

Elsevier Editorial System(tm) for Desalination
Manuscript Draft

Manuscript Number: DES-D-13-01196R2

Title: Ionic liquids as a carrier for chloride reduction from brackish water using hollow fiber renewal liquid membrane

Article Type: Special Issue: Desmembranetechnology

Keywords: chloride reduction; ammonium and phosphonium ionic liquid; supported liquid membrane; hollow fiber renewal liquid membrane

Corresponding Author: Dr. Agustin Fortuny,

Corresponding Author's Institution: Universitat Politecnica de Catalunya

First Author: Agustin Fortuny, Dr.

Order of Authors: Agustin Fortuny, Dr.; Maria T Coll, Dr.; Ana M Sastre, Dr.

Manuscript Region of Origin: SPAIN

Abstract: High concentration of chloride ions in continental water is a great problem for the exploitation of these natural resources. In industry, the use of this water involves additional conditioning steps. For drinking water and irrigation uses, the Cl⁻ must be reduced by conventional water treatment processes, like ion exchange or reverse osmosis, but for large scale production these techniques could be very expensive due to resin regeneration or energy costs. The possibility of using supported liquid membranes (SLM) with ionic liquids (IL), Aliquat 336, Cyphos IL 101 and Cyphos IL 167, as carriers to exchange Cl⁻ for HCO₃⁻ anion has been shown to work. The reversibility of this anion exchange was corroborated by solvent extraction experiments and implemented in flat sheet supported liquid membrane (FSSLM) and hollow fiber renewal liquid membrane technologies (HFRLM). About double rate transport values was been obtained in HFRLM compared to SLM and one hour is time enough to reduce the chloride concentration up to 250 mg/L using HFRLM at the best experimental conditions. The results obtained allow us to be optimist about the implementation of this technology on a large scale to chloride reduction in drinking water when the source is inadequate for direct use.

Highlights

- Different ILs were successfully used as ion-exchange extractants to reduce the chloride in water.
- Equilibrium constants have been obtained.
- The reversibility of the $\text{Cl}^-/\text{HCO}_3^-$ interchange process has been verified.
- The ILs shown a promising behaviour with SLM.
- This technique could be applied to exchange any other anion present in aqueous solutions.

Ionic liquids as a carrier for chloride reduction from brackish water using hollow fiber renewal liquid membrane

Agustin Fortuny, Maria Teresa Coll, Ana Maria Sastre

EPSEVG. Universitat Politècnica de Catalunya,. Chemical Engineering Dep
Av. Victor Balaguer, 1. 08800 Vilanova i la Geltru, Spain.
tel. +34 938967754 e-mail: agustin.fortuny@upc.edu; fax: +34 938967700.

Abstract

High concentration of chloride ions in continental water is a great problem for the exploitation of these natural resources. In industry, the use of this water involves additional conditioning steps. For drinking water and irrigation uses, the Cl^- must be reduced by conventional water treatment processes, like ion exchange or reverse osmosis, but for large scale production these techniques could be very expensive due to resin regeneration or energy costs. The possibility of using supported liquid membranes (SLM) with ionic liquids (IL), Aliquat 336, Cyphos IL 101 and Cyphos IL 167, as carriers to exchange Cl^- for HCO_3^- anion has been shown to work. The reversibility of this anion exchange was corroborated by solvent extraction experiments and implemented in flat sheet supported liquid membrane (FSSLM) and hollow fiber renewal liquid membrane technologies (HFRLM). About double transport values was obtained in HFRLM compared to SLM and one hour is time enough to reduce the chloride concentration up to 250 mg/L using HFRLM at the best experimental condition. The results obtained allow us to be optimist about the implementation of this technology on a large scale to chloride reduction in drinking water when the source is inadequate for direct use.

Keywords: chloride reduction; ammonium and phosphonium ionic liquid; supported liquid membrane; hollow fiber renewal liquid membrane

Introduction

Because water is the main solvent in nature, the presence of different species in ground water is very variable and its quality is dependent on the climate and geological factors. Salinity in continental waters is one of the most serious problems in many places on the planet, making it unsuitable for irrigation or as a source for potabilization treatment plants.

In the conventional processes to produce drinking water chloride is not eliminated. For this reason, when brackish water is used, it is necessary to apply other additional processes to achieve the limit (250 mg/L) established by the 98/83/EC Directive.

Reverse osmosis, electrodialysis and membrane distillation are the most generalized processes to reduce salts from seawater (about 35000 mg/L) and from brackish (500-30000 mg/L) water. All these processes use energy to produce adequate water and the associated energetic cost is considerable. Of course more efficient membrane designs [1], inclusion of the energy saving steps [2], utilization of renewable energies [3-5], emerging adsorption methods [6, 7], etc. have been applied to improve the profitability of plant operations.

1 When the concentration of salts in the water is lower than in the above cases, like some
2 river water with chloride concentration less than 1000 mg/L, processes based on
3 chemical separation may be able to reduce the chloride content. The advantage of these
4 technologies is their low energetic requirements [8]. Ion exchange membranes [9] and
5 other membrane processes like those shown in this work are examples of this tendency.
6 Liquid membrane technologies are an attractive alternative for chloride reduction in
7 salty water; it allows simultaneous extraction and stripping processes in the same stage,
8 non-equilibrium mass transfer, high selectivity and low solvent consumption.
9 In this study, we have worked with extraction using supported liquid membranes (SLM)
10 to reduce the chloride concentration in water up to the specification for drinking water
11 chloride contents. To achieve this goal, ammonium and phosphonium based ionic
12 liquids have been used as a carrier.

13 Ionic liquids (ILs) are compounds with an organic cation and either organic or inorganic
14 anions. They are very interesting because they remain liquid over a wide temperature
15 range including room temperature. The greatest advantage of the ILs is their practically
16 zero vapour pressure compared with the commonly used volatile organic solvents.
17 Actually the ILs can be designed for specific proposals, and their applications are
18 extended to different fields: media for green synthesis [10-12], CO₂ capture [13-18],
19 removal of fermentation products [19, 20] and pharmaceuticals [21], and as solvents or
20 extractants for liquid-liquid extraction [21-25] and hence, for supported liquid
21 membrane processes [26].

22 This work proposes an alternative solution to chloride ions reduction from brackish
23 water. The aim of this paper is to investigate the ability of hollow fiber renewal liquid
24 membrane technique use to desalt ground and superficial brackish water for drinking
25 and irrigation purposes.

