

Recycling of Cr(VI) by membrane solvent extraction: Long term performance with the mathematical model

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Abstract

This work focuses on the analysis of the long-term performance of a non-dispersive extraction process applied to the separation and concentration of hexavalent chromium contained in ground waters using Aliquat 336 as a extractant. Working with raw ground waters of high Cr(VI) concentration (700 mg/l), the influence of the temperature (20, 40 and 60 °C) and the influence of those interferences caused by the presence of competitive anions in the ground waters were studied in discontinuous mode. In continuous mode, the performance of the system for long periods of time was analysed and it was observed that the system is stable since the outlet concentration of Cr(VI) in the ground water and in the back-extraction solution (10–20 g/l) remains constant. Finally, the kinetic model of the separation is included at 40 °C and the value of the diffusivity and mass transport constants ($K_m = 1.47 \times 10^{-7}$ m/s and $D = 6.66 \times 10^{-11}$ m²/s) are calculated using equations from the literature and the values of the extraction equilibrium parameter (0.035) and repart constant in the back-extraction (13) were obtained by a comparison of experimental and simulated data.

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1. Introduction

Chromium (VI) is a highly toxic metal that can easily be encountered in the environment. Besides the huge amount of waste waters generated during rinsing steps of metal finishing industries, leaks, unsuitable storage or improper disposal deposits of different forms of the metal in the ground may lead to filtration and transport of the pollutant to ground water sites [1].

Some of the main methods used to recover Cr(VI) in the electroplating and metal finishing industries involve the use of various types of evaporators and ion exchange resins [2]. Reverse osmosis, electrolytic recovery techniques, and liquid–liquid extraction, biosorption, among others, have also been demonstrated to work [3,4]. New membrane technologies have been investigated by different research groups since membranes offer a flexible, modular energy-efficient device with a high specific surface. When microporous hollow fiber modules are used as

liquid–liquid contactors, aqueous and organic phases come into contact through the pores of the fiber wall. Phase entrainment can be avoided by applying a differential static pressure in the aqueous phase when using hydrophobic membranes [5]. Mass transfer occurs from the aqueous phase to the organic phase and from latter to the back-extraction aqueous phase. This configuration guarantees that saturation of the carrier does not occur since it is continuously regenerated and consequently the carrier concentration is reduced while still maintaining the mass-transfer rate [6].

Applications of solvent extraction to the separation-concentration of Cr(VI) from wastewaters using microporous hollow fibre modules have appeared in the literature under different configurations as shown in Table 1. Simultaneous extraction and stripping of the Cr(VI) has been developed using one or two hollow fiber modules. In the single module mode, or supported liquid membrane, SLM, the organic phase is placed in the pores of the fiber walls and the extraction and stripping is carried out by passing the feed and stripping solution through the lumen and shell sides, respectively. In non-dispersive solvent extraction, NDSX, two modules are required, one for the extraction and one for the stripping mode and the organic phase

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Nomenclature

A	contact area
C_e	concentration of Cr(VI) in the feed aqueous phase
C_i	concentración inicial de Cr(VI)
C_o	concentration of Cr(VI) in the organic phase
C_s	concentration of Cr(VI) in the back-extraction phase
CT	total concentration in the organic phase
d_i	inner diameter of hollow fiber
d_{lm}	mean logarithmic diameter of hollow fiber
d_o	outer diameter of hollow fiber
D	diffusivity value of the organic solute complex
F_e	flowrate of the feed aqueous phase
F_o	flowrate of the organic phase
F_s	flowrate of the back-extraction aqueous phase
H	repart coefficient of Cr(VI) between the aqueous phase and the organic phase in the BEX step
I	ionic strength
K_{eq}	equilibrium constant
K_m	membrane mass transport coefficient
L	effective length of the module
n_f	number of fibres
r_i	inner radius of hollow fiber
r_o	outer radius of hollow fiber
t	time
T	temperature
V_a	molar volume of the solute
V_b	molar volume of the dissolvent
V_k	tank volume
V_{me}	volume of the aqueous phase in the module
V_{mo}	volume of the organic phase in the module
V_{ms}	volume of the back-extraction aqueous phase in the module
z	length of the fibre
<i>Greek letters</i>	
δ	thickness of the fiber
ε	porosity of the fiber
γ	activity coefficient
μ	viscosity of the organic phase
σ	standard deviation
τ	tortuosity of the fibers
ψ_b	Wilke–Chang coefficient
<i>Subscript</i>	
e	extraction
i	interface
o	organic
p	purge
s	back-extraction
t	tank

usually circulates through the shell sides of the two modules while the feed and stripping solutions are passed through the lumen of each module. Emulsion pertraction, PERT, is a newer process which uses one membrane module and the water phase is kept separate from an emulsion phase by the membrane. The emulsion consists of an organic solvent with a dissolved extractant as a continuous phase with aqueous droplets of strip liquid dispersed on it.

