

Kinetics of the recovery of Cd from highly concentrated aqueous solutions by non-dispersive solvent extraction

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Abstract

In this paper, the kinetics of the non-dispersive extraction and back-extraction of cadmium from high concentration aqueous solutions using D2EHPA as selective extractant are reported. Batch experiments were performed in order to analyse the influence of the initial Cd concentration in the feed, organic and back-extraction phases. The proposed kinetic model consists of a system of partial differential and algebraic equations describing the mass balances of Cd in the fluid phases of the hollow-fibre contactors and homogenisation tanks. The main hypothesis is that membrane mass transport controls the extraction kinetics. Two design parameters K_m , membrane mass transport coefficient, and K_{eq} , equilibrium parameter of the extraction reaction have been calculated from the correlation of the experimental results by the reported model. The comparison of experimental and simulated data confirmed the validity of the kinetic analysis. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Cd recovery; Di(2-ethylhexyl) phosphoric acid; Non-dispersive solvent extraction; Kinetic model

1. Introduction

Various liquid–liquid extraction processes have been proposed for recovery and recycling of metal waste through the years [1]. The manufacture of nickel–cadmium batteries or the recycling of battery scrap are examples of processes where solvent extraction can be used in order to solve environmental problems [2,3]. In this application, the separation of Ni and Cd from high concentration solutions resulting after leaching of the scrap can be achieved successfully by solvent extraction [4]. The use of an appropriate selective extractant followed by an efficient back-extraction process could allow the recycling of both metals.

In recent years, non-dispersive solvent extraction (NDSX) has been suggested for several applications as an option to conventional processes. This technology presents several advantages in comparison to conventional processes that have been widely reported in recent literature [5–9]. These benefits include low maintenance, no dispersion of the phases and the high interfacial area provided when a hollow-fibre configuration is applied.

Before industrial application of NDSX technology, further studies are needed on features such as quantification of the losses of the organic phase into the aqueous phase due

to solubility, and determination of the life time of the membrane. Losses of organic phase could be minimised by using compounds with low solubility in water solutions. Long life of the membrane could be expected since membrane fouling tends to be more of a problem with pressure-driven devices than with concentration-driven ones [6].

The large number of bibliographic references to NDSX technology published during the last decade reveals great interest in this process. A general review of the technology and the applications has been included in a publication dedicated to process separation with membranes by Ho and Sirkar [7], and, more recently, Gabelman and Hwang [6] provided a review of hollow-fibre membrane contactors. Among the most recent references on the application of the technology, Alonso et al. [8] and Urriaga et al. [9] studied the separation of Cd from phosphoric acid in order to avoid the presence of the metal in phosphate fertilisers; different extractants such as Aliquat 336 or Cyanex 302 were checked and a mathematical model and characteristic parameters needed for process design were obtained. The study of the separation-concentration of Cr(VI) with Aliquat 336 using NDSX at pilot plant scale has been reported by Alonso et al. [10].

In a previous paper [4], the viability of the application of NDSX technology to the separation of nickel and cadmium from highly concentrated solutions was reported, carrying out the extraction and back-extraction processes simultane-

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Nomenclature

a_A	solute activity in the feed phase
a_{H^+}	proton activity in the feed phase
C	solute concentration in the stirred tanks (feed, organic and stripping) (mol/l)
C_i	initial concentration of Cd in the stirred tanks (feed, organic and stripping) (mol/l)
C_{IN}	inlet solute concentration in the stirred tanks (feed, organic and stripping) (mol/l)
C_A	solute concentration in the feed phase (mol/l)
C_O	solute concentration in the organic phase (mol/l)
C_S	solute concentration in the stripping phase (mol/l)
C_{OI}	interfacial solute concentration in the organic phase (mol/l)
C_T	total carrier concentration (mol/l)
F	inlet and outlet flowrate in the stirred tanks (feed, organic and stripping) (l/h)
F_A	aqueous flowrate in the extraction and back-extraction modules (l/h)
F_O	organic flowrate in the extraction and back-extraction modules (l/h)
K_{eq}	extraction equilibrium constant
K'_{eq}	apparent extraction equilibrium constant
K''_{eq}	apparent extraction equilibrium constant
K_m	membrane mass transport coefficient in extraction and back-extraction module (m/s)
n_f	number of fibres
n	stoichiometric parameter
r_f	inner radius of the hollow fibre (m)
t	time (h)
V	tank volume (feed, organic, stripping) (l)
v_A	linear velocity in the aqueous phase (feed and stripping)
v_O	linear velocity in the organic phase
Z	ion charge
z	axial distance (cm)

