

Hybrid neutralization and membrane process for fluoride removal from an industrial effluent

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Abstract. This study aims to investigate at a laboratory scale fluorides removal from an industrial wastewater having excessive F⁻ concentration through a hybrid process combining neutralization and membrane separation. For the membrane separation operation, both Reverse Osmosis (RO) and Nanofiltration (NF) were investigated and confronted. The optimized neutralization step with hydrated lime allowed reaching fluoride removal rates of 99.1± 0.4 %. To simulate continuous process, consecutive batch treatments with full recirculation of membrane process brines were conducted. Despite the relatively high super saturations with respect to CaF₂, no membrane cloaking was observed. The RO polishing treatment allowed decreasing the permeate fluoride concentration to 0.9± 0.3 mg/L with a fluoride rejection rate of 93± 2% at the optimal transmembrane pressure of around 100 psi. When NF membrane was used to treat neutralization filtrate, the permeate fluoride concentration dropped to 1.1± 0.4 mg/L with a fluoride rejection rate of 88± 5% at the optimal pressure of around 80 psi. Thus, with respect to RO, NF allowed roughly 20% decrease of the driving pressure at the expense of only 5% drop of rejection rate. Both NF and RO permeates at optimal operating transmembrane pressures respect environmental regulations for reject streams discharge into the environment.

Keywords: industrial wastewater; fluoride removal; hybrid treatment process; neutralization; reverse osmosis; nanofiltration; optimization

1. Introduction

More production and less pollution are the challenges facing the industry in all areas, to meet the expectations of public opinion and policy makers to ensure a safe environment.

Aluminum fluoride manufacturing industries should abide by sustainability criteria. These industries have to deal with effluents with excessive fluoride concentrations encompassing a potential environmental threat (Ezzeddine *et al.* 2014a, b). It is necessary to treat this effluent in order to respect the environmental standards before discharge and reuse. In Tunisia, the maximum fluoride discharge limit is 3 mg/L in industrial effluent (Tunisian standard NT.106.002 1989).

Fluorine is the most electronegative element; therefore, it acquires a negative charge and forms F⁻ ions in aqueous media (Dhillon *et al.* 2016). Fluorides are very reactive compounds. They cannot be found in free forms in the environment. Fluorides exist in nature in different forms

such as fluorspar (CaF₂), cryolite (3NaF. AlF₃) and fluorapatite (3Ca₃(PO₄)₂. Ca(F,Cl)₂) (Adimalla *et al.* 2019). Fluoride has both beneficial and harmful effects on individual health depending upon its concentration (Ahada and Suthar 2017, Kabira *et al.* 2019). Discharging effluents containing fluorides into the environment is extremely harmful to all living species. Extensive research work has focused on fluorides in drinking waters (Kawakami *et al.* 2018, Bouhadjar *et al.* 2019). The benefits and impacts of fluoride in drinking water have been a matter of several searches. They allowed unfolding fluoride concentration limits in drinking water, preventing tooth decay. The harmful effects of fluorides increase proportionately with the amount and duration of ingestion (WHO 2017). Fluoride intake at low fluoride concentration, usually between 0.5 and 1 mg/L, helps prevent dental caries and strengthen bones, especially in children (Ahada and Suthar 2017, WHO 2017, Ram 2017). The danger of dental fluorosis will depend on the total absorption of fluoride from all sources and not just the concentration in drinking water. Conversely, exposure to excessive fluoride amount can lead to dental fluorosis (Ram 2017), skeletal fluorosis (Kabira *et al.* 2019). Impacts on the bone are considered as the most relevant outcomes in assessing the adverse effects of long-term exposure of humans to excess fluoride. The effects of fluoride on the osteon depend on the type of bone and its organic and inorganic constituents. Among the

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structural changes in fluorosis bones, we can remind increased bone mass and density, exostosis (bony outgrowth) at bone surfaces and increased osteoid seam and re-sorption surfaces. The most dangerous effect of fluoride in bone is its skeletal accumulation from long-term excessive exposure. Consequently, it can occur severe forms of skeletal deformities. Fluoride can damage such organs as the nervous system (Dhillon *et al.* 2016) inducing even skeletal cancer (Fordyce 2011).

Fluoride linked harmful effects are not only related to drinking waters but also extend to wastewaters. Excessive fluorides in reject streams could affect all leaving species. Industrialization activities such as aluminum fluoride production encompass streams and effluents with high F concentrations. Nowadays, stringent environmental constraints on F in effluents are imposed. Environmental regulations have consolidated the efforts to treat all effluents prior to discharge into the sea and various water streams. Reusing and recycling F rich wastewaters are considered the best solution for saving the ever-shrinking fresh water resources and preventing their pollution.