As regards the organic solution, different extractants have been researched for the removal of Cr(VI) working under different extraction equipments: LIX84, Aliquat 336, Alamine 336, Cyanex 921, among others. Table 1 show the applications where the extraction of Cr(VI) is carried out by hollow fiber membrane systems such as SLM, MFH or PERT.

The advantage of the hollow fiber membranes is lost if the performance of the techniques is not stable in long term tests. The instability can be attributed to the combination of a number of factors such as solubility of the organic phase in the aqueous phase, hydrodynamic or interfacial instabilities, etc. SLM have received much attention, but the technique's lack of stability has reduced the number of industrial application possibilities [7]. PERT is a novel technique and the main difficulty is the stability of the emulsion phase. Although NDSX requires two hollow fiber modules, it has been selected for use in this study since the separation of the organic and aqueous phases through the membrane and the circulation of the three phases at the same time provides as results a more stable behaviour. For this very reason, one of the aims of this work is to test the long term performance of the NDSX technique for the separation and recovery of Cr(VI).

In the treatment of the ground waters, two main separation requirements are considered at the same time: (i) reducing the concentration of chromium in the ground waters and (ii) increasing the concentration of the metal in the back-extraction phase up to a level that enables it to be reused (10–20 g/l). In order to make the two objectives simultaneously possible Aliquat 336 was selected as the organic extractant in this work and the performance of the system under long term test are studied.

2. Experimental method

The main components of the membrane assisted liquid–liquid extraction, NDSX, are two hollow fibre modules, one for the extraction (EX module) and the other one for the stripping process (BEX module). The modules are both Liqui-Cel Extra-Flows 2.5" × 8" membrane contactors purchased from Hoechst Celanese Corporation.

Table 2 gives the physico-chemical characterization of the ground waters being used in this study. For the separation and concentration of Cr(VI) from these ground waters, Aliquat 336, a commercial mixture of trialkylmethylammonium chlorides, was used as extractant. The concentration of Aliquat 336 used in all the tests was 30% (v/v) and to avoid segregation of a second phase, the modifier isodecanol, in the same proportion, was added. Finally, kerosene, a commercial mixture with maximum percentage of 20% in aromatic compounds, was used

Table 1
Applications of liquid–liquid extraction to the separation to Cr(VI)

Type of extraction	Bibliography	Concentration of Cr(VI) in the effluent (mg/l)	Extractant	Back-extractant
SLM	Hochhauser and Cussler [8]	100	Tridodecilamina	NaOH
	Mori et al. [9]	100	TOA	H ₂ SO ₄
	Alonso et al. [7]	100–250	Aliquat 336	NaOH
	Chaudry et al. [10]	2500–8000	TOA	NaOH
	Banerjea et al. [11]	75–100	Aliquat 336	NaOH
	Bhowal y Datta [12]	50–100	Aliquat 336	NaOH
	Castillo et al. [13]	20–40	Aliquat 336	DPC and H ₂ SO ₄
MFH	Yun et al. [14]	100	TOA y LIX 84	–
	Alonso et al. [15]	10–500	Aliquat 336	–
	Yang et al. [16]	250	TOA among others	–
	Alonso et al. [17]	40–50	Aliquat 336	CINa
	Young et al. [18]	400–2500	Radiamine 6336	NaOH
	Harrington and Stevens [19]	250	Radiamine 6336	KOH
PERT	Ho and Poddar [20]	100–1000	Amberlite LA-2	NaOH
	Galán et al. [21]	700–2100	Aliquat 336, Alamine 336	NaOH
	Ortiz et al. [22]	2170–2692	Alamine 336	NaOH

Table 2
Physico-chemical characterization of the ground waters

Cr(VI) (mg/l)	700–2000
Ca ²⁺ (mg/l)	550
Al ³⁺ (mg/l)	60
SO ₄ ²⁻ (mg/l)	1750
Cl ⁻ (mg/l)	1200
DQO (mg/l)	170
TOC (mg/l)	50
pH	7.3
Conductivity (mS/cm)	7

as solvent being supplied by Petróleos del Norte SA. NaCl (1–1.5 mol/L) was used as the stripping agent in the aqueous phase.

During the NDSX process, the pressure of the aqueous phase was maintained 2.5 psi higher than the pressure of the organic

phase, ensuring that no displacement of the organic phase from the pores of the hollow fibres took place due to fiber hydrophobicity.