Greek letters

γ	activity coefficient
μ	ion strength
σ_w	weighted standard deviation, defined by Eq. (17)

ously. Working with initial concentrations of 0.37 M of Cd and 0.37–0.68 M of Ni in the feed aqueous phase, 0.3 M of H_2SO_4 in the back-extraction phase (BEX) and using di(2-ethylhexyl) phosphoric acid (D2EHPA) as extractant, the separation process gave a selectivity factor in the BEX solution of 67 mol Cd/mol Ni. The separation was achieved working with a pH in the range 2.5–3.5 in the feed aqueous phase and a pH value equal to 0.5 in the BEX aqueous solution.

In this paper, as the first part in a study of the kinetics of the separation process of Cd and Ni from highly concentrated solutions, the kinetics of NDSX of Cd from high concentration solutions (0.2–0.4 M) is analysed.

The kinetic modelling of the system is an essential part of the paper, needed for the optimal design of the NDSX process for industrial applications.

2. Experimental set-up

The use of organophosphorous acids has been widely reported for the extraction of heavy metals and rare earths [11–16]. In this paper, D2EHPA (Merck) with a concentration of 60% (v/v) was used as selective extractant and kerosene (Petronor) was used as solvent. In order to avoid the formation of a third phase (second organic), a modifier component TBP was used; it was added to the organic phase in a concentration of 10% (v/v). Finally, H_2SO_4 was used as BEX agent.

The experimental set-up includes two hollow-fibre membrane modules, one for the extraction and the other one for the back-extraction process. In the extraction module, the feed aqueous phase contacted the organic phase and the reaction between D2EHPA and Cd took place. In the back-extraction module, the loaded organic phase reacted with the back-extraction agent transferring the Cd to the aqueous phase. Three stirred tanks were also employed for homogenisation of the three liquid solutions: feed aqueous phase, organic phase and back-extraction phase. A schematic diagram of the set-up is shown in Fig. 1 and the main characteristics of the hollow-fibre membrane modules are given in Table 1.

The non-dispersive experimental system included two diaphragm pumps capable of supplying up to 1 l/min of the aqueous phases and a gear pump capable of supplying up to 0.6 l/min for the organic phase. To ensure that no displacement of the organic phase from the pores of the fibre wall took place, the pressure of the aqueous phase was maintained about 5 psia higher than the pressure of the organic phase.

Both EX and BEX operations were carried out working in a recirculating mode with the fluid phases flowing co-currently in each module. Samples were withdrawn every 30 min from the aqueous solution tanks and the cadmium

Table 1
Hollow-fibre membrane module characteristics

Characteristics of the modules	Values
Fibre	X-30/polypropylene
Internal diameter	240 μm
Wall thickness	30 μm
Number of fibres	10 200
Nominal porosity	40%
Effective mass-transfer length	150 mm
Effective mass-transfer area	1.4 m^2

