

See discussions, stats, and author profiles for this publication at:
<https://www.researchgate.net/publication/228474859>

Preliminary design and optimization of PEUF process for Cr(VI) removal

ARTICLE in DESALINATION · MARCH 2008

Impact Factor: 3.76 · DOI: 10.1016/j.desal.2007.01.214

CITATIONS

22

READS

41

4 AUTHORS, INCLUDING:



[Pablo Cañizares](#)

University of Castilla-La Mancha

262 PUBLICATIONS 6,741 CITATIONS

SEE PROFILE



[Angel Perez](#)

University of Castilla-La Mancha

22 PUBLICATIONS 435 CITATIONS

SEE PROFILE



[Javier Llanos](#)

University of Castilla-La Mancha

39 PUBLICATIONS 342 CITATIONS

SEE PROFILE

Preliminary design and optimisation of a PEUF process for Cr(VI) removal

Pablo Cañizares, Ángel Pérez*, Javier Llanos, Guiomar Rubio

*Department of Chemical Engineering, Faculty of Chemistry, University of Castilla-La Mancha,
Av. Camilo José Cela, 10. 13004 Ciudad Real, Spain
Tel. +34-926-295300; Fax +34-926-295318; email: angel.perez@uclm.es*

Received 21 December 2006; accepted 3 January 2007

Abstract

The main purpose of this work is the study of the viability of a polyelectrolyte enhanced ultrafiltration (PEUF) process for the chromate recovery using poly(diallyldimethylammonium chloride) (PDADMAC) as water-soluble polymer. First of all, the interaction between PDADMAC and chromate ions was studied by potentiometric titrations of different poly(acrylic acid) (PAA) solutions in which its acidity constant (pK_a) was determined using the Henderson–Hasselbach equation. This interaction is linked to the influence of the presence of PDADMAC and chromate in the PAA pK_a value. Next, the operation conditions (pH, temperature and trans-membrane pressure) that optimize the membrane hydrodynamic behaviour were studied with ultrafiltration runs in mode operation of total recirculation. Furthermore, working at the operation conditions determined in the previous stage and with solutions of PDADMAC and chromate, the influence of ionic strength on design parameters was studied. Finally, the viability of a chemical method to regenerate the polyelectrolyte, based on the addition of NaCl and subsequent ultrafiltration, was checked. We conclude that this method is not suitable, mainly because of the great amount of water spent in the diafiltration stage necessary to reduce the polyelectrolyte solution chloride concentration.

Keywords: Chromate removal; PDADMAC; Ultrafiltration; Diafiltration

1. Introduction

Chromium is a well known toxic heavy metal, especially in its hexavalent form. As chromate, chromium is produced in several and different industries such as leather tanning and metal surface

treatment. Its toxicity has been deeply studied and it represents a high risk to health. Amongst its toxic effects, it has been linked to cancer in humans by inhalation and it is highly toxic in water even at low concentrations [1].

Different alternatives have been applied to the elimination of chromate anions in water effluents. For instance, a traditional way to remove

*Corresponding author.

Presented at the conference on Desalination and the Environment. Sponsored by the European Desalination Society and Center for Research and Technology Hellas (CERTH), Sani Resort, Halkidiki, Greece, April 22–25, 2007.

chromate in water effluents has been the reduction of Cr(VI) to Cr(III) and a subsequent increase in pH that leads to the precipitation of $\text{Cr}(\text{OH})_3$. The main inconvenience of this method is the presence of a solid waste with a high content in this heavy metal ion. One more advanced method is photocatalysis [2,3], where the removal of organic compounds and chromate, by oxidation of the former and reduction of the latter, can be reached simultaneously. Another option is ion-exchange technologies. Although ion-exchange resins are easily available, Galán et al. demonstrate that this technology presents the main disadvantage of the complexity of the regeneration step [4]. Moreover, membrane technologies have also been applied to the removal of chromate from aqueous effluents. Amongst them, it has been utilized low selective membrane processes such as nanofiltration (NF) [5] or a combination of NF and reverse osmosis (RO) [6], ultrafiltration with modified charged carbon membrane [7], micellar enhanced ultrafiltration (UF) [8,9] and hybrid processes comprising adsorption in activated carbon and microfiltration (MF) [10]. Finally, polymer enhanced ultrafiltration (PEUF) using cationic polyelectrolytes, a more selective technique than RO or NF, has been applied to recover chromate ions [11,12].