31 **Experimental**

32 **Reactants**

33 Quaternary ammonium salt, Aliquat 336 (methyl trioctyl/decyl amine) and two other
34 phosphonium ionic liquids, Cyphos IL 101 (triethyl(tetradecyl)phosphonium chloride)
35 and Cyphos IL 167 (tributyl(tetradecyl)phosphonium chloride), supplied by Cytec
36 Industries Inc, were mixed with 10% decanol/kerosene (v/v) and used as extractants in
37 liquid extraction or as a carrier in the liquid membrane experiments. A mixture of 10%
38 decanol/kerosene (v/v) was the diluent used to prepare the organic phase.

39 Water with 1 g NaCl/L, has been used in the experiments because it is one of the most
40 commonly found concentrations.

41 Stock solution was prepared dissolving the adequate amount of NaCl in distilled water.
42 The stripping solution used was NaHCO₃. All the used reactives were analytical reagent
43 grade.

44 **Determination of the chloride concentration**

45 The concentration of Cl⁻ in the samples was determined by titration with AgNO₃ using
46 the potentiometric method. The potential has been measured using a Ag || Ag/AgCl
47 Crison 5260 electrode.

48 The AgNO₃ standard solution 0.02 M was previously standardized with a solution of
49 0.028 M NaCl (1000 mg/L Cl⁻). The experimental error did not exceed 2%.

Liquid liquid extraction

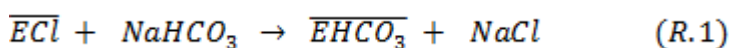
The anion exchange mechanism by liquid liquid extraction between the Cl^- in the water and the HCO_3^- in the ionic liquid molecules (E^+HCO_3^-) allows us to determine the viability of this operation.

The liquid liquid extraction by anion exchange was carried out in typical glass separatory funnels. Equal volume of the aqueous phase containing 1000 mg/L of Cl^- was mechanically shaken with the corresponding liquid ionic ($\text{R}_4\text{N}^+\text{HCO}_3^-$) phase in a SBS horizontal shaker at 140 rpm for 20 minutes at room temperature ($21 \pm 1^\circ\text{C}$). After separation of the phases, an aliquot of the aqueous phase was taken for chloride concentration analysis and the loaded organic phase was stripped with 0.9 M of NaHCO_3 solution.

Measuring the Cl^- concentration before and after the contact, made it possible to determine the extraction extension. The concentration of Cl^- in the stripping samples allows us to balance the mass and in this way corroborate the results.

R_4NHCO_3 and R_4PHCO_3 preparation

Preliminary conditioning of Aliquat 336, Cyphos IL 101 and Cyphos IL 167 (ECl) by contact with a NaHCO_3 solution allows us to generate the EHCO_3 molecule. A generalized chemical reaction associated with this exchange could be:



where E is the cationic part of each ionic liquid : (R_4N^+ or R_4P^+) and the bar denotes the compound present in the organic phase.

These new species provide us with the possibility to carry out the anion exchange between Cl^- and HCO_3^- . In this sense, successive contacts between the IIs, at different concentrations, and fresh solutions of NaHCO_3 0.9 M have been done. The aqueous phase was completely replaced after each step and the concentration of chloride anion was measured to know the remaining Cl^- in the organic phase. High concentration of HCO_3^- compared to IL concentration was used to assure maximum exchange in each step.

FSSLM transport

The flat sheet supported liquid membrane (FSSLM) is the simplest form of the liquid membrane. The support in FSSLM, as is well-known, must be on a porous and hydrophobic material, with good thermal stability and high chemical resistance to the organics used. The experimental setup consists of two acrylic cylindrical compartments, feed cell and receiving cell, with the hydrophobic support placed in between. Both aqueous solutions were mixed by mechanical stirrers. The support membrane was previously impregnated with the ionic liquid to be used as a carrier. Table 1 gives the characteristics of the polymeric support provided by Millipore.

Table 1.

The feed cell was filled with 210 mL of the solution of sodium chloride and the stripping cell with 210 mL of sodium bicarbonate solution. Chloride ions from the feed

1 phase are exchanged with the HCO_3^- of the membrane, this process takes place in the
2 feed-membrane interphase. After that, the ionic liquid loaded with Cl^- anions crosses the
3 membrane by a diffusional process. Finally, on the membrane-stripping interphase the
4 reverse exchange $\text{Cl}^-/\text{HCO}_3^-$ occurs. In this way, chloride anions are continuously
5 removed from the feed.

6 Samples from feed and receiving phases were withdrawn at regular time intervals, and
7 the evolution of the Cl^- concentrations was quantified.
8

9 HFRLM transport

10
11 Hollow fiber modules give a better ratio area transfer/volume. However, not all hollow
12 fiber membrane technologies are appropriate for this implementation, because
13 membrane stability is one of the most important problems with this kind of membrane.
14 The stability of the supported liquid membrane has been improved by using renewal
15 liquid membrane technique, where the diluted ionic liquid used as a carrier is mixed
16 with the stripping solution. While the feed flows along the shell side of the module, the
17 mixture of stripping phase and carrier flows along the lumen side, preventing any loss
18 of organic solution from the membrane pores.

19 The hollow fiber module used in the experimental part is a Liqui-Cel contactor (G-261).
20 The scheme of the experimental set-up and the operational mode was described by
21 Rathore et al. [27]. The characteristics of the hollow fiber module are provided in table
22 2.
23
24
25
26

27 Table 2.

28
29
30 The lab- scale plant worked with 5 litres of the feed solution containing 600 mg/L of the
31 Cl^- (from NaCl), this value is representative of river water with high salt content. The
32 stripping/organic emulsion was made up of an emulsion of HCO_3^- aqueous solution
33 (500mL) and the ionic liquid (50mL).
34

35 The stirred mixture of stripping and organic phase (aqueous/organic ratio 10:1) was
36 pumped through the lumen side of the module and the feed phase circulated through the
37 shell side. Both streams flow at 50 L/h and a low transmembranar pressure ($P_f - P_s = 0.2$
38 bar) between shell side and lumen side was applied in order to avoid the transfer of
39 organic phase to the feed reservoir.
40

41 The concentration of Aliquat 336 in the liquid membrane was changed after each
42 experiment. In order to assure the new liquid membrane concentration, it is necessary to
43 totally replace the IL present in the pores and to refill them with the IL at the required
44 concentration. Inverting the transmembranar pressure to 0.5 bar, the organic is forced to
45 cross the fibers to the feed flow. Taking into account that the total volume of the pores
46 is about 50 mL, when 150 mL of the ionic liquid appear in the feed tank, it means that
47 the pore liquid has been completely renewed and the membrane is ready for the next
48 run.
49

50
51 The small size of the module used, allows us to evaluate the transport performance of
52 the system without having to prepare large amounts of the dissolutions. The process
53 expects a reduction of the Cl^- in the feed phase up to adequate values and allows us to
54 concentrate (ten times) the Cl^- in the stripping compartment.
55
56

57 Experiments and results

58 59 Extraction equilibrium

60
61
62
63
64
65

The conditioning of Aliquat 336, Cyphos IL 101 and Cyphos IL 167 to produce the new ILs in bicarbonate form has been carried out at 0.36 and 0.18 M. As the exchange reaction is 1:1, the same concentrations of EHCO₃ IL have been obtained after the contacts. This is made clear because after the contacts, the sum of the accumulative chloride extracted was close to the initial IL concentration and it implies that all the Cl⁻ in this compound have been completely replaced by HCO₃⁻.