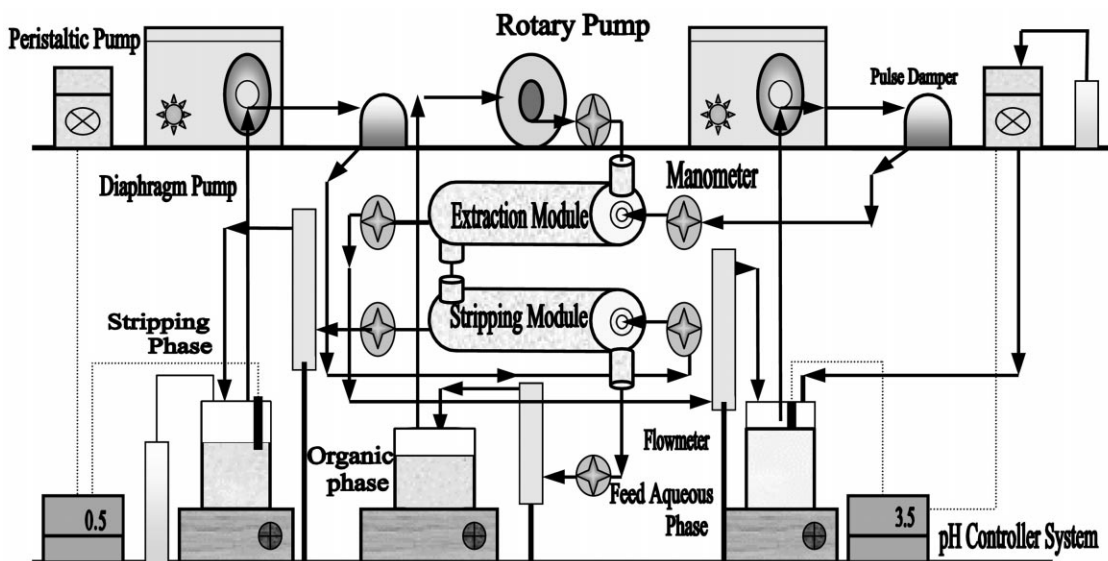


Fig. 1. Schematic diagram of the simultaneous hollow-fibre EX and BEX processes.

concentration was analysed, after sample preparation, in a Perkin Elmer 3100 Atomic Absorption Spectrophotometer.

The feed phase consisted of aqueous solutions of CdSO_4 with an initial concentration of Cd between 0.2 and 0.4 M while the back-extraction solution was a 0.3 M H_2SO_4 solution. The pH of both aqueous phases was kept constant during the runs: 3.5 for the feed phase and 0.5 for the BEX solution, through the addition of NaOH (9 M) in the feed aqueous phase and H_2SO_4 (0.3 M) in the back-extraction solution. Adjustment of the pH was carried out by a pH controller system (Metrohm 691-01) and the change of volume due to the addition of NaOH and H_2SO_4 was negligible compared to the total volume of the aqueous solutions. The experiments were carried out at room temperature, $20 \pm 1^\circ\text{C}$.

3. Theoretical background

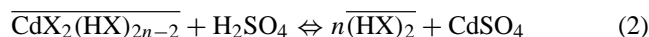
Modelling a NDSX system requires the knowledge of the equilibrium (stoichiometry and equilibrium parameters) and kinetic parameters (mass transfer coefficients) since it is assumed that the complexing reactions are very fast.

3.1. Chemical reaction stoichiometry

The system under study is the reversible extraction reaction of Cd with D2EHPA



and the back-extraction reaction,



where $\overline{(\text{HX})}_2$ represents the initial carrier concentration and $\overline{\text{CdX}_2(\text{HX})_{2n-2}}$ is the solute-carrier complex species.

The complexity of the description of the extraction behaviour of phosphorous compounds has been widely reported in the literature [16,17]. D2EHPA has been reported to exist as a dimer in the organic phase and therefore it complexes as a dimer with the metal [18,19], but there is no agreement in the literature about the stoichiometry of the ion exchange reaction of Cd with the organic carrier D2EHPA; Table 2 gives a summary of the stoichiometric coefficients and equilibrium constants reported previously.

Working with highly loaded organic phases, the situation is even more complex since successively larger aggregated metal complexes appear. The monomeric species D2EHPA can also exist [20].