Polyelectrolyte enhanced ultrafiltration is a reactive membrane process extensively applied to retain metal ions [13–15]. In this method, a reaction between a metal ion and a water-soluble polyelectrolyte takes place followed by an ultrafiltration step where this metal ion is rejected. Poly(diallyldimethylammonium chloride) (PDADMAC) is a polyelectrolyte used as flocculant [16,17] and in the drinking water production [18]. The latter use is gathered in the Order SCO/3719/2005 of the Spanish Ministry of Public Health and Consumption (published in the Spanish Official State Gazette in December 1st, 2005). Furthermore, PDADMAC has been applied to PEUF processes for the removal of

different anions such as arsenate [18,19] or nitrate [20] and to the decolorization of dye-containing solutions [21]. To recover the polymer used in a PEUF process, traditionally, it is necessary to break the polymer-metal complex and to carry out a later ultrafiltration stage. In PEUF processes to recover metal cations, this chemical regeneration can consist of an increase in pH to get the macromolecular complex breakage [15,22–25].

Apart from the above mentioned works, very few articles have pay attention to chromate removal by PEUF, regarding not only chromate retention but also polymer regeneration and the study of polyelectrolyte-chromate interaction. In the present work, a polyelectrolyte enhanced ultrafiltration process is proposed to retain chromate ions from a diluted aqueous stream using PDADMAC as water-soluble polyelectrolyte. In a first stage, the interaction between PDADMAC and chromate has been evaluated by potentiometric titrations, analyzing the influence that the presence of PDADMAC and chromate ions has in the acidity constant of poly(acrylic acid) (PAA). Next, the influence of temperature (T), transmembrane pressure (ΔP), pH and ionic strength in design parameters (permeate flux and rejection coefficient) has been studied. Finally, it has been checked the viability of a chemical method to carry out the polyelectrolyte regeneration. Here, we propose the addition of certain amount of NaCl to break the chromate-PDADMAC complex, followed by an ultrafiltration step. Furthermore, a final diafiltration stage is necessary to decrease the polyelectrolyte chloride content to a value low enough to allow a subsequent retention cycle.

2. Theory

2.1. Potentiometric titrations

Regarding only base-acid behaviour, in a mixture of PAA and PDADMAC, carboxylic

groups of PAA are the only type of titratable groups [26]. The PAA acidity constant has been calculated from the titration data, applying the Henderson–Hasselbach equation, Eq. (1):

$$\text{pH} = \text{p}K_a + n \log \left[\frac{\alpha}{1-\alpha} \right] \quad (1)$$

where $\text{p}K_a$ is the antilogarithm of the PAA acidity constant, n is an empirical constant and α is the dissociation degree of PAA.

2.2. Diafiltration stage modelling

In order to model the diafiltration stage, a chloride mass balance can be applied to the reactor, Eq. (2):

$$V \frac{d[\text{Cl}]_R}{dt} = -Q_P [\text{Cl}]_P \quad (2)$$

where V is the reactor volume (L), $[\text{Cl}]_R$ and $[\text{Cl}]_P$ are the chloride concentration (ppm), respectively, in the reactor and the permeate stream and Q_P is the permeate flow rate ($\text{L h}^{-1} \text{m}^{-2}$). Taking into account the definition of chloride rejection coefficient (R_{Cl}), Eq. (2) can be transformed into Eq. (4):

$$R_{\text{Cl}} = 1 - \frac{[\text{Cl}]_P}{[\text{Cl}]_R} \quad (3)$$

$$V \frac{d[\text{Cl}]_R}{dt} = -Q_P [\text{Cl}]_R (1 - R_{\text{Cl}}) \quad (4)$$

Chloride rejection coefficient evolution with time can be adjusted to an empirical equation, Eq. (5):

$$R_{\text{Cl}} = B_1 \log(t + B_2) + B_3 \quad (5)$$

where, B_1 , B_2 and B_3 are empirical constants. If Eq. (5) is substituted in Eq. (4), it gives a

differential equation, Eq. (6), from which resolution the evolution of chloride concentration with time can be calculated:

$$\frac{d[\text{Cl}]_R}{dt} = \frac{-Q_P [\text{Cl}]_R (1 - B_1 \log(t + B_2) - B_3)}{V} \quad (6)$$

To solve this model, first of all, parameters B_1 , B_2 and B_3 have been calculated by adjustment of the evolution of chloride rejection coefficients with time, applying the Marquardt algorithm. Secondly, Eq. (6) has been solved using the fourth order Runge-Kutta procedure.