Figure 1 shows the evolution of the organic chloride fraction during the successive exchanges for a particular case of 0.36 M of Aliquat 336. As can be seen, eight contact steps are enough to exchange completely the Cl⁻ for HCO₃⁻. In every step, about 50% of the remaining chloride in the organic phase is transferred to the aqueous phase.

Figure 1.

By this procedure the IL EHCO₃ 0.36 M in 10% decanol/kerosene was produced and it will be used as a carrier in the liquid membrane. Similar behaviour was observed for the other commercial ionic liquids used in this study.

The liquid-liquid experiments provided details about the easiness of this exchange but, it is necessary to investigate the reversibility of the process too. In this sense, alternated contacts of NaCl (1000 mg Cl⁻/L) and NaHCO₃ (1 M) aqueous solutions with the organic phase were carried out.

The experiment contacts the ionic liquid in bicarbonate form (E⁺HCO₃⁻) conditioned previously with the solution of NaCl. Then the organic phase loaded with Cl⁻ was contacted with a fresh solution of NaHCO₃. This process has been repeated several times.

Figure 2 shows the reversibility of the Cl⁻/HCO₃⁻ exchange for Cyphos IL 101 0.18M in 10% decanol/kerosene. The figure shows the complete process: three conditioning steps (C1, C2, C3) from 6353 mg/L of Cl⁻ (0.18 M) of Cyphos IL 101 (C0) and six alternate exchange steps (E loading Cl⁻ and S loading HCO₃⁻).

Figure 2.

The results in figure 2 give information about the viability of using these compounds in an intensification membrane separation process because the two processes Cl⁻/HCO₃⁻ and HCO₃⁻/Cl⁻ are reversed and the effectiveness is maintained.

The liquid liquid extraction experiments have also been used to model the extraction exchange. The extraction equilibrium was planned taking into account the reaction R1 with the associated equilibrium constant:

$$K_{eq} = \frac{[EHCO_3][Cl^-]}{[ECl][HCO_3^-]} \quad (Eq. 1)$$

Knowing the concentration of chloride and bicarbonate added in each step and the initial concentration of the extractant species, it is possible to derive:

$$K_{eq} = \frac{([Cl^-]_0 + [Cl^-]_i) \cdot ([EHCO_3]_{i-1} + [Cl^-]_i)}{([ECl]_{i-1} - [Cl^-]_i) \cdot ([HCO_3^-]_0 - [Cl^-]_i)} \quad (Eq. 2)$$

1 Where:

2 i denotes the step number or the contact number and

3 $[Cl^-]_0 = 0$ for the conditioning and stripping steps

4 $[HCO_3^-]_0 = 0$ for the extraction steps

5
6
7 Supposing one K_{eq} value, the chloride aqueous concentration for every step can be
8 obtained by Eq. 2. This allows us to simulate the evolution of the Cl^-/HCO_3^- exchanged
9 for each value of the K_{eq} . Fitting the theoretical chloride concentration values with the
10 experimental ones, the equilibrium constant can be obtained.

11 The SOLVER macro of Excel software was used to minimize the error function defined
12 as:

13
14
15
16
17
$$Error = \sum_{i=1}^N ([Cl^-]_{theoric} - [Cl^-]_{experimental})_i^2 \quad (Eq.3)$$

18
19
20 The extraction equilibrium constants for the three ILs tested in this work are
21 summarized in table 3.

22 Table 3.

23
24
25
26 The equilibrium constant for Aliquat 336 is larger than that obtained by the Cyphos
27 ionic liquids tested. The methyl group in the structure of Aliquat 336 provides better
28 access for the anion exchange. The difference of the size between the groups, butyl
29 compared to hexyl in the Cyphos ILs can also explain the values of their constants.
30 Figure 3 allows us to visualize the concordance between the experimental and the
31 theoretical data obtained from the model when Aliquat 336 0.36 M was used. With the
32 equilibrium constant global process, conditioning, and alternated anion exchanges can
33 be simulated. The remaining chloride in the organic phase obtained using Cyphos IL
34 101 and Cyphos IL 167 fit as well as Aliquat 336 data.

35 Figure 3.

36 FSSLM

37
38
39
40
41
42
43 Some operational parameters like the ionic liquid used, its concentration, the chloride
44 concentration in the water to be treated, the concentration of bicarbonate as a counter-
45 ion have influence on the chloride reduction in the supported liquid membrane systems.
46 In order to analyze its effect on the mass transfer, a series of experiments using flat
47 sheet supported liquid membrane have been carried out.

48
49
50 Figure 4 compares the evolution of the remaining $[Cl^-]$ in the feed cell for all the ionic
51 liquids chosen. The experiments were carried out with a feed cell containing 1000 mg/L
52 of chloride and a receiving phase with 1M of bicarbonate.

53
54 No significant differences have been observed between Aliquat 336, Cyphos IL 101, or
55 Cyphos IL 167 at 0.18 M. In fact, all the ILs show the same behaviour.

56
57 Even knowing that Aliquat 336 has the most favourable equilibrium constant, the
58 cationic part of the IL seems not to have significant influence on the transport at these
59 operating conditions.

60
61
62
63
64
65

Figure 4.

In order to give quantitative information about the transport, the chloride flux must be determined. At working conditions, the mass balance can be written as eq 4. where the diminution of the $[Cl^-]$ in the feed cell is a consequence of the Cl^- transfer through the membrane.

$$V \frac{d[Cl^-]_f}{dt} = -J_{Cl^-} A \quad (Eq.4)$$

where:

$[Cl^-]_f$: concentration of Cl^- in the feed cell, mol/L

t: time, min

J_{Cl^-} : chloride flux, mol/min.m²

V: volume of feed cell, L

A: transfer area, m²

Taking into consideration that at these working conditions the evolution of the chloride concentration in the feed is practically linear, the flux through the SLM can be directly determined from the slope of this line. The obtained values of chloride flux for the Aliquat 336, Cyphos IL 101 and Cyphos IL 167 were very similar. All of them are about $1.53 \cdot 10^{-4}$ mol/min.m².