Besides the complexity of the extraction system itself, the reaction can be also influenced by the presence of the diluent or solvent, the modifier agent, as well as by the presence of other inorganic common anions. In this respect, Rao et al. pointed out the effect of the sulphate ion in the aqueous phase on the extraction of cobalt and nickel; the authors indicated that the diluent acted not only as a carrier of the

Table 2
Stoichiometric coefficients and equilibrium parameters for the system Cd–D2EHPA

n	Authors	Metal concentration	Organic phase	Diluent	K_{eq}
2	Daiminger et al. (1996)	0.1–10 mg/l Cd	0.05 M < D2EHPA < 0.5 M	Isodecane	$6 + 1.5 \times 10^{-3}$
2.5	Grimm and Kolarik (1974)	0.2 mol/l CdCl_2	0.5 M D2EHPA + 0.34 TBP	<i>n</i> -dodecane	
	Raghuraman et al. (1995)	1 g/l Cd	5–10% D2EHPA	Tetradecane	$2.58 \times 10^{-2} (\text{l/mol})^{0.5}$

extractant and extracted metal but also as a participant in the extraction process [21,22].

3.2. Chemical equilibrium description

Considering the stoichiometric equation (1) with a value of n equal to 2, an expression for the equilibrium constant for the extraction process is formulated using activities in the feed aqueous and organic phases [23] as follows:

$$K_{\text{eq}} = \frac{[a_{\overline{\text{CdX}_2(\text{HX})_2}]}[a_{\text{H}^+}]^2}{[a_{\text{Cd}}][a_{\overline{(\text{HX})_2}}]^2} = \frac{[\overline{\text{CdX}_2(\text{HX})_2}][\text{H}^+]^2 [\gamma_{\overline{\text{CdX}_2(\text{HX})_2}}][\gamma_{\text{H}^+}]^2}{[\text{Cd}^{+2}][\overline{(\text{HX})_2}]^2 [\gamma_{\text{Cd}}][\overline{\gamma_{(\text{HX})_2}}]^2} \quad (3)$$

In a first approach, in this paper, it has been assumed that the ratio $\gamma_{\overline{\text{CdX}_2(\text{HX})_2}}/\gamma_{\overline{(\text{HX})_2}}^2$ remained constant in the range of experimental conditions, so that Eq. (3) is transformed into

$$K'_{\text{eq}} = K_{\text{eq}} \frac{[\overline{\gamma_{\text{CdX}_2(\text{HX})_2}}]}{[\overline{\gamma_{(\text{HX})_2}}]^2} = \frac{[\overline{\text{CdX}_2(\text{HX})_2}][\text{H}^+]^2 [\gamma_{\text{H}^+}]^2}{[\text{Cd}^{+2}][\overline{(\text{HX})_2}]^2 [\gamma_{\text{Cd}^{+2}}]} \quad (4)$$

As a_{H^+} remained constant in the extraction and back-extraction processes, Eq. (4) can be simplified to

$$K''_{\text{eq}} = \frac{K'_{\text{eq}}}{[\gamma_{\text{H}^+}]^2 [\text{H}^+]^2} = \frac{[\overline{\text{CdX}_2(\text{HX})_2}]}{[\text{Cd}^{+2}][\overline{(\text{HX})_2}]^2} \frac{1}{[\gamma_{\text{Cd}^{+2}}]} \quad (5)$$

During the experiments, the concentration of Cd in the feed aqueous solution decreased to values below 10% of the initial concentration. The corresponding values of the activity coefficient of the Cd ion in the aqueous solution have been calculated using the Debye–Hückel equation [24]:

$$\ln \gamma_i = \left(\frac{0.5Z^2 \sqrt{\mu}}{1 + \sqrt{\mu}} \right) \quad (6)$$

where the ionic strength is expressed as

$$\mu = \frac{1}{2} \sum C_i Z_i^2 \quad (7)$$

where Z is the ion charge and C_i is the concentration of each ion in the solution.

3.3. Separation kinetics

In NDSX systems, overall mass transfer coefficients are a weighted average of the individual mass transfer coefficients in the feed aqueous phase, across the membrane and in the organic phase [25–27]. Often, one of the three individual coefficients will be much smaller than the others, dominating the overall mass transport coefficient. As a first assumption, it can be considered that the mass transfer is dominated by the resistance of the membrane [28], due to the low permeability and the thickness of the membrane.