The use of raw ground waters complicates the extraction process because of the presence of different anions and cations in the feed solutions as shown in Table 2. Thus, the presence of high concentration of calcium cation interferes with the process due to the precipitation of CaSO₄ into the pore of the hollow fibers, making it necessary to eliminate the calcium present in the waters. Fig. 1 shows the cationic ion exchange column used to reduce calcium concentration in the inlet ground waters previous to the NDSX process set-up. The cationic ion exchange column was filled with Lewatit Monoplus S-100 resins. The concentration of calcium after the cation exchange process is always lower than 10 mg/l.

Two types of experiments were carried out in this study: discontinuous and continuous mode. Discontinuous experiments

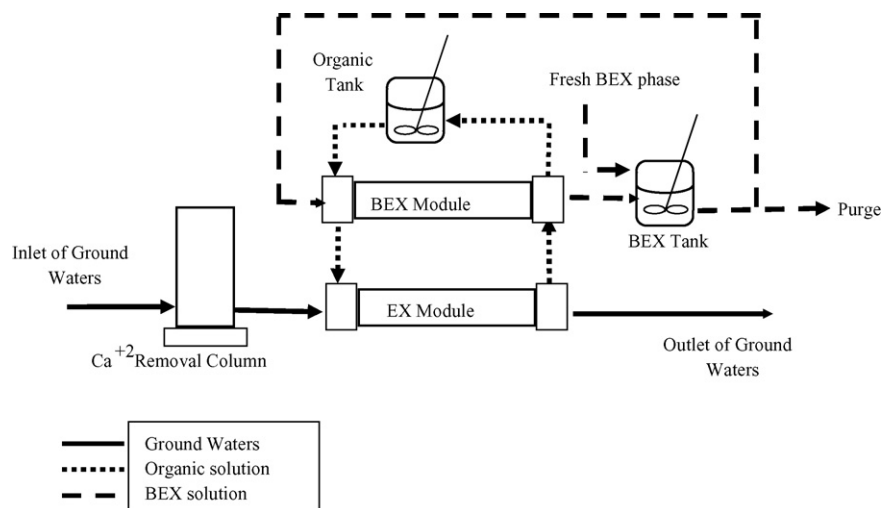


Fig. 1. Experimental set-up for the continuous process.

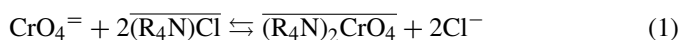
were carried out with the three solutions in a recycling mode and therefore three tanks were required [24]. The continuous experiments were carried out in one-pass mode for the ground waters, recycling mode for the organic solution and semi-continuous mode for the BEX solution. Fig. 1 shows the experimental set-up when working in a continuous process. It is observed in Fig. 1 that there is a purge to take out part of the concentrated chromate solution and one stream to introduce the fresh BEX solution into the system. The volume of the BEX tank remains constant since the flowrate for both the purge and the fresh BEX inlet stream is the same.

The continuous tests of the present work were carried out with an inlet ground water flowrate of 1.8 l/h and two different operational modes were used; in the first one the process ran for 100 h and therefore used 180 l of raw ground water but in the second one runs for 700 h with five cycles of 140 h for each cycle and used 15 l of row water in each cycle. So, in this second test when the raw ground water was passed through the extraction module, the depleted outlet ground water was collected in a second tank and CrO_4Na_2 was added to this second tank to once again reach the inlet Cr(VI) concentration (774 mg/l) and then these 15 l were reused as fresh ground water. The results of Cr(VI) separation of this second tank are affected by the presence of a higher concentration of Cl^- coming from the interchange of Cl^- with CrO_4^{2-} in the extraction module during the first run of the tank. So that, in the second tank, the concentration of Cl^- was around 1700 mg/l compared to 1200 mg/l in the first run of the tank. After using the tank several times, the Cl^- concentration was around 3000–4000 mg/l, a concentration that was considered too high and therefore a new cycle was initiated with raw ground waste, i.e., 1200 mg/l of Cl^- concentration and 774 mg/l of Cr(VI).

In some of the experiments, hollow fibres were thermostated and three heater systems were included in the plant: one on-line system for pipes and tubes and two electrical resistances placed inside the organic and BEX tanks in order to increase the temperature of the process.