The influence of the ionic liquid concentration in the supported liquid membrane on the chloride feed reduction is visualized in figure 5. In this figure, the concentration of Aliquat 336 in the membrane was changed maintaining the concentration of Cl^- (1000 mg/L) and HCO_3^- (1 M) in the feed and the receiving cells respectively.

Figure 5.

Of course, more Aliquat 336 in the membrane facilitates the Cl^- transport through the membrane but this increase is not directly proportional to the IL concentration because the viscosity of the IL increases so much with the IL concentration. The chloride fluxes determined for these Aliquat 336 concentrations are shown in figure 8.

Results in figure 6 show the influence of the HCO_3^- concentration in the receiving cell on the chloride transport. The ionic liquid used as a carrier was 0.36 M Aliquat 336 in 10% decanol/kerosene and the feed cell was filled with 1000 mg Cl^- /L. The bicarbonate provides the driving force to control the mass transfer and hence lower concentrations of bicarbonate give slower transport.

Figure 6.

The experiments on FSSLM open the possibility of using the Aliquat 336, Cyphos IL101 and Cyphos IL 167 as carriers in the intensification membrane processes to reduce the chloride from the aqueous solutions.

HFRLM experiments

The experiments on hollow fiber modules working with renewal ionic liquid membrane technique have been carried out using Aliquat 336 as a transfer agent. Figure 7 shows

1 the evolution of the $[Cl^-]$ in the feed tank for various Aliquat 336 concentrations (0.09,
2 0.18, 0.27 and 0.36 M) mixed with a 0.9 M HCO_3^- stripping solution.

3 **Figure 7.**

4
5
6 The mass transfer velocity is faster at higher concentrations of Aliquat 336 but this
7 effect is dampened by the rise of the viscosity of liquid membrane. The chloride fluxes
8 determined are shown in figure 8. In comparison with the flux on SLM membranes
9 these values are bigger as a consequence of the membrane characteristics as the ratio
10 porosity/thickness.
11

12 **Figure 8.**

13
14
15 The circulation in closed loop along this membrane module (feed- membrane-feed, and
16 emulsion/membrane/emulsion) produces an accumulative effect in the stock tanks.
17 Because of this functioning, after a long operation time the $[Cl^-]$ in the feed tank
18 achieves a constant value (about 124 mg/L) and the chloride transfer is stopped due to
19 the high content of chloride in the stripping solution (about 4770 mg/L).

20
21 In figure 9, the influence of the bicarbonate concentration in the stripping solution,
22 between 0.2 and 0.9M, has been shown. In this case, the experiments were carried out at
23 constant concentration of the carrier (0.36M of Aliquat 336 in 10% decanol/kerosene).
24 As can be seen, higher concentration of bicarbonate in the receiving phase promotes
25 faster transport of chloride
26

27 The effect of accumulative mass in the stock tanks is also shown in figure 9 where the
28 concentration of Cl^- in the feed seems to be getting stabilized after a long running time.
29 The equilibration value obtained in each case is dependent on the bicarbonate
30 concentration used. The higher the bicarbonate concentration the lower the final value
31 of chloride concentration achieved.
32
33

34 **Figure 9.**

35
36
37 After one hour of operation time the reduction of the chloride concentration in the feed
38 is about 54%, 48% and 35% for 0.9, 0.5 and 0.2 M of bicarbonate.
39
40

41 **Conclusions**

42
43 Different ionic liquids, Aliquat 336, Cyanex IL 101 and Cyphos IL 167 have been
44 successfully used as ion-exchange extractants to reduce the chloride concentration in
45 water. Solvent extraction experiments have been designed to obtain equilibrium data
46 and to analyze the equilibrium behaviour. The reversibility of the Cl^-/HCO_3^- interchange
47 process has been verified.
48

49 Chloride anion can be effectively transported through the liquid membranes containing
50 Aliquat 336, Cyphos IL 101 or Cyphos IL 167 as carriers.
51

52 The chloride reduction efficiency of the process is higher than 80% after 4 hours of
53 running at the best working conditions.
54

55 Renewal ionic liquid membrane technology prevented the organic losses and allowed us
56 to increase the efficiency of the separation. This technique could be also applied to
57 exchange any other anion present in aqueous solutions choosing adequately the counter-
58 ion and the IL.
59
60
61
62
63
64
65

Acknowledgements

This work was supported by the Spanish Ministry of “Educacion, Cultura y Deporte” with grant number CTQ2011-22412. The authors also acknowledge Markus Hofmeister and Rafal Madaj’s contribution to the lab work.

References

- [1] M. Chapman, Evaluation of high productivity brackish desalination membrane, *Desalination* 308 (2013) 41-46.
- [2] M. Kurihara, M. Hanakawa, Mega-ton water system: Japanese national research and development project on seawater desalination and wastewater reclamation, *Desalination* 308 (2013) 131-137.
- [3] M.R. Otaishat, F. Banat, Desalination by solar powered membrane distillation systems, *Desalination* 308 (2013) 186-197.
- [4] X. Wang, L. Zhang, H. Yang, H. Chen, Feasibility research of potable water production via solar-heated hollow fiber membrane distillation system, *Desalination* 247 (2009) 403-411.
- [5] M. Rommel, M. Wieghaus, J. Koschikowski, Solar powered desalination: an autonomous water supply. *Desalination* 3 (2008) 22-24.
- [6] K.C. Ng, K. Thu, Y. Kim, A. Chakraborty, G. Amy, Adsorption desalination: an emerging low-cost thermal desalination method *Desalination* 308 (2013) 161-179.
- [7] K. Thu, Y. Kim, A. Myat, A. Charaborty, K.C. Ng, Performance investigation of advanced adsorption desalination cycle with condenser-evaporator heat recovery scheme, *Desalin. Water Treat.* (2012) 1-14.
- [8] E. Bringas, M.F. San Roman, J.A. Irabien, I. Ortiz, An overview of the mathematical modelling of liquid membrane separation processes in hollow fibre contactors. *J. Chem. Technol. Biotechnol.* 84 (2009) 1583-1614.
- [9] S. Fox, Z. Ronen, Y. Oren, J. Gilron, Treating ground water contaminated with high perchlorate concentrations by an ion exchange membrane bioreactor, *Procedia Engineering* 44 (2012) 809-811.
- [10] C.P. Mehnert, Supported ionic liquid catalysis, *Chem. Eur. J.* (2005) 50-56.
- [11] J.S. Wilkes, properties of ionic liquid solvents for catalysis, *J. Mol. Catal. A. Chem.* 214 (2004) 11-17.
- [12] M. Gamba, A.A.M. Lapis, J. Dupont, Supported ionic liquid enzymatic catalysis for the production of biodiesel, *Adv. Synth. Catal.* 350 (2008) 160-164.

