *Chem. Eng. J. (Amsterdam, Neth.)* **2009**, *151*, 1.
28. Martínez, C.; Torres, L. M.; *Quim. Nova* **2013**, *36*, 1227.
29. Subbaiah, M. V.; Yuvaraja, G.; Vijaya, Y.; Krishnaiah, A.; *J. Taiwan Inst. Chem. Eng.* **2011**, *42*, 965.
30. Hall, K. R.; Eagleton, L. C.; Acrivos, A.; Vermeulen, T.; *Ind. Eng. Chem. Fundam.* **1966**, *5*, 212.
31. Hamdaoui, O.; Naffrechoux, E.; *J. Hazard. Mater.* **2007**, *147*, 401.
32. Harris, P. O.; Ramelow, G. J.; *Environ. Sci. Technol*. **1990**, *24*, 220.
33. Mullen, M. D.; Wolf, D. C.; Beveridge, T. J.; Bailey, G. W.; *Soil Biol. Biochem*. **1992**, *24*, 129.
34. Lodi, A.; Solisio, C.; del Borghi, M.; *Bioprocess Biosyst. Eng*. **1998**, *19*, 197.
35. Shaker, M. A.; *Am. J. Appl. Sci.* **2007**, *4*, 605.
36. Aryal, M.; Liakopoulou-Kyriakides, M.; *Colloids Surf., A* **2011**, *387*, 43.

Submitted: January 20, 2016