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ANALYSIS OF THE BACK-EXTRACTION OF CADMIUM–NICKEL–D2EHPA ORGANIC PHASES

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ABSTRACT

In this work the back-extraction reaction and equilibrium parameter of organic phases containing Cd, Ni, and di(2-ethylhexyl)phosphoric acid (D2EHPA) are presented. Using sulphuric acid solution as stripping agent, this study is part of the analysis of the integral separation process of Cd and Ni acidic mixtures by means of non-dispersive solvent extraction. Discrimination of different back-extraction mechanisms was achieved from the comparison of kinetic results to simulated data with a previously-reported mathematical model. Finally, it was concluded that the formation of the organic complex species $\overline{CdX_2NiX_2}$ is responsible for the back-extraction of both metals with the equilibrium parameter $K_{BEX\_Cd\text{–}Ni} = 8.8 \times 10^{-5}\ m^3/mol$.

INTRODUCTION

Among the alternatives for the treatment of aqueous streams containing heavy metals, one of the most promising techniques is solvent extraction. Metal

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solvent extraction has been used extensively in hydrometallurgical operations. More recently, dispersion-free solvent extraction using microporous hollow-fiber (HF) contactors has received considerable attention and was proven to be very effective (1). Membrane-based non-dispersive extraction is characterized by the stabilization of the organic–aqueous interface at a porous material, avoiding the dispersion of the organic phase into the aqueous phase or vice versa and thus eliminating emulsion formation and phase entrainment (2). Additional advantages of non-dispersive solvent extraction (NDSX) are widely mentioned in the literature (3–6).

Membrane separations, in HF modules, that combine the solvent extraction and stripping processes in two steps, deserve special attention because of their potential applications, which include the separation and concentration of specific chemical species, the decontamination of wastes or biological fluids, and direct analysis for a particular compound in a mixture (7). The efficient removal of toxic heavy metals like Cd^{+2}, Cr^{+6}, Cu^{+2}, Zn^{+2}, Ni^{+2}, etc., and other contaminants like phenol from industrial wastewater (2,8–17) and the recovery of valuable solutes from aqueous phases, e.g., citric acid, carboxylic acids, aminoacids, L-phenylalanine, etc. (18,19), are well-demonstrated applications of this technique.

In previous works, the authors (20–22) studied the viability and kinetics of the non-dispersive solvent extraction of aqueous mixtures of Cd and Ni using di(2-ethylhexyl)phosphoric acid (D2EHPA) as the organic extractant and a concentrated sulphuric acid solution as the stripping phase. Besides the complexity of the extraction reactions that involve metallic components and organophosphorous acids (23–27), only few references are found on the mechanisms of the back-extraction processes (9,16,18,28,29). Thus, in this work the analysis of the back-extraction of organic phases loaded with Cd and Ni is reported as an important part in the design of the integral separation process.

EXPERIMENTAL SETUP

The feed aqueous solutions were prepared with $CdSO_4 \cdot 8/3H_2O$ and $NiSO_4 \cdot 6H_2O$ (AR grade); D2EPHA (MERCK, Schuchardt, Germany) was used as selective extractant in a concentration of 60% (v/v) and kerosene (REPSOL S.A., Bilbao, Spain) was used as solvent. Tri-butyl phosphate (TBP), 10% v/v (MERCK) was added to the organic phase in order to avoid segregation of a third phase (second organic). All the components of the organic phase were used as received, without further purification. Finally, H_2SO_4 was used as back-extraction (BEX) agent.

For the simultaneous extraction (EX) and BEX two HF modules were used in series where the organic phase flowed from the EX module to the BEX one. In the first module, extraction of solutes was accomplished by the organic phase that was in contact with the BEX solution in the second module, flowed to the homogenisation tank of the organic phase, and entered again in the extraction step. Aqueous phases flowed through the inner side of the microporous HF membranes whose pores were filled with the organic extractant, and the organic extractant flowed concurrently in the shell side in both HF modules. Figure 1 shows the experimental setup comprising of two HF modules, three stirred tanks, and accessories.

The pH of both the aqueous phases was kept constant along the runs by means of two pH controller systems (Metrohm 691-01, Metrohm A. G., Herisau, Switzerland). The feed phase (extraction phase) pH was kept equal to 3.5 by the addition of a $9\times10^{-3}\,\mathrm{mol/m^3}$ sodium hydroxide solution. The back-extraction solution (stripping phase) pH was kept equal to 0.5 by addition of a $10\times10^{-3}\,\mathrm{mol/m^3}$ H_2SO_4 solution. The volume added to the aqueous phases was considered negligible compared to the total volume of the tanks. The experiments were carried out at room temperature, 20 ± 1°C.