When dealing with ionic species in the extraction step, it is widely assumed that the chemical reactions are sufficiently fast to be considered as instantaneous so that the reacting species are everywhere present in equilibrium concentration at the interface.

For systems working under non-steady state, it is necessary to describe the change of the solute concentration with time, requiring solution of the system of partial differential equations. Previously, use of overall mass balances incorporating overall mass transport coefficients has been made for the description of the separation kinetics of different solutes from aqueous solutions. However, the dependence of the kinetic parameters on the operating conditions suggests that a more complex model is needed. In this paper, the experimental system incorporates two hollow-fibre modules and three reservoir tanks where the liquid phases are mixed homogeneously [29]. The mass balance equations can be expressed as follows.

3.3.1. Extraction module

Aqueous solution:

$$-\frac{1}{v_A} \frac{\partial C_A}{\partial t} = \frac{\partial C_A}{\partial z} + \frac{2\pi n_f r_f}{F_A} K_m (C_{\text{OI}} - C_O),$$

$$z = 0, C_A = C_{\text{out}} \text{ (extraction tank),}$$

$$t = 0, C_A = C_{A,\text{initial}} \quad (8)$$

Organic solution:

$$\frac{1}{v_O} \frac{\partial C_O}{\partial t} = -\frac{\partial C_O}{\partial z} + \frac{2\pi n_f r_f}{F_O} K_m (C_{\text{OI}} - C_O),$$

$$z = 0, C_O = C_{\text{out}} \text{ (organic tank),}$$

$$t = 0, C_O = C_{O,\text{initial}} \quad (9)$$

where C_{OI} can be calculated by the equilibrium condition at the interface,

$$K_{\text{eq}} = \frac{[C_{\text{OI}}][a_{\text{H}^+}]^2}{[a_A][\overline{(\text{HX})_2}]^2} \quad (10)$$

where C_{OI} can be determined from the mass balance to the organic phase,

$$C_T = 2\overline{(\text{HX})_2} + 4\overline{C_{\text{OI}}} \quad (11)$$

3.3.2. Back-extraction module

Working with a high concentration H_2SO_4 solution as BEX phase, it can be assumed that the reaction is completely shifted to the right and therefore that the mass transport rate of the cadmium to the BEX solution is maximised.

Aqueous solution:

$$\frac{1}{v_S} \frac{\partial C_S}{\partial t} = -\frac{\partial C_S}{\partial z} + \frac{2\pi n_f r_f}{F_S} K_m (C_O),$$

$$z = 0, C_S = C_{\text{out}} \text{ (stripping tank),}$$

$$t = 0, C_S = C_{S,\text{initial}} \quad (12)$$

Organic solution:

$$\frac{1}{v_O} \frac{\partial C_O}{\partial t} = \frac{\partial C_O}{\partial z} + \frac{2\pi n_f r_f}{F_O} K_m(C_O),$$

$$z = 0, C_O = C_O \text{ (outlet extraction module),}$$

$$t = 0, C_O = C_{O,\text{initial}} \quad (13)$$

3.3.3. Stirred tanks

The dynamic response of the system is determined by simultaneously solving the system of differential equations describing the behaviour of the membrane modules (Eqs. (6)–(11)) and the modelling equations for the three vessels considered as ideal stirred tanks:

$$V \frac{dC_{\text{out}i}}{dt} = F(C_{\text{in}} - C_{\text{out}}), \quad t = 0,$$

$$C_{\text{out}} \text{ (organic tank)} = C_{O,\text{initial}},$$

$$C_{\text{out}} \text{ (extraction tank)} = C_{A,\text{initial}},$$

$$C_{\text{out}} \text{ (stripping tank)} = C_{S,\text{initial}} \quad (14)$$

As a result, the system is described by four partial differential equations (hollow-fibre modules), three algebraic equations (equilibrium condition, mathematical expression for the determination of the activity coefficients and overall mass balance of the organic extractant) and three total differential equations (stirred tanks); two parameters have to be estimated, K_{eq} , the equilibrium constant of the extraction chemical reaction, and K_m , the membrane mass transport coefficient.