3. Results and discussion

The extraction reaction of Cr(VI) using Aliquat 336 are represented by the following equation:



When using NaCl as back-extractant agent the corresponding BEX reaction is represented by the following equation:

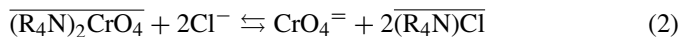


Table 3
Experimental conditions for the discontinuous mode experiments

Experiment	Initial Cr(VI) concentration in the ground water (mg/l)	Temperature (°C)	Feed volume (l)	Initial Cr(VI) concentration in the BEX phase (mg/l)	Initial Cr(VI) concentration in the organic phase (mg/l)	Feed flowrate (l/h)
1	580	20	4	0	0	6
2	520	20	4	0	0	6
3	630	20	1.5	0	0	6
4	630	40	1.5	1573	180	6
5	630	60	1.5	2670	1346	6

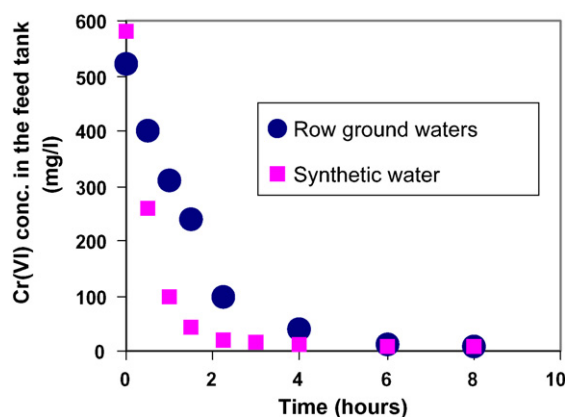


Fig. 2. Evolution of the Cr(VI) concentration in the feed tank for synthetic and row ground water.

3.1. Characterization of Cr(VI) separation from ground waters by NDSX

Although the planned objective in this work was the study of Cr(VI) recovery from groundwater using the NDSX system and working over long periods of time, it was initially necessary to carry out several experiments in which the ground waters were worked with for only short periods of time (2–4 h). For the first type of short time tests, recycling mode cycles with initial concentrations of about 500–650 mg/l of Cr(VI) were selected and the influence of variables such as the presence of competitive anions and temperature were studied.

Taking into account that Aliquat 336 is an anionic exchanger the presence of anions in the ground water may interfere with the Cr(VI) separation process. In relation to the influence of the anions present in the ground water, two separation experiments were done, the first one using raw ground waters (experiment 1) and the second one using synthetic laboratory water containing only CrO_4Na_2 with a pH of 8.1 (experiment 2). Table 3 shows the experimental conditions and Fig. 2 the differences in the separation process between raw ground waters and laboratory waters for Cr(VI) separation purposes.

From Fig. 2, it can be seen that the presence of Cl^- and SO_4^{2-} anions in the ground waters clearly reduces the chromium separation process since Cl^- and SO_4^{2-} are competitive with CrO_4^{2-} . Therefore, the lower the anion concentrations in the ground water the better.

The optimization of the separation process is very important with these real ground waters where the extraction process is affected by the presence of competitive anions. Chaudry et al.

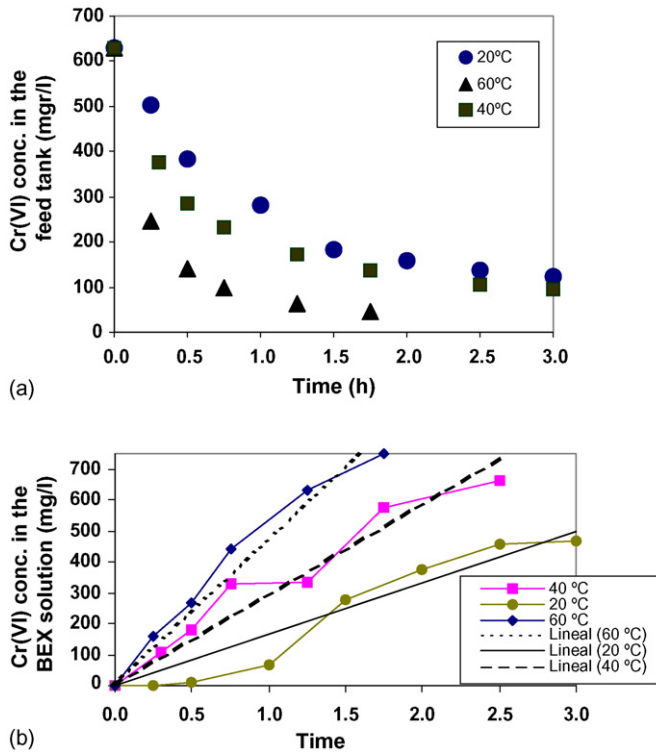


Fig. 3. (a) Kinetic of the Cr(VI) concentration in the feed solution at different temperatures. (b) Kinetic of the Cr(VI) concentration in the BEX solution at different temperatures.

[11] show an increase of 27% in the separation of Cr(VI) using supported liquid membranes by increasing the temperature of the process by 20 °C. Therefore, the second variable study at discontinuous mode in this work is the influence of temperature on the Cr(VI) separation and recycling processes. For this study, a thermostated system was used and Table 3 shows the experimental conditions of the series of experiments done working at 20, 40 and 60 °C (experiments 3–5) and Fig. 3 show the results for these experiments.