Many treatment technologies to remove fluoride from aqueous environments have been applied. These methods can be divided into four categories: chemical coagulation/precipitation (Ezzeddine *et al.* 2014a, b), ion exchange (Patnaik *et al.* 2018), adsorption (Ezzeddine *et al.* 2014a, Ezzeddine and Hannachi 2017, Benamor *et al.* 2018) and membrane processes (Ezzeddine *et al.* 2014b, Meftah *et al.* 2019, Owusu-Agyeman *et al.* 2019). When the concentration of fluorides are very high, the most commonly used method for fluoride removal is precipitation using calcium salt, such as lime (Ezzeddine *et al.* 2014b), limestone (Ezzeddine *et al.* 2014a), hydrocalumite or calcium chloride (Albustami 2014). These calcium salts are added to the wastewater to induce supersaturation allowing CaF₂ precipitation. In practice, these precipitating agents can only reduce the fluoride concentration to a range of 20–100 mg/L. Consequently, an additional defluoridation process must be performed. The study of Ezzeddine *et al.* (2014a) demonstrated that the hybrid Neutralization- adsorption could effectively remove fluoride from wastewater. Membrane process is an alternative technology for post lime neutralization of water and wastewater defluoridation systems. This has been reported in many recent investigations. Membrane processes such as reverse osmosis (RO) (Ezzeddine *et al.* 2014b, Owusu-Agyeman *et al.* 2019), nanofiltration (NF) (Bejaoui *et al.* 2014, Bouhadjar *et al.* 2019, Meftah *et al.* 2019), dialysis and electro-dialysis (Sahli *et al.* 2007, Boubakri *et al.* 2014) were also investigated to reduce fluoride concentrations in water and wastewater.

In a previous work, removal of fluoride from a real industrial wastewater effluent by a hybrid process involving Neutralization and RO processes was studied (Ezzeddine *et al.* 2014b). This polishing treatment permitted decreasing the permeate fluoride concentration to 8 mg/L, allowing to reach an overall fluoride removal rate of 99.7%. NF, compared to RO, is a low-pressure process that has a relatively equivalent selectivity allowing to remove fluorides in water effluents. The duality between these

competing membrane processes, for providing drinking water has been reported (Harrak *et al.* 2015, Minyaoui *et al.* 2017). The aim of this work is to optimize and compare NF to RO as polishing treatment in a hybrid process involving membrane separation as a post-neutralization operation. Optimal operating conditions for these rival membrane processes will be unfolded in the hereafter reported experimental investigating. The comparison will extend to investigate the compliance of treated reject streams with environmental Tunisian standard NT 106 002 (Tunisian standard NT.106.002 1989).

2. Materials and methods

2.1 Industrial fluoride effluent

A genuine industrial effluent was used in this study. The effluent is generated by an aluminum fluoride manufacturing unit. It has an excessive fluoride content ranging between 2900 and 5700 mg/L. The industrial wastewater physico-chemical properties, after mild treatment before discharge into the marine environment, were previously reported (Ezzeddine *et al.* 2014b, Ben Rejeb *et al.* 2019). Within the hybrid treatment process, the industrial wastewater is diluted with fresh water or recycled brine to obtain a water stream containing about 1177 - 2288 mg/L of fluoride with a pH, a conductivity and a turbidity of around 2.4, 9 mS/cm and 6 NTU, respectively.

2.2 Chemicals and reagents

Various techniques have been utilized to determine fluoride in different aqueous medium (Yahyavi *et al.* 2015), however, the most important methods can be categorized into six principal classes: chromatography, electrochemical methods, sensors, micro fluidic analysis, titration and spectroscopy. Fluoride is usually measured using an ion-selective electrode, which allows determining the total amount of free and complex-bounded fluoride dissolved in water as described by the standard method of the American Public Health Association (APHA 1998, Ezzeddine *et al.* 2014a, b, WHO 2017, Ezzeddine and Hannachi 2017). The method detection limit of fluoride anions in aqueous solutions is 0.02 ppm. For F analysis by ion selective electrode method, water samples need to be buffered using Total Ionic Strength Adjustment Buffer (TISAB). The addition of TISAB solution before the measurement keeps the pH value and the ionic strength constant. The TISAB solution has the supplementary effect to attach interfering cations and thereby liberating complexed fluoride. In practical, various reactants are required to prepare the fluoride standard and TISAB (Ezzeddine *et al.* 2014b).