4. Results and interpretation

Several experiments were carried out in order to analyse the influence of three operation variables: (a) initial Cd concentration in the aqueous feed phase, (b) initial Cd concentration in the organic phase, and (c) initial Cd concentration in the BEX phase. Experimental conditions are shown in Table 3.

The volume of the aqueous solutions was equal to 600 cm³ and the volume of the organic solution was 1200 cm³. Each run was carried out until the concentration of the metal in the

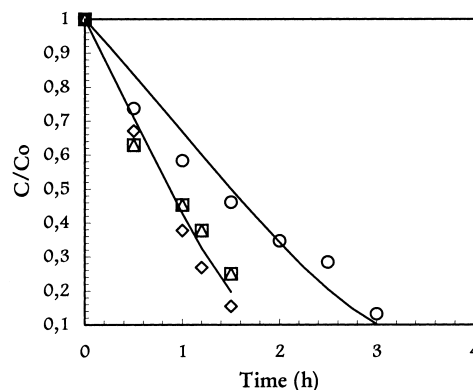


Fig. 2. Kinetics results of the extraction process: experiment I (\diamond), experiment II (\square), experiment III (\triangle) and experiment IV (\circ); simulated data (—).

aqueous phase was below 10% of the initial concentration value. The duration of each run thus depended on the initial concentration of the metal in the aqueous phase and varied from 1.5 to 4 h.

4.1. Initial concentration of cadmium in the organic phase equal to 0.2 M

Fig. 2 shows the kinetic results of the extraction and Fig. 3 of the back-extraction processes. All the experiments were duplicated and average concentration values have been plotted.

In Fig. 2, the dimensionless concentration of the metal in the aqueous phase has been plotted in order to remove the effect of the initial concentration of the metal on the kinetic curves. It is clearly observed that the rate of extraction in experiment IV (initial Cd concentration equal to 0.4 M) is lower than the rate of extraction in the other experiments. When the results of runs I, II and III are compared, no significant difference between the kinetic data was observed. Fig. 3, where the BEX Cd concentration is plotted versus time, shows a linear kinetic behaviour for all experiments.

Experiment V was performed working with three batch cycles in the extraction process and the results are given in Fig. 4. Each cycle was run until the concentration of Cd

Table 3
Values of the initial Cd concentration in the experiments

Number of the experiment	Initial feed concentration (M)	Initial organic concentration (M)	Initial BEX solution concentration (M)
I	0.186	0.214	0
II	0.212	0.191	0.201
III	0.212	0.193	0.396
IV	0.422	0.195	0.315
V			
(a)	0.426	0.195	0.315
(b)	0.402	0.053	0.943
(c)	0.402	0.057	1.262
VI	0.422	0.387	0.396
VII	0.406	0.396	0.807

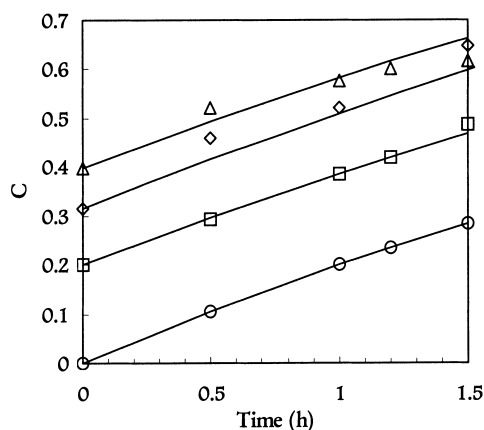
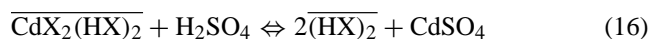


Fig. 3. Kinetics results of the back-extraction process: experiment I (\diamond), experiment II (\square), experiment III (\triangle) and experiment IV (\circ); simulated data (—).

in the feed solution dropped below 0.04 M; at this moment a new batch with a fresh solution was started as feed. The following two cycles were performed with the same initial conditions. In the BEX stirred tank, the same solution was kept throughout the experiment.

