



## Nanofiltration polishing membrane process for fluoride removal

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### ABSTRACT

The objective of this experimental study is to investigate, at a laboratory scale, the removal efficiency of a process combining dilution, neutralization, and nanofiltration (NF) membrane separation of real industrial wastewater. The considered effluent is produced by an aluminum fluoride manufacturing plant with a fluoride concentration in the range of  $4,606 \pm 547$  mg/L. First, the effect of drying of technical grade hydrated lime, used as a neutralizing agent has been explored. Drying allowed the considerable saving of lime with slightly better fluoride removal efficiency giving a removal rate of  $98.7\% \pm 0.3\%$  at the optimal lime excess of around 36% for the neutralization step. The polishing NF membrane separation, conducted on a laboratory pilot unit, yielded a fluoride rejection rate of  $77.3\% \pm 0.3\%$  at the optimal operating transmembrane pressure of nearly 85 psi. The overall fluoride removal rate at optimized operating conditions has reached  $99.85\% \pm 0.02\%$  with a permeate effluent having fluoride contents of  $6.6 \pm 0.1$  mg/L.

**Keywords:** Industrial wastewater; Fluoride; Removal process, Hydrated lime neutralization; Nanofiltration; Laboratory scale experiments, Optimization

### 1. Introduction

Despite their harmful effects, several industrial wastewater effluents are still rejected in the marine environment. It is necessary to treat this effluent in order to respect the environmental standards before discharge into the sea. In Tunisia, the recommended fluoride value is 3 mg/L in industrial effluents [1]. Tunisia is among the most stringent countries concerning fluoride contents of waste streams. However, because of intense industrial activities, fluorides are a major issue in the Gulf of Gabes. Fluoride ( $F^-$ ) is the anionic form of the fluorine element (F), the most electronegative and reactive halogen. It is not found in nature as elemental form but always occurs under a valence of (-1). High fluoride concentrations in surface water or groundwater may be natural or anthropogenic [2]. Several methods

were developed to determine fluoride in aqueous solutions. Most common techniques use electrochemical methods, such as potentiometry [3,4], voltammetry [5], polarography [6]. The fluoride detection by the ion-selective electrode is not limited to water analysis but is used as well for toothpaste and mouthwash [7], milk [8], drug [9].

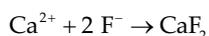
Fluoride in drinking water has been extensively investigated. Nonetheless, it is still a hot research subject [10–12]. A low fluoride concentration in drinking water (0.5–1 mg/L) is essential to help prevent dental caries and strengthen bones, especially for children below 8 y of age [13,14]. Children need fluoride to protect their newly formed teeth, while adults necessitate fluoride for teeth health [13]. Conversely, exposure to high fluoride concentrations can lead to various serious health problems such as tooth decay [15], dental fluorosis [13,16], skeletal fluorosis [2,15]

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or cancer [17] and neurotoxicological effects [2]. Ahada and Suthar [13] studied seven classes of fluoride concentrations and their effects on human health.

Various fluoride diseases occur through fluoride-contaminated drinking waters and wastewaters. Several industries using fluorine or its derivatives may increase fluoride concentration in various natural matrices. Among industries that generate fluoride-rich waste are: Phosphate processing and fertilizer production [18–20], aluminum fluoride production [3,4,21], zinc processing [22], magnesium melting, semiconductor production [23], ceramic and fertilizer industry [24]. Agricultural activities could generate some F contaminated effluents [25]. All these activities could contribute to the contamination of water assets with fluoride. Excessive fluoride amounts are harmful to marine wildlife as for humans [26]. This is the reason why environmental regulations are stringent with respect to fluoride contents of waste streams imposing effluent proper treatment before disposal or reuse. Fluoride removal from water can be achieved by several treatment technologies among which: coagulation/precipitation [27,28], adsorption [3,21,29,30] and ion-exchange [31]. Membrane processes such as nanofiltration (NF) [32–37], reverse osmosis (RO) [4,33,35], electrodialysis (ED) [38] and Donnan dialysis [39], were also considered to reduce fluoride concentrations in water and wastewater.