Pumping of both aqueous phases was achieved using polytetrafluoroethylene (PTFE) diaphragm pumps capable of flows up to $4.8\times10^{-2}\,\mathrm{m^3/hr}$, and powered by a variable speed DC motor, and the organic phase utilised a gear pump capable of flows up to $6\times10^{-2}\,\mathrm{m^3/hr}$. Three teflon flowmeters were used to monitor the flow rates of the feed, stripping, and organic streams. The flowmeters were equipped with backpressure control valves in order to maintain the appropriate control of differential pressure in both modules. Table 1 gives the characteristics of the modules used in this work that were purchased from Hoechst Celanese Corp., NC.

Initially, the organic phase was loaded using only the extraction module with Cd and/or Ni according to the experimental schedule shown in Table 2, i.e., the BEX part of the experimental system was excluded in this process. Cadmium loading was carried out contacting the initial organic phase with a feed aqueous solution containing $0.2\times10^3\,\mathrm{mol/m^3}$ of $CdSO_4$ for 3 hr until the concentration of Cd in the organic phase was about $0.2\times10^3\,\mathrm{mol/m^3}$ (Exp. I, III, IV). Nickel loading was performed by contacting feed aqueous solutions of $NiSO_4$ $0.2\times10^3\,\mathrm{mol/m^3}$ for 5 hr until the concentration of Ni in the organic phase reached a value $0.2\times10^3\,\mathrm{mol/m^3}$ (Exp. II, III, IV). When the organic phase was conveniently loaded, the BEX part of the experimental system was included and the EX and BEX processes were carried out by recirculation of the aqueous and organic phases through the modules and back into the reservoirs.

The volume of the aqueous solutions in the stirred tanks was $0.6\times10^{-3}\,\mathrm{m^3}$ and the volume of the organic solution was $1.2\times10^{-3}\,\mathrm{m^3}$. The kinetic experiments were carried out until the concentration of Cd in the aqueous phase (feed phase) decreased below 10% of the initial concentration value. The duration of the runs was between 1.5 and 3 hr, depending on the initial conditions of the organic phase. The metallic content of the samples was analysed in a Perkin–Elmer 1100 B Atomic Absorption Spectrometer (Perkin Elmer, CT).

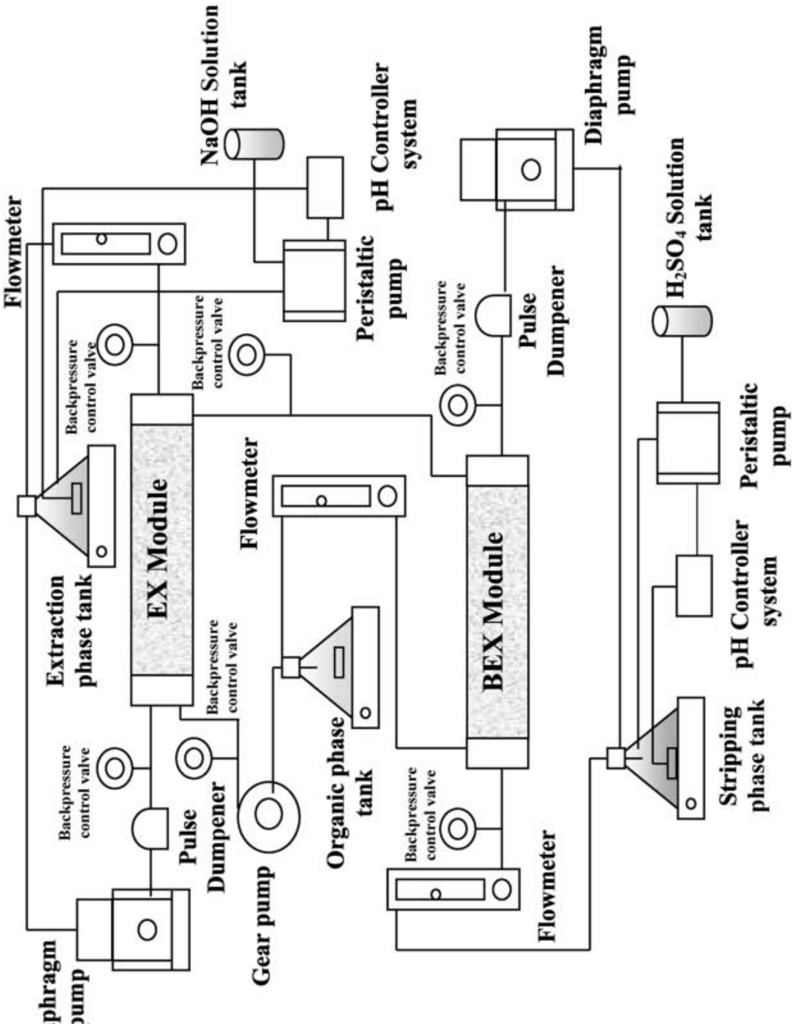

Figure 1. Schematic view of the experimental setup.