Working with concentrations lower than or equal to 0.2 M of cadmium in the organic phase, according to the literature (Table 2), the chemical reactions can be expressed as



Modelling the separation system requires knowledge also of the mass transport coefficient in the membrane, K_m , and the equilibrium parameter, K_{eq} defined by Eq. (5). The solution of the partial differential equations was carried out using the chemical engineering simulation process software called gPROMS with K_m and K_{eq} as optimisation parameters in the comparison between simulated and experimental results. The minimum standard deviation between the experimental and simulated results was selected as the basis

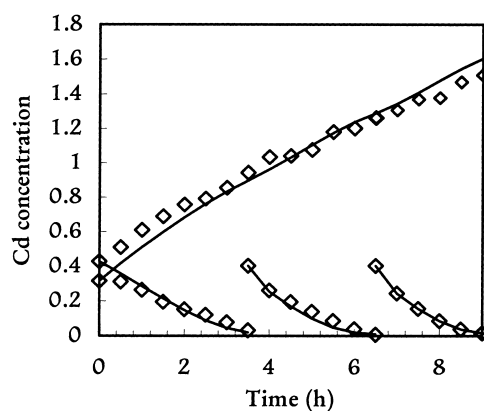


Fig. 4. Kinetics results of the extraction and back-extraction process: experiment V (\diamond); simulated data (—).

Table 4

Standard deviation values of the comparison between the experimental and simulated results with the parameters $K_{eq}=1.88 \times 10^{-5}$ and $K_m=1.57 \times 10^{-7}$ m/s

Experiment	σ_w (%)	
	Extraction	Back-extraction
I	5.64	6.82
II	5.60	4.40
III	5.47	7.13
IV	6.60	8.70
V	5.90	7.90
VI	5.46	2.70
VII	6.50	9.00

for the optimisation sequence. The absolute dimensionless standard deviation is defined as

$$\sigma_w = \left(\frac{\sum ((C_{exp} - C_{sim})/C_i)^2}{n - 1} \right)^{1/2} \quad (17)$$

where C_i is the initial concentration of the cadmium in the feed aqueous solution, C_{exp} the experimental data and C_{sim} is the simulated data.

The standard deviation values obtained for runs I–VII are given in Table 4. Simulated lines corresponding to experiments I–V are also shown in Figs. 2–4. There is good agreement between the experimental and simulated results and the optimum values of the model parameters are $K_{eq}=1.82 \times 10^{-5}$ and $K_m=1.57 \times 10^{-7}$ m/s.

4.2. Initial concentration of cadmium in the organic phase equal to 0.4 M

The kinetic results obtained with an initial concentration of Cd in the organic phase equal to 0.4 M are shown in Fig. 5 for the extraction and in Fig. 6 for the back-extraction processes. These experiments were also duplicated and average concentration values have been plotted. Fig. 5 shows that there is a negligible difference between the extraction kinetic

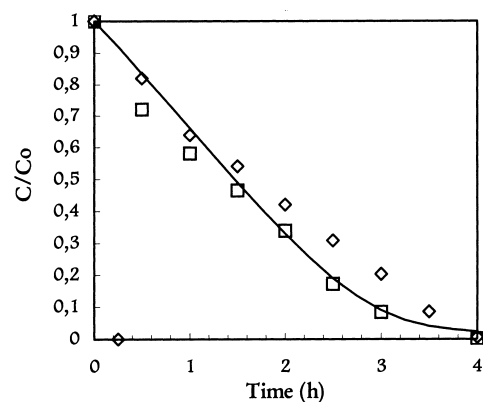


Fig. 5. Kinetics results of the extraction process: experiment VI (\diamond) and experiment VII (\square); simulated data (—).