Technical grade lime (Ca(OH)₂) was the neutralizing agent for precipitating calcium fluoride (CaF₂). More effective solid–water separation was obtained, in the neutralization process, by adding analytical grade Iron III Chloride hexahydrate (FeCl₃, 6H₂O) acting as flocculent.

2.3 Analytical tools

A conductivity meter (OHAUS model starter 3100C)

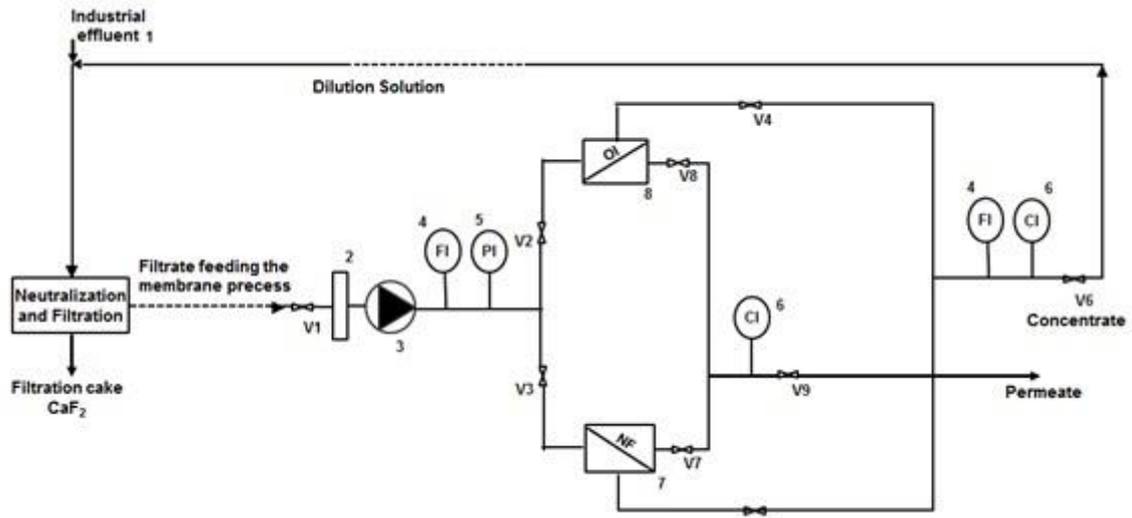


Fig. 1 Schematic diagram of the laboratory pilot

(Legend: 1: Industrial effluent; 2: Pre-filters; 3: Pump; 4: Flow-meters; 5: Pressure-gauges; 6: Conductivity-meters; 7: NF module; 8: RO module; V1-9: Valves.)

and pH meter (Metrohm 827 pH meter) were employed. Fluoride analysis were carried out by fluoride ion-selective electrode (Thermo Scientific Orion, model 9609BNWP) connected to an ion meter (OHAUS model starter 2100). The accuracy on fluoride contents in process streams water samples and raw water was determined by replications with a relative inaccuracy ranging between 2% and 16% when fluoride contents decrease from 1400 ppm to 0.6 ppm, respectively. Calcium analysis was carried out by complexometric titration with EDTA in the presence of Murexide as indicator within an imprecision of less than 1%. Turbidity was measured by means of a turbidity meter (HF-scientific Micro 100).

2.4 Experimental procedure

2.4.1 Neutralization step

Lime was sieved with 125 μm size sieve and was dried in the oven at 110°C. The industrial effluent was diluted with 2.5-dilution factor with tap water or recycled brine from the membrane process. The diluted effluent was mixed with the optimal excess of lime at 500-800 rpm for 20-40 min, resulting in the precipitation of CaF_2 (Ezzeddine *et al.* 2014b, Meftah *et al.* 2019). Iron III Chloride hexahydrate was used to speed up settling of suspended matters.

An hybrid process involving neutralization and a membrane separation to remove F^- from the waste effluent was investigated. Laboratory scale experiments were conducted simulating a continuous treatment process. Several batch treatments were performed with full stream recycling.

After neutralization, the formed CaF_2 and the remaining unreacted lime were separated from the liquid by 0.45 μm filtration. The filtrate will then undergo the NF or RO treatment.