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Table 1. Hollow-Fiber Membrane Module Characteristics

Characteristics of the Modules	Values
Fiber	X-30/polypropylene
Internal diameter	240 μm
Wall thickness	30 μm
Number of fibers	10200
Nominal porosity	40%
Effective mass-transfer length	150 mm
Effective mass-transfer area	1.4 m^2

RESULTS AND INTERPRETATION

This paper reports the analysis of the back-extraction mechanism of cadmium- and nickel-loaded organic phases. In the experiments the back-extraction process was coupled to the extraction process as described in the previous section. Table 2 shows the initial concentration of the metals in the organic and stripping phases of the experiments. Experiments I and II were carried out with an organic phase that had been loaded with only one of the metals, Cd or Ni respectively; whereas the organic phase of experiments III and IV had been loaded with both metals.

The Cd ion was transported to the BEX phase due to the initial loading of the organic phase and also due to the transport of Cd from the feed phase; whereas in the case of Ni, the back-extraction was only due to the initial presence of the metal in the organic phase, since under the experimental conditions ($pH_{EX} = 3.5$) there was no extraction of Ni. Figures 2–4 show the kinetic results of experiments I–IV.

Table 2. Initial Conditions of the Experimental Runs

	Initial Concentration, ORG Phase (mol/m^3) 10^3		Initial Concentration, Stripping Phase (mol/m^3) 10^3	
Experiment	Cd	Ni	Cd	Ni
I	0.202	—	0.20	—
II	—	0.192	0.20	—
III	0.20	0.20	0.21	0.20
IV	0.194	0.20	0.21	—

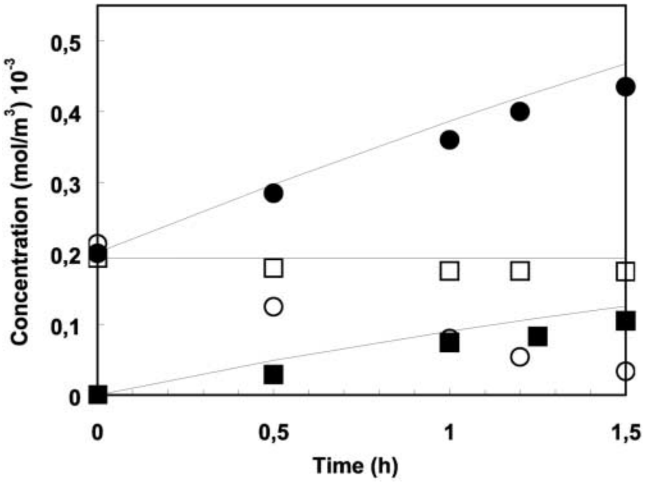

Figure 2. Cadmium evolution in experiment I and Ni evolution in experiment II. ○: Cd concentration of the solution in the extraction phase tank. ●: Cd concentration of the solution in the stripping phase tank. □: Ni concentration of the solution in the extraction phase tank. ■: Ni concentration of the solution in the stripping phase tank.

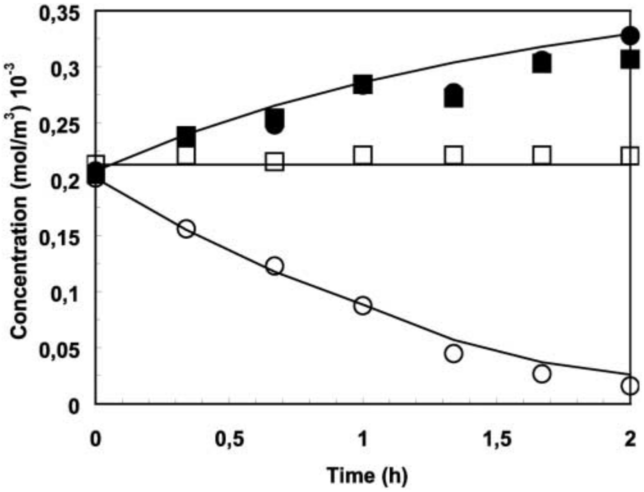

Figure 3. Cadmium and Ni kinetic results in the extraction and back-extraction processes of experiment III. ○: Cd concentration of the solution in the extraction phase tank. ●: Cd concentration of the solution in the stripping phase tank. □: Ni concentration of the solution in the extraction phase tank. ■: Ni concentration of the solution in the stripping phase tank.

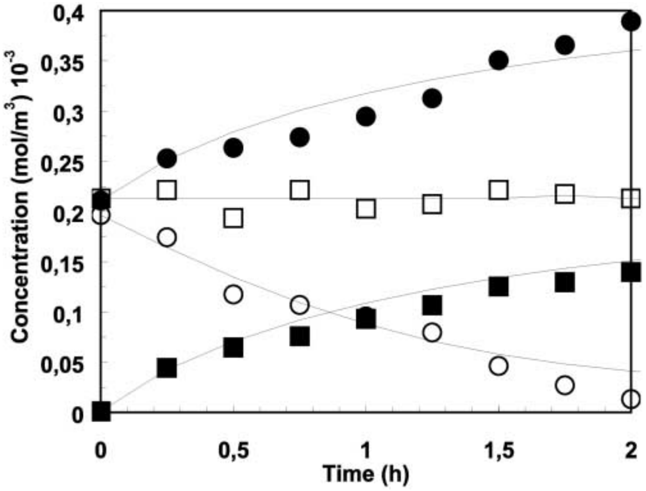

Figure 4. Cadmium and Ni kinetic results in the extraction and back-extraction processes of experiment IV. ○: Cd concentration of the solution in the extraction phase tank. ●: Cd concentration of the solution in the stripping phase tank. □: Ni concentration of the solution in the extraction phase tank. ■: Ni concentration of the solution in the stripping phase tank.