3. Experimental

3.1. Materials and apparatus

Ultrafiltration experiments were carried out using a laboratory-scale plant described in a previous paper [15]. It works with a tubular Micro Carbosep 20 UF module with an inner ceramic membrane (MWCO 10 kDa, TiO_2 active layer, effective membrane area of 0.004 m^2 , and internal diameter of 6 mm).

The selected polyelectrolyte was poly(diallyldimethylammonium chloride) ($M_w < 100,000 \text{ Da}$) and concentration 35% w/w supplied by Aldrich. PDADMAC solutions were prepared using Milli-Q water and were previously diafiltered to eliminate low molecular weight fractions. The experimental concentration of PDADMAC was always 0.1% w/w, measured with a total organic carbon (TOC) analyser (Shimadzu 5050 A). Cr(VI) solutions were prepared with sodium chromate 4-hydrate supplied by Panreac. Chromate ion concentrations were measured with an atomic absorption spectrophotometer (Varian, SpectrAA 220). Both, NaOH and HCl, for potentiometric titrations were known title solutions supplied by Panreac.

Potentiometric titrations were carried out with a 686 titroprocessor (Methrohm) automatic titrator equipped with an electronic burette

(Metrohm, 665 Dosimat) and fitted with a glass combined electrode (Metrohm) and a temperature meter (Metrohm). Potentiometric titration cell possesses a jacket connected to a thermostated bath.

3.2. Procedure

In experiments in total recirculation mode, both streams, permeate and retentate, were returned to the reactor. In the diafiltration experiment, the rejected stream was recirculated to the reactor but the permeate stream was removed and its flow rate was measured in order to pump the same volume of water from the reservoir to the reactor.

With respect to potentiometric titrations, the procedure was similar to that describe by Petrov et al. [26]. First of all, NaOH 1 N was added in order to begin from a value of pH equal to 11.6. Next, the titration was done by stepwise addition of 50 μ L of 0.2 M HCl at 25°C and under a N_2 inert atmosphere.

4. Results and discussion

4.1. PDADMAC titrations

The first step was the study of the interaction between PDADMAC and CrO_4^{2-} by potentiometric titrations. The influence of the CrO_4^{2-} presence in the PAAH-PDADMAC polyelectrolyte complex was evaluated. Three solutions were titrated: a solution of PAA (0.05% w/w), a mixture of PAA (0.05% w/w) and PDADMAC (0.05% w/w) and a mixture of PAA (0.05% w/w), PDADMAC (0.05% w/w) and CrO_4^{2-} (25 ppm). In the titration with chromate, it has been used the same PDADMAC/chromate molar relation than that utilised in ultrafiltration runs. The titration curves are plotted in Fig. 1 and the results of the Henderson–Hasselbach equations adjustment are gathered in Table 1.

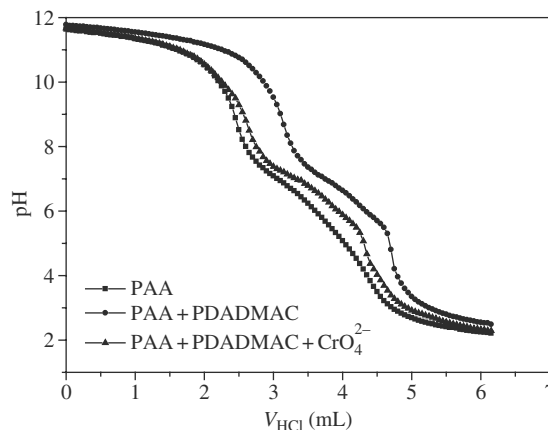


Fig. 1. Titration curves of PAA (0.05% w/w), PAA (0.05% w/w) + PDADMAC (0.05% w/w) and PAA (0.05% w/w) + PDADMAC (0.05% w/w) + CrO_4^{2-} (25 ppm). Stepwise addition of 50 μ L of 0.2 M HCl at 25°C after addition of NaOH 1 N until pH 11.6.