2.4.2 Membrane separation process

Tests were performed on a low-pressure Laboratory scale pilot unit. The unit is designed for a maximum

operating pressure of 10 bar. The pilot allows to alternate between RO and NF or even combine both membrane processes.

The hybrid process flow sheet is shown in Fig. 1. For NF, NanoRO K1812 module supplied by Membranium was used. Also, the pilot is equipped with commercial spiral wound reverse osmosis membrane (75 GPD), manufactured by Aquapro. A commercial brand antiscalant was used to inhibit membrane fouling. NF and RO membrane modules intrinsic perspectives were monitored. Membrane permeability was checked before and after each membrane batch treatment with pure water.

Conductivity, turbidity and pH were monitored along with fluoride and calcium concentrations for both permeate and concentrate solutions of the membrane separation operation.

The membrane process recovery rate (τ %) 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. They were determined with an accuracy of 2% by replications for at least three times.

The recovery rate varies with the imposed pressure which was varied between 20 and 150 psi. Volumetric pumps were used to create the trans-membrane pressure drive within ± 2.5 psi.

Membrane selectivity is expressed by Fluoride rejection rate (R_F %) 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, respectively.

In all experiments and for any given operating conditions, the membrane operation was continued until a

pseudo-steady state prevailed. This was confirmed by constant flow rates and conductivities for permeate and concentrate 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 retentate flow rate and fluoride concentration, respectively. In all experiments F balance was holding within $\pm 10\%$. It is worthy to note that a similar balance on conductivity was also holding within an accuracy of 3 to 4%. Thus, tracking conductivity could be easily used for quick monitoring of the performances of membrane processes such as desalination or similar applications.

As the industrial effluent along with all water streams, except permeates, are supersaturated with respect to calcium fluoride, it is important to estimate calcium fluoride supersaturation values using the following equation:

$$\Omega_{CaF_2} = \frac{[Ca^{2+}]\gamma_{Ca^{2+}}[F^-]^2\gamma_{F^-}^{-2}}{Ksp_{CaF_2}} \quad (4)$$

where $[Ca^{2+}]$ and $[F^-]$ are the calcium and fluoride concentrations, respectively; $\gamma_{Ca^{2+}}$ and γ_{F^-} are the calcium and fluoride activity coefficients, respectively. Calcium fluoride equilibrium constant, Ksp_{CaF_2} , or the ionic activities product (IAP) for saturated solution, was experimentally determined by McCann H.G. (1968) at 34°C and found to be $3.58 \pm 0.18 \times 10^{-11}$. This value was determined using the extended Debye-Huckel model for estimating calcium and fluoride activity coefficients for weak solutions, i.e. having Ionic strengths (IS) below 0.2 (Elfil and Hannachi, 2006). The IAP is very much dependent on solution IS given by:

$$IS = \frac{1}{2} \sum z_i^2 C_i \quad (5)$$

where z_i and C_i are the i^{th} ion species charge and concentration, respectively. In this work, the same model was used to predict activity coefficients.

3. Results and discussion

3.1 Chemical precipitation

Since a real effluent, the properties of which were constantly varying, has been used, the neutralization had to be optimized. The adopted procedure has been reported in our previous investigations (Ezzeddine *et al.* 2014a, b, Ezzeddine and Hannachi 2017). Consistently with the pH variation, the optimal lime excess was identified to give the lowest conductivity and lower mineral contents in the neutralized effluent. The optimal lime excess varies according to the variation of the initial fluoride concentration in the raw effluent (see Fig. 2).

The industrial wastewater characteristics after laboratory scale neutralization are given in Table 1. The variations in conductivity, pH, turbidity, calcium concentration and the residual contents of fluoride are due to the changing industrial wastewater properties. Neutralization with hydrated lime using optimal excesses led to fluoride removal rates higher than $99.1 \pm 0.4\%$.