In experiment III the initial concentration of Cd and Ni in the organic phase are equal to 0.2×10^{-3} mol/m^3; Fig. 3 shows that the evolution of the concentration of both metals in the stripping solution is very similar for the duration of the experimental runs.

Modelling of the Back-Extraction Process

Previous works on the removal of Cr(VI) (13,14) and on the removal of Cd (2) reported the kinetic modelling of the separation of metallic mixtures by non-dispersive solvent extraction when the process also included the back-extraction step for concentration of the separated metal and regeneration of the organic phase. The mathematical model consisted of a set of coupled differential equations, solute mass balances to the fluid phases together with the equilibrium expressions of the interfacial chemical reactions between aqueous solutes and the organic extractant (Appendix A). In those works it was considered that the main resistance to solute transport lies in the microporous membrane and that the reagent species are present in equilibrium concentration at the whole interface.

For the modelling of a NDSX system that includes the extraction and the back-extraction steps the requirements are the knowledge (i) of the equilibrium (stoichiometry and equilibrium parameter) of the chemical reactions involved, since it is assumed that complexing reactions are very fast, and (ii) the kinetic parameters of the process (mass transfer coefficients). Thus, in the case under study (after the proper description of the extraction process (21,22)), it is necessary to be able to describe the reactions responsible for the BEX of Cd and Ni from the organic phase.

The complexity of the description of the behaviour of chemical reactions of phosphorous compounds has been studied extensively in the literature (30,31). Di(2-ethylhexyl)phosphoric acid is an important acidic organophosphorous extractant because of its high separation and extraction efficiency. In the last decades, D2EHPA has been applied extensively to the separation and purification processes of uranium, rare earths, and other metals such as copper and zinc. In general, the metal ion is extracted into the organic phase by forming a complex species with D2EHPA (32,33). Solutions of this extractant in organic diluents can be heavily loaded by divalent metal ions without formation of a third phase or becoming unacceptably viscous, while a favourable metal to D2EHPA ratio of 1:2 is reached (24,34,35). However, there is no agreement about the stoichiometry of the ion exchange reactions of Cd and Ni with the organic carrier D2EHPA; among other possibilities the stoichiometries 1:2 and 1:2.5 (Eqs. (1,2)) have been reported,

$$Cd^{+2} + 2\overline{(HX)_2} \overset{K_{EX-Cd}}{\longleftrightarrow} \overline{CdX_2(HX)_2} + 2H^+ \tag{1}$$

$$Ni^{+2} + 2.5\overline{(HX)_2} \overset{K_{EX-Ni}}{\longleftrightarrow} \overline{NiX_2(HX)_3} + 2H^+ \tag{2}$$

Discrimination of the Back-Extraction Mechanisms

The first attempt to describe the back-extraction kinetic results made use of the previously-reported chemical equilibria, which in the case of Cd would lead to the following BEX reaction,

$$\overline{CdX_2(HX)_2} + 2H^+ \overset{K_{BEX-Cd}}{\longleftrightarrow} Cd^{+2} + 2\overline{(HX)_2} \tag{3}$$

and in the case of Ni according to the stoichiometry 1:2.5, the BEX reaction would be,

$$\overline{NiX_2(HX)_3} + 2H^+ \overset{K_{BEX-Ni}}{\longleftrightarrow} Ni^{+2} + 2.5\overline{(HX)_2} \tag{4}$$

After introduction of Eqs. (3,4) in the kinetic model (Appendix A) the equilibrium parameters were estimated by the comparison of experimental and simulated results using the minimum-weight standard deviation as optimization criterion. In these runs, the value of the membrane mass transport parameter previously estimated, $K_m = 5.69 \times 10^{-4}$ m/hr, was used (22). As a representative example Fig. 5 gives the comparison between simulated and experimental results of experiment IV when Eqs. (3,4) are included in the mass transport model. Similar trends were observed in the rest of the experiments.

It is observed that the simulated concentration data are higher than the experimental values for both metals. The standard deviations lay in the range 33–43% for the results of Cd and in the range 12–14% in the case of Ni (Table 3). Due to the bad agreement between the simulated and experimental data, it was concluded that the mathematical model that included Eqs. (3,4) is not able to describe the BEX process successfully.

