



# Fluoride removal from natural waters by polymer inclusion membranes

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## ABSTRACT

A polymer inclusion membrane (PIM) containing commercial ionic liquid methyltrioctylammonium chloride (Aliquat 336) as a carrier and cellulose triacetate (CTA) as a base polymer has been used for the first time to remove fluoride from natural waters. Due to the anion-exchange characteristics of the carrier, a 1 M NaCl solution has been used as a receiving phase. It has been found that the addition of tributyl phosphate (TBP) in the formulation of the PIM increased the membrane's performance. Several parameters have been investigated using a PIM made of 30% CTA, 50% Aliquat 336, and 20% TBP (% in mass) including the effect of other ions such as chloride and sulphate and the effect of pH. Only when the feed phase contains high amounts of chloride (concentration 10 times higher than fluoride) a slight decrease on PIM's efficiency is observed (85% defluoridation).

The separation system developed here has been used satisfactorily for fluoride removal from different naturally occurring waters. Moreover, the membrane's reusability has also been investigated, showing that the membrane can be used for four cycles without loss of efficiency in removing fluoride.

## 1. Introduction

Fluoride water pollution from natural geological sources has been recognized as a worldwide problem in many areas of the world [1,2], and the content found depends on the geology, chemistry, physical characteristics, and the climate of the area. Besides the release of fluoride into groundwater by the slow dissolution of fluorine-containing rocks, various industries such as glass and ceramic production, electroplating, and semiconductor manufacturing can also contribute to fluoride pollution to a great extent through the discharge of wastewaters [3].

Even though the ingestion of small amounts of fluoride through water is usually considered to have a beneficial effect on human health, it is well known that an excess intake leads to various diseases including embrittlement of bones, effects on thyroid activity, and neurological damage, in severe cases [4].

The World Health Organization (WHO) has set the maximum permissible limit of fluoride in drinking water at 1.5 mg L<sup>-1</sup> [5], which is far below the concentrations found in several water sources around the globe. Some East African countries exhibit high fluoride content in natural waters, with values of 250 mg L<sup>-1</sup> in groundwater in the Shinyanga region and 528 mg L<sup>-1</sup> in the Arumeru District lakes in Tanzania. Furthermore, other countries such as China, India, and Mexico are also particularly vulnerable to fluoride contamination [6,7]. In our own area of Girona (North-East Spain), many people are often exposed to fluoride

content that is above the permissible limit (EU directive adopted the value of 1.5 mg L<sup>-1</sup> for fluoride in drinking water) mainly in dry periods of the year.

Given the need to tackle the toxicity of fluoride and how widespread excess content is, different defluoridation techniques of natural waters have been developed. Recently, C.F.Z. Lacson et al. [6] reviewed existing fluoride removal technologies, finding that the most popular were sorption, precipitation/crystallization, membranes, hybrid treatments, and bioremediation. Amongst these, sorption and precipitation processes are conventional techniques that have simple methodologies but which have a high consumption of reagents [3]. On the other hand, separation with membranes is a one-step technique that is easy to operate and with very low chemical usage that has shown to effectively remove fluoride even at low concentrations. Recently, M.M. Damtie et al. have extensively reviewed the performance of various membrane processes for the removal of fluoride in water and wastewater technologies [8]. Generally, nanofiltration (NF) and reverse osmosis (RO) are the most established membrane processes for defluoridation [9–12]. Water permeation of NF/RO is a pressure-driven membrane process that is widely used both in drinking water production and wastewater treatment. Pressure exerted on the solution at one side of the membrane acts as a driving force to separate into a permeate and a retentate. RO is highly efficient in rejecting fluoride but the extremely high pressure required gives it a correspondingly high operational cost. NF, with larger

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pores, requires lower pressure.

Electrodialysis (ED) is an electro-membrane process in which ionic substances are removed from aqueous solutions by ion exchange membranes using electricity as the driving force. In this case, instead of having hydraulic pressure as the driving force, ED uses an applied electric field and/or the Donnan effect. ED is a well-established technique for water desalination and salt production and is also used for the treatment of water with high levels of contaminants. ED using anion exchange membranes has successfully been used for defluoridation processes [13,14].

Donnan dialysis (DD) is another membrane-based equilibrium process that exchanges ions between two solutions separated by a semi-permeable membrane. The driving force for the transport of ions is the difference in their concentrations between the two solutions. Although DD has slow kinetics compared to ED, it is more economic, energy-saving, and only needs simple technology [15]. DD using anion exchange membranes with quaternary ammonium groups has successfully been used for the removal of fluoride from water. Usually, NaCl solutions, alone or in combination with aluminium salts, have been used as the receiving phase [16–18].

The use of polymer inclusion membranes (PIMs) can be an attractive alternative to DD, maintaining the simplicity and minimum energy requirement, but with an increase in the kinetics of operation. PIMs are a type of functionalized membrane that can be tailor-made for the target analyte to be removed and that support separation based on chemical reactions. These membranes are easily prepared by the solvent casting method by mixing a proper polymer (for instance, cellulose triacetate (CTA) or polyvinyl chloride (PVC)) with an extractant (called a carrier), which is responsible for the interaction with the analyte. Depending on the nature of the carrier, different extraction mechanisms are possible, such as ion exchange or chelation. Therefore, the analyte and the carrier form a hydrophobic ion-pair or a complex that is able to diffuse through the membrane. Using an appropriate receiving solution, the analyte will then be released, and the carrier will again be able to repeat the transport process. The net result of this process is the removal of the analyte from its source.

There are many compounds that can act as carriers in PIMs, and, in principle, all the extractants used in solvent extraction may be suitable carriers. The choice of the appropriate carrier depends on the characteristics of the analyte to be transported. When the target species is an anion, such as fluoride, suitable extractants are those able to form ion-pairs. This is the case of the ionic liquid (IL) Aliquat 336, a commercial quaternary ammonium salt mainly composed of trioctylmethyl ammonium chloride which exchanges the chloride anion by other anions present in the aqueous solution. As an example, Aliquat 336 incorporated in PIMs has successfully been used for the transport of metallic species (such as  $\text{CdCl}_3^-$  [19],  $\text{PtCl}_4^{2-}$  [20],  $\text{Cr(VI)}$  [21]); anions (as  $\text{HAsO}_4^{2-}$  [22], orthophosphate [23]), and also organic molecules such as antibiotics [24]. In many studies, the affinity of PIMs made of Aliquat 336 towards different anions has been explored, but until now, the extraction of fluoride using this carrier has not been reported.