As it can be deduced, the value of the PAA pK_a decreased in the presence of PDADMAC, as described by Petrov et al. [26]. This result can be explained by an interaction between ammonium cations of PDADMAC and carboxylic groups of PAA. This interaction leads to a higher dissociation degree of PAA at the same pH value and, consequently, a lower value of pK_a and a stronger acidic behaviour. When chromate is placed in the titration media, the above-mentioned interaction between PAA and PDADMAC will be weakened if a complex between chromate and PDADMAC is formed. This is the result obtained in this study. The value of pK_a obtained when chromate is present

Table 1
 pK_a and n values for PAA titrations. 0.05% w/w PAA, 0.05% w/w PDADMAC, 25 ppm CrO_4^{2-} ; $T = 25^\circ C$

	n	pK_a	pK_a [26]
PAA	1.9	6.2	6.4
PAA + PDADMAC	5.5	4.3	3.6
PAA + PDADMAC + CrO_4^{2-}	2.3	5.8	—

in the initial solution is higher than that reached for the mixture of PDADMAC and PAA and slightly lower than the pK_a value for PAA by itself.

Furthermore, the value of the empirical constant n is especially high for the PAA-PDADMAC mixture. The unusual high value of this constant is indicative of the bond between poly-electrolytes of different charge (polyacrylate groups of PAA and ammonium groups of PDADMAC). Once again, the similarity between the values of this constant for PAA and for the mixture with chromate demonstrates the existence of a complex $PDADMA-CrO_4^{2-}$. A more quantitative study could be done and will be carried out in next works.

4.2. Ultrafiltration of PDADMAC solutions

Once the interaction between chromate and PDADMAC was studied, the influence of four operational parameters (pH, transmembrane pressure, temperature and ionic strength) in both, permeate flux and polymer rejection coefficient, was analysed. The best operational conditions are those with maximum rejection coefficient and permeate flux. The optimum must be a compromise between a great permeate flux and a reasonable capacity of metal rejection [14]. The operational conditions have been optimized in experiments with 0.1% w/w PDADMAC solutions in total recirculation mode, because the presence of a macromolecule is what governs the hydrodynamic behaviour of the membrane [15–23]. This concentration is far away from PDADMAC gel concentration [20,27] in order to minimize concentration polarization. A feed flow rate of 300 L/h (tangential velocity = 3 m s^{-1}) was applied. This feed flow rate ensures turbulent conditions that minimise both, fouling and concentration polarization phenomena.

Fig. 2 depicts the evolution of permeate fluxes and polymer rejection coefficients with

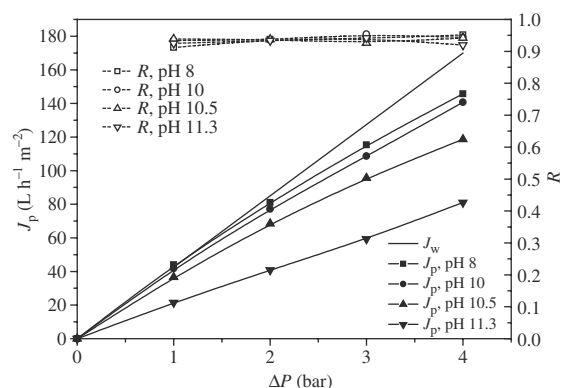


Fig. 2. Influence of transmembrane pressure and pH on permeate fluxes and polymer rejection coefficients. 0.1% w/w PDADMAC; $v = 3 \text{ m s}^{-1}$; $T = 25^\circ\text{C}$.

transmembrane pressure at different values of pH at 25°C . Values of pH higher than 8 have been used because chromate ions are not stable at lower pH values [28]. Polymer rejection coefficients remain almost unaltered with pH, reaching values always higher than 90%. On the contrary, permeate flux decreases slightly until pH = 10, but suffers a deep drop at higher pH values. This result can be explained by the fact that the membrane is negatively charged at pH values higher than 10.4 [23]. This charge allows an electrostatic interaction between the membrane active layer and the PDADMAC quaternary ammonium groups that leads to the appearance of fouling phenomena.

Next, Fig. 3 shows the evolution of permeate fluxes and rejection coefficients with transmembrane pressure in experiments at 50°C and in the optimal pH interval determined in the previous stage (from 8 to 10). On the one hand, from these experiments one can deduce that permeate flux is clearly enhanced meanwhile rejection coefficients remain unaltered with respect to the experiments at 25°C . On the other hand, maximum values of permeate flux are obtained at pH of 9. For this reason, a value of pH equals to 9 is chosen for the rest of the study.