Several authors pointed to the possibility of the formation of different stoichiometric metal–organic complexes $\overline{(MX_2 \cdot H_2X_2)}$ or $\overline{((MX_2)_2 \cdot H_2X_2)}$ depending on the metallic loading of the organic phase (36,37).

With these considerations, it was proposed that in the presence of a concentrated aqueous solution containing two metals the organic extractant would form a mixed complex species with both metals. According to the experimental procedure the organic phase was first loaded with Ni, forming a

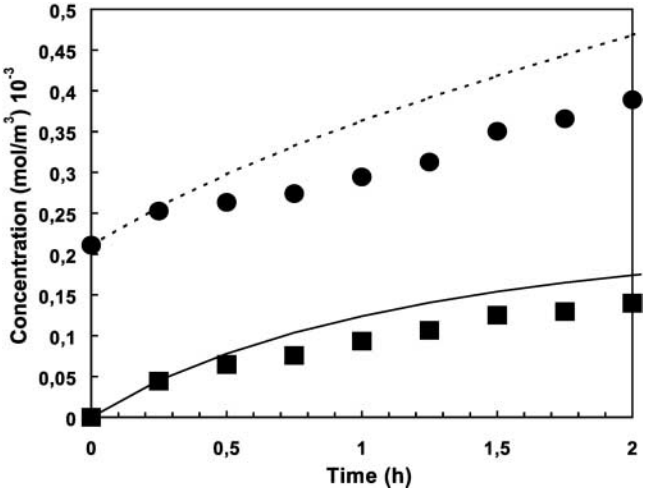

Figure 5. Simulated data of back-extraction of Cd and Ni in experiment IV with the model that includes Eqs. (3–4). ●: Experimental Cd concentration of the solution in the stripping phase. - - -: Simulated Cd concentration of the solution in the stripping phase. ■: Experimental Ni concentration of the solution in the stripping phase. —: Simulated Ni concentration of the solution in the stripping phase.

Table 3. Values of the Standard Deviation

BEX Equations	Equilibrium Constant	Cd (%)	Ni (%)
Eqs. (3)–(4)	$K_{\mathrm{BEX-Cd}} = 5.5 \times 10^4$ $K_{\mathrm{BEX-Ni}} = 0.6 \times 10^{1.5} (\mathrm{mol/m^3})^{0.5}$	33–43	12–14
Eqs. (5)–(7)	$K'_{\mathrm{BEX-Cd}} = 2 \times 10^{-2} (\mathrm{mol/m^3})^{-1}$ $K_{\mathrm{BEX-Ni}} = 0.6 \times 10^{1.5} (\mathrm{mol/m^3})^{0.5}$	34–47	16–18
Eqs. (3) and (8)	$K_{\mathrm{BEX-Cd}} = 5.5 \times 10^4$ $K_{\mathrm{BEX-Cd–Ni}} = 6.87 \times 10^{-5} (\mathrm{m^3/mol})$	12–13	10–11
Eq. (11)	$K_{\mathrm{BEX-Cd–Ni}} = 8.8 \times 10^{-5} (\mathrm{m^3/mol})$	7–9	4–7

complex species $\overline{\mathrm{NiX_2(HX)_3}}$ and after that with Cd following the equation,

$$\overline{\mathrm{NiX_2(HX)_3}} + \mathrm{Cd}^{+2} \overset{K'_{\mathrm{EX-Cd}}}{\longleftrightarrow} \overline{\mathrm{NiX_2CdX_2(HX)}} + 2\mathrm{H}^+ \tag{5}$$

and the back-extraction process of both metals would take place following the reactions,

$$\overline{\mathrm{NiX_2CdX_2(HX)}} + 2\mathrm{H}^+ \overset{K'_{\mathrm{BEX-Cd}}}{\longleftrightarrow} \mathrm{Cd}^{+2} + \overline{\mathrm{NiX_2(HX)_3}} \tag{6}$$

$$\overline{\mathrm{NiX_2(HX)_3}} + 2\mathrm{H}^+ \overset{K_{\mathrm{BEX-Ni}}}{\longleftrightarrow} \mathrm{Ni}^{+2} + 2.5\overline{\mathrm{(HX)_2}} \tag{7}$$

Figure 6 shows the simulated results corresponding to experiment III as a representative example obtained after inclusion of Eqs. (5–7) in the kinetic model.

Due to the high value of the standard deviation of the back-extraction results that lay in the range 34–47% for Cd and 16–18% for Ni, Eqs. (5–7) were discarded in the description of the back-extraction of both metals.

Next, the formation of a different stoichiometric complex species $\overline{\mathrm{CdX_2NiX_2}}$ was considered, which supposed the maximum metallic occupation of the extractant and therefore allowed to get higher concentrations of free extractant in the organic phase; the BEX of the metals proceeded according to Eq. (8),

$$\overline{\mathrm{CdX_2NiX_2}} + 4\mathrm{H}^+ \overset{K_{\mathrm{BEX-Cd–Ni}}}{\longleftrightarrow} \mathrm{Cd}^{+2} + \mathrm{Ni}^{+2} + 2\overline{\mathrm{(HX)_2}} \tag{8}$$

The comparison of the results simulated with this model to the experimental data of experiment IV, as a representative example, is given in Fig. 7.