Fluorides can be precipitated as calcium fluoride according to the following reaction:



In practice, for extremely high fluoride concentration the precipitation can only reduce the fluoride concentration to a range of 20–100 mg/L [4]. Thus, neutralization alone is not sufficient to eliminate fluoride. Consequently, another defluoridation process must be performed. A neutralization associated with a membrane process can achieve this objective [4]. NF is an efficient fluoride rejection technique that rivals RO and ED. NF is a relatively low-pressure process that selectively rejects large dissolved chemical species having a size in the range of 1–10 nanometer. This technique is considered an intermediary between ultrafiltration and RO [40–44]. Membranes present several advantages such as high flux, high retention of multivalent anion salts and organic contaminants, relatively low operation, and maintenance costs compared to other treatment techniques.

Tahaik et al. [32] studied groundwater defluoridation using an NF pilot plant. They studied the performance of two commercial spiral wound membranes and the influence of experimental parameters on F elimination, including the initial concentration reduction, pressure, and effluent volume. Pontie et al. [34] compared performances in terms of hydraulic permeability, total salinity rejection, and fluoride removal from brackish groundwater of two commercial membranes (NF90 and BW30) [34]. Fluoride removal from synthetic water and metal packaging industrial effluent with two commercial membranes (NF90 and RO-SG) was studied by Imen et al. [35]. The highest rejection was obtained from the NF90 membrane (>97.6%), however, it was between 92%–97% from RO-SG. For fluoride partial removal, Diallo et al. [36] examined at a laboratory scale

the performance of two commercial membrane separation processes namely TFC-SR3 and SelRO MPF-34. Results confirmed that the TFC-SR3 membrane was very efficient with fluoride rejection rates of 83%–96%. For the SelRo MPF-34 membrane, retention rates of 25%–52% were obtained for fluoride ions. Bouhadjar et al. [37] studied the sustainability and suitability of a low-cost, pilot-scale NF plant for groundwater defluoridation in northern Tanzania. The plant was able to remove more than 98% F.

Ezzeddine et al. [4] considered a process combining neutralization and RO form fluoride removal for highly contaminated waste streams. The laboratory-scale experimental investigation allowed reducing the permeate fluoride concentration to 8 mg/L; therefore reach an overall fluoride removal rate of 99.7%. In the present work, the NF membrane process is used as a polishing treatment after the neutralizing step for the same water effluent. The objective of this investigation is to find the optimal operating conditions for neutralization and the membrane process allowing the best removal performance of fluorides. Although fluoride removal using calcium salts has been extensively investigated in the literature, none had given the interest in the drying effect of neutralizing agents on treatment process performances. In this study, the effect of pre-drying of the hydrated lime will be unfolded allowing determining the optimal lime excess giving the minimum conductivity with the lowest fluoride concentration. For the NF polishing step, the optimal transmembrane pressure allowing the highest F rejection rate will be identified.

## 2. Materials and methods

### 2.1. Materials

In the experiments, analytical grade chemicals were used to prepare the total ionic strength adjustment buffer solution required for fluoride analysis. Standard solutions were obtained by diluting analytical grade sodium fluoride (NaF) in different concentrations with distilled water. Neutralization tests were carried out using slaked lime technical grade calcium hydroxide, a product of INTERCHAUX-Tunisia, titrating  $86.2\% \pm 0.9\% \text{ Ca(OH)}_2$ . Aluminum sulfate ( $\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$ ) was dosed as a coagulant to accelerate the separation of solid-water in the neutralization step.

Real industrial effluent was provided by the aluminum fluoride manufacturing industry. The industrial water has a fluoride concentration of about  $4,606 \pm 547 \text{ mg/L}$ . The characteristics of such effluent have been reported in Ezzeddine et al. [4]. Tap water was used for dilution of industrial effluents.

### 2.2. Analytical methods

Fluoride concentrations were measured by a fluoride-selective electrode (Orion, 9609BNWP) connected to an ion meter (OHAUS model starter 2100) according to the standard method given by the American Public Health Association [45,46]. A conductivity meter (OHAUS model starter 3100C) and pH meter (Metrohm 827 pH meter) were used for measurement. The solution's turbidities were determined through "HF-scientific Micro 100 turbidity meter". X-ray

fluorescence (XRF) using the “AXIOS model PANalytical XRF spectrometer” was adopted for characterizing lime and neutralization cake obtained by filtration.

