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ScienceDirect
Journal of Hazardous Materials 152 (2008) 795–804
Journal of Hazardous Materials
www.elsevier.com/locate/jhazmat

Integration of ion exchange and non-dispersive solvent extraction processes for the separation and concentration of Cr(VI) from ground waters

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Received 24 April 2007; received in revised form 29 June 2007; accepted 17 July 2007
Available online 31 July 2007

Abstract

The focus of this work has been the study of simultaneous removal and recovery of Cr(VI) from ground waters with a high concentration of the metal (700 mg/l). The main objectives of water cleaning were the decrease of the Cr(VI) concentration down to the limits indicated by the Spanish regulations for discharge into channel waters (0.5 mg/l) and the recovery of the chromate compounds up to 15 g/l. The integration of two technologies: non-dispersive solvent extraction and anion exchange is presented as an environmental compatible solution. The final hybrid process allows the individual shortcomings of each technology to be overcome and leads to an optimum process configuration. Non-dispersive solvent extraction (NDSX) is used mainly for the concentration of the metal in a back-extraction solution and ion exchange (IE) is used for the depuration of the metal in the ground water down to 0.5 mg/l. The integrated process has been carried out on two different scales: laboratory and pilot plant, with satisfactory results being obtained.
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Keywords: Chromium (VI); Membrane; High concentrated; Ground water; Anion exchange

1. Introduction

Several industries such as paint and pigment manufacturing, stainless steel production, corrosion control, leather tanning, chrome plating, wood preservation, fertilizers, textile, photography, etc., discharge effluents containing Cr(VI). The effluents of these industries contain hexavalent chromium at concentrations ranging from tenths to hundreds of mg/l, metal finishing industries being the main generators of wastes containing Cr(VI) [1,2]. It is particularly difficult to substitute the use of chromium in metal finishing industries because of chromium's hardness, bright appearance, resistance to commonly encountered corrosive environments, ease of application, and low cost. Furthermore, leakage, 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 [3,4].

Installation of a physico-chemical treatment plant to destroy or remove toxic materials is the main method used to treat the wastes generated from electroplating operations. Physical–chemical treatment of chromium (VI) consists of three steps: (i) hexavalent chromium in water is reduced to very low concentrations using reducing agents such as bisulfites and sulfur dioxide, which reduces the Cr(VI) to Cr(III), (ii) once the decrease is completed, an alkali is added to neutralize the acid and precipitate the trivalent chromium as $Cr(OH)_3$, and (iii) the waste is then allowed to settle and usually lagooned. This technology produces large amounts of metal sludge containing trivalent chromium that, once disposed of, can be reoxidized to Cr(VI), thereby increasing the hazard of disposed wastes, and the reutilization of the metal is not possible. Treatment methods differ depending on the conditions of the process and properties of wastewaters [5].

The goal of all industry should be the recovery and reuse of the valuable material contained in the generated wastes, and especially in the case of hazardous wastes. Ion exchange is commonly used for separation and concentration of Cr(VI) [6]. The main advantages of ion exchange (IE) over chemical precipitation are the potential recovery of the metal, higher selectivity, lesser

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doi:10.1016/j.jhazmat.2007.07.084

Nomenclature

C_{BEX}	concentration of the fresh back-extraction (BEX) solution (NaCl) (mol/l)
C_i	concentration of Cr(VI) in inlet ground waters (mg/l)
C_{out}	concentration of Cr(VI) in outlet ground waters after a process (mg/l)
C_p	concentration of Cr(VI) in the purge (g/l)
F	flow rate of the ground waters (l/h)
F_{BEX}	flow rate of the back-extraction solution (l/h)
F_p	flow rate of the purge (l/h)

volume of produced sludge and the meeting of strict discharge specifications [7,8].

Different technologies, i.e., reverse osmosis, electrolytic recovery techniques, and liquid–liquid extraction, among others, have also been shown to work [9,10]. Membrane assisted liquid–liquid extraction using porous hollow fiber membranes, which is also known as non-dispersive solvent extraction (NDSX), has been investigated for the removal and recovery of Cr(VI) [11–14]. Concerning the removal of chromate compounds from aqueous effluents, the technology allows the easy coupling to a back-extraction step where the pollutant is separated from the organic extractant, the latter being regenerated while at the same time the chromate becomes concentrated in a suitable stripping phase. The extraction and concentration of Cr(VI) and other metals from wastewaters by liquid–liquid extraction using hollow fiber membranes has been previously studied by the authors and the viability of the technology demonstrated [15,16].

When hollow fiber modules are used as liquid–liquid contactors, aqueous and organic solutions flow continuously, one through the lumen of the fiber and the other through the shell side, and both 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 [17].

Both technologies, NDSX and IE, are based on the same chemical reactions, the main difference lying in the way the regeneration of the selective functional groups is carried out once they become depleted with chromate ions. In many cases, the environmentally most compatible and cost effective solution comprises a combination of two or more processes [18–21]. Taking into account the difficulties for the separation and recovery of the contaminant contained in wastes, and especially so for highly concentrated wastewaters, sometimes the best option is the integration of two technologies to take advantage of the best characteristics of each.

In the treatment of the wastewaters containing Cr(VI), two main separation requirements should be considered at the same time: (i) lowering the concentration of chromium in the ground waters and (ii) concentration of the metal in the back-extraction phase up to a level that enables us to reuse it. On one hand, ion exchange resins are easily available and meet strict discharge specifications, but their main disadvantage is that the regeneration process is complex, requiring several sequential steps. On the other hand, the great advantage of a newer technology such as non-dispersive solvent extraction technology is that the regeneration step is carried out simultaneously and automatic control is easily achieved.