From Fig. 3a, it can be observed that the separation of Cr(VI) in the ground waters was clearly improved when working with higher temperatures. In relation to the back-extraction solution, Fig. 3b, the concentration of Cr(VI) increases linearly with time for the three temperatures and the tendency line has a higher slope at higher temperatures: 214, 272 and 381 mg/l/h at 20, 40 and 60 °C, respectively.

Although the higher the temperature the best response of the process, the following experiments were done at 40 °C since that is the maximum temperature for the polypropylene fibers recommended by the Hoechst Celanese Corporation when working over long periods of time.

3.2. Long term performance of NDSX system

The following experiments focused on a system stability analysis for long periods of time at laboratory scale. So, this second set of experiments were carried out in one-pass mode for the ground waters and recycling mode for the organic solution. The concentration and volume of the back-extraction solution was

Table 4
Experimental conditions for the continuous mode experiments

	Experiment 6	Experiment 7
Total time (h)	100	750
Temperature (°C)	20	40
Inlet Cr(VI) concentration in the raw ground water (mg/l)	626	774
Flowrate of the ground water (l/h)	1.8	1.8
Back-extraction volume (l)	1.56	1.56
Back-extraction Cr(VI) target concentration (g/l)	7	10–20
Cl ⁻ concentration in the outlet solution (mol/l)	1.311	1.385
Flowrate of the purge solution (l/h)	0.05	0.048

kept constant by a purge which takes out part of the Cr(VI) concentrated BEX solution and by introducing fresh BEX solution as shown in Fig. 1. Table 4 shows the experimental data for the two types of continuous tests, the main difference between them being the total time, the temperature of the system and the Cr(VI) concentration in the purge stream.

Fig. 4 shows the results obtained for experiment 6 carried out over a 100 h period. It can be observed that the concentration of the feed solution drops to 200 mg/l initially, but then rises to 400 mg/l due to the increase in the concentration of solute in the organic solution. When the stability of the solute in aqueous-organic-aqueous solutions is reached the concentration of Cr(VI) in the outlet ground waters remains stable in 400 mg/l and the concentration of Cr(VI) in the back-extraction solution remains constant around the target value (7 g/l) during the whole experiment. The results obtained in this experiment were clearly satisfactory and a second long-time experiment working at higher temperature (40 °C) was planned in order to achieve a higher separation and higher back-extraction target concentration (10 and 20 g/l).

Taking into account the good results of the previous experiment working for 100 h, the second experiment was planned in five cycles of around 140 h each cycle (experiment 7 in Table 4). Each cycle has an initial concentration of Cr(VI) in the ground water of 774 and 1200 mg/l of Cl⁻, as shown in Table 4, and the experimental methodology is explained in Section 2. Fig. 5 shows the results of this experiment during a 700 h period. The outlet concentration of Cr(VI) in the ground water is represented by square points associated to the left axis and the Cl⁻ concen-

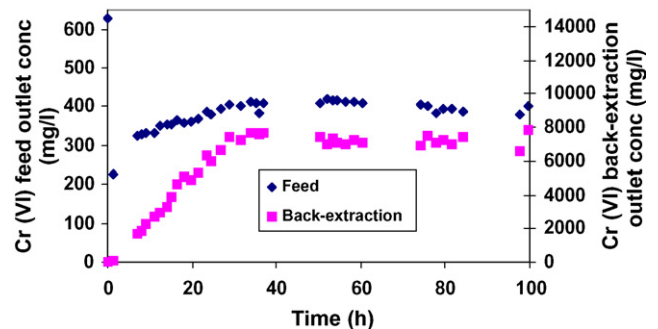


Fig. 4. Evolution of extraction and back-extraction Cr(VI) in experiment 6.

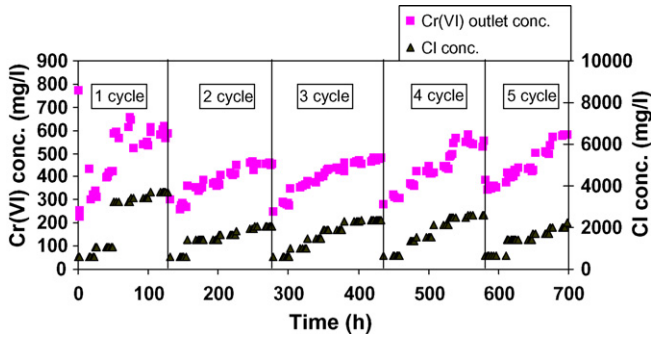


Fig. 5. Kinetics of the outlet Cr(VI) concentration and inlet Cl^- concentration in the ground waters in experiment 7.