### 2.3. Experimental procedure

The flowsheet of the overall treatment process is shown in Fig. 1. The process combines a neutralization operation using the hydrated lime (neutralization or first step) and NF membrane separation or polishing step. Batch wise experiments were conducted for both steps. All experiments were replicated at least three times to assess experimental errors.

#### 2.3.1. Neutralization step

Prior to use, the neutralizing agent, technical grade lime, was subject to grinding and sieving with 125  $\mu\text{m}$  size sieve. It could be used as-is or dried at 110°C until reaching constant weight. The effluent excessive fluoride concentration was first reduced by a 2.5-dilution factor with tap water. This allowed decreasing the fluoride concentration to  $1,842 \pm 219$  mg/L with a  $2.6 \pm 0.2$  pH, a conductivity of  $9.5 \pm 0.5$  mS/cm and turbidity of around 6 NTU at  $26^\circ\text{C} \pm 1^\circ\text{C}$ . Operations were performed in a closed batch polyethylene reactor of 1 L capacity. 500 mL of the diluted effluent volume was mixed with different lime excesses and stirred at 800 rpm for 20 min. Then, the solution was settled until obtaining a stable pH and conductivity. For dried and un-dried lime, samples were taken to monitor the pH, conductivity, and fluoride concentration. Aluminum sulfate was used to speed up settling of suspended matters. A jar test was performed to determine the adequate flocculent dose.

The neutralization was then performed at a larger scale with batches of 20 L at 500 rpm for 40 min with previously determined optimal amounts of dried lime excesses. The same final pH, conductivity, and fluoride concentration were obtained for smaller batches.

After neutralization, the cake made up of the neutralization product ( $\text{CaF}_2$ ) and the remaining unreacted lime was

separated from the liquid by 0.45  $\mu\text{m}$  filtration. The filtration cake was analyzed by XRF. A laboratory-scale NF pilot unit was later used for treating the neutralization filtrate in the polishing step.

#### 2.3.2. Membrane separation process

Experiments were performed on a low-pressure laboratory-scale pilot unit as shown in Fig. 1. A NanoRO K1812 module, kindly provided by “Membranium®”, was used the membrane separation. The NF membrane type is a spiral wound organic polyamide-based composite membrane with approximately 0.4  $\text{m}^2$  of filtration area. The maximum operating pressure is 10 bar. An antiscalant was added to prevent membrane fouling.

Membrane integrity was systematically checked before and after membrane treatment with pure distilled water. Conductivity, turbidity, and pH were monitored along with fluoride and calcium concentration for both permeate and concentrate solutions.

The recovery rate is obtained by:

$$\tau = 100 \frac{Q_p}{Q_f} \quad (1)$$

where  $Q_f$  and  $Q_p$  are the feed and permeate flow rates, respectively. The recovery rate changes with the imposed pressure, which was varied between 20 and 150 psi.

Fluoride rejection rate is given by:

$$R_F = 100 \frac{[F^-]_f - [F^-]_p}{[F^-]_f} \quad (2)$$

where  $[F^-]_f$  and  $[F^-]_p$  are the feed and permeate fluoride concentrations in the solution, respectively.

At each pressure, the membrane separation was continued until reaching a steady state. This was demonstrated by