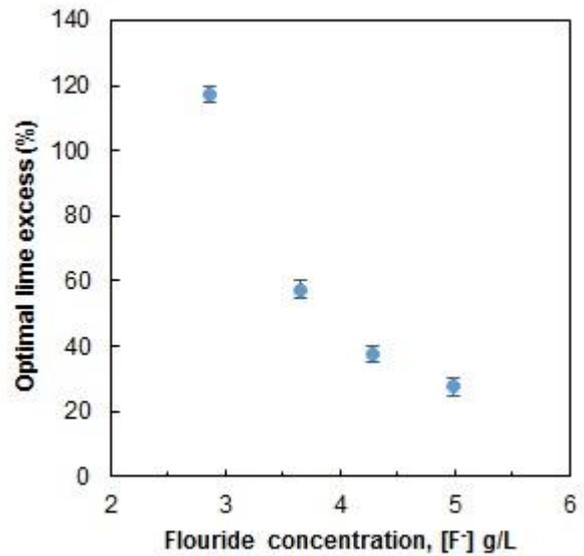


Fig. 2 Variation of optimal lime excess with feed fluoride concentration

Table 1 Neutralized Industrial wastewater properties

Parameter	Units	After Neutralization
Conductivity at 25°C	μS/cm	160-276
pH	-	6.5-7.5
Turbidity	NTU	0.5 ± 0.2
Ca ²⁺	mg/L	55.8 ± 11.8
F ⁻	mg/L	7-30

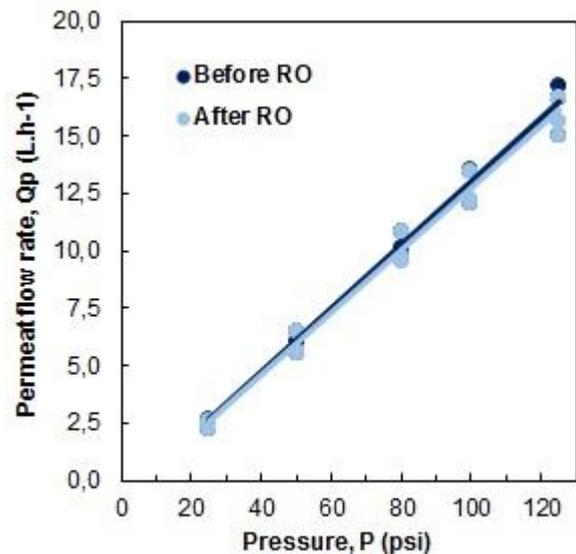


Fig. 3 RO permeate flow rate vs. transmembrane pressure

3.2 Membrane polishing treatment

As described earlier, a laboratory scale low pressure membrane unit was used. It was fed with the optimally neutralized stream effluent obtained by dilution of the industrial effluent with tap water or recycled brines. Before

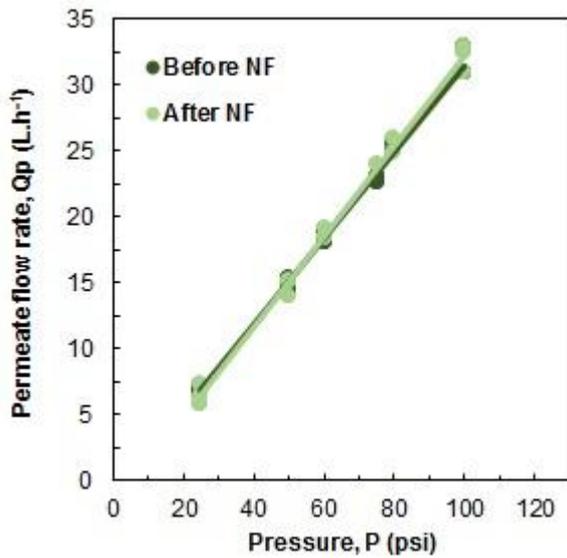


Fig. 4 NF permeate flow rate vs. transmembrane pressure

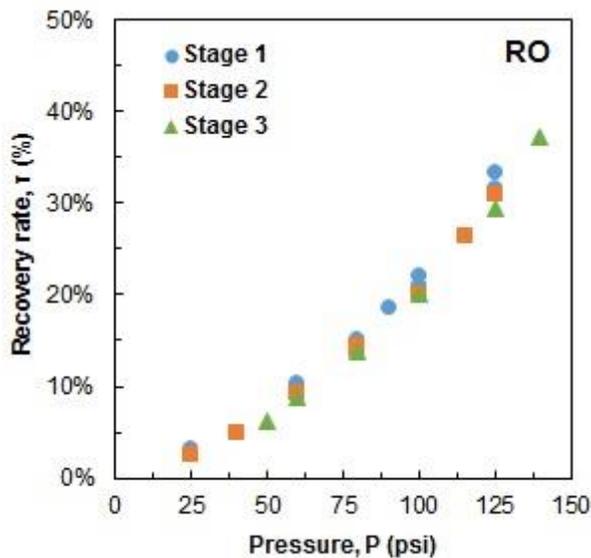


Fig. 5 RO recovery rate vs. transmembrane pressure

and after all membrane batch treatments, the membrane modules permeability was assessed with pure water to detect any membrane fouling phenomenon. No fouling was observed in this study as shown in Figs. 3 and 4. There is no significant variation of the membrane characteristic line.