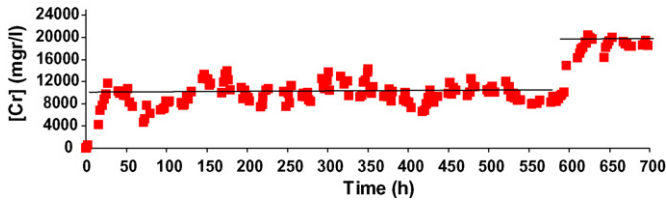


Fig. 6. Evolution of Cr(VI) concentration in the BEX solution in experiment 7.

tration is represented by the triangles associated to the right axis. So, in Fig. 5, the five cycles are clearly observed, since in each of these cycles, the concentration of Cr(VI) increases continuously depending on Cl^- concentration, showing that the Cl^- and Cr(VI) concentrations follow a parallel path.

Furthermore, in Fig. 5 it can be observed that the outlet concentration of Cr(VI) during the process varies from 250 to 450 mg/l. In relation to the back-extraction solution shown in Fig. 6, the concentration remains stable around the target values: 10 g/l (0–600 h) and 20 g/l (600–700 h).

Looking at Fig. 5 carefully, the response of the system at the beginning of each cycle can also be observed, i.e., when the concentration of Cl^- is at its lowest (1200 mg/l). Table 5 shows the outlet concentration of Cr(VI), when the concentration of Cl^- is 1200 mg/l and it is observed that the concentration of Cr(VI) is around 260 mg/l in cycles 1–4. In the last cycle the concentration goes up to 344 mg/l, although in this last cycle the concentration of the back-extraction solutions increases to 20 g/l.

In both continuous experiments (6 and 7), the outlet concentration of chromium in the extraction module was too high to consider that the ground waters were sufficiently clean. Further reduction of chromium concentration would either require

Table 5
Outlet concentration of Cr(VI) in each of the cycles of experiment 7 when the concentration of Cl^- is 1200 mg/l

Cycle	Time (h)	Outlet Cr(VI) concentration in the ground water (mg/l)
1	1	255
2	144	259
3	278	250
4	436	280
5	583	344

working with lower values of flow rates of the ground waters or carrying out a second NDSX step. The study of the sensitivity of the process to changes in the feed flow rate or carrying out a second NDSX makes it necessary to first obtain the mathematical model and parameters of the process.

3.3. Mathematical model

The dynamic response of the continuous experiments was modelled based on several equations (partial differential and algebraic) describing the mass transport through the membrane modules, tanks and streams. It is considered that the main resistance to the solute transport in the modules lies in the microporous membrane and that the species are present in equilibrium concentration at the interface everywhere. The mathematical model proposed in this work is based on the previous mathematical model carried out for separation and recovery of Cr(VI) by NDSX, but taking into account the differences in the configuration of the experimental system of this work and the different type of water [15,17,23,24]. Therefore two modifications were included: (i) the presence of the purge stream in the back-extraction process, (ii) taking into account the high concentration of the metal in the ground water, the activity coefficients of the aqueous solutions are considered using a modification of the Debye–Huckel equation [25] such as shows in Eq. (10) and (iii) the influence of the temperature. Finally, all the equations included in the mathematical model are presented.

- Extraction module:

- Ground water:

$$\frac{V_{me}^E}{F_e L^E} \frac{\partial C_e^E}{\partial t} = -\frac{\partial C_e^E}{\partial z^E} + \frac{A^E}{F_e L^E} K_m^E (C_{oi}^E - C_o),$$

$$t = 0, \quad C_e^E = C_{e,initial}^E; \quad z^E = 0, \quad C_e^E = C_{e,in}^E \quad (3)$$

- Organic phase:

$$\frac{V_{mo}^E}{F_o L^E} \frac{\partial C_o^E}{\partial t} = -\frac{\partial C_o^E}{\partial z^E} + \frac{A^E}{F_o L^E} K_m^E (C_{oi}^E - C_o^E),$$

$$t = 0, \quad C_o^E = C_{o,initial}^E; \quad z^E = 0, \quad C_o^E = C_o^T \quad (4)$$

- Back-extraction module.