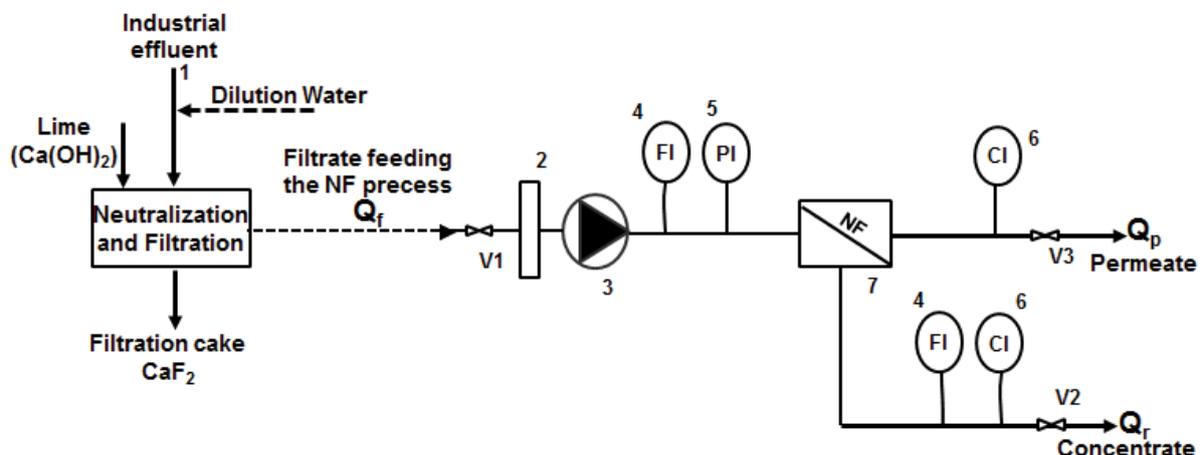


Fig. 1. Flowsheet of the treatment process and the pilot NF unit (Legend: 1: industrial effluent; 2: pre-filters; 3: pump; 4: flow meters (FI); 5: pressure gauges (PI); 6: conductivity meters (CI); 7: NF module; V1-3: valves).

constant flow rates and conductivities for concentrate and permeate streams.

A balance on fluoride was systematically performed according to:

$$Q_f [F^-]_f = Q_p [F^-]_p + Q_r [F^-]_r \quad (3)$$

where  $Q_r$  and  $[F^-]_r$  are the retentate flow rate and fluoride concentration, respectively. Fluoride balance was always holding within an error below 10%.

### 3. Results and discussion

#### 3.1. Neutralization step

##### 3.1.1. Drying effect of hydrated lime on precipitation

Real industrial effluents originating from an aluminum fluoride industry were used in this study. Ezzeddine et al. [4] studied the removal of fluoride by neutralization using calcium hydroxide from the same effluent. Precipitation alone has reduced the fluoride concentration to  $60 \pm 2$  mg/L at 50% of lime excess. This allowed obtaining a fluoride removal rate of 98.1%. In the previous investigation, the drying of lime has not been considered. In this work, the effect of neutralizing agent drying will be studied. Sieving and drying of lime allowed further upgrading these results with respect to fluoride reduction and lime consumption.

As shown in Fig. 2, lime reactivity is sensitive to moisture requiring its drying. Fluoride post neutralization concentration, influenced by lime excess, has drastically changed when lime was sieved and dried as described in section 2.3.1. Increasing lime excess minimizes fluoride content quickly in the effluent up to 15% excess for dried lime. Beyond this excess, the fluoride removal reaches a plateau with a residual F concentration of  $25.9 \pm 5.6$  mg/L. Dried lime

is much more reactive than un-dried lime where the same F concentration limit is almost reached for excesses higher than 70%.

Fluoride concentration after the neutralization step is still high requiring additional membrane treatment. Since NF was chosen to further reduce fluoride concentration, effluent conductivity and pH must be monitored. Fig. 3 illustrates the pH evolution as a function of lime excess and drying effect. Three stages of pH variations were obtained for the two curves. First, the solution pH slowly increases up to a certain lime excess. Then, the pH undergoes a sharp increase after which a pseudo plateau is obtained. This figure also demonstrates the reactivity of dried lime as the pH curve shifting behavior occurs for much lower lime excesses. To avoid membrane damaging in the post neutralization NF separation, the solution pH should range between 6 and 7. This is why the lime excess for the neutralization with dried lime should be kept between 30% and 40%.

Fig. 4 summarizes the conductivity evolution as a function of lime excess used for neutralization of the effluent for both dried and un-dried lime. After a certain excess, lime will continue to dissolve without the further formation of  $CaF_2$  this will give the conductivity curve an increasing trend. According to solution pH variation, the optimal lime excess is about  $36\% \pm 1\%$  corresponding to the lowest solution conductivity, that is, lesser mineral contents in the filtrate feeding the NF separation.

Neutralization with dried lime at optimized conditions was able to reduce the fluoride concentration to  $25 \pm 4$  mg/L with a pH ranging between 6 and 7. Thus, neutralization with dried lime alone allowed reaching an interesting fluoride removal rate as high as  $98.7\% \pm 0.3\%$ . Lime drying allowed substantial savings of the neutralization agent of nearly 28% and an improvement of the overall removal rate of about 0.6% compared to what was previously reported [4].