This work reports the integration of NDSX and IE technologies in a process for the cleaning of waters containing a high concentration of Cr(VI). The main objective of water cleaning was for it to come within the limits Spanish regulations (0.5 mg/l of Cr(VI)), while a second objective of the process was to recover the chromate compounds in a concentration of 15 g/l. Both objectives led to the development of an innovative process that was integrated by NDSX step with high concentration of Cr(VI) in the stripping agent coupled to an anion resin process (IE) that decrease the concentration of Cr(VI) to below the required limit.

The results of the integrated process, NDSX–IE, obtained under laboratory and pilot plant scale are presented in this paper. The integration of both technologies allows to overcome the individual shortcomings and leads to an optimum process configuration.

2. Experimental

Two different processes have been integrated for the remediation of waters containing chromium (VI) as the main pollutant in order to simultaneously achieve the separation of the pollutant down to discharge levels and the concentration of the metal in a regeneration solution: non-dispersive solvent extraction and ion exchange.

First of all, the ground waters were characterized by different analytical methods. Table 1 shows the main physico-chemical parameters.

2.1. Non-dispersive solvent extraction

The main components of the liquid–liquid extraction assisted by a membrane system are two hollow fiber modules, one for the extraction (EX module) and the other one for the stripping process (BEX module). The organic phase coming out of the extraction module was sent to the back-extraction module in order to accomplish two different objectives: (i) concentration of the removed chromium and (ii) regeneration of the organic phase. In the back-extraction module chromium was transported from the organic solution to the BEX solution that flowed to the

Table 1
Physico-chemical characterization of the ground waters

Cr^{6+} (mg/l)	600–2000
Ca^{2+} (mg/l)	550
Al^{3+} (mg/l)	60
SO_4^{2-} (mg/l)	1750
Cl^- (mg/l)	1200
DQO (mg/l)	170
COT (mg/l)	50
pH	7.3

Table 2
Characteristics of the membrane modules at laboratory and pilot plant scale

	Laboratory scale Normal flow 2.5 in. × 8 in.	Pilot plant scale Extra flow 4 in. × 28 in.
Number of fibers	10,200	32,500
Effective surface area (m^2)	1.4	19.3
Effective length (cm)	15	63
Fiber type	Celgard X-30 polypropylene	Celgard X-30 polypropylene
Inner diameter (μm)	240	240
Thickness (μm)	30	30
Pore size (μm)	0.05	0.05
Porosity (%)	30	30

storage tank; a continuous purge was applied to the tank, thereby a concentrated chromate solution was obtained; the tank volume was kept constant by continuous addition of fresh BEX solution.

The modules are both Liqui-Cel membrane contactors from Hoechst Celanese Corporation, normal flow 2.5 in. × 8 in. for the laboratory scale system and extra flow 4 in. × 28 in. for the pilot plant scale system. Their characteristics are shown in Table 2. In addition, four homogenisation tanks were also necessary, one for the organic phase, one for the feed aqueous phase and two tanks for the back-extraction aqueous streams.

On the laboratory scale the tank of the organic solution, back-extraction and purge had 2 l capacity and the tank of the feed aqueous solutions had 20 l capacity, and all the pipes were made of teflon and polypropylene. In the pilot plant, the tank of the organic solution had 90 l capacity and was made of stainless steel and the tanks of the aqueous solutions: feed, back-extraction and purge had a capacity of 5000, 100 and 60 l, respectively, and were made of polyethylene. Finally, the pipes of the aqueous phases were made of teflon and polypropylene while the pipes of the organic phase were stainless steel. In both systems, hollow fibers were thermostatized working at a temperature of 20–40 °C. Three heater systems were included in the plant, an on-line system for pipes and tubes and electrical resistances being placed inside the organic and BEX tanks.

In the modules, the aqueous phases run through the lumen of the hollow fibers and the organic phase flows through the shell side. Due to the use of hydrophobic fibers, the pressure of the aqueous phase is maintained higher than the pressure of the organic phase, ensuring that no displacement of the organic phase from the pores of the hollow fibers takes place. The working differential pressure is 2.5 psi [22].

When necessary, the feed solution was passed through a sand filter to remove remaining suspended solids and then through a 10 μm filter before entering the modules to prevent fouling in the hollow fibers. The feed ground waters flowed through the extraction module in a continuous mode.

Aliquat 336, a commercial mixture of trialkylmethylammoinium chlorides, was used as the extractant, and kerosene was used as diluent. To avoid the segregation of a third phase the addition of a modifier, isodecanol, was employed. NaCl was used as stripping agent.

Table 3
Physical and chemical properties of Lewatit MP-64 resins

Bead size (mm)	0.3–1.25
Density (g/ml)	1.03
Volume change (%)	Maximum 35
Operating pH range	0–8
Bed depth (m)	0.8–1.5
Water retention (%)	57–63
Useful capacity (eq/l)	1.4

2.2. Ion exchange

Anion exchange involves the exchange of one anion for another, resin being the main component of the process. Lewatit MP 64 is a weakly basic resin, macroporous-type anion exchange resin of standard bead size distribution based on styrene–divinylbenzene copolymer. It contains tertiary and quaternary amine group characterized by medium basicity and high stability. Table 3 shows the main characteristics of this type of resin.