Plasticizers are also sometimes added to the formulation of PIMs. Nowadays, it is accepted that the role of the plasticizer on PIMs affects both the physical and chemical properties of the membrane. Initially plasticizers were added to the formulation of PIMs to separate the chains of the polymer, so improving the flexibility of the membrane. However, it has been proved that the addition of plasticizers in PIMs does not only affect their mechanical properties but can also sometimes lead to an improvement in transport. Plasticizers can act as a solvating medium of carriers, creating continuous pathways between the two interfaces of the membrane through which the species can diffuse. Fontàs et al. [25] demonstrated using different characterization techniques that the addition of a plasticizer to a PIM made of CTA and Aliquat 336 acted as a solvent and constituted a medium for the extractant mobility within the CTA polymer. Several plasticizers with different chemical structures, dielectric constants, and viscosities have been used to produce PIMs. The

most common plasticizer used in PIMs is 2-nitrophenyloctyl ether (NPOE), but others, such as bis(2-ethylhexyl) adipate (DEHA), dibutylphthalate (DBP), dibutylsebacate (DBS), and tributyl phosphate (TBP) [26] are also used.

In the present study, we report, for the first time, the use of a PIM containing Aliquat 336 for the removal of fluoride from natural waters with special emphasis on membrane composition and water characteristics. The developed PIM system has been tested for its ability to remove fluoride from different naturally occurring fluoride waters and for its reusability. To the best of our knowledge, this is the first study on the use of this simple and affordable functionalized membrane for the removal of fluoride.

## 2. Materials and methods

### 2.1. Reagents and solutions

A stock solution ( $1000 \text{ mg L}^{-1}$ ) of fluoride from Merck (Darmstadt, Germany) was used to prepare the calibration standards. NaF, NaCl, and HCl, purchased from Panreac (Castellar del Valles, Spain), and  $\text{Na}_2\text{SO}_4$ , from Merck (Darmstadt, Germany), were used to prepare the working and the receiving solutions.

For the preparation of the PIMs, the followings reagents were used: the extractant Aliquat 336, the plasticizers NPOE, DBS, and TBP, and the organic solvent chloroform ( $\text{CHCl}_3$ ), all purchased from Sigma-Aldrich (Saint Louis, Missouri, USA), and the polymer CTA, from Acros Organics (Geel, Belgium).

All reagents and solvents were of analytical grade and the ultrapure water used to prepare the aqueous solutions was obtained using the Milli-Q Plus water purification system (Millipore Ibérica S.A., Barcelona, Spain).

### 2.2. Instruments and analysis

Total fluoride in the feed and the receiving phase was determined potentiometrically using a fluoride combination ion-selective electrode (ISE), ISE F-9655C model (Hach Lange, Hospitalet de Llobregat, Spain), and the ionic strength was adjusted, when necessary, with 1 M NaCl. In experiments where the pH was evaluated, TISAB solution (Merck, Darmstadt, Germany) was used. The ionic composition of the water samples was determined by ion chromatography (IC) DIONEX IC5000 equipped with an autosampler AS-AP, and a conductivity detector. The columns used were an IonPac® AS18 anion-exchange column ( $4 \times 250 \text{ mm}$ ) with the AG Guard column ( $4 \times 50 \text{ mm}$ ) for anions and a IonPac® CS16 cation-exchange column ( $4 \times 250 \text{ mm}$ ) with the CG16 Guard columns ( $4 \times 50 \text{ mm}$ ) for cations. When needed, fluoride content was also analysed by IC. The pH and the conductivity values were determined with a Crison Model GLP 22 pH meter (Barcelona, Spain) and Ecosan, Entech Instruments, portable conductivity meter (Katey, Texas, EEUU), respectively.

PIM thickness was measured using a Digimatic Micrometer (Mitutoyo, Tajatsu-ku, Japan).

The scanning electron microscopy (SEM) observations were made using a field emission with a field emission electron source (FE-SEM) Zeiss, model DSM 960 A (Germany). The samples were placed on a stub and coated with carbon (model K950 turbo evaporator, Emitech, Germany).

### 2.3. Preparation of PIMs

PIMs were prepared by the solvent casting method as reported in Vázquez et al. [27] with some modifications. Briefly, the appropriate amount of CTA was dissolved in 15 mL of chloroform and left in contact 5 h under continuous magnetic agitation. After this, the carrier (Aliquat 336) and, when needed, plasticizers (TBP, NPOE, or DBS), were added to the chloroform solution and mixed again for 1 h. This solution was then

poured into a 7.0 cm diameter flat-bottom glass Petri dish which was set horizontally and covered loosely. The solvent was allowed to evaporate over 24 h at room temperature and then the resulting film was carefully peeled off the bottom of the Petri dish. Table 1 collects the composition (% mass) of the PIMs tested in this study and the amount of each component needed for the preparation. The resulting membranes showed a similar thickness ( $55 \pm 2 \mu\text{m}$ ).

#### 2.4. Fluoride transport experiments

A two-compartment transport cell described elsewhere [28] was used to study the effectivity of the PIMs in removing fluoride. The exposed membrane area was  $11.4 \text{ cm}^2$  which contacted both the feed phase, on one side, and the receiving phase, on the other (190 mL each). As a feed phase, solutions usually containing  $10 \text{ mg L}^{-1}$  fluoride in ultrapure water or natural waters spiked at this level were used for the evaluation of parameters affecting the fluoride removal experiments using PIMs. To evaluate the effect of chloride and sulphate, solutions with  $10 \text{ mg L}^{-1}$  fluoride (i.e., 0.5 mM) and 35–350  $\text{mg L}^{-1}$  of chloride (i.e., 1–10 mM) or 10–96  $\text{mg L}^{-1}$  of sulphate (i.e., 0.1–1 mM) were also prepared in ultrapure water. The effect of pH between 2 and 7 was investigated by adding HCl to the feed solution. The receiving phase composition was set to 1 M NaCl, except when evaluating the effect of its concentration. These solutions were continuously stirred using a magnetic multistirrer KS 260 basic (IKA, Staufen, Germany) and samples were withdrawn at regular time intervals during the 24 hours of the experiment to follow the transport profile. Experiments were performed at room temperature ( $22 \pm 1 \text{ }^\circ\text{C}$ ) and in duplicate as a minimum.