- Back-extraction solution:

$$-\frac{V_{ms}^S}{F_s L^S} \frac{\partial C_s^S}{\partial t} = \frac{\partial C_s^S}{\partial z^S} + \frac{A^S}{F_s L^S} K_m^S (C_{oi}^S - C_o^S),$$

$$t = 0, \quad C_s^S = C_{s,in}^S; \quad z^S = 0, \quad C_s^S = C_s^T \quad (5)$$

- Organic phase:

$$\frac{V_{mo}^S}{F_o L^S} \frac{\partial C_o^S}{\partial t} = -\frac{\partial C_o^S}{\partial z^S} + \frac{A^S}{F_o L^S} K_m^S (C_{oi}^S - C_o^S),$$

$$t = 0, \quad C_o^S = C_{o,initial}^S; \quad z^S = 0, \quad C_o^S = C_o^E (z^E = L^E) \quad (6)$$

- Back-extraction tank with purge:

$$F_p [C_{p,out} - C_{p,in}] = F_s [C_{s,in}^T - C_{s,out}^T] \quad (7)$$

Table 6
Mathematical correlation from the literature for the estimation of the K_m

References	Equations	Fiber types	K_m (m/s)
Lin and Juang [26]	$K_m = \frac{\varepsilon D}{\tau^2 r_i \ln(r_o/r_i)}$	Hoechst: Celgard X-30	1.47×10^{-7}
Coelhoso et al. [27], Yeh and Huang [28]	$K_m = \frac{\varepsilon D d_{lm}}{\tau \delta d_i}$	Hoechst: Celgard X-10	3.80×10^{-7}
Ho and Poddar [29], Yang et al. [30]	$K_m = \frac{\varepsilon D d_{lm}}{\tau \delta d_o}$	Hoechst: Celgard X-10	3.0×10^{-7}
Yun et al. [31], Prasad and Sirkar [32]	$K_m = \frac{\varepsilon D}{\tau \delta}$	Hoechst: Celgard X-20	3.40×10^{-7}

- Organic tank:

$$\frac{dC_k^T}{dt} = \frac{F_k}{V_k} (C_{k,in}^T - C_k^T) \quad \text{being } k = o, s, e,$$

$$t = 0, \quad C_s^T = C_{s,initial}, \quad C_o^T = C_{o,initial}, \quad C_e^T = C_{e,initial} \quad (8)$$

- Extraction equilibrium equation:

$$K_{eq} = \frac{4C_{oi}^E (C_i - C_e^E)^2}{C_e^E (CT - 2C_{oi}^E)^2} \times \frac{(\gamma_{Cl^-})^2}{\gamma_{CrO_4^{2-}}} \times (CT \times 10^{-3})^{0.6} \quad (9)$$

$$\frac{\log(\gamma)}{z^2} = \frac{0.511 \times \sqrt{I}}{1 + 1.2 \times \sqrt{I}} - 0.2 \times I \quad (10)$$

- Constant for the back-extraction:

$$H = \frac{C_s^s}{C_{oi}^s} \quad (11)$$

This mathematical model to be applied requires the knowledge of three characteristic parameters, two parameters related to the extraction and back-extraction chemical reactions (K_{eq} and H), and one mass transport parameter (K_m).

Several expressions have been considered in the literature to estimate the value of mass transport parameter and Table 6 shows the expression proposed by different authors. The values of the parameters included in the equations were obtained from the manufacturer $\varepsilon = 0.4$, $\delta = 30 \mu\text{m}$ and $d_o = 300 \mu\text{m}$ and the value of the tortuosity, $\tau = 2.6$, was taken from the bibliography.

The prediction of diffusivities for long chain hydrocarbon molecules when complexes are formed is complicated. In order to estimate the diffusivity (D) of the organic solute complex, $(R_4N)_2CrO_4$, in the organic phase, several expressions from the bibliography were considered, and these are shown in Table 7. The value of the diffusivity calculated at the conditions of this work for each equation are shown in the last column of Table 7 and it is observed that similar values were obtained with all the expressions. Finally, the Scheibel equation, which was also used by other authors such as Coelhoso et al. [27], Haring and Stevens [19] and Alonso and Pantelides [15] and because, moreover, it represents an average value, was selected.

Once the value of diffusivity was calculated, the membrane mass transfer coefficient value (K_m) was also calculated for the different expression of Table 6 and the values obtained are presented in the last column of that table. Similar values were obtained using the different equations and the value obtained with the first expression was selected ($K_m = 1.47 \times 10^{-7}$ m/s) since the same type of fibers as those of Lin and Juang were used in this work. Previous K_m values reported in the literature for Cr(VI) separation using Aliquat 336 and X-30 microporous membrane at 20 °C are 2.2×10^{-8} m/s [17,23] and 8.0×10^{-8} m/s [15]; the difference between them and the actual value can be explained based on: (i) the difference in the temperature of the process since in this work the temperature is higher (40 °C), (ii) since Alonso and Pantelides [15] and Alonso et al. [17] obtained the value by adjustment between experimental and simulated data, whilst in this work it has been calculated mak-

Table 7
Mathematical correlations for diffusivity value of the organic solute complex