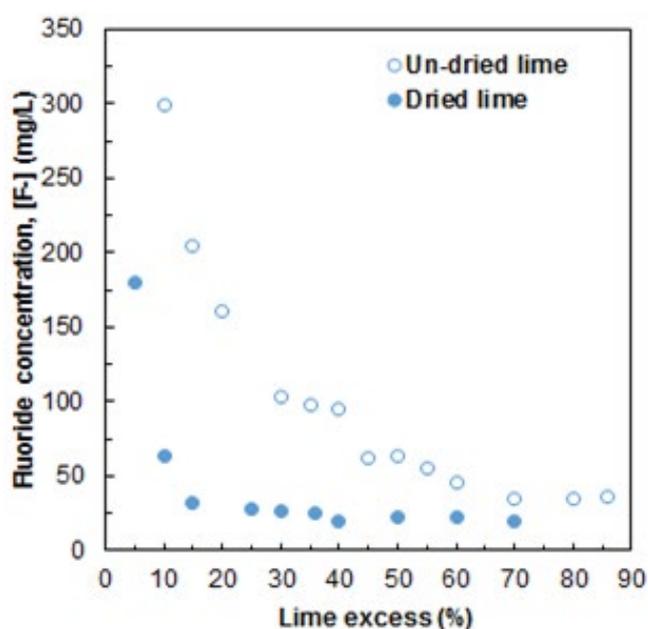


Fig. 2. Fluoride concentration vs. lime excess.

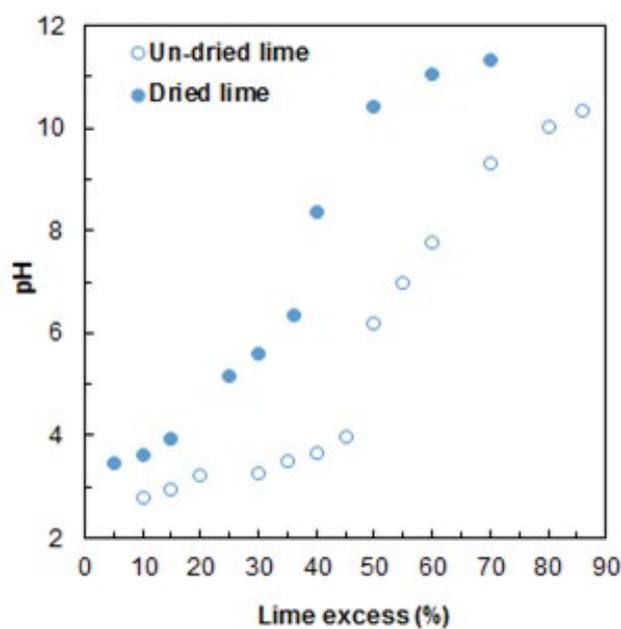


Fig. 3. pH vs. lime excess.

3.1.2. Evolution of the turbidity with coagulant doses

As shown in Fig. 5, adding aluminum sulfate as coagulant reduced very much solution turbidity. The optimal coagulant dose is about 200 mg/L giving a solution of about 2 NTU.

3.1.3. Chemical analysis of filtration cake

The solid residue of the neutralization step, filtration cake, was characterized by XRF after drying at 110°C. Post neutralization filtration cake characteristics are given in

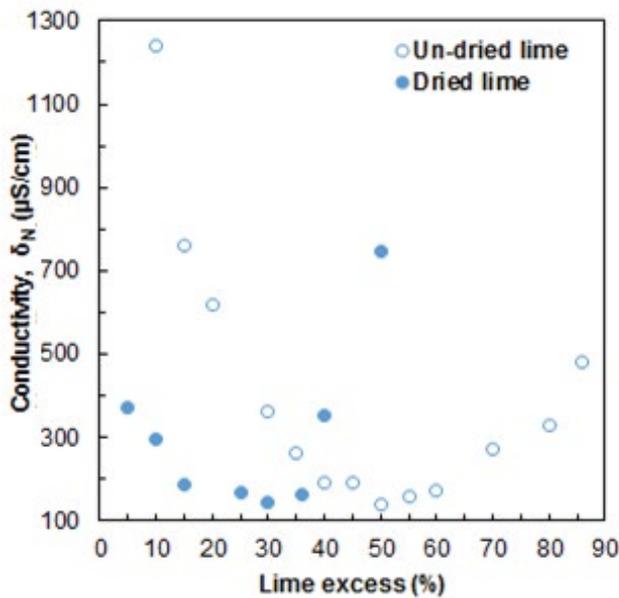


Fig. 4. Conductivity vs. lime excess.