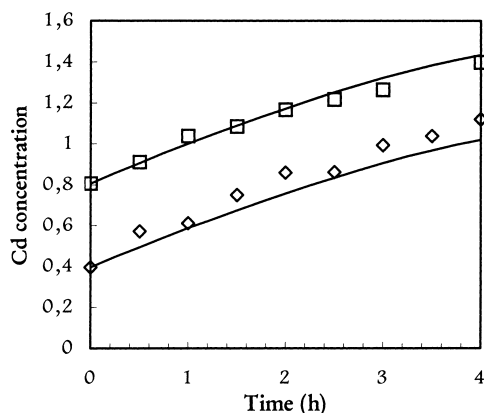


Fig. 6. Kinetics results of the back-extraction process: experiment VI (\diamond) and experiment VII (\square); simulated data (—).

results of experiments VI and VII corresponding to different initial Cd concentrations in the BEX solution (Table 3).

When the organic phase concentration of Cd is higher than or equal to 0.4 M, the stoichiometric equations (15) and (16) together with the mass balance to the organic phase could not explain the experimental results. Taking into account previous bibliographic references [30], the following stoichiometric equations are therefore proposed:



Following the same procedure, previously described in Section 4.1, the simulated curves shown in Figs. 5 and 6 were obtained. Standard deviation values obtained from the comparison of experimental results to simulated data with the parameter values previously reported are given in Table 4.

Finally, Figs. 7 and 8 show the parity graphs corresponding to the extraction results and to the back-extraction data. We observe that more than 90% of the results of C_{sim} fall within the range of $C_{\text{exp}} \pm 10\%$, confirming the validity of the mathematical model, and the parameters obtained in this study for the kinetics of Cd extraction with D2EHPA

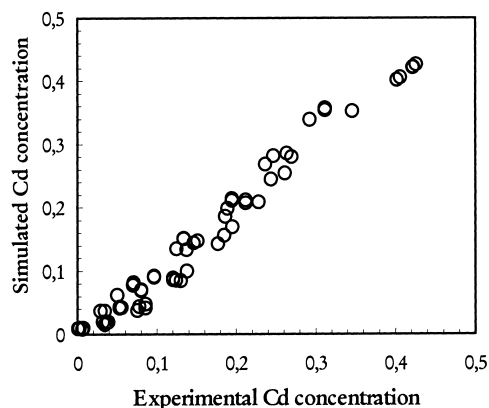


Fig. 7. Parity graph: results of the extraction process.

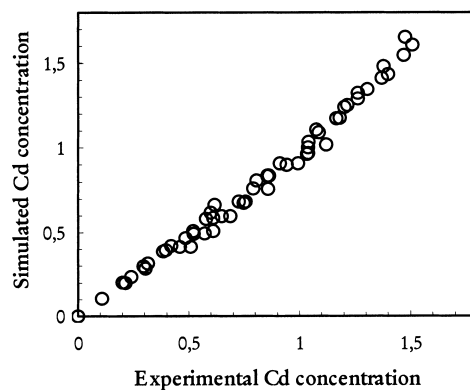


Fig. 8. Parity graph: results of the back-extraction process.

in hollow-fibre modules, with high concentration aqueous solutions.

5. Conclusions

In this paper, the kinetics of the non-dispersive extraction and back-extraction of Cd from high concentration aqueous solutions using D2EHPA as selective extractant are reported. Batch experiments were performed in order to analyse the influence of the initial Cd concentration in the feed, organic and back-extraction phases. The kinetic model consisted of a system of partial differential and algebraic equations describing the mass balances of Cd in the fluid phases of the hollow-fibre contactors and homogenisation tanks. We assumed that the membrane mass transport of cadmium governed the extraction kinetics. Two design parameters $K_m = 1.57 \times 10^{-7}$ m/s, membrane mass transport coefficient, and $K_{\text{eq}} = 1.82 \times 10^{-5}$, equilibrium parameter of the extraction reaction were calculated from the correlation of the experimental results. The comparison of experimental and simulated data in a parity graph confirmed the validity of this kinetic analysis.

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