1 [13] M.B. Shiflett, A.D. Shiflett, A. Yokozeki, Separation of tetrafluoroethylene and
2 carbon dioxide using ionic liquid, *Sep. Purif. Technol.* 79 (2011) 357-364.

3 [14] P. Scovazzo, D. Havard, M. McShea, S. Mixon, D. Morgan, Long-term, continuous
4 mixed-gas dry fed CO₂/CH₄ and CO₂/N₂ separation performance and selectivities for
5 room temperature ionic liquid membranes, *J. Membr. Sci.* 327 (2009) 41-48.

6 [15] W. Zhao, G. He, L. Zhang, J. Ju, H. Dou, F. Nie, C. Li, H. Liu, Effect of water in
7 ionic liquid on separation performance of supported ionic liquid membrane for CO₂/N₂,
8 *J. Membr. Sci.* 350 (2010) 279-285.

9 [16] J. Martak, S. Sshlosser, Extraction of lactic acid by phosphonium ionic liquids,
10 *Sep. Purif. Technol.* 57 (2007) 483-494.

11 [17] S. Yoo, J. Won, S.W. Kang, Y.S.Kang, S. Nagase, CO₂ separation membranes
12 using ionic liquids in a Nafion matrix, *J. Membrane Sci.* 363 (2010) 72-79

13 [18] J. Albo, P. Luis, A. Irabien, Carbon dioxide capture from flue gases using a cross-
14 flow membrane contactor and the ionic liquid 1-ethyl-3-methylimidazolium
15 ethylsulfate, *Ind. Eng. Chem. Res.* 49 (2010) 11045-11051.

16 [19] H.R. Cascon, S.K.Choudhari, G.M. Nisola, E.L. Vivas, D-J Lee, W-J Chung,
17 Partitioning of butanol and other fermentation broth components in phosphonium and
18 ammonium -based ionic liquids and their toxicity to solventogenic clostridia, *Sep.*
19 *Purif. Technol.* 78 (2011) 164-174.

20 [20] N. Kouki, R. Tayeb, R. Zarrougui, M. Dhabi, Transport of salicylic acid through
21 supported liquid membrane based on ionic liquids, *Sep. Purif. Technol.* 76 (2010) 8-14.

22 [21] A. Rout, S. Karmakar, K.A. Venkatesan, T.G. Srinivasan, P.R. Vasudeva Rao,
23 Room temperature ionic liquid diluents for the mutual separation of europium (III) from
24 americium(III), *Sep. Purif. Technol.* 81 (2011) 109-115.

25 [22] X. Sun, Y. Ji, L. Guo, J. Chen, D. Li, A novel ammonium ionic liquid based
26 extraction strategy for separating scandium from yttrium and lanthanides, *Sep. Purif.*
27 *Technol.* 81 (2011) 25-30.

28 [23] Y.-H. Kim, Y.-K. Choi, J. Park, S. Lee, Y.-H. Yang, H. J. Kim, T-J, Park, Y. H.
29 Kim, S. H. Lee, Ionic liquid-mediated extraction of lipids from algal biomass,
30 *Bioresource Technology* 109 (2012) 312-315

31 [24] M.F. San Roman, E. Bringas, R. Ibañez, I. Ortiz, Liquid membrane technology:
32 fundamentals and review of its applications, *J. Chem. Technol. Biotechnol.* 85 (2010) 2-
33 10.

34 [25] M. Regal-Rosocka, Extractive removal of zinc(II) from chloride liquors with
35 phosphonium ionic liquids/toluene mixtures as novel extractants, *Sep. Pur. Thecn.* 66
36 (2009) 19-24

[26] R.D. Noble, D.L. Gin, Perspective on ionic liquids and ionic liquid membranes, J. Memb. Sci. 369 (2011) 1-4.

[27] N.S. Rathore, A. Leopold, A.K. Pabby, A. Fortuny, M.T. Coll, A.M. Sastre, Extraction and permeation studies of Cd(II) in acidic and neutral chloride media using Cyanex 923 on supported liquid membrane, Hydrometallurgy 96 (2009) 1-4.

1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
19
20
21
22
23
24
25
26
27
28
29
30
31
32
33
34
35
36
37
38
39
40
41
42
43
44
45
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60
61
62
63
64
65

1
2
3 **Figure captions**

4
5 Figure 1. Remaining chloride in the organic phase during successive contacts from 0.36
6 M Aliquat 336.

7
8 Figure 2. Reversibility of the $\text{Cl}^-/\text{HCO}_3^-$ exchanges for 0.18 M Cyphos IL.

9
10
11 Figure 3. Experimental and theoretical data for the production of R_4NHCO_3 from 0.36
12 M of Aliquat and the successive $\text{HCO}_3^-/\text{Cl}^-$ exchanges.

13
14 Figure 4. Evolution of the chloride remaining in the feed cell for the three ILs tested.

15
16 Figure 5. Effect of Aliquat concentration (Feed 1000 mg Cl^-/L , Stripping 1M NaHCO_3)

17
18
19 Figure 6. Effect of NaHCO_3 concentration on the transport. (Aliquat 0.36 M, Feed 1000
20 mg Cl^-/L)

21
22
23 Figure 7. Influence of the Aliquat 336 concentration on the chloride transport in
24 FSSLM. Stripping phase was 0.9 M of NaHCO_3

25
26
27 Figure 8. Effect of the concentration of the carrier (Aliquat 336) on the chloride flux.

28
29
30 Figure 9. Influence of bicarbonate concentration in the stripping phase on the chloride
31 transferred. Aliquat 336 0.56M in 10% decanol/kerosene was used as carrier.