#### 2.5. Description of transport kinetics

Different authors have proposed mathematical models to explain the transport of different substances across a membrane [29,30]. Transport description can be expressed by the initial flux,  $J$  ( $\text{mol m}^{-2} \text{ s}^{-1}$ ). From the slope of the straight line obtained when representing the metal concentration in the receiving phase in function of time (during the first 3 h of the experiment), the initial flux can be calculated according to the following equation (1):

$$J = - \frac{d[F]_{r,t}}{dt} \frac{V}{A} \quad (1)$$

Where  $[F]_{r,t}$  denotes the fluoride concentration in the receiving phase at a given time (t), V the volume of the stripping solution, and A the area of the used membrane.

The effectivity of the PIM in removing fluoride from the water was calculated using the removal efficiency (RE), defined by Eq. (2) and calculated after 24 h:

$$RE = \frac{[F]_{r,t}}{[F]_{f,0}} \times 100 \quad (2)$$

Where  $[F]_{f,0}$  is the initial fluoride concentration in the feed phase.

**Table 1**

PIM composition expressed in % mass. The amount of each component is indicated in parentheses.

Membrane	% CTA	% Aliquat 336	% Plasticizer
50/50/0	50 (0.155 g)	50 (0.155 g)	–
50/0/50-TBP	50 (0.155 g)	–	50 (0.155 g)
30/50/20-TBP	30 (0.093 g)	50 (0.155 g)	20 (0.062 g)
20/50/30-TBP	20 (0.062 g)	50 (0.155 g)	30 (0.093 g)
30/40/30-TBP	30 (0.093 g)	40 (0.124 g)	30 (0.093 g)
30/50/20-DBS	30 (0.093 g)	50 (0.155 g)	20 (0.062 g)
30/50/20-NPOE	30 (0.093 g)	50 (0.155 g)	20 (0.062 g)

#### 2.6. Water samples

Waters with different fluoride contents and sources were used. These were tap water (obtained from Girona, Spain), two kinds of bottled mineral water (labelled as Mineral-1 and Mineral-2), and different waters naturally containing fluoride. These waters were used to evaluate the effectiveness of the developed separation system. Natural waters were collected at different locations in North-East Catalonia (Spain). Two of these locations were at the town of Santa Coloma de Farners ( $41^\circ 51' 08.3'' \text{ N}$ , and  $2^\circ 40' 09.2'' \text{ E}$  as the sampling georeferenced point): one corresponds to spring water (labelled as Spring Water), and the other is groundwater taken from the Sant Salvador spring (labelled as Groundwater). Another sample was from a hot spring ( $60 \text{ }^\circ\text{C}$ ) from Caldes de Malavella (labelled as Hot Spring Water) ( $41^\circ 50' 12.8'' \text{ N Lat.}$ , and  $2^\circ 48' 30.7'' \text{ E long.}$  as the sampling georeferenced point). The main chemical characteristics of the different water types used are shown in Table 2.

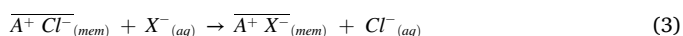
### 3. Results and discussion

#### 3.1. Fundamentals of fluoride transport

As stated in the introduction, the carrier Aliquat 336 can extract anions by an ion-exchange mechanism. This reaction can easily take place when the anion to be extracted has a higher affinity for the cationic part of Aliquat 336 (the trioctylmethyl ammonium cation) than chloride. Several authors have investigated the ion-exchange capacity of PIMs containing this IL for different anions. S. Kagaya et al. [31] used a PIM made of 60% PVC and 40% Aliquat 336 (expressed in % mass) to evaluate the extraction of nitrate and sulphate by immersing a piece of PIM in 10 mM  $\text{NaNO}_3$  and 10 mM  $\text{Na}_2\text{SO}_4$  solutions. In both cases, a near stoichiometric ion-exchange reaction was found, showing the high affinity of Aliquat 336 for these anions. Similar results were observed for the anions  $\text{CH}_3\text{COO}^-$ ,  $\text{ClO}_4^-$ , and  $\text{SCN}^-$  [32] using a membrane composed of 70% PVC, 20% Aliquat 336, and 10% 1-tetradecanol (expressed in % mass). Kumar et al. [33] studied the diffusional transport of the anions  $\text{I}^-$ ,  $\text{NO}_3^-$ ,  $\text{SO}_4^{2-}$ ,  $\text{Cl}^-$ , and  $\text{ClO}_4^-$  by equilibrating PIMs made of Aliquat 336, CTA, and incorporating various plasticizers, specifically, NPOE, tris (2-ethylhexyl)-phosphate (TEHP), and dioctyl phthalate (DOP) with 0.1 M aqueous salt solutions containing relevant anions. The quantitative displacement of anions in the membrane samples was monitored by using  $^{131}\text{I}$  as a radiotracer. It was demonstrated that the self-diffusion mobility of the  $\text{I}^-$  ions was affected by the plasticizer used in the preparation of the PIM and also that the amount of the carrier and the nature of the plasticizer play an important role in the transport process in this type of membranes. However, none of these studies investigated the possibility of exchanging chloride for fluoride. Sodaye et al. [34] used a PIM made of Aliquat 336, CTA, and NPOE to evaluate the selectivity coefficients of monovalent anions in anion-exchange PIMs. First, Aliquat 336 in  $\text{I}^-$  form was prepared and, afterwards, it was placed into contact with solutions containing several anions including fluoride. It was found that for a large number of anions the selectivity with respect to  $\text{I}^-$  was very low. This was the case of  $\text{F}^-$ ,  $\text{OH}^-$ ,  $\text{HCO}_3^-$ ,  $\text{CH}_3\text{COO}^-$  and  $\text{IO}_3^-$ , showing that extraction was not possible.