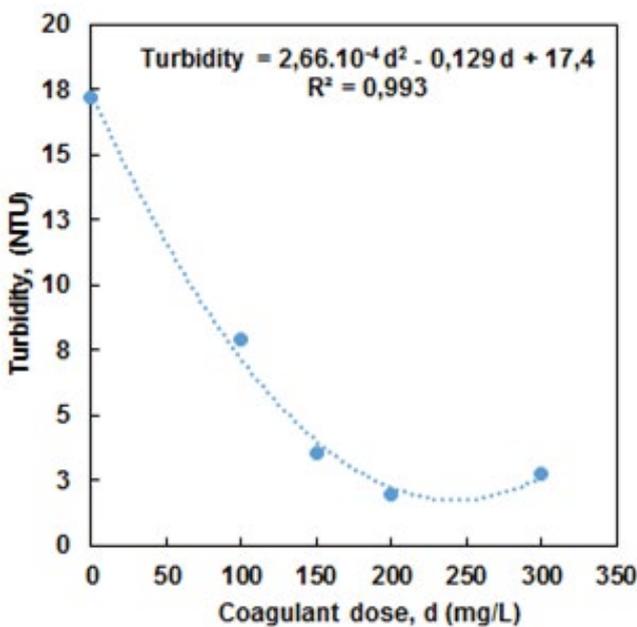


Fig. 5. Turbidity vs. coagulant dose.

Table 1. The filtration cake CaF<sub>2</sub> content is relatively very high reaching around 80%, which could make it suitable for use as raw spath fluor for aluminum fluoride industry.

3.2. NF polishing treatment

The fluoride content in the filtrate is still relatively very high. The filtrate recovered from the neutralization step is used to feed a low-pressure membrane separation laboratory pilot unit for polishing treatment. Before and after each membrane experiment, the membrane permeability was assessed with distilled water to detect any membrane fouling occurrence. No fouling was observed in the study as shown in Fig. 6 where there is no significant difference in the membrane characteristic line.

Several experiments were conducted to investigate the transmembrane pressure effects on the unit recovery rate. Fig. 7 presents the variation of the recovery rate up to a transmembrane pressure of 125 psi. As the transmembrane pressures increase the recovery rate raises with the near-perfect quadratic trend.

Table 1  
Filtrate cake contents

Elements	%
CaF <sub>2</sub>	79.74
CaCO <sub>3</sub>	6.5
Fe <sub>2</sub> O <sub>3</sub>	0.035
Al <sub>2</sub> O <sub>3</sub>	0.158
P <sub>2</sub> O <sub>5</sub>	0.038
S	0.023
Mg(OH) <sub>2</sub>	0.065
SiO <sub>2</sub>	12.442

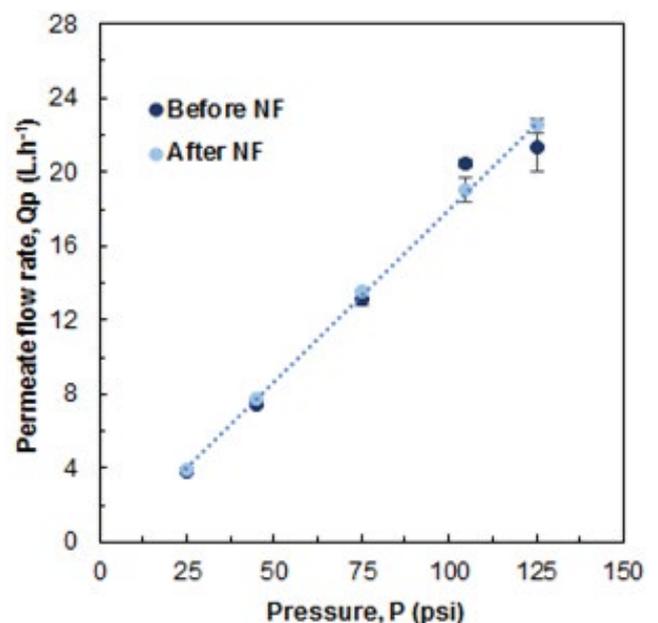


Fig. 6. Permeate flow rate vs. transmembrane pressure.