References	Mathematical correlations	D (40 °C) (m ² /s)
Wilke and Chang [33], Reid et al. [34]	$D = \frac{7.4e^{-8}(\psi_b M)^{1/2} T}{\mu V_a^{0.6}}$	7.16×10^{-11}
Geankoplis [35]	$D = \frac{9.96e^{-12} T}{\mu z V_a^{0.33}}$	4.07×10^{-11}
Scheibel [36], Alvarez et al. [37]	$D = 8.2e^{-8} \left[1 + \left(\frac{3V_b}{V_a} \right)^{2/3} \right] \frac{T}{\mu V_b^{1/3}}$	6.66×10^{-11}
Reddy-Doraiswamy [38], Alvarez et al. [37]	$D = \frac{10e^{-8}(\psi_b M)^{1/2} T}{\mu V_b^{1/3} V_a^{1/3}}$	8.77×10^{-11}
Lusis and Ratcliff [39], Alvarez et al. [37]	$D = 8.52e^{-8} \left[1.4 \left(\frac{V_b}{V_a} \right)^{1/3} + \left(\frac{V_b}{V_a} \right) \right] \frac{T}{\mu V_b^{1/3}}$	6.55×10^{-11}

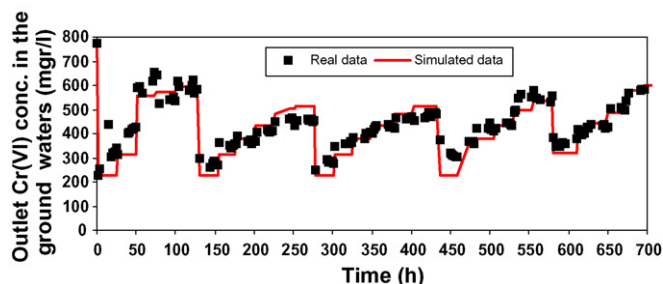


Fig. 7. Comparison between experimental data and simulated correlation for experiment 7.

ing use of the bibliography and (iii) the ground waters with the much higher concentration of Cr(VI).

To solve the mathematical model it is necessary to calculate the equilibrium parameters for extraction (K_{eq}) and the back-extraction processes (H). However these parameters were calculated by simulation since no references were found in the bibliography for this type of waters and working with such a high concentration as this. Therefore, the equilibrium parameters of the extraction and back-extraction processes were calculated by comparison between the experimental and simulated data. The dynamic response was obtained by simultaneously solving the equations using the process simulator gPROMS.

$$K_{eq} = 0.035, \quad H = 13$$

The values of standard deviation, σ , were calculated according to the following equation:

$$\sigma = \sqrt{\frac{\sum [(C_{exp} - C_{sim})/C_{sim}]^2}{n - 1}} \quad (11)$$

A σ -value of 9.8 was obtained for the extraction solution in experiment 7.

Finally, the theoretically predicted behaviour was checked with the experimental results for experiment 7 and Fig. 7 shows the experimental and simulated data for the Cr(VI) outlet concentrations in the ground waters for that experiment. The good agreement between the experimental and simulated data concluded that the mathematical model and design parameters can be used for the description of the ground waters behaviour for the NDSX system.

4. Conclusion

This work presents a theoretical and experimental analysis of the behaviour of a non-dispersive extraction process applied to the separation and concentration of hexavalent chromium contained in ground waters using Aliquat 336 as an extractant. Two main separation objectives were considered, i.e., reducing the concentration of chromium in the ground waters whilst at the same time increasing the concentration of the metal in the back-extraction phase up to a level that enables it to be reused (10 or 20 g/l). Discontinuous experiments working with different temperatures and anions concentrations were carried out, obtaining that the best temperature for the process for long term tests is

40 °C and determining the strong competition of the other anions present in the ground waters for the free anions of the extractant.

The stability of the system for long periods of time in continuous mode and working at 40 °C was also analyzed. These continuous experimental tests working with different initial conditions checked the stability of the membrane process up to as much as 700 h and it can be observed that the system is stable in the extraction and back-extraction steps, reaching a concentration of the metal in the BEX solution up to 20 g/l.

The kinetic model of the separation of Cr(VI) from ground water by non-dispersive solvent extraction working in a continuous mode at 40 °C is included. The value of the diffusivity and mass transport constant ($K_m = 1.47 \times 10^{-7}$ m/s and $D = 6.66 \times 10^{-11}$ m²/s) were obtained from equations taken from the literature and the values of the extraction equilibrium parameter (0.035) and repart constant in the back-extraction (13) were obtained by comparison between experimental and simulated data. Finally, the validity of the model has been checked against the experimental kinetic results of the separation and concentration of Cr(VI) and good agreement is shown.

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