Even though the affinity of Aliquat 336 towards fluoride seems to be low, when this IL acts as a carrier in a PIM, the transport process can be possible using a highly concentrated saline solution as a receiving phase (a 1 M NaCl solution in this study). Aliquat 336 will pump chloride ions from the receiving phase to the feed phase until equilibrium is reached at the two membrane interfaces. In this process, anions present in the feed phase will be transported to the receiving phase.

Hence, at the interface feed solution-PIM, the extraction reaction takes place as shown in Eq. (3):

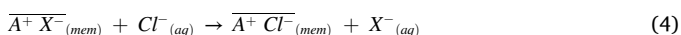


**Table 2**Chemical characteristics of water samples used in this study. Conductivity values are expressed in  $\mu\text{S cm}^{-1}$  while ions concentrations are in  $\text{mg L}^{-1}$ .

Water	Conductivity	pH	[Na <sup>+</sup> ]	[Mg <sup>2+</sup> ]	[Ca <sup>2+</sup> ]	[K <sup>+</sup> ]	[Cl <sup>-</sup> ]	[SO <sub>4</sub> <sup>2-</sup> ]	[HCO <sub>3</sub> <sup>-</sup> ]	[F <sup>-</sup> ]
Tap Water	170	7.71	14.6	9.2	52.2	2.8	22.5	42.0	64	0.1
Mineral-1 Water	239	7.89	8.0	6.1	27.9	1.2	4.4	9.6	114	0.7
Mineral-2 Water	1353	6.67	507.1	27.6	49.0	17.5	167.7	69.3	1550	2.5
Spring Water	399	8.09	115.1	0.6	9.5	3.6	58.6	97.0	116	9.6
Groundwater	115	6.62	24.6	2.2	12.7	1.7	15.7	3.7	76	1.6
Hot Spring Water	2793	7.55	1178.5	8.8	10.3	52.6	630.3	45.8	2037	8.8

Where  $\text{A}^+\text{Cl}^-$  is Aliquat 336 and  $\text{X}^-$  is a general representation for anions present in the feed phase (fluoride or other possible anions). It should be taken into account that in the case of divalent anions, such as sulphate, for example, the stoichiometry of the reaction is 2:1 (Aliquat 336:  $\text{SO}_4^{2-}$ ).

Similarly, at the interface of the receiving phase, the back-extraction reaction can be represented as Equation (4).



Hence, Aliquat 336 can diffuse back to the interphase of the feed phase and repeat the process.

A schematic diagram of this transport process for fluoride is shown in Fig. 1.

### 3.2. Effect of PIM composition

Membrane composition has a central role in the transport process. For this, we evaluated the transport of fluoride using a PIM made of CTA and Aliquat 336 (50/50/0), and also PIMs containing this reagent as well as plasticizers. In this latter case, in order to evaluate the nature of the plasticizer, the amount of Aliquat 336 was maintained at 50%, while CTA was lowered to 30% and the plasticizers NPOE, DBS, and TBP were 20% (30/50/20-NPOE; 30/50/20-DBS and 30/50/20-TBP PIMs, respectively). These plasticizers exhibit different viscosity and dielectric constant values, as shown in Table 3 (data from Pabby et al., 2015).

All the prepared membranes were flexible and mechanically stable, with a similar thickness (about 55  $\mu\text{m}$ ). PIMs made of only CTA and Aliquat 336 (50% each component) are known to be homogeneous and non-porous, as shown in Vera et al. [35]. The morphological characterization of the new PIMs 30/50/20-NPOE, 30/50/20-DBS, and 30/50/20-TBP was also investigated (Fig. 2). The surface images (Fig. 2 a-c) revealed that all membranes present a uniform surface with no apparent porosity. Cross-section images of the membranes (Fig. 2 d-e) showed a homogeneous and dense structure.

Therefore, all the PIMs were tested for the fluoride transport using a feed solution of 10  $\text{mg L}^{-1}$  of  $\text{F}^-$  in ultrapure water. The transient concentration curves for each PIM composition are shown in Fig. 3.

As can be observed, even though the PIM without any plasticizer (*i.e.* 50/50/0) is able to quantitatively remove fluoride after 24 h of

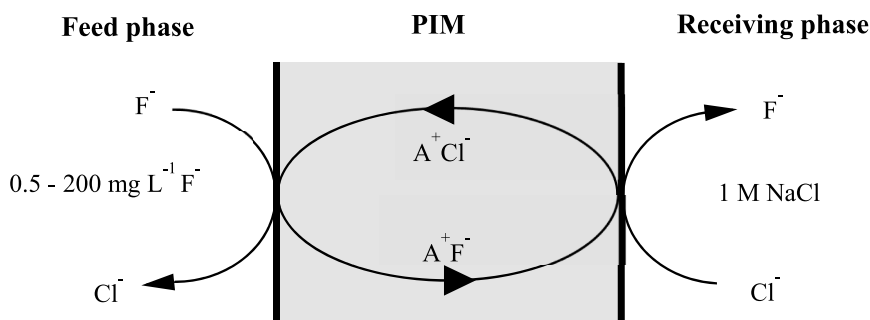
**Table 3**Effect of membrane composition (CTA/Aliquat 336/Plasticizer) on initial J and RE (%). Feed solution: ultrapure water with 10  $\text{mg L}^{-1}$   $\text{F}^-$ ; receiving solution: 1 M NaCl.