The basis of ion exchange is quite simple: a variable speed pump with a flow rate indicator and a glass column with filter disks fitting both top and bottom parts. Ion exchange resins go through shrink/swell changes during ion exchange processing, therefore only 60% of the column was filled up with resins. Once the bed was packed the freeboard space was filled with the process solution.

The length of the laboratory scale column was 0.3 m and the width was 0.04 m. The length of the pilot plant column was 1.4 m and the width was 0.25 m and two parallel columns were used.

Column tests were performed to elucidate the shape of the breakthrough curve and to evaluate the effect of changes to operating conditions. Test were carried out in a five-stage procedure: (1) the feed solution was passed through the anion exchange column to saturate the resin; (2) the resin was regenerated by passing a solution of NaOH; (3) the resin was sponged by passing water through it; (4) HCl was passed through the resin to restore the resin to its original form; and (5) water was passed through the resin in order to remove the HCl.

Cation exchange resins are used due to the high content of calcium in the feed waters, so it was necessary to decrease its concentration previous to the NDSX process in order to avoid precipitation of calcium sulfate in the hollow fibers. Thus, a cationic ion exchange column was incorporated to the pilot plant to eliminate the presence of Ca^{2+} in the feed waters. The cationic ion exchange column was filled with Lewatit Monoplus S-100 resins.

Finally a schematic diagram of the plant with both technologies operating at the same time is shown in Fig. 1. If only one technology was used only half of the plant would be working while the other half was stopped.

3. Results

First of all, several of experiments for each technology were done separately and then the integration of both processes was

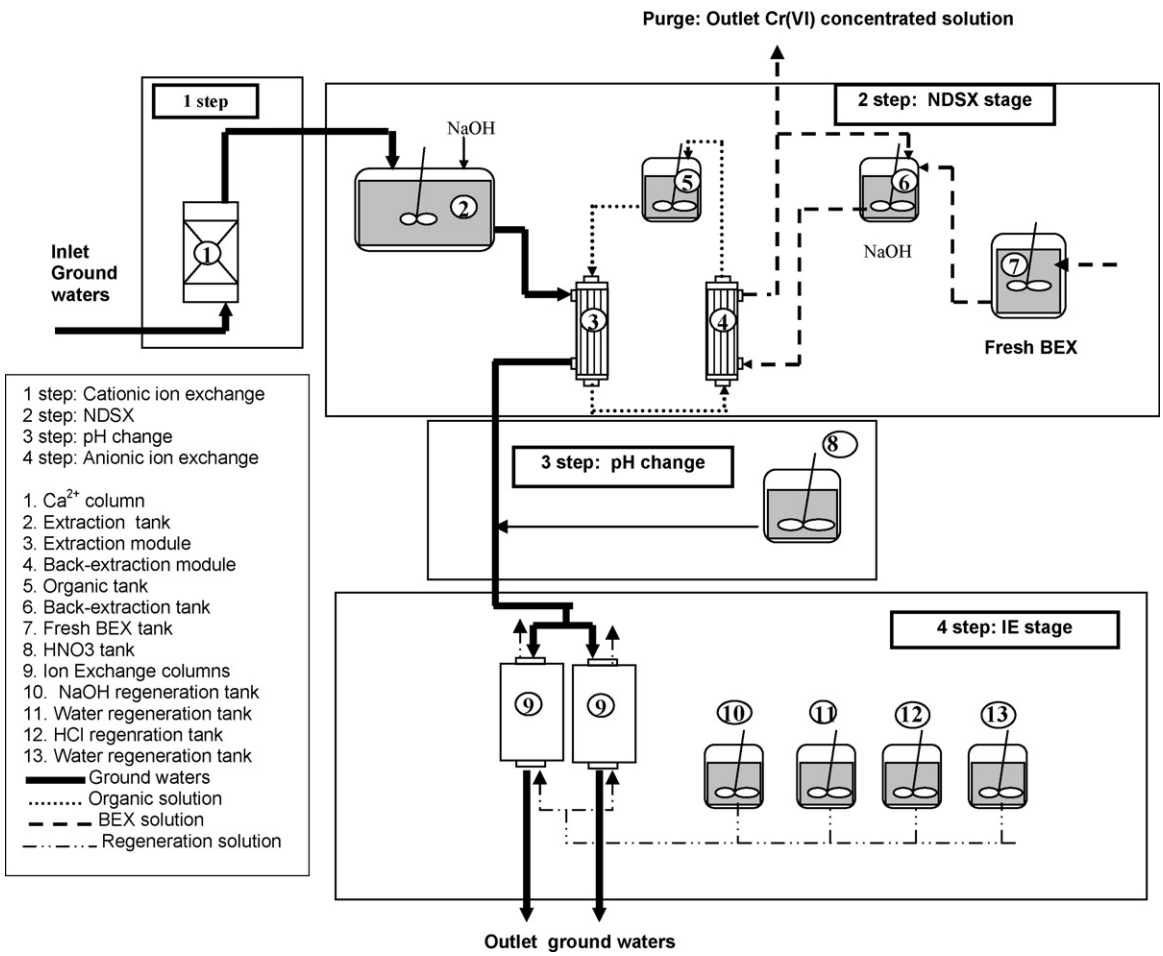

Fig. 1. Experimental set-up of the integrated NDSX–IE process.

considered. The kinetic results of Cr(VI) removal and concentration with the technological alternatives is presented as follows.