To simulate a continuous treatment process, the NF or RO retentate was recycled and utilised for diluting the industrial effluent before neutralization. The investigation was limited to three consecutive batch treatments or stages.

For each stage of the membrane process, the feed pressure was changed allowing obtaining various recovery rates. Fig. 5 shows that the conversion rate ranged between 3 and 37% for a pressures ranging from 25 to 140 psi in the RO process polishing treatment. As shown in Fig. 6, the conversion rate ranges between 5 and 60 % for transmembrane pressures ranging between 20 and 100 psi for the NF process.

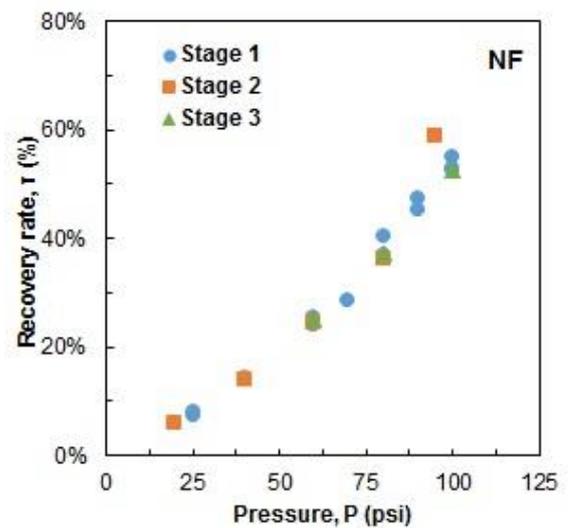


Fig. 6 NF recovery rate vs. transmembrane pressure

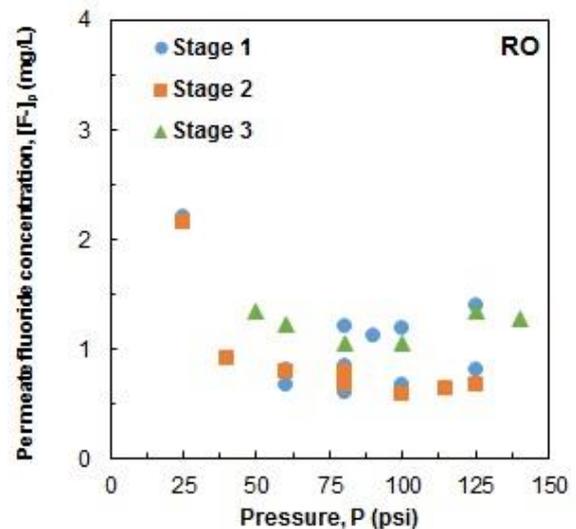


Fig. 7 RO permeate fluoride concentration vs. transmembrane pressure

The RO polishing treatment allowed decreasing the permeate fluoride concentration to 0.9 ± 0.3 mg/L (see Fig. 7) for the optimal transmembrane pressures of around 100 psi for which the fluoride rejection rate was $93 \pm 2\%$ (see Fig. 8). As shown in Fig. 9, the NF treatment permitted to reduce the permeate fluoride concentration to 1.1 ± 0.4 mg/L for all stages (see Fig. 9). NF, at the optimal pressure of around 80 psi, allowed a fluoride rejection rate of $88 \pm 5\%$ as indicated in Fig. 10.

Imposing higher transmembrane pressures, above optimal values, for both RO and NF leads to a decrease of fluoride rejection. The existence of an optimal pressure range for better separation performances in membrane modules is well known (Minyaoui *et al.* 2017). This is resulting from competing transport processes for water and other ionic species along and cross the active membrane, for varying hydrodynamic conditions corresponding to changing transmembrane pressures.