Plasticizer	Membrane	J ( $\times 10^{-6} \text{ mol m}^{-2} \text{ s}^{-1}$ )	RE (%)
–	50/50/0	3 ( $\pm 1$ )	100
NPOE ( $\eta = 11.1 \text{ cP}$ ; $\epsilon_r = 24.0$ )	30/50/20	4.3 ( $\pm 0.3$ )	100
DBS ( $\eta = 9.5 \text{ cP}$ ; $\epsilon_r = 4.5$ )	30/50/20	2.67 ( $\pm 0.03$ )	86 ( $\pm 10$ )
TBP ( $\eta = 3.3 \text{ cP}$ ; $\epsilon_r = 8.3$ )	30/50/20	5.9 ( $\pm 0.8$ )	100
	20/50/30	3.7 ( $\pm 0.6$ )	100
	30/40/30	3.3 ( $\pm 0.8$ )	100
	50/0/50	0	0

experimentation, better results were found for the PIM containing TBP (30/50/20-TBP) which gave the highest initial flux value (see Table 3) and the achievement of the transport of fluoride after less than 5 h. In the case of the other plasticizers tested, the resulting J was similar to that of the PIM made only with CTA and Aliquat 336. TBP is the reagent exhibiting the lowest viscosity value, and this parameter is often related to the improvement on the transport features, as shown in Ref. [36]. However, taking into account that TBP is a compound that can also act as a solvating extractant and, for example, is able to extract Fe(III) [37], we tested a PIM made of only CTA and TBP (50/0/50 – TBP; *i.e.*, without the carrier Aliquat 336) for fluoride transport experiments. In this case, no fluoride was found in the receiving phase, showing that the transport process is governed by the interaction of fluoride with Aliquat 336. The better performance of the PIM with TBP can probably be due to both the decrease in the membrane viscosity and the formation of a solvating environment in which the formed ion pair Aliquat336-F<sup>-</sup> can be easily transported.

Two other PIM compositions were tested using TBP as a plasticizer: 30/40/30 (in which the amount of organic phase is maintained; *i.e.* 70%), and 20/50/30 (a PIM with the same Aliquat 336 content but with 10% more TBP than the previous PIM tested). Transient fluoride concentration curves for these two PIMs are shown in Fig. 4.

As can be observed, the increase in TBP content did not result in faster transport, and similar initial J values, which were lower than those attained with the PIM 30/50/20-TBP, were obtained in both cases (see Table 3).

**Fig. 1.** Schematic transport of  $\text{F}^-$  through a PIM containing Aliquat 336 ( $\text{A}^+\text{Cl}^-$ ) as a carrier.

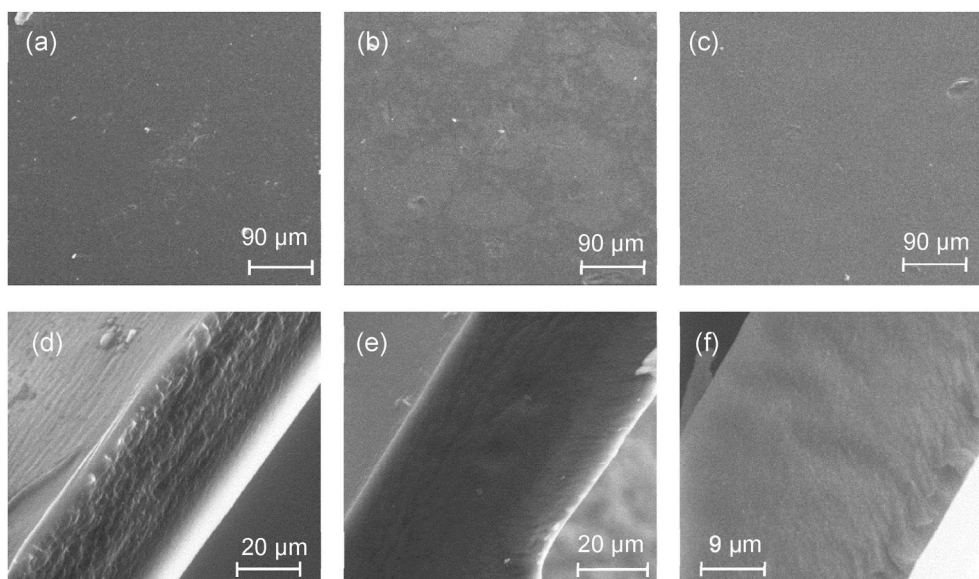


Fig. 2. SEM Images of PIMs. 30/50/20-DBS surface (a), cross-section (d); 30/50/20-NPOE surface (b), cross-section (e); 30/50/20-TBP surface (c), cross section (f).

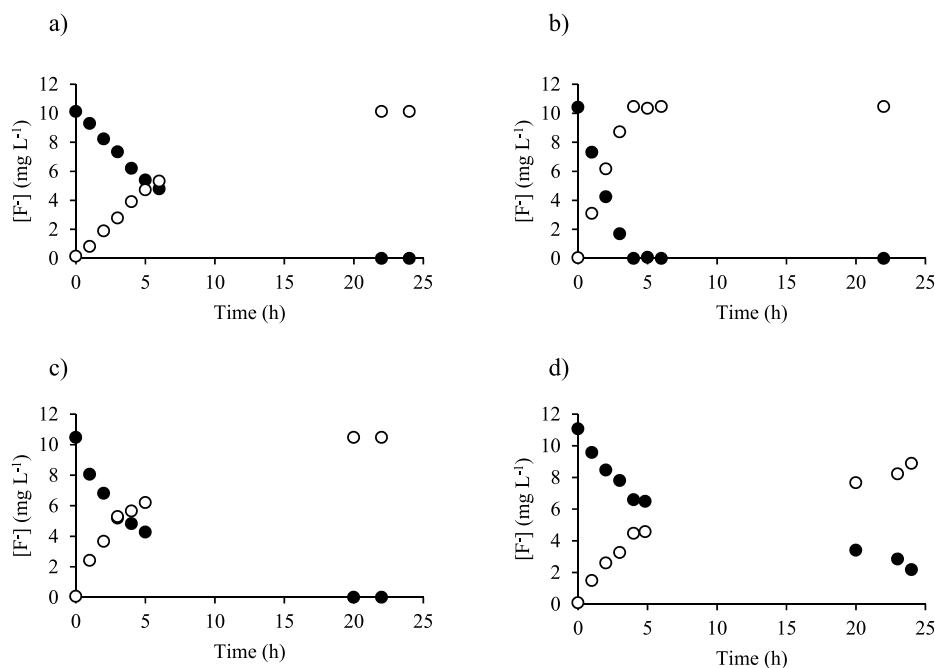


Fig. 3. Transient fluoride concentration curves for the feed (●) and receiving (○) phases for (a) 50/50/0 membrane, (b) 30/50/20-TBP membrane, (c) 30/50/20-NPOE membrane, and (d) 30/50/20-DBS membrane. Feed solution: Ultrapure water with 10 mg L<sup>-1</sup> F<sup>-</sup>; receiving solution: 1 M NaCl.