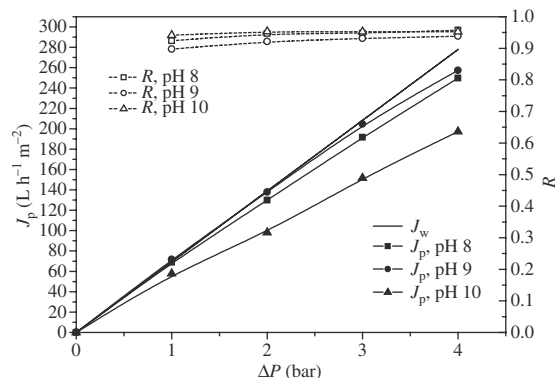


Fig. 3. Influence of transmembrane pressure and pH on permeate fluxes and polymer rejection coefficients. 0.1% w/w PDADMAC; $v = 3 \text{ m s}^{-1}$; $T = 50^\circ\text{C}$.

4.3. Chromate retention by PEUF

Fig. 4 represents the influence of temperature and transmembrane pressure on design parameters at pH = 9. Permeate flux in experiments with chromate follows the same trend than that without metal, but suffers a 20% decrease. This decrease can be caused by the change in the anion charge. The fact that chromate has a charge of -2 , makes necessary that two polyelectrolyte repetitive units bind each chromate molecule, what makes polymer configuration less rigid.

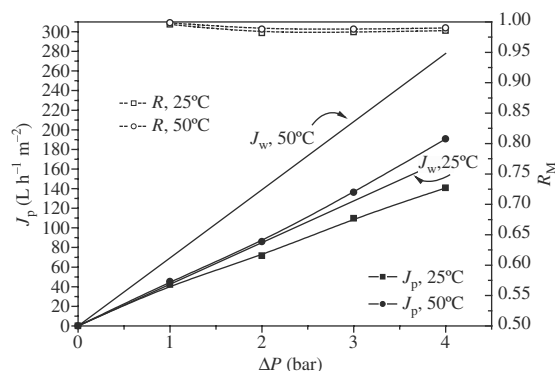


Fig. 4. Influence of temperature and transmembrane pressure on permeate fluxes and metal rejection coefficients. 0.1% w/w PDADMAC; 50 ppm CrO_4^{2-} ; pH = 9; $v = 3 \text{ m s}^{-1}$.

This higher flexibility favours the decrease in the polymer hydrodynamic radius, which facilitates the appearance of fouling phenomena by pore blocking. Furthermore, metal rejection coefficients are similarly high at both temperatures, with values above 99%. As is the way with experiments without metal, working at 50°C is preferable to working at 25°C , as higher permeate fluxes are obtained as well as similar, and very high, retention coefficients are reached.

The influence of ionic strength on permeate fluxes and rejection coefficients has been studied. These experiments were carried out at pH = 9 and 50°C , the optimal conditions determined in the previous step. Fig. 5 depicts the evolution of permeate fluxes and metal rejection coefficients with different concentrations of NaCl in an interval of transmembrane pressures between 0 and 4 bar. The main conclusion derived from this figure is that chromate rejection suffers a deep decrease with the addition of NaCl. As expected, the presence of high quantities of NaCl displaces the formation equilibrium of the complex PDADMA- CrO_4^{2-} to its decomposition, as it is represented by Fig. 6.

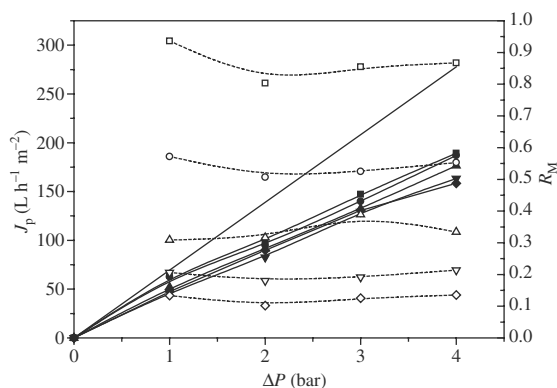


Fig. 5. Influence of transmembrane pressure and ionic strength on permeate fluxes and metal rejection coefficients. 0.1% w/w PDADMAC; 50 ppm CrO_4^{2-} ; pH = 9; $T = 50^\circ\text{C}$; $v = 3 \text{ m s}^{-1}$. ■ [NaCl] = 0.01 M; ● [NaCl] = 0.03 M; ▲ [NaCl] = 0.05 M; ▼ [NaCl] = 0.07 M; ◆ [NaCl] = 0.09 M. J_p : Solid symbols and lines. R_M : open symbols and dash lines.