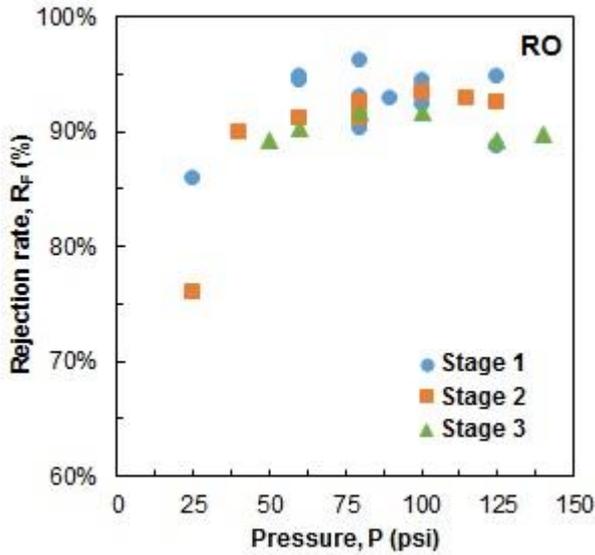


Fig. 8 RO fluoride rejection rate vs. transmembrane pressure

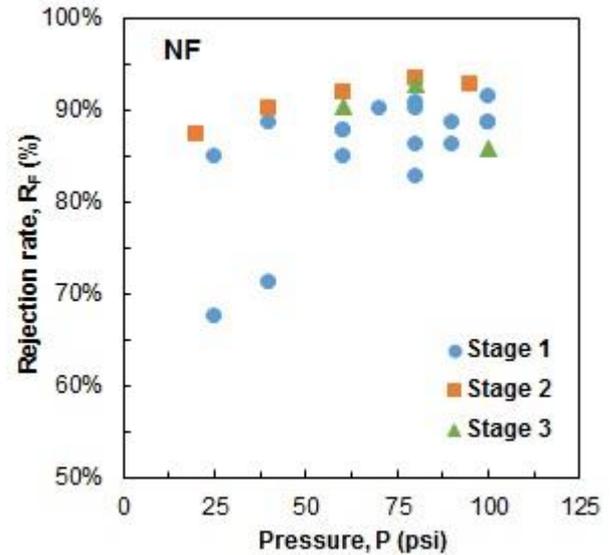


Fig. 10 NF fluoride rejection rate vs. transmembrane pressure

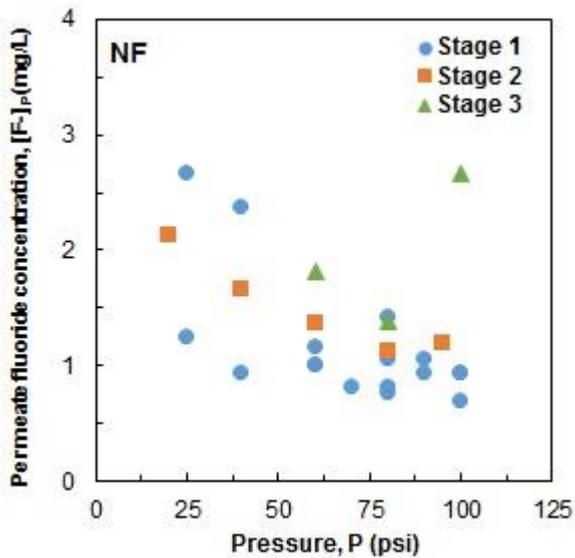


Fig. 9 NF permeate fluoride concentration vs. transmembrane pressure

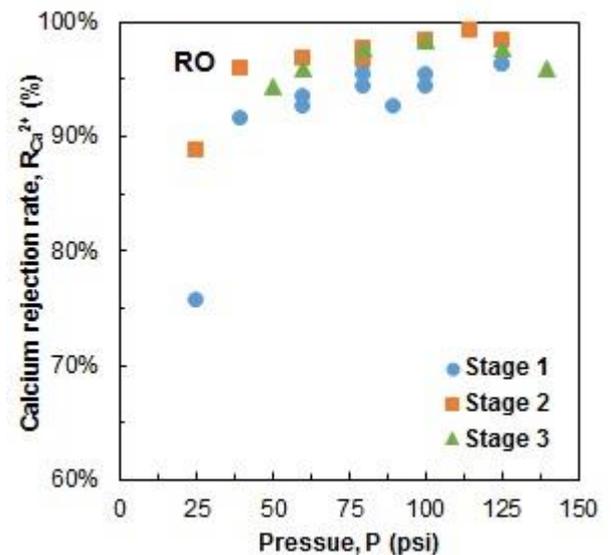


Fig. 11 RO calcium rejection rate vs. transmembrane pressure

Fig. 11 indicates that the maximum RO calcium rejection rates were 96.2 ± 1.8 % for the optimal transmembrane pressure. In the case of NF, the best rejection rates were 87 ± 3 % for the corresponding optimal transmembrane (see Fig. 12). As for fluorides, increasing the pressure leads to slight decrease of membrane selectivity.