It is worth mentioning that no fluoride accumulation was observed in the membrane in any of the cases. Moreover, the obtained  $J$  values are similar to those from other studies using a PIM with Aliquat 336, as is the case of Cd [19] or As [22], for example.

Taking into account all the above details, a PIM composition of 30/50/20-TBP was used in the subsequent experiments.

Moreover, before evaluating other parameters affecting the separation system, the effect of NaCl concentration in the receiving phase was studied using this PIM composition and a feed phase containing 10 mg L<sup>-1</sup> fluoride in ultrapure water. When using an 0.5 M NaCl solution, the initial flux was  $4.0 (\pm 0.5) \times 10^{-6} \text{ mol m}^{-2} \text{ s}^{-1}$  whereas a concentration of 0.7 M increased this value to  $4.9 (\pm 0.4) \times 10^{-6} \text{ mol m}^{-2} \text{ s}^{-1}$ . As expected, these values were lower than  $J$  when using a 1 M NaCl solution, and, therefore, this solution was set as the receiving phase.

### 3.3. Effect of fluoride concentration

Taking into account that water samples can contain different amounts of fluoride, as seen in the Introduction, the effectivity of the PIM in removing the anion at higher concentration levels was evaluated. The relationship of the initial flux vs.  $F^-$  concentration at the range 10 - 200 mg L<sup>-1</sup> is shown in Fig. 5, where it can be seen that flux values proportionally increase as fluoride concentration increases. This fact is very important since a decrease in the flux is related to the saturation of the membrane, as reported in various studies [19,38], which leads to a decrease in the membrane efficiency. This does not occur in the PIM system designed for the removal of fluoride. Moreover, it is important to highlight that the removal efficiency was 100% after 24 h of experimentation within the concentration range studied.

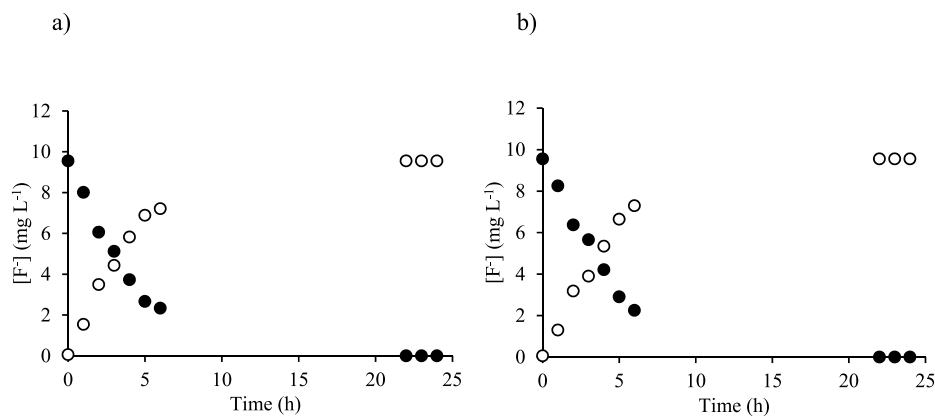


Fig. 4. Transient fluoride concentration curves for the feed (●) and receiving (○) phases for PIMs made of (a) 30/40/30-TBP and (b) 30/50/30-TBP. Feed solution: ultrapure water with 10 mg L<sup>-1</sup> F<sup>-</sup>; receiving solution: 1 M NaCl.

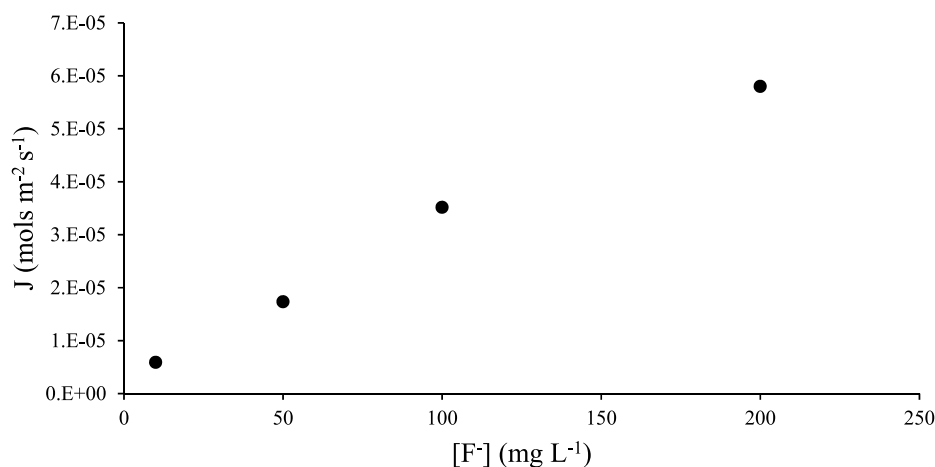


Fig. 5. Initial J vs. fluoride concentration in ultrapure water; PIM: 30/50/20-TBP; receiving solution: 1.0 M NaCl.