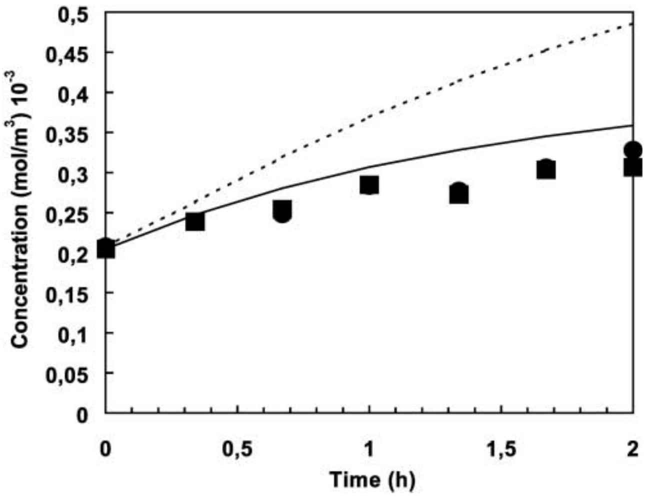

Figure 6. Simulated data of BEX results of experiment III with a model that includes Eqs. (5–7). ●: Experimental Cd concentration of the solution in the stripping phase. - - -: Simulated Cd concentration of the solution in the stripping phase. ■: Experimental Ni concentration of the solution in the stripping phase. —: Simulated Ni concentration of the solution in the stripping phase.

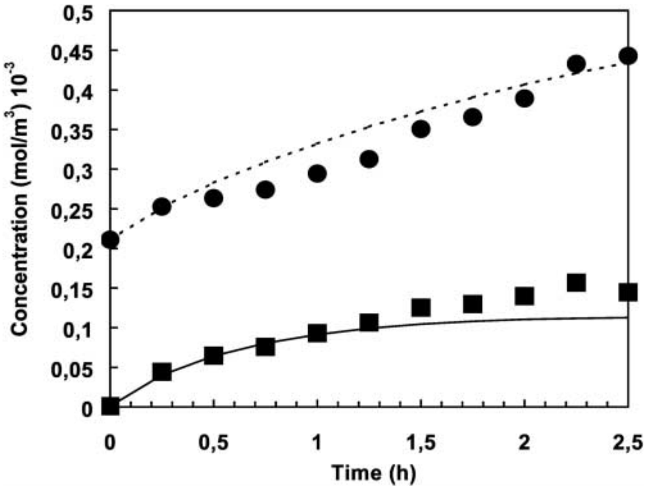

Figure 7. Experimental and simulated results of the BEX process of the experiment IV with a model that includes Eqs. (3,8). ●: Experimental Cd concentration of the solution in the stripping phase. - - -: Simulated Cd concentration of the solution in the stripping phase. ■: Experimental Ni concentration of the solution in the stripping phase. —: Simulated Ni concentration of the solution in the stripping phase.

It is observed that the description of the BEX results of both the metals is pretty good—the values of standard deviation considering all the experiments were less than 13% for both metals. The use of the mathematical model still needed three parameters to describe the kinetic behaviour of the back-extraction process: $K_{\mathrm{BEX-Cd}} = 5.5 \times 10^4$, $K_m = 5.69 \times 10^{-4}\ \mathrm{m/hr}$, and $K_{\mathrm{BEX-Cd\text{–}Ni}} = 6.87 \times 10^{-5}\ \mathrm{m^3/mol}$.

Finally and in order to simplify the modelling, it was considered that the two reactions responsible for the BEX of Cd, Eq. (3) and Eq. (8) could be combined as follows,

$$\overline{\mathrm{CdX_2NiX_2}} + 2\mathrm{H}^+ \overset{K'_{\mathrm{BEX-Ni}}}{\longleftrightarrow} \mathrm{Ni}^{+2} + \overline{\mathrm{CdX_2(HX)_2}} \tag{9}$$

$$\overline{\mathrm{CdX_2(HX)_2}} + 2\mathrm{H}^+ \overset{K_{\mathrm{BEX-Cd}}}{\longleftrightarrow} \mathrm{Cd}^{+2} + 2\overline{\mathrm{(HX)_2}} \tag{10}$$

$$\overline{\mathrm{CdX_2NiX_2}} + 4\mathrm{H}^+ \overset{K_{\mathrm{BEX-Cd\text{–}Ni}}}{\longleftrightarrow} \mathrm{Cd}^{+2} + \mathrm{Ni}^{+2} + 2\overline{\mathrm{(HX)_2}} \tag{11}$$

requiring the knowledge of only one parameter for the BEX of both metals (Eq. 11 is the sum of Eqs. 9 and 10.)