Thus, NF vs. RO allows a reduction of the transmembrane pressure by about 20 psi at the expense of a loss of rejection rate of only 5 %. For both NF and RO the permeate fully comply with Tunisian environmental regulations. Both for RO and NF, the overall rejection rate for the hybrid process was in excess of 99.99%. The permeate is the only effluent of the hybrid fluoride removal process.

At all investigated transmembrane pressures, this effluent was complying with the Tunisian environmental regulations for reject streams discharge into the environment for both RO and NF membrane separation processes. This effluent could also be easily valorized within the manufacturing factory delivering the waste stream.

It is interesting to note that the best operating conditions could have been unfolded using only conductivity measurements. The variation of permeate and concentrate conductivity for RO are summarized in Figs. 13 and 14, respectively. It is clear that the concentrate conductivity increases with the recycling rate of brine streams from stages 1 to 3 approaching a pseudo-continuous hybrid

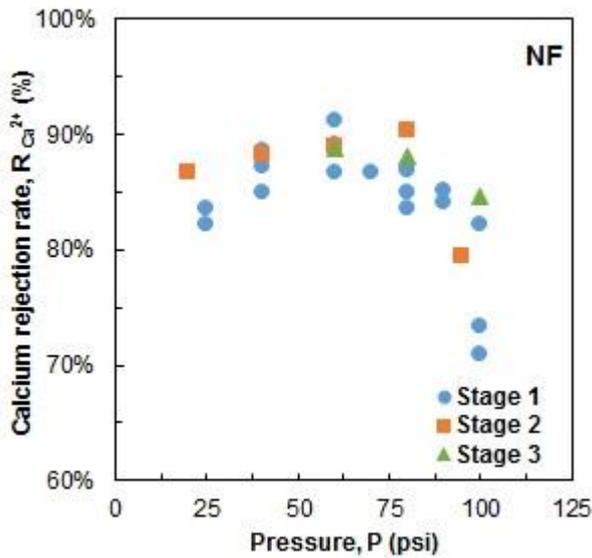


Fig. 12 NF calcium rejection rate vs. transmembrane pressure

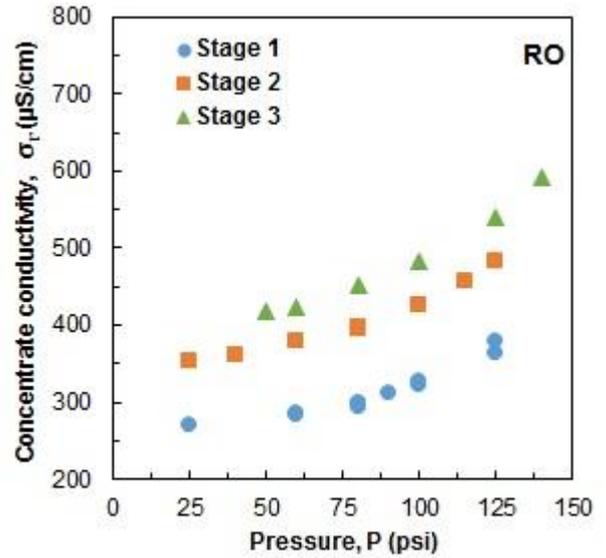


Fig. 14 RO Concentrate conductivity vs. transmembrane pressure

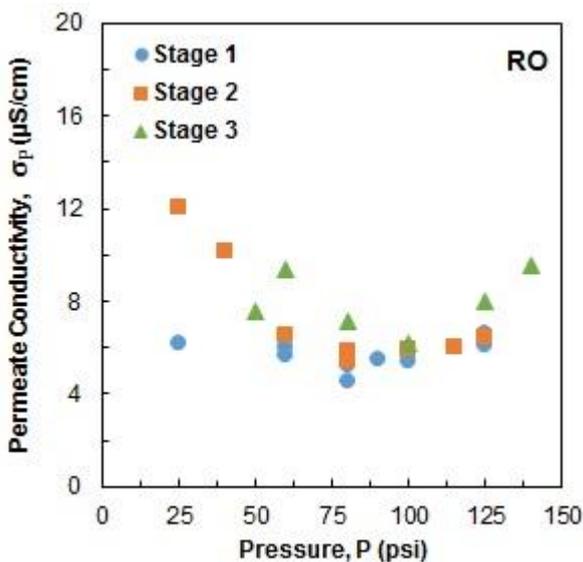


Fig. 13 RO Permeate conductivity vs. transmembrane pressure