3.4. Effect of other anions and pH

Taking into account that Aliquat 336 is a non-selective extractant, as in the case of anion-exchange membranes, we evaluated whether the

presence of other anions could hamper the transport of fluoride. In a previous study using a PIM made of CTA and Aliquat 336 for the transport of arsenate in natural waters, it was observed that even though the transport efficiency for As(V) was not altered by the presence of

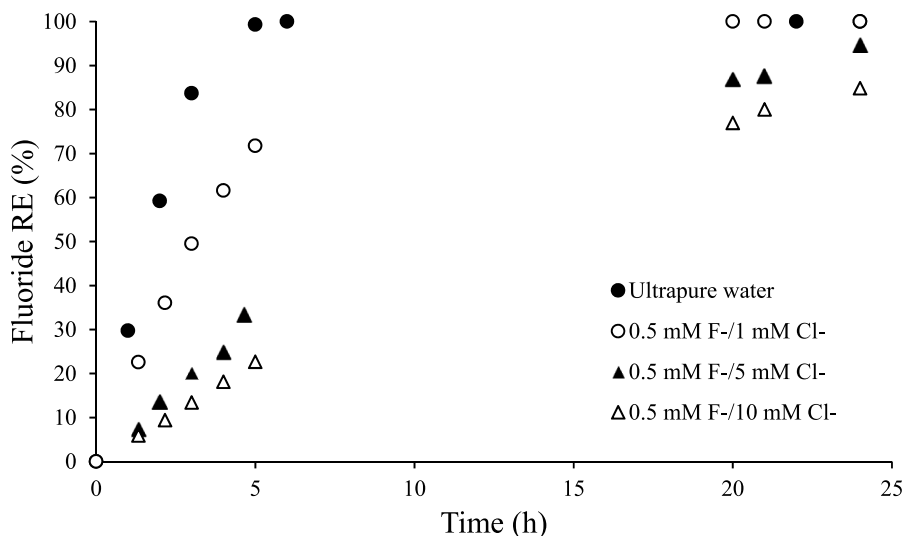


Fig. 6. Effect of chloride concentration in the feed solution, at different levels, on fluoride removal efficiency. PIM: 30/50/20-TBP; receiving phase: 1.0 M NaCl.

anions such as  $\text{Cl}^-$ ,  $\text{HCO}_3^-$  and  $\text{SO}_4^{2-}$  in the feed solution, the anions were also transported to the receiving solution along with arsenate [22]. Therefore, it is important to evaluate the effect of other anions on fluoride transport.

To this end, different solutions containing  $10 \text{ mg L}^{-1} \text{ F}^-$  (i.e.  $0.5 \text{ mM}$ ) and  $1\text{--}10 \text{ mM Cl}^-$ , which corresponds to the  $35\text{--}350 \text{ mg L}^{-1}$  range, were used as a feed phase. This is a typical anion present in natural waters, and the concentrations tested encompass usual content. Fig. 6 shows the effect of chloride concentration on fluoride removal. As can be seen, the removal kinetics is affected by chloride content, and the initial fluxes obtained varied as follows:  $4 \times 10^{-6}$ ,  $2 \times 10^{-6}$ , and  $1 \times 10^{-6} \text{ mol m}^{-2} \text{ s}^{-1}$  for 1.0, 5.0, and  $10 \text{ mM}$  chloride concentration, respectively. Taking into account that the transport is based on the chemical pumping of chloride from the receiving phase to the feed phase, it is clear that an increase of chloride anions in the feed phase is unfavourable. However, the global efficiency of the system was very good. Quantitative transport of fluoride was achieved at both  $1 \text{ mM}$  and  $5 \text{ mM}$  chloride, and the RE was only slightly affected when water contained the maximum chloride permissible content in drinking water, i.e.,  $350 \text{ mg L}^{-1}$ , reaching an acceptable removal value of 85% after 24 h.

The effect of sulphate was also investigated using solutions with  $10 \text{ mg L}^{-1} \text{ F}^-$  and  $\text{SO}_4^{2-}$  at two levels of concentration:  $0.1$  and  $1 \text{ mM}$ , (i.e.,  $10\text{--}96 \text{ mg L}^{-1}$ ). At these concentration levels, the transport of fluoride was not affected and quantitative removal was achieved after 24 h.

The effect of pH was also checked by adding HCl to  $10 \text{ mg L}^{-1} \text{ F}^-$  solutions. Taking into account that the pKa of HF is 3.17, we investigated the transport efficiency at  $\text{pH} = 3$  ( $1 \text{ mM HCl}$ ) and at  $\text{pH} = 2$  ( $10 \text{ mM HCl}$ ). In the first case, where both HF and  $\text{F}^-$  are present in a similar concentration in the solution, the RE (%) was 100%. However, at  $\text{pH} = 2$  this value decreased to 44%. Taking into account that RE (%) at this chloride content was 85% (see section 3.4), it is clear that the decrease in the efficiency is due to the presence of HF, which is a neutral species that cannot be extracted by Aliquat 336. Nevertheless, the pH of natural waters is between 6.5 and 8, where fluoride exists as an anion.

### 3.5. Fluoride removal from natural water samples

Different types of waters were used to evaluate the effectiveness of the developed separation system (Table 2 for their chemical characteristics and Table 4 for the results).

Tap water, with almost negligible fluoride content, was spiked at a level of  $10 \text{ mg L}^{-1}$  and was used as a feed phase. It was found that fluoride was quantitatively removed after a running time of 24 h. Moreover, two

**Table 4**

Fluoride concentration of feed solutions ( $\text{mg L}^{-1}$ ), initial  $J$  ( $\text{mols m}^{-2} \text{ s}^{-1}$ ), fluoride and RE (%) for water samples with naturally occurring fluoride. PIM: 30/50/20-TBP; receiving phase:  $1.0 \text{ M NaCl}$ .

Water sample	[F] <sup>-</sup> initial ( $\text{mg L}^{-1}$ )	[F] <sup>-</sup> (initial + added) ( $\text{mg L}^{-1}$ )	$J$ ( $\times 10^{-6} \text{ mol m}^{-2} \text{ s}^{-1}$ )	RE (%)
Tap water	0.1	10.3	2.3 ( $\pm 0.4$ )	100
Mineral-1	0.7	–	–	100
		9.6	3.4	100
		95	–	72
				( $\pm 5$ )
Mineral-2	2.5	–	–	68
				( $\pm 4$ )
Spring water	9.6	–	1.2 ( $\pm 0.3$ )	86
				( $\pm 6$ )
Groundwater	1.6	–	0.57	100
			( $\pm 0.02$ )	
Hot	8.6	–	0.4	36
Spring				( $\pm 6$ )
Water				
	Dilution	0.4	–	100
	1:20		0.3	
	Dilution +	0.4	7.3	2.0
	added			100

bottled mineral water samples containing  $0.7 \text{ mg L}^{-1}$  (Mineral-1) and  $2.5 \text{ mg L}^{-1}$  (Mineral-2) were also used as a source solution. In the case of Mineral-1, the PIM system successfully removed fluoride, also when fluoride content was increased to  $10 \text{ mg L}^{-1}$ . When this water sample was spiked at a level of  $95 \text{ mg L}^{-1}$  the removal efficiency was 72%. Solutions of the same concentration but in ultrapure water allowed the quantitative removal of fluoride. Therefore, the presence of other anions can affect the efficiency of the membrane at this high fluoride concentration, but it is important to highlight the high RE value achieved nevertheless.