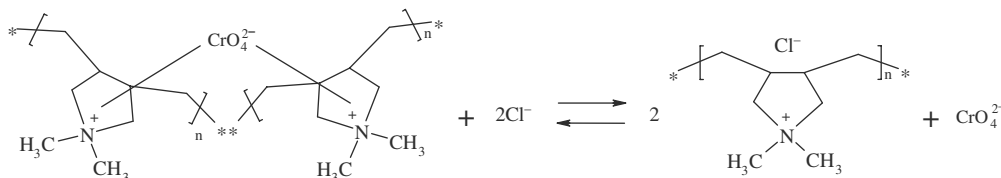


Fig. 6. PDADMA- CrO_4^{2-} complex breakage equilibrium by addition of chloride.

It is greatly noticeable, that it is necessary a very much higher concentration of chloride anions to displace the complex formation equilibrium of PDADMAC and chromate. Without added ionic strength, the concentration of chloride ions is the strictly necessary to compensate PDADMAC ammonium groups charge. With a 0.1% w/w PDADMAC solution, this chloride concentration equals to 5.6 mM, thirteen times higher than chromate concentration. Even in these conditions, chromate rejection coefficient is above 99%. It is necessary to add a supplementary 90 mM chloride concentration (chloride/chromate molar relation of 222) to diminish chromate retention under 20%. With respect to permeate fluxes, there exists a slight decrease when increasing ionic strength. It can be explained because of a change in the polyelectrolyte structure from a cylindrical to a spherical form [29].

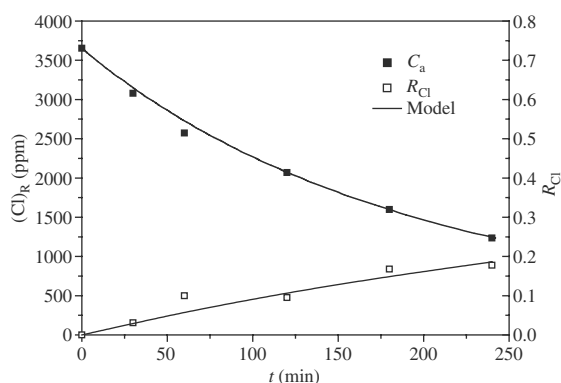


Fig. 7. Evolution of Cl^- concentration in the reactor of a 4 h diafiltration experiment. Initial solution: 0.1% w/w PDADMAC; 0.09 M NaCl; pH = 9; $T = 50^\circ\text{C}$; $\Delta P = 4$ bar; $v = 3 \text{ m s}^{-1}$.

This polymer configuration can produce a fouling phenomenon by pore blocking that caused the observed decrease in permeate flux.

4.4. Polyelectrolyte regeneration

In order to carry out the polyelectrolyte regeneration, the viability of a chemical procedure by addition of NaCl and subsequent ultrafiltration has been checked. If this via is selected, it is necessary to reduce the chloride concentration in polyelectrolyte solution by a diafiltration stage until its original value (200 ppm). With this aim, a four hours diafiltration experiment was set up with an initial solution of 0.1% w/w PDADMAC, 0.09 M NaCl, at 50°C , 4 bar of transmembrane pressure and a feed flow rate of 300 L/h. The experimental results have been modelled according to the procedure explained in point 2.2. Fig. 7 resumes the experimental data as well as the model adjustment. The value of permeate flux was almost constant around a value of $150 \text{ L h}^{-1} \text{ m}^{-2}$ and has not been reported in Fig. 7.

The adjustment of Eq. (5) to chloride rejection experimental data gives Eq. (7):

$$R_{Cl} = 0.2675 \log(t + 233.39) - 1.4619 \quad (7)$$

As it can be observed, the proposed model accurately adjusts the experimental data. The final chloride concentration reached was, approximately, 1000 ppm, considerably higher than the target concentration of 200 ppm. Therefore, the evolution of chloride concentration in the reactor with time has been simulated to know the needed

time of operation as well as the water consumption. From this simulation, it would be necessary 12 h of operation time and 7.2 L of water consumption to reach the desired chloride concentration. This water volume is more than threefold the treated volume (2 L). For this reason, we consider unviable this chemical method and further research must be carried out in subsequent works with respect to the polyelectrolyte regeneration stage.