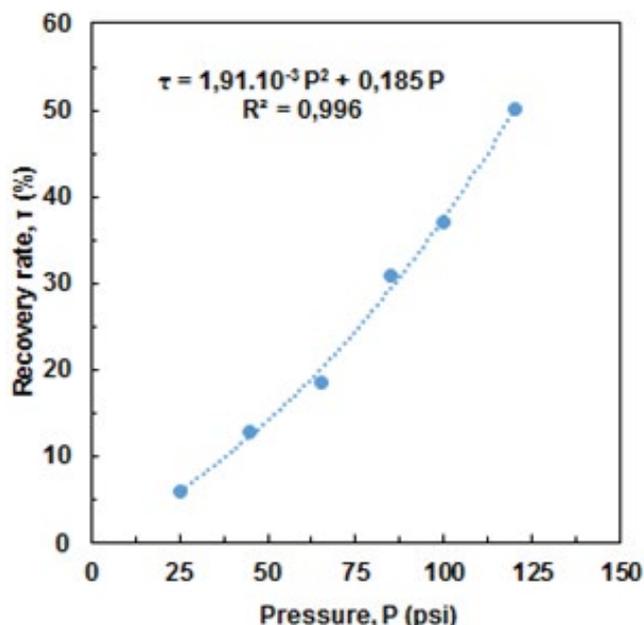


Fig. 7. Recovery rate vs. transmembrane pressure.

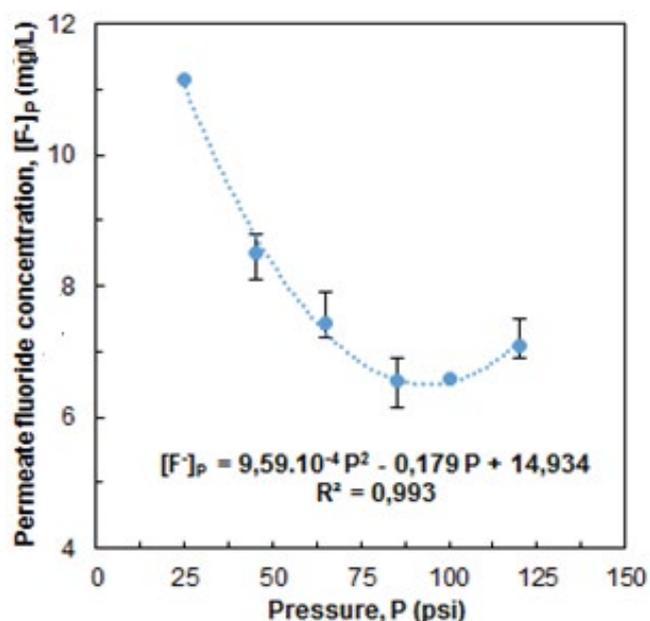


Fig. 8. Permeate fluoride concentration vs. transmembrane pressure.

Fig. 8 shows the permeate fluoride contents for different transmembrane pressures. It is clear that there is an optimal pressure for which the fluoride concentration is minimal. This trend is well known for large-scale modules as shown in Minyaoui et al. [40]. It reflects competing transport processes for water and fluoride species along and across membrane modules, for various transmembrane pressures. The NF treatment allowed decreasing the permeate fluoride concentration to  $6.6 \pm 0.1$  mg/L for the optimal transmembrane pressure ranging between 85 and 100 psi. NF provided treated water with a fluoride rejection rate of  $77.3\% \pm 0.3\%$  (Fig. 9).

Calcium concentration in the neutralized industrial effluent was 36 ppm. Fig. 10 illustrates that the calcium rejection follows a similar trend as for F. The best rejection rate, 97%, corresponds to the same optimal transmembrane pressure of 85 psi.