32
33
34
35
36
37
38
39
40
41
42
43
44
45
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60
61
62
63
64
65

Table 1. Characteristics of the polymeric support Durapore GVHP04700

material	PVDF
pore diameter	45 μ m
porosity	75%
thickness	125 μ m
effective area	11.4 cm ²

Table 2. Details of hollow fiber membrane module

Module diameter (cm)	8
Module length (cm)	28
Cartridge configuration	Extra-flow with centre baffle
Membrane surface area (m ²)	1.4
Porosity (%)	40
OD/ID (μm)	300/220
Membrane/potting material	PP/PE
Hold-up volume shell side, mL	400
Hold-up volume side, mL	150

Table 3. Equilibrium constants values for the IL

IL	K_{eq}
Aliquat 336	0.210
Cyphos IL 101	0.097
Cyphos IL 167	0.166

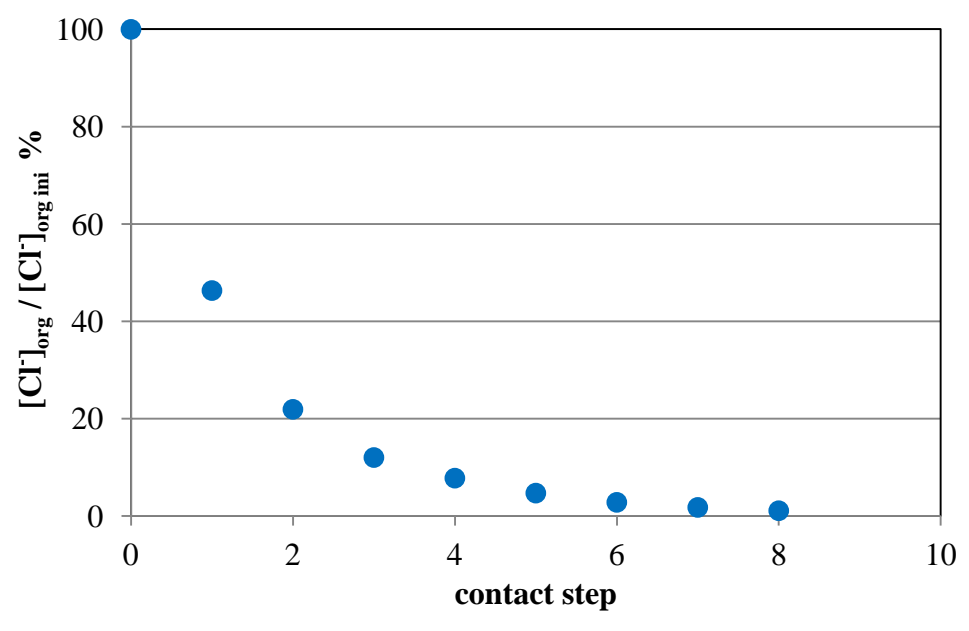


Figure 1

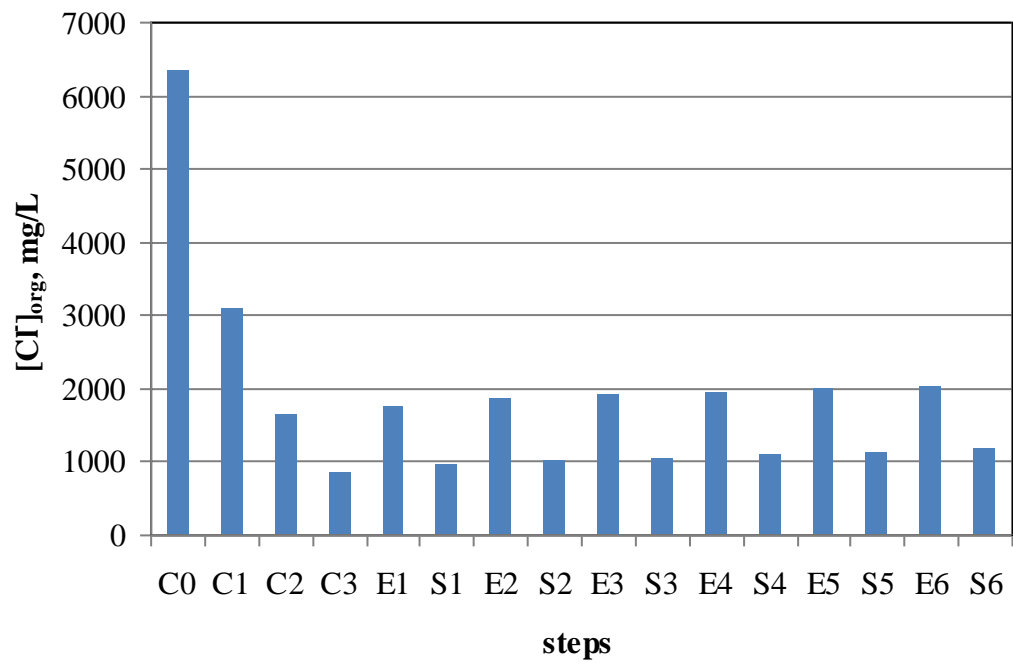