Mineral-2, spring water, groundwater and hot spring water were used as a feed solution. All four contained different fluoride concentrations as they were natural sources. The RE (%) results varied depending on the type of water, even though, in general, initial flux values were of the same order of magnitude, as seen in Table 4. In both the cases of Mineral-2 and of spring water, even though the removal of fluoride is not quantitative, the remaining concentration fulfils the WHO standards of  $<1.5 \text{ mg L}^{-1}$ . The differences in the performance of the separation system are due to the different composition of the water samples. In the case of Mineral-2, for example, the conductivity was 5.6 times higher than that of Mineral-1, and the chloride content was 38 times higher. In the case of the groundwater, the sample with the lowest mineralization, fluoride was effectively removed from the feed phase. Moreover, for Mineral-1, Mineral-2 and Groundwater samples, the transport of sulphate was also monitored. It was found that, for all cases, the sulphate anion was quantitatively transported to the receiving phase. This result was expected due to the non-selective characteristics of the carrier used in the PIM.

Moreover, a water sample from a hot spring water, which is not intended to be used as drinking water, was also tested due its high natural fluoride content despite having an extremely high conductivity value ( $2793 \mu\text{S cm}^{-1}$ ) and a chloride content of  $630 \text{ mg L}^{-1}$ . Under these unfavourable conditions, the PIM system achieved an RE of 36%. Dilution of this water sample resulted in a conductivity value of  $140 \mu\text{S cm}^{-1}$ ,  $32 \text{ mg L}^{-1} \text{ Cl}^-$ , and  $0.4 \text{ mg L}^{-1}$  fluoride. By lowering the ionic content of the water, fluoride was completely removed from the feed phase. Similar results were obtained when the diluted hot spring water sample contained  $7.3 \text{ mg L}^{-1}$ . Therefore, it can be seen that the PIM system is able to remove fluoride from typical natural water samples containing this anion to achieve at the permissible levels required.

### 3.6. Membrane reusability

The performance of the PIM in terms of RE (%) was investigated using the same membrane for several cycles of experiments (one cycle corresponds to 24 h long experiment). After each cycle, both feed and receiving phases were changed for fresh ones but the PIM was maintained. Experiments were done in both ultrapure water and tap water, both spiked with  $10 \text{ mg L}^{-1} \text{ F}^-$ . The results in Fig. 7 show that the membrane may be used for four cycles with just a minor reduction in transport efficiency when using ultrapure water, whereas no reduction in RE (%) is observed in the treatment of tap water. These results are important in demonstrating the possible utility of this membrane in water treatment.

## 4. Conclusions

In this study, we have investigated a polymer inclusion membrane to remove fluoride from natural waters. A PIM composition of 30% CTA, 50% Aliquat 336, and 20% TBP has been shown to effectively transport fluoride to a receiving phase consisting of  $1 \text{ M NaCl}$ . Even though high concentrations of other anions, basically chloride, can hamper fluoride removal, it has been found that the PIM can successfully treat waters with naturally occurring fluoride to reach the WHO standards. Moreover, the membrane can be used several times without loss of efficiency.

This is the first time that PIMs have been used for fluoride removal in natural waters. These membranes are easy to prepare, stable over time,

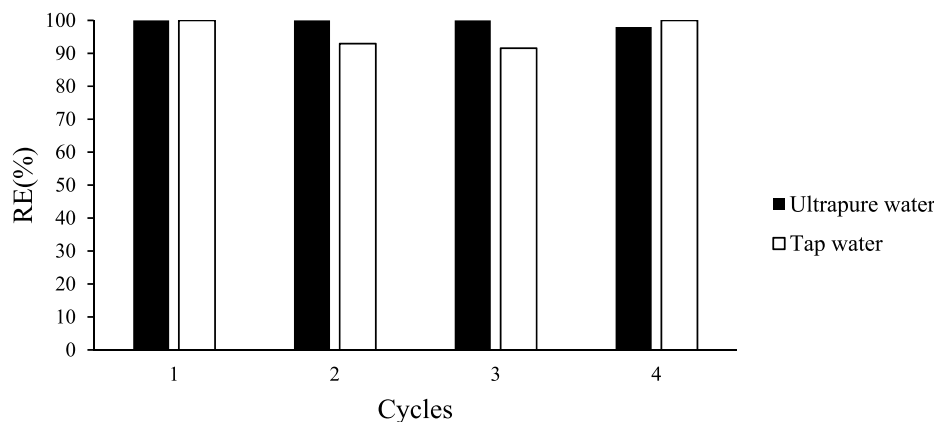


Fig. 7. RE (%) for membrane reusability experiment. Feed solution: ultrapure water and tap water with  $10 \text{ mg L}^{-1} \text{ F}^{-}$ ; PIM: 30/50/20-TBP; receiving solution:  $1.0 \text{ M NaCl}$ .

and do not require specific infrastructures or a power source to operate. As such, PIMs can be viewed as a particularly attractive option for the treatment of fluoride-rich waters in remote areas.

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### CRedit authorship contribution statement

**Berta Alcalde:** Investigation, Methodology, Validation, Writing – original draft. **Enriqueta Anticó:** Conceptualization, Funding acquisition, Methodology, Resources, Supervision, Validation, Writing – review & editing. **Claudia Fontàs:** Conceptualization, Data curation, Funding acquisition, Methodology, Project administration, Resources, Supervision, Validation, Visualization, Writing – review & editing.

### Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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