5. Conclusions

It has been demonstrated the existence of an interaction between PDADMAC and chromate anions by potentiometric titrations. Due to the concordance between characterization and ultrafiltration results, we conclude that the proposed semi-quantitative method, apart from being a simple approach, can be potentially applied to determine formation constants between cationic polyelectrolytes and anions and, therefore, be used as a useful tool in prediction and modelling of PEUF processes results.

With respect to the ultrafiltration experiments results, on the one hand, it has been studied and optimised the chromate retention stage using PDADMAC as water soluble polyelectrolyte in a PEUF process. Chromate rejection coefficients up to 0.99 and permeate fluxes of around $200 \text{ L h}^{-1} \text{ m}^{-2}$ have been reached working at 50°C , 4 bar of transmembrane pressure and a PDADMAC and chromate concentration of, respectively, 0.1% w/w and 50 ppm. Furthermore, this polymer demonstrates very much higher affinity to bind chromate than chloride ions, even with a very much higher concentration of the latter and it does not lead to neither concentration-polarization nor important fouling. These results demonstrate the complete technical viability of the PEUF process to retain chromate ions.

On the other hand, it has been checked that the chemical regeneration stage by addition of NaCl is not a viable option to carry out the polymer regeneration. Two main reasons can be given to

support this conclusion. On the one hand, the higher affinity of PDADMAC to bind chromate better than chloride, makes necessary a very high concentration of chloride to get the complex breakage. As a consequence, in the subsequent diafiltration stage, it is necessary to spend a water volume more than threefold the treated solution volume. For this reason, we conclude that if the polymer must be recycled, chemical regeneration is not a suitable option.

References

- [1] US Environmental Protection Agency, 1998, Toxicological review of hexavalent chromium.
- [2] X.R. Xu, H.B. Li and J.D. Gu, Simultaneous decontamination of hexavalent chromium and methyl tertbutyl ether by UV/TiO₂ process, *Chemosphere*, 63 (2006) 254–260.
- [3] J.K. Yang and S.M. Lee, Removal of Cr(VI) and humic acid by using TiO₂ photocatalysis, *Chemosphere*, 63 (2006) 1677–1684.
- [4] B. Galán, D. Castañeda and I. Ortiz, Removal and recovery of Cr(VI) from polluted ground waters: a comparative study of ion-exchange technologies, *Water Res.*, 39 (2005) 4317–4324.
- [5] H.F. Shaalan, M.H. Sorour and S.R. Tewfik, Simulation and optimization of a membrane system for chromium recovery from tanning wastes, *Desalination*, 141 (2001) 315–324.
- [6] I. Frenzel, D.F. Stamatialis and M. Wessling, Water recycling from mixed chromic acid waste effluents by membrane technology, *Sep. Purif. Technol.*, 49 (2006) 76–83.
- [7] G. Pugazhenth, S. Sachan, N. Kishore and A. Kumar, Separation of chromium (VI) using modified ultrafiltration charged carbon membrane and its mathematical modeling, *J. Membr. Sci.*, 254 (2005) 229–239.
- [8] K. Baek and J.W. Yang, Simultaneous removal of chlorinated aromatic hydrocarbons, nitrate, and chromate using micellar-enhanced ultrafiltration, *Chemosphere*, 57 (2004) 1091–1097.
- [9] J. Lee, J.S. Yang, H.J. Kim, K. Baek and J.W. Yang, Simultaneous removal of organic and inorganic contaminants by micellar enhanced ultrafiltration with mixed surfactant, *Desalination*, 184 (2005) 395–407.