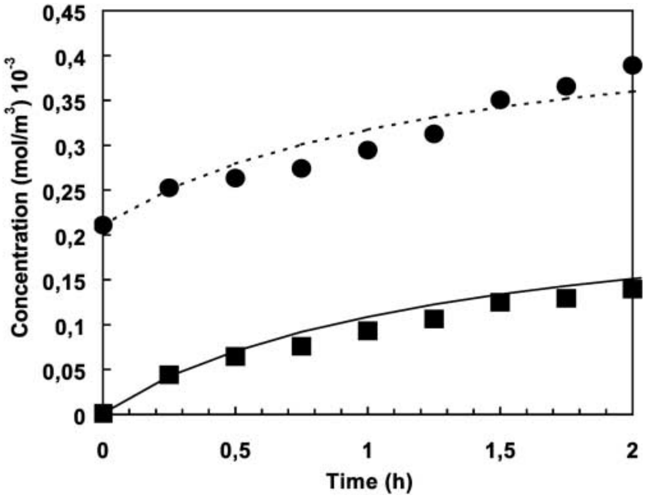

Figure 8. Experimental and simulated data with a model that include Eq. (11). Results of experiment IV. ●: Experimental Cd concentration of the solution in the stripping phase. - - -: Simulated Cd concentration of the solution in the stripping phase. ■: Experimental Ni concentration of the solution in the stripping phase. —: Simulated Ni concentration of the solution in the stripping phase.

The optimization procedure described previously was followed, obtaining the value of $K_{\mathrm{BEX\_Cd\text{–}Ni}} = 8.8 \times 10^{-5}\ \mathrm{m^3/mol}$. Figure 8 shows the comparison of data of experiment IV with results simulated according to this model.

Besides the good agreement between experimental and simulated data observed in Fig. 8, the values of standard deviation were also lower than the values obtained with previous models, lying below 9% for both metals. Therefore it was concluded that the simultaneous Extraction and BEX process was successfully described with a kinetic model that considered the formation of an organic complex species where both metals were present and that was responsible for the simultaneous BEX of Cd and Ni, needing only three parameters $K_{\mathrm{EX}} = 1.82 \times 10^{-5}$, $K_{\mathrm{BEX\_Cd\text{–}Ni}} = 8.8 \times 10^{-5}\ \mathrm{m^3/mol}$, and $K_{\mathrm{m}} = 5.69 \times 10^{-4}\ \mathrm{m/hr}$ to describe successfully the dynamic behaviour of the integral separation process.

Table 3 summarizes the values of standard deviation obtained from the comparison of experimental and simulated results with the considered models.

CONCLUSIONS

In this work the analysis of the back-extraction process of organic phases containing Cd, Ni, and D2EHPA is reported. The back-extraction step took place simultaneous to the extraction step in an integral separation process of Cd–Ni mixtures. Using the kinetic model developed previously by the authors (22), the discrimination of the back-extraction mechanism was performed by the comparison of experimental results with model predictions after inclusion of different equations of the BEX equilibria. Finally, the best description of the process was achieved when the formulation of the organic complex species $\overline{\mathrm{CdX_2NiX_2}}$ was considered, which was responsible for the back-extraction of both metals with a value of the equilibrium parameter of $K_{\mathrm{BEX\_Cd\text{–}Ni}} = 8.8 \times 10^{-5}\ \mathrm{m^3/mol}$.

APPENDIX A

For the development of the mass balances of both solutes in the components of the NDSX system the following assumptions were considered: (i) fully developed laminar flow inside the hollow fibers, (ii) lack of backmixing inside the modules, and (iii) linear concentration gradients, leading to the following expressions:

Extraction Module

Differential mass balances of the solutes in the feed and organic solutions in the extraction module are expressed through the following equations, (where $i = 1$ for cadmium and $i = 2$ for nickel).

EX, Aqueous Solution

$$-\frac{\partial C_{A_i}}{v_A \partial t} = \frac{\partial C_{A_i}}{\partial z} + \frac{2\pi n_f r_f}{F_A} K_m (C_{OI_i} - C_{O_i}) \tag{A.1}$$

with boundary conditions:

$$z = 0 \qquad C_{A_j} = C_{out_i}\ \text{(extraction tank)} \tag{A.2}$$

$$t = 0 \qquad C_{A_i} = C_{A_i,\text{initial}}, \quad i = 1, 2 \tag{A.3}$$

C_{OI_i} is the interfacial concentration of the metal in the organic phase that is related to the aqueous metal concentration through the thermodynamic chemical equilibrium equation:

$$K_{eq} = \frac{[a_{\overline{CdX_2(HX)_2}}][a_{H^+}]^2}{[a_{Cd^{+2}}][a_{\overline{(HX)_2}}]^2} = \frac{[\overline{CdX_2(HX)_2}][H^+]^2}{[Cd^{+2}][\overline{(HX)_2}]^2} \frac{[\gamma_{\overline{CdX_2(HX)_2}}][\gamma_{H^+}]^2}{[\gamma_{Cd^{+2}}][\gamma_{\overline{(HX)_2}}]^2} \tag{A.4}$$