3.1. Non-dispersive solvent extraction

NDSX technology enables the separation and the concentration of Cr(VI) to be carried out simultaneously; therefore this technology was used first in order to separate and concentrate the higher quantity of Cr(VI).

The NDSX experiments were carried out in one-pass mode for the ground waters, recycling mode for the organic solution and semi-continuous for the BEX solution. The concentration and volume of the back-extraction solution was 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 [23].

Table 4 shows the experimental data of the NDSX process for two tests (Experiments 1 and 2) at laboratory scale. Fig. 2 shows the results obtained for experiment 1 carried out over an 80 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 Cr(VI) in the organic solution over time. When the stability of the metal 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 as is shown in Fig. 3.

The results obtained in this experiment were satisfactory and a second experiment working at a lower flow rate was planned in order to achieve a higher separation in the removal of Cr(VI). As observed in Table 4, the main difference between experiments 1 and 2 is the flow rate of the inlet waters and the Cr(VI)

Table 4
Inlet conditions of experiments 1 and 2 carried out by NDSX process

	C_i (mg/l)	F (l/h)	F_{BEX} (l/h)	F_p (l/h)	C_{BEX} (mol/l)	C_p (g/l)
Experiment 1	626	1.8	18	0.05	1.311	7
Experiment 2	597	1.2	18	0.01	1.153	4

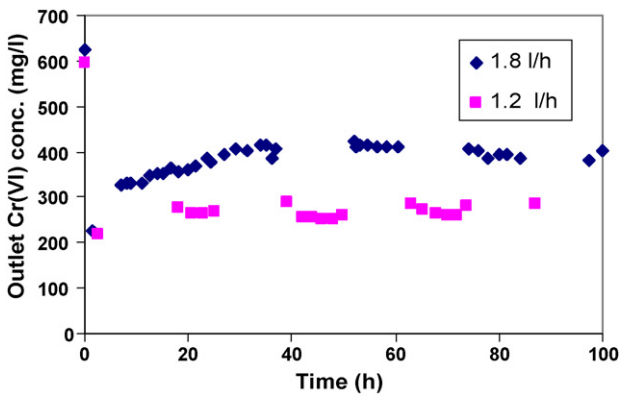

Fig. 2. Comparison of the outlet Cr(VI) concentration in the ground waters versus time in experiments 1 and 2 carried out at 1.8 and 1.2 l/h, respectively, and at pH of 7.3.

concentration in the purge stream. The decrease of the Cr(VI) concentration in the purge also contributes for increasing the decrease of the Cr(VI) in the feed waters.

So, Fig. 2 also shows the results of the outlet Cr(VI) concentration when the flow rate of the ground water decreases to 1.2 l/h. It is observed that the outlet concentration of Cr(VI) remains stable around 250 mg/l, thereby achieving a better decrease of Cr(VI) in the feed water. However, another variable has also been varied to increase the separation factor, since the concentration of the metal in the back-extraction solution is 4 g/l, as shown in Fig. 3.

Experiments 1 and 2 show the adequate behaviour of the NDSX process for the concentration of the metal in the BEX solution; however, the behaviour of these experiments is not adequate for the separation process since the concentration of Cr(VI) in the outlet feed waters is very high.

A further decrease of the chromium concentration in the outlet waters would either need to work with lower values of flow rates of the feed ground waters or to carry out a second NDSX step following the same methodology as in the first step. In this work, both possibilities have been analysed through mathematical simulation tasks using gPROMS (general Process Modelling System Ltd.). The extraction and concentration of Cr(VI) from

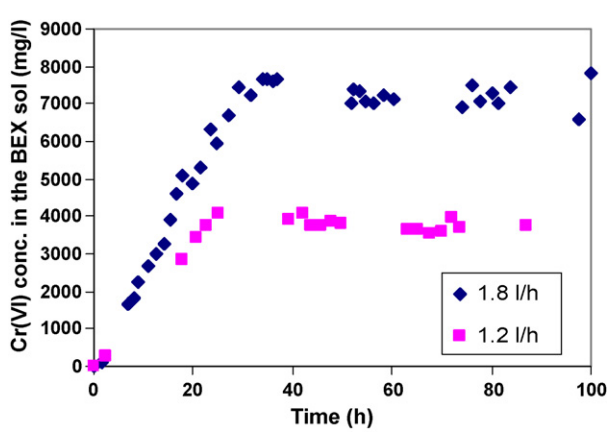

Fig. 3. Comparison of the Cr(VI) concentration in the BEX solution in experiments 1 and 2 versus time carried out at 1.8 and 1.2 l/h, respectively.

Table 5
Sensitivity of the Cr(VI) outlet concentration to feed flow rate and to a second NDSX step obtained by simulation with gPROMS

	Flow rate (l/h)						
	3	1.8	1.2	0.8	0.6	0.4	0.2
1 stage NDSX: C_{out} (mg/l)	540	460	330	260	160	72	50
2 stage NDSX: C_{out} (mg/l)	330	230	110	50	18	5	2

rinse waters, using hollow fiber membranes and Aliquat 336 as the extractant, has been previously studied by the authors and the mathematical model and design parameters have been obtained [15,22,23].

The mathematical model to describe NDSX processes consisted of six non-linear partial differential equations describing the mass transport through the membrane modules and two algebraic equations describing the equilibrium reactions. The mathematical model also required the knowledge of three characteristic parameters, two chemical equilibrium parameters of the interfacial reactions and the membrane mass transport coefficient [23].