The overall performances for neutralization and NF separation at optimized operating conditions, 36% dried lime excess and a transmembrane pressure of 85 psi, is a removal rate of  $99.85\% \pm 0.02\%$ . The NF permeate fluoride contents is  $6.6 \pm 0.1$  mg/L down from  $25 \pm 4$  mg/L in the neutralized effluent. To ensure a continuous treatment process, the NF retentate could be recycled and used for diluting the effluent before neutralization.

#### 4. Conclusions

This work reports a laboratory-scale experimental investigation for treating an aluminum fluoride manufacturing plant industrial wastewater having an excessive fluoride concentration of  $4,606 \pm 547$  mg/L. The treatment process combined a dilution, a neutralization step using dried and un-dried technical grade lime, and an NF membrane separation. Dried lime was much more reactive allowing better neutralization performances and neutralizing

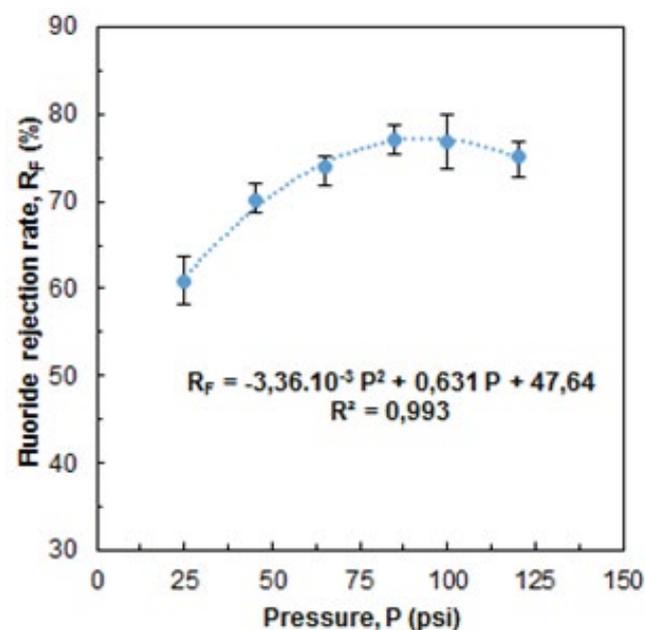


Fig. 9. Fluoride rejection rate vs. transmembrane pressure.

agent savings. Neutralization alone with optimal dried lime excess of around 36% allowed reducing the solution fluoride concentration to  $24.9 \pm 4$  mg/L. The dried filtration cake titrated a calcium fluoride ( $CaF_2$ ) content of nearly 80%. Neutralized effluents with optimally dried lime excesses were further treated with a laboratory pilot NF unit. This polishing treatment allowed, at unfolded optimal transmembrane pressure of around 85 psi, additional fluoride removal giving a permeate fluoride contents of  $6.6 \pm 0.1$  mg/L, permitting to reach an overall fluoride

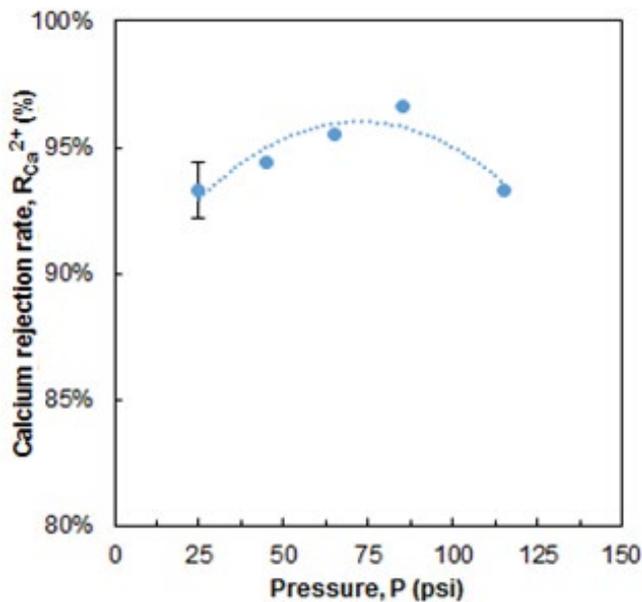


Fig. 10. Calcium rejection rate vs. transmembrane pressure.

removal rate of  $99.85\% \pm 0.02\%$ . The concentrate could be recycled and used for the effluent dilution prior to neutralization.

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