EX, Organic Solution

$$\frac{\partial C_{O_i}}{v_O \partial t} = -\frac{\partial C_{O_i}}{\partial z} + \frac{2\pi n_f r_f}{F_O} K_m (C_{OI_i} - C_{O_i}) \tag{A.5}$$

Boundary conditions of the organic phase:

$$z = 0 \qquad C_{O_i} = C_{out_i}\ \text{(organic tank)} \tag{A.6}$$

$$t = 0 \qquad C_{O_i} = C_{O_i,\text{initial}}, \quad i = 1, 2 \tag{A.7}$$

Back-Extraction Module

BEX Aqueous solution

$$\frac{\partial C_{S_i}}{v_S \partial t} = -\frac{\partial C_{S_i}}{\partial z} + \frac{2\pi n_f r_f}{F_S} K_m (C_{O_i} - C_{OI_i}) \tag{A.8}$$

Boundary conditions for the stripping aqueous phase:

$$z = 0 \qquad C_{S_i} = C_{out_i}\ \text{(stripping tank)} \tag{A.9}$$

$$t = 0 \qquad C_{S_i} = C_{S_i,\text{initial}}, \quad i = 1, 2 \tag{A.10}$$

with the equilibrium back-extraction reactions represented by Eqs. (3–11).

BEX Organic Solution

$$-\frac{\partial C_{\mathrm{O_i}}}{v_{\mathrm{O}}\partial t} = \frac{\partial C_{\mathrm{O_i}}}{\partial z} + \frac{2\pi n_{\mathrm{f}} r_{\mathrm{f}}}{F_{\mathrm{O}}} K_{\mathrm{m}}(C_{\mathrm{O_i}} - C_{\mathrm{OI_i}}) \tag{A.11}$$

Boundary conditions of the organic phase:

$$z = 0 \qquad C_{\mathrm{O_i}} = C_{\mathrm{O_i}}\ \text{(outlet extraction module)} \tag{A.12}$$

$$t = 0 \qquad C_{\mathrm{O_i}} = C_{\mathrm{O_i,initial}}, \quad i = 1, 2 \tag{A.13}$$

Stirred Tanks

$$V\frac{\mathrm{d}C_{\mathrm{out_i}}}{\mathrm{d}t} = F(C_{\mathrm{in_i}} - C_{\mathrm{out_i}}) \tag{A.14}$$

$$t = 0 \qquad C_{\mathrm{out_i}}\ \text{(organic tank)} = C_{\mathrm{O_i,initial}} \tag{A.15}$$

$$C_{\mathrm{out_i}}\ \text{(extraction tank)} = C_{\mathrm{A_i,initial}} \tag{A.16}$$

$$C_{\mathrm{out_i}}\ \text{(stripping tank)} = C_{\mathrm{S_i,initial}} \tag{A.17}$$

SYMBOLS

a	activity, (mol/m^3) 10^{-3}
C	solute concentration in the stirred tanks (feed, organic, stripping), (mol/m^3) 10^{-3}
C_{in}	inlet solute concentration to the stirred tanks (feed, organic, stripping), (mol/m^3) 10^{-3}
C_{O}	solute concentration in the organic phase, (mol/m^3) 10^{-3}
C_{OI}	interfacial solute concentration in the organic phase, (mol/m^3) 10^{-3}
C_{out}	outlet solute concentration from the stirred tanks (feed, organic, stripping), (mol/m^3) 10^{-3}
F	flowrate of the fluid phases, feed, organic and stripping (m^3/hr)
$K_{\mathrm{BEX\_Cd}}$	chemical equilibrium constant of the back-extraction of cadmium
$K_{\mathrm{BEX\_Cd-Ni}}$	back-extraction equilibrium constant of cadmium and nickel
$K_{\mathrm{EX\_Cd}}$	extraction equilibrium constant of cadmium
K_{m}	membrane mass transport coefficient (m/hr)
n_{f}	number of fibers

r_f	inner radius of hollow fiber (m)
t	time (hr)
V	tank volume (feed, organic, stripping) (m^3)
v_A	linear velocity in the feed aqueous phase (m/hr)
v_O	linear velocity in the organic phase (m/hr)
v_S	linear velocity in the stripping aqueous phase (m/hr)
z	axial distance (m)

Greek letters

σ	standard deviation

Subscript

A	feed aqueous phase
BEX_Cd	cadmium in the back-extraction process
BEX_Cd–Ni	cadmium and nickel in the back-extraction process
EX_Cd	cadmium in the extraction process
i	metallic solute, cadmium, or nickel
O	organic phase
S	back-extraction phase
w	aqueous phase

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