The sensitivity analysis of the process for the feed flow rate and for an additional NDSX step was performed by simulation. Table 5 reports a summary of results and it was observed that it is possible to decrease the outlet concentration levels of Cr(VI) by both situations: reducing the flow rate and/or adding a new NDSX step. However, it is very difficult to achieve those concentration levels which permit the discharge of the outlet ground waters into water channels in accordance with Spanish legislation by means of NDSX since many NDSX steps were necessary or flow rates were very low. In this sensitivity study the concentration of Cr(VI) in the BEX solution was 15 g/l and the flow rate was 18 l/h.

Therefore, another separation process based on anion interchange resins (IE) will be added to the NDSX step in order to lower the Cr(VI) concentration in the ground waters down to an acceptable level for discharge. However, some IE experiments were first done separately as shows as follows.

3.2. Ion exchange

Several experiments were carried out working with the IE column described in the experimental section. The flow rate of the water is equal to the NDSX experiments (1.8 l/h) and the concentration of Cr(VI) in the feed waters is similar to the outlet Cr(VI) concentration in those experiments (350–450 mg).

Table 6 shows the inlet conditions and results of the experiments 3–10. The first four columns of Table 6 represent the conditions of the feed ground waters and the others show the results of the experiments. There is a considerable difference between experiments 3–5 and the others, resulting from the pH of the feed waters. The pH value in experiments 3–5 is basic and in experiments 6–10 is acid and the results of two type of experiments are also different.

Chromate ions exist in the aqueous phase in different ionic forms, with total chromate concentration and pH dictating which

Table 6
Inlet conditions and results of experiments 3–10 carried out by ion exchange (IE) process

Experiment	C_i (mg/l)	F (l/h)	pH	C_{out} (mg/l)	Breaktime (h)	Capacity (mol/l)
3	324–406	1.2	8–2	>5	0	–
4	440	2.4	10–2	>5	0	–
5	440	2.4	10–2	>5	0	–
6	220–460	2.4	2–2.5	0.1	31	1.75
7	434–440	2.4	2–2.5	0.3–0.4	20	1.80
8	430–460	2.4	2–2.5	0.3–0.4	31	1.67
9	430–440	2.4	2–2.5	0.3–0.4	39	
10	430–456	2.4	2–2.5	0.2–0.3	38	

particular chromate species will predominate. The following are the important equilibrium reactions [24,25]:

Reaction	log K (25 °C)	
$H_2CrO_4 \Leftrightarrow H^+ + HCrO_4^-$	−0.8	(1)
$HCrO_4^- \Leftrightarrow H^+ + CrO_4^{2-}$	−6.5	(2)
$2HCrO_4^- \Leftrightarrow Cr_2O_7^{2-} + H_2O$	1.52	(3)
$HCr_2O_7^- \Leftrightarrow H^+ + Cr_2O_7^{2-}$	0.07	(4)

Working at Cr(VI) concentrations lower than 1 g/l, it seems more attractive to work at acidic pH than at alkaline pH since the major species at lower pH is $HCrO_4^-$, which removes more chromium atoms per exchange site than the main species at alkaline pH, CrO_4^{2-}. Therefore, anion exchange resins offer much greater chromate removal capacity at acidic pH compared to alkaline pH, and that is why acidic pH operation is universal practice in treating wastewater and contaminated groundwater for Cr(VI) removal.

As shown in the fifth column of Table 6, in experiments 3–5 the outlet Cr(VI) concentration in the waters is always higher than 5 mg/l, while in the experiments 6–10 the outlet concentration is lower than 0.3 mg/l for 20 h or more. Therefore, acidic pH conditions were selected for the ion exchange process. Furthermore, it is observed in Table 6 that the value of the useful capacity at acidic pH is around 1.67–1.8 mol/l, which is slightly higher than the capacity given by the manufacturer.

Fig. 4 represents the experimental breakthrough curves for experiments 6–10, and it can be observed that the breakthrough

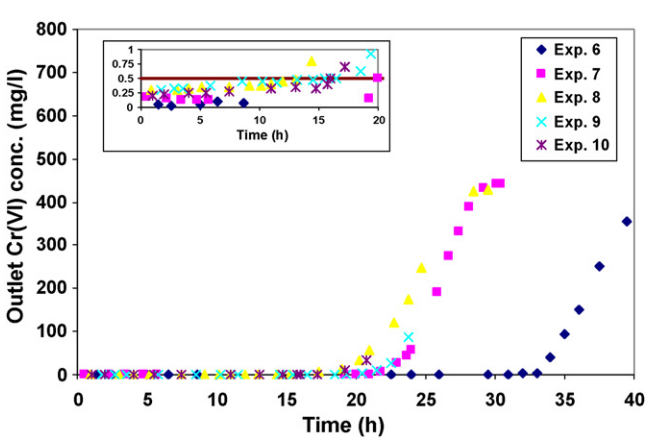

Fig. 4. Breakthrough curves for experiments carried out at acidic pH, with inlet Cr(VI) concentration around 400 mg/l.