- [10] C.A. Basar, C. Aydiner, S. Kara and B. Keskinler, Removal of CrO_4 anions from waters using surfactant enhanced hybrid PAC/MF process, *Sep. Purif. Technol.*, 48 (2006) 270–280.
- [11] J. Bohdziewicz, Removal of chromium ions (VI) from underground water in the hybrid complexation-ultrafiltration process, *Desalination*, 129 (2000) 227–235.
- [12] S. Tangvijitsri, C. Saiwan, C. Soponvuttikul and J.F. Scamehorn, Polyelectrolyte-enhanced ultrafiltration of chromate, sulphate, and nitrate, *Sep. Sci. Technol.*, 37 (5) (2002) 993–1007.
- [13] K. Volchek, E. Krentsel, Y. Zhilin, G. Shtereva and Y. Dytnersky, Polymer binding/ultrafiltration as a method for concentration and separation of metals, *J. Membr. Sci.*, 79 (1993) 253–272.
- [14] K. Geckeler and K. Volchek, Removal of hazardous substances from water using ultrafiltration in conjunction with soluble polymers, *Environ. Sci. Technol.*, 30 (1996) 725–734.
- [15] P. Cañizares, A. Pérez, R. Camarillo and J.J. Linares, A semi-continuous laboratory-scale polymer enhanced ultrafiltration process for the recovery of cadmium and lead from aqueous effluents, *J. Membr. Sci.*, 240 (2004) 197–209.
- [16] B. Tian, X. Ge, G. Pan, B. Fan and Z. Luan, Adsorption and flocculation behaviours of polydi-allyldimethylammonium (PDADMA) salts: influence of counterion, *Int. J. Miner. Proc.*, 79 (2006) 209–216.
- [17] <http://www.cyttec.com/pdf/WaterTreatment/WTT-1199.pdf>, Accessed December 19, 2006.
- [18] D. Gallo, E.J. Acosta, J.F. Scamehorn and D.A. Sabatini, Pilot-scale study of polyelectrolyte-enhanced UF for arsenic removal, *J. AWWA*, 98 (1) (2006) 106–116.
- [19] P. Pookrod, K.J. Haller and J.F. Scamehorn, Removal of arsenic anions from water using polyelectrolyte-enhanced ultrafiltration, *Sep. Sci. Technol.*, 39 (4) (2004) 811–831.
- [20] X. Zhu, K.H. Choo and J.M. Park, Nitrate removal from contaminated water using polyelectrolyte-enhanced ultrafiltration, *Desalination*, 193 (2006) 350–360.
- [21] X. Tan, N.N. Kyaw, W.K. Teo and K. Li., Decolorization of dye-containing aqueous solutions by the polyelectrolyte-enhanced ultrafiltration (PEUF) process using a hollow fiber membrane module, *Sep. Purif. Technol.*, 52 (2006) 110–116.
- [22] P. Cañizares, Á. Pérez and R. Camarillo, Recovery of heavy metals by means of ultrafiltration with water-soluble polymers: calculation of design parameters, *Desalination*, 144 (2002) 279–285.
- [23] P. Cañizares, A. de Lucas, Á. Pérez and R. Camarillo, Effect of polymer nature and hydrodynamic conditions on a process of polymer enhanced ultrafiltration, *J. Membr. Sci.*, 253 (2005) 149–163.
- [24] P. Cañizares, Á. Pérez, R. Camarillo and M.T. Villajos, Improvement and modelling of a batch polyelectrolyte enhanced ultrafiltration process for the recovery of copper, *Desalination*, 184 (2005) 357–366.
- [25] P. Cañizares, Á. Pérez, R. Camarillo, J. Llanos and M.L. López, Selective separation of Pb from hard water by a semi-continuous polymer-enhanced ultrafiltration process (PEUF), *Desalination*, 206 (2007) 602–613.
- [26] A.I. Petrov, A.A. Antipov and G.B. Sukhorukov, Base-acid equilibria in polyelectrolyte systems: from weak polyelectrolytes to interpolyelectrolyte complexes and multilayered polyelectrolyte shells, *Macromolecules*, 36 (2003) 10079–10086.
- [27] S. Sriratana, J.F. Scamehorn, S. Chavadej, C. Saiwan, K.J. Haller, S.D. Christian and E.E. Tucker, Use of polyelectrolyte-enhanced ultrafiltration to remove chromate from water, *Sep. Sci. Technol.*, 31 (18) (1996) 2493–2504.
- [28] F.B. Martí, F.L. Conde, S.A. Jimeno and J.H. Méndez, 11th edn., *Química analítica cualitativa*, Paraninfo, 1983, pp. 597–598.
- [29] C.S. Dunaway, S.D. Christian, E.E. Tucker and J.F. Scamehorn, Study of the binding of anions by a cationic polyelectrolyte using equilibrium dialysis. 1, Chromate anions, *Langmuir*, 14 (1998) 1002–1012.