Figure 2

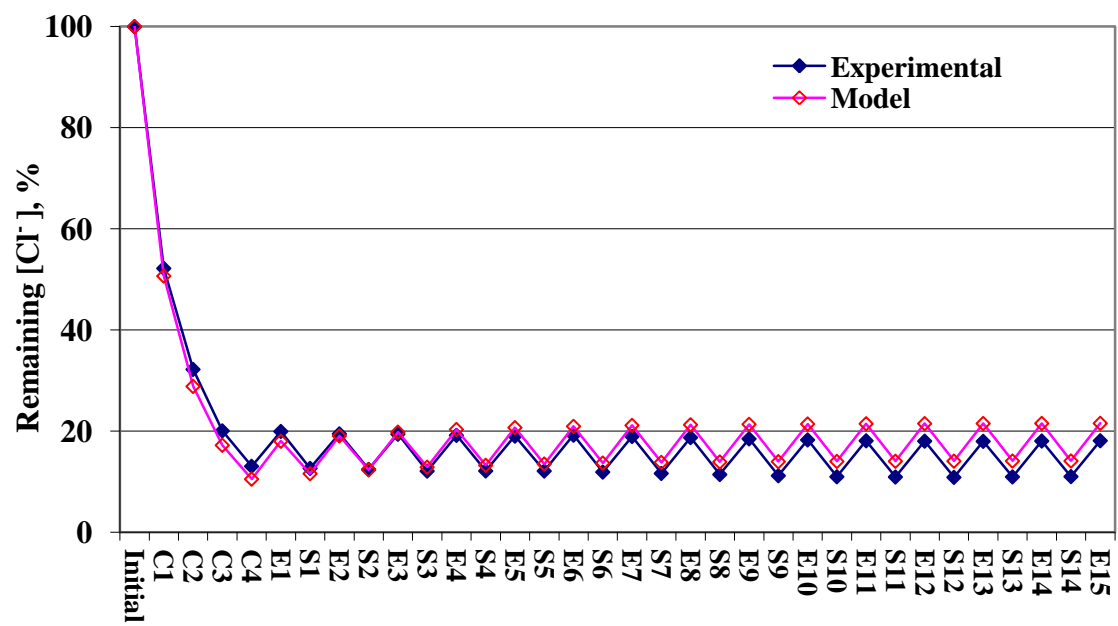


Figure 3

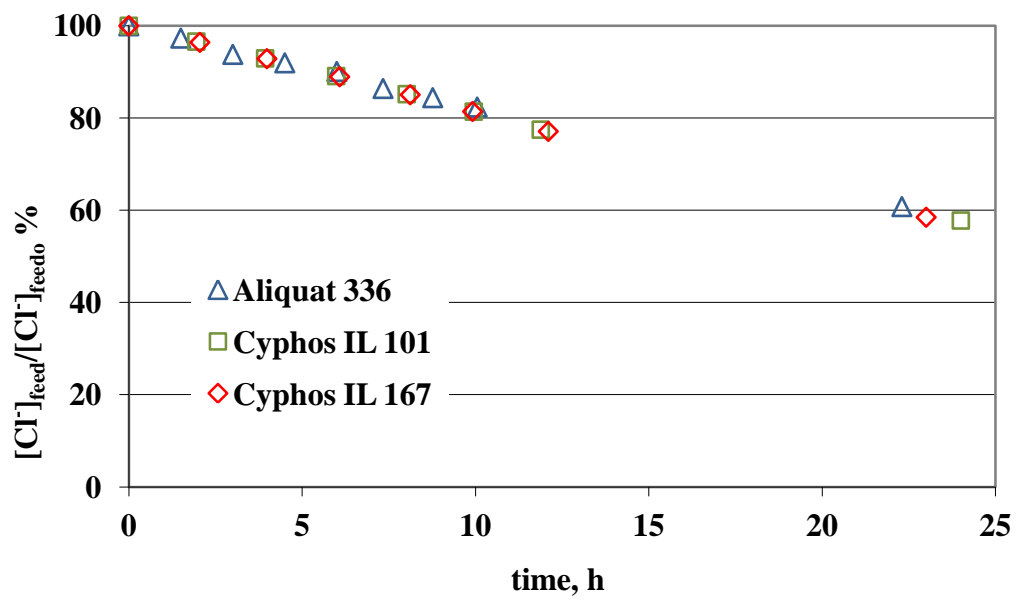


Figure 4

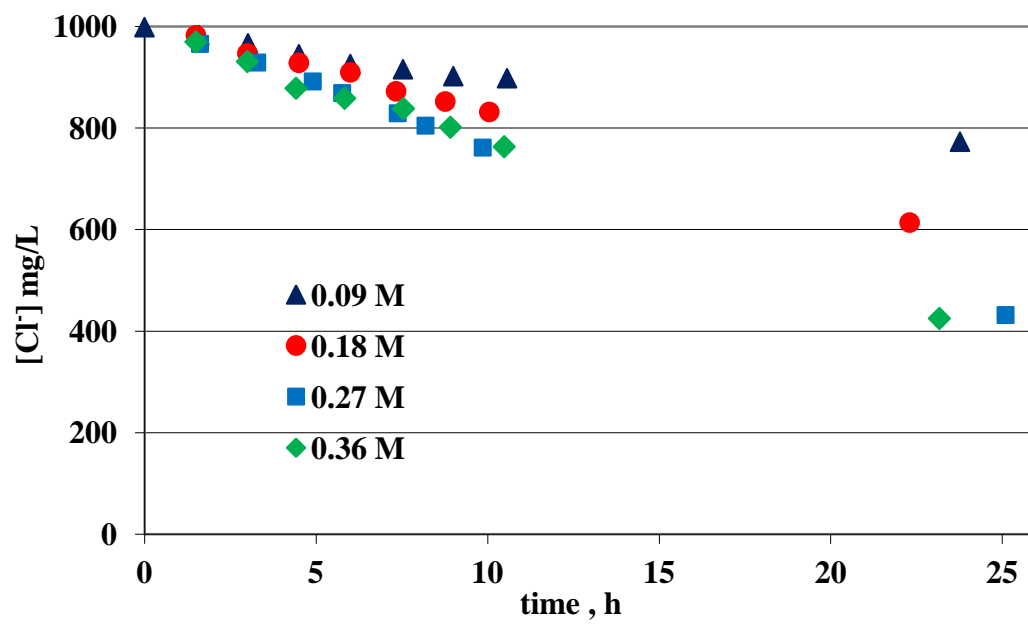


Figure 5

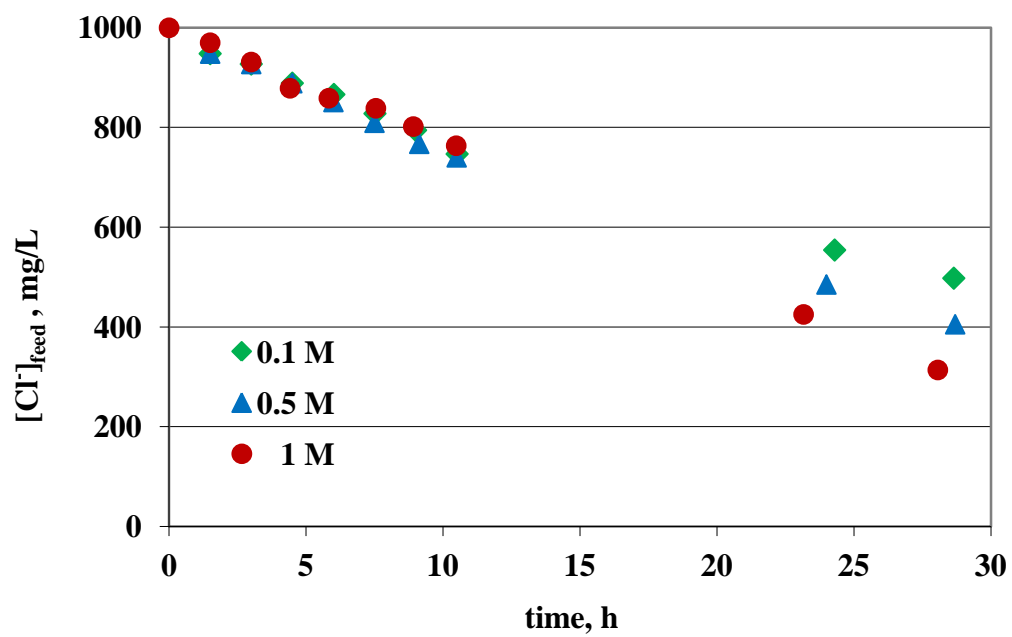


Figure 6

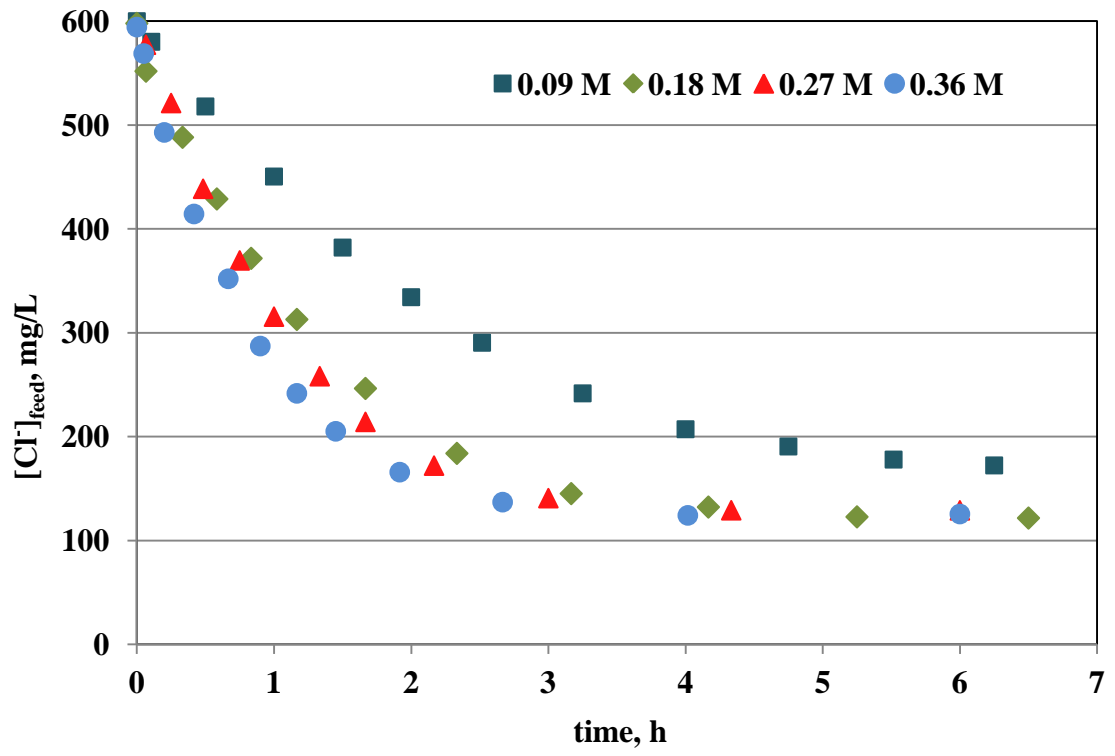


Figure 7

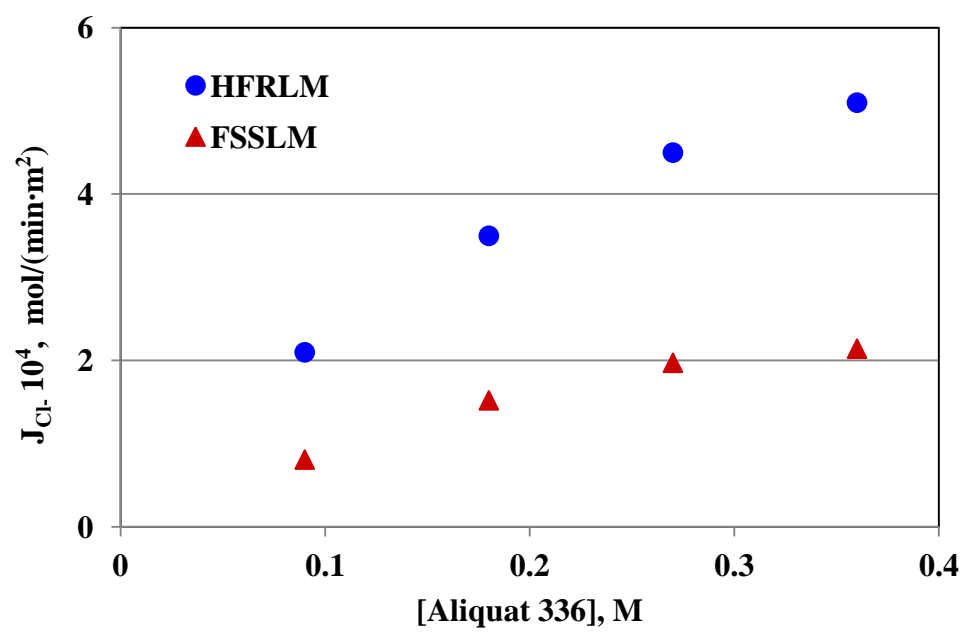


Figure 8

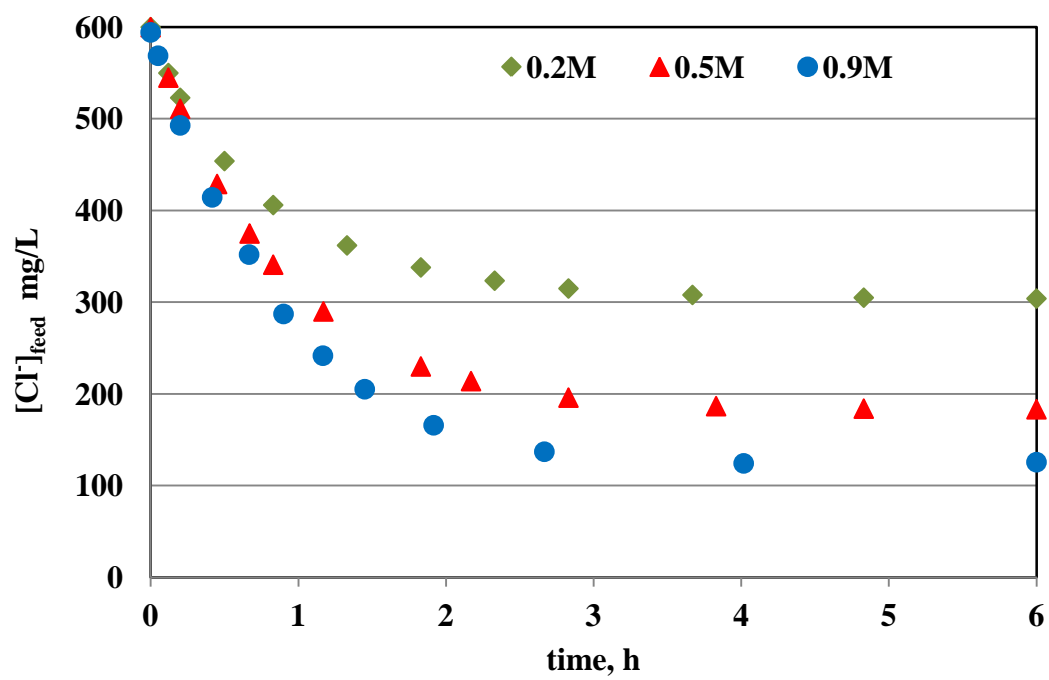


Figure 9