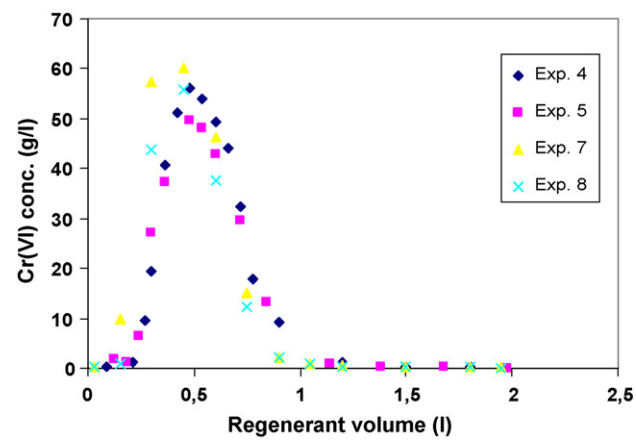

Fig. 5. Regeneration curves for ion-exchange experiments 4, 5, 7 and 8.

curve is favourable because has a self-sharpening slope and the chromium concentration values at outlet ground water are lower than 0.5 mg/l for more than 20 h (breaktime) and then the slope of the curve rises sharply. Experiment 6 presents the breaktime at 30 h since a lower initial concentration is used as is shown in Table 6.

Fig. 5 represents the experimental regeneration curve corresponding to experiments 4, 5, 7 and 8. In this regeneration stage the concentration of the Cr(VI) reaches 60 g/l and by the end of the regeneration process almost all the resin is regenerated. The quantity of Cr(VI) recovery depends on the volume and concentration of regenerant used.

From the small graph in Fig. 4 it is also observed that the average values of outlet concentration before the breaktime (C_{out}) fluctuate between 0.1 and 0.4 mg/l. It is important to remember that Spanish legislation establishes the discharge limit at 0.5 mg/l; therefore, all of the experiments were sufficiently successful. The situations shown in Figs. 4 and 5 allow us to demonstrate the viability of the anion exchange resins (Lewatit MP-64) to eliminate Cr(VI) from groundwater and recovery of the metal in the regeneration solution working under acid pH.

Ion exchange resins, which are easily available and meet of strict discharge specifications, have as one disadvantage: the complexity of the regeneration process that requires four sequential steps: (i) regeneration with NaOH, (ii) washing with water, (iii) acidification with HCl, and (iv) final washing.

Industrial experience and the development of efficient ion exchange resins would in some cases recommend the use of

this technology. However, considering the favourable characteristics of both options (NDSX and IE), the integration of the technologies into a hybrid process, that overcomes the individual shortcomings, could lead to the optimum process configuration.

3.3. Integration of both technologies

Two main objectives are considered simultaneously in the treatment of the waters: (i) decrease of the Cr(VI) concentration in waters down to 0.5 mg/l of Cr(VI) and (ii) recovery of the chromate compounds up to 15 g/l. As explained in Section 3.1, it is possible to decrease of the Cr(VI) concentration in wastewaters down to very low concentration levels using NDSX; however, either very high membrane area or very low flow rate is required. On the other hand, IE technology is a well known process for the separation of Cr(VI) from wastewaters particularly when the concentration of Cr(VI) is low, but the regeneration process is long and that is particularly costly when highly concentrated solutions are treated since the fill capacity of the resins is rapidly reached.

Taking into account the high concentration of Cr(VI) in the waters and the planned objectives, this work integrates both technologies (NDSX and IE) as is shown in Fig. 1. NDSX and IE processes are simultaneously carried out and the waters flows firstly through the NDSX process and then trough the IE process. The main objective of the NDSX is the concentration of Cr(VI) in the BEX solution and the main objective of IE process is the decrease of the concentration of Cr(VI) to below the required limit.

The integration of NDSX and IE technologies is presented in this paper working on two different scales: laboratory scale and pilot plant scale.

3.3.1. Laboratory scale

Table 7 shows the characteristics of the hybrid process NDSX–IE at laboratory scale (experiment 11) as well as the initial concentrations of the wastewater.

Fig. 6 represents the results of the hybrid process during 120 h. It shows that the NDSX process decreases the concentration of the inlet ground water (700 mg/l) to a value of around 400 mg/l, which remains stable during the whole run. Besides that, the Cr(VI) concentration in the BEX process was around 7 g/l all the time because that was the set concentration. Simultaneously to the NDSX process, the ion exchange process was carried out to lower the concentration of the metal from 400 mg/l. It is observed that at around 35 h the concentration of the Cr(VI) starts to increase since the resin is close to being saturated. At the end of the breakthrough curve, the concentration of the metal in the outlet waters was similar to the inlet concentration and a new IE process begins using a different column which contains fresh resin. Therefore, two IE columns were used to carry out the integrated process, in order to work simultaneously on the regeneration of the resins in one column and to carry out the IE separation process in the other column. During the 120 h three separation–regeneration cycles were carried out and therefore three breakthrough curves appear clearly in Fig. 6. The small figure included in Fig. 6 shows the results of IE process down to 5 mg/l and it can be observed that the concentration of Cr(VI) in the outlet waters when the resin is not completely charged is lower than 3 mg/l.

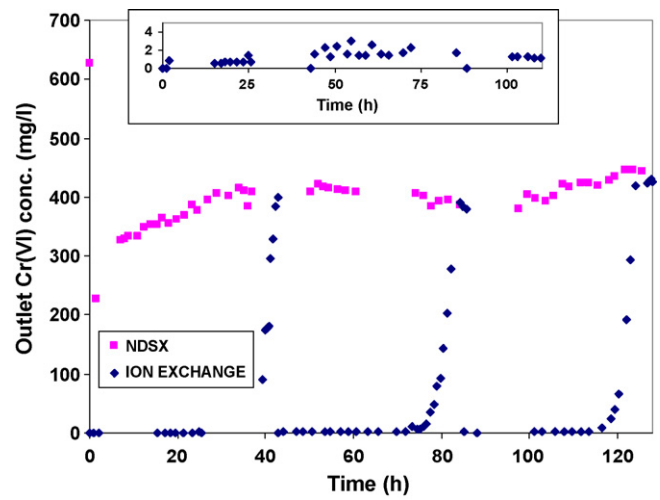

Fig. 6. Changes in Cr(VI) concentration in the ground waters from inlet concentration (700 mg/l) for the integrated NDSX–IE process versus time at laboratory plant scale and 40 °C.

The laboratory scale results are good enough to indicate that the integrated process runs well and the process is stable. Besides, the objective of each technology has been reached and therefore new experiments were carried out at pilot plant scale.

3.3.2. Pilot plant scale

Taking into account the results obtained at laboratory level, the scale-up of the process to pilot plant level was undertaken. In the NDSX process, the main scale-up variable is the mass transfer area that was increased by almost 20 times, i.e., from 1.2 m^2 corresponding to laboratory scale to 19.3 m^2 in the pilot plant set-up [26,27] and in the IE process the main scale-up variable is the resin volume which increases by almost 50 times, i.e., from 0.3 l corresponding to laboratory scale to 16 l of resin in the pilot plant set-up.

Table 7
Inlet conditions of experiments carried out by integration of NDSX and ion exchange at laboratory scale and pilot plant scale

Experiment	Scale	C_i (mg/l)	F (l/h)	C_p (g/l)	pH
11	Laboratory	NDSX: 700 IE: outlet of NDSX	1.8	7	NDSX: 7 IE: 2
12	Pilot plant	NDSX: 684 IE: outlet of NDSX	40	15	NDSX: 7 IE: 2

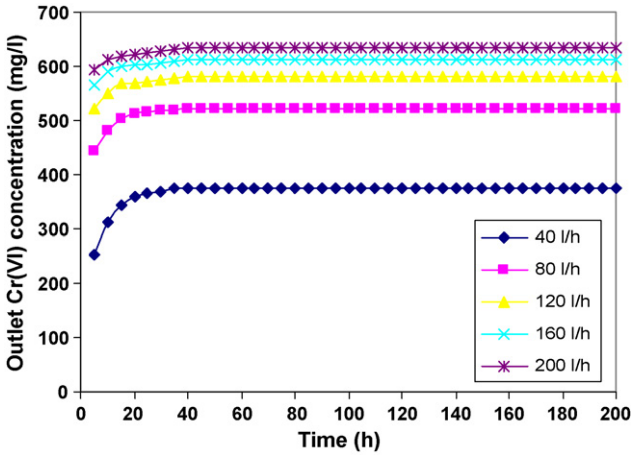

Fig. 7. Comparison of the outlet Cr(VI) concentration in the ground waters obtained by simulation for different flow rates using the NDSX process at pilot plant scale at 40 °C.

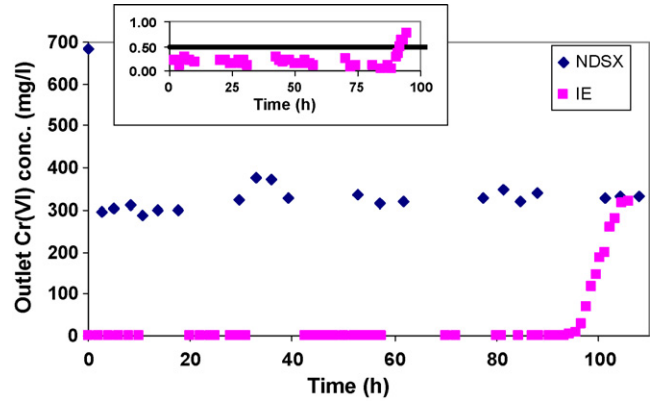

Fig. 8. Changes in Cr(VI) concentration in the ground waters from inlet concentration (684 mg/l) for the integrated NDSX–IE process versus time at pilot plant scale and 40 °C.

Initially, at the pilot plant scale, simulation tests were carried out to know which flow rate of feed water was appropriate for the plant. The temperature of the process was increased since the higher the temperature the better the response of the process [23]. However, 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. The same mathematical model used in laboratory scale experiments was used in order to describe NDSX processes with the adequate modifications derived from the higher area of the NDSX module and the temperature. gPROMS software was also used. Fig. 7 shows the outlet concentration of Cr(VI) of the ground waters obtained by simulation for flow rates, which varies from 40 to 200 l/h. As expected, lowering the flow rate of the feed waters, the outlet concentration in the waters also drops.

The final hybrid process proposed in this paper to take advantage of the best aspect of each technology can be defined with the following steps (Fig. 1):

i. *Ion exchange with cationic resins*. In this work, besides the high concentration of Cr(VI) in the waters, the use of real ground waters complicates the extraction process due to the presence of anions and cations in the feed solutions. So, the presence of calcium cation interferes with the process due to the precipitation of $CaSO_4$ being necessary to eliminate the calcium present in the waters by ion exchange. Lewatit Monoplus S-100 is used as the cation exchanger in order to lower the concentration of Ca^{2+} to avoid precipitation of calcium salts in the porous hollow fiber membranes. Regeneration is carried out with NaOH.
ii. *The NDSX step* that incorporates two membrane modules: one for the extraction and a second one for the back-extraction process. Ground waters flow continuously from the cation exchange column to the extraction module and then towards the third step. The organic phase circulates in a recycling mode from the extraction module to the back-extraction module. In the BEX tank a purge stream takes out the concentrated solution and the volume is kept constant by feeding fresh back-extraction solution. In the NDSX step a decrease of Cr(VI) concentration below 50% of the initial value is sought, whereas the stripping phase works with a concentration of 15 g/l. The temperature of the process is 40 °C in order to increase the separation velocity process.
iii. *pH change* of the waters coming from the NDSX process by adding HNO_3 in order to bring the pH down to 2.
iv. *Ion exchange* process using Lewatit MP-64 resins and working in continuous mode in order to decrease the concentration of Cr(VI) in the feed water down to 0.5 mg/l. Two columns are used, one for the separation process and the other one for the regeneration. The resin is regenerated by passing a concentrated solution of NaOH, and then later, the resin is sponged by passing water through it and finally HCl is passed through the resin to return the resin to its original Cl^- form and water was passed through the resin in order to remove the HCl.

Experiment 12 is carried out at pilot plant scale with the steps explained above and the experimental conditions shown in Table 7. Figs. 8 and 9 show the kinetics result of the integrated

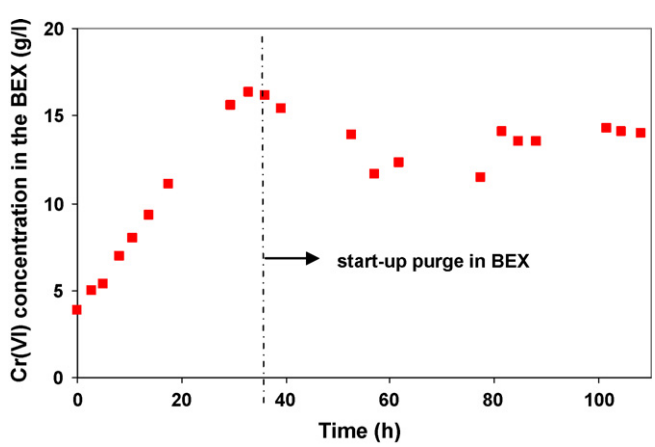

Fig. 9. Changes of Cr(VI) concentration in the back-extraction solution for the integrated NDSX–IE process versus time at pilot plant scale at 40 °C being 15 g/l the target concentration.

process over 110 h. The results of this integrated process are good since it can be observed that the two initial objectives are achieved simultaneously: (i) decrease of the Cr(VI) concentration in the outlet waters as shown in Fig. 8 and (ii) recovery of the chromate compounds in the BEX solution as shown in Fig. 9. In Fig. 8, it is also observed that only one IE run is represented since the volume of the resin is large and runs adequately for nearly 100 h. The small graph inside Fig. 8 shows in detail the outlet concentration of Cr(VI) in the waters.

Fig. 9 shows the evolution of the concentration of Cr(VI) in the BEX solution which contains around 15 g/l of Cr(VI). During the first part of the figure, the concentration of Cr(VI) increases up to 15 g/l since the purge is not working; however, once the concentration of Cr(VI) in the BEX solution reaches that value, the purge starts up in order to recover the metal.

Therefore, the stability of the integrated system in continuous mode was satisfactorily analyzed, it being observed that the system is stable in the extraction and back-extraction steps, a concentration of the metal in the BEX solution of up to 15 g/l being reached. A higher concentration of metal in the BEX solution is also possible.

The good agreement between the experimental tests and objectives allow us to conclude that the integrated NDSX and IE process can be satisfactorily used for the treatment of ground waters. The optimization of the processes, such as, the flow rate of the feed water, intermediate concentrations, configuration of the NDSX process, . . . will be done in a near future as will also the economic evaluation of the optimized process.

4. Conclusion

The goal of all industries should be the separation and recovery of the valuable material contained in the generated, and especially so in the case of hazardous waste such as Cr(VI). However, it is difficult to find one technology that simultaneously achieves both objectives. In many cases, the environmentally most compatible and cost effective solution comprises a combination of two or more of these processes.

This work presents an experimental analysis of the behaviour of the integration of a non-dispersive extraction process and ion exchange processes applied to the separation and concentration of hexavalent chromium contained in ground waters. Two main separation objectives were considered, i.e., to be able to lower the concentration of chromium in the ground waters until the discharge limits established by Spanish legislation (0.5 mg/l) while 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 (15 g/l).

Firstly, several experiments were done with both technologies working separately. NDSX experiments were done at different flow rates and it is observed that it is possible to decrease the outlet concentration levels of Cr(VI); however, to achieve the concentration levels which allow the discharge of the outlet waters into water channels it is required that there be very low flow rates or very high surface membrane area. IE tests were carried out satisfactorily since a low outlet Cr(VI) concentration was achieved; however, IE requires separated depletion and regeneration times, which is especially important when highly concentrated waters are treated. Besides, the IE regeneration process requires four sequential steps, while NDSX technology allows for a continuous regeneration process working at the same time with a high concentration stripping phase.

The final hybrid process proposed in this paper to take advantage of the best aspect of each technology can be defined with the following steps, (i) ion exchange with cationic resins, (ii) the NDSX step using Aliquat 336 as an extractant, (iii) pH change of the waters down to 2, and (iv) ion exchange process using anionic resins as Lewatit MP-64. The good agreement between the experimental tests and objectives conclude that the integrated NDSX and IE processes can be satisfactorily used for the treatment of ground waters.

Acknowledgement

This work has been financially supported by the project: 1FD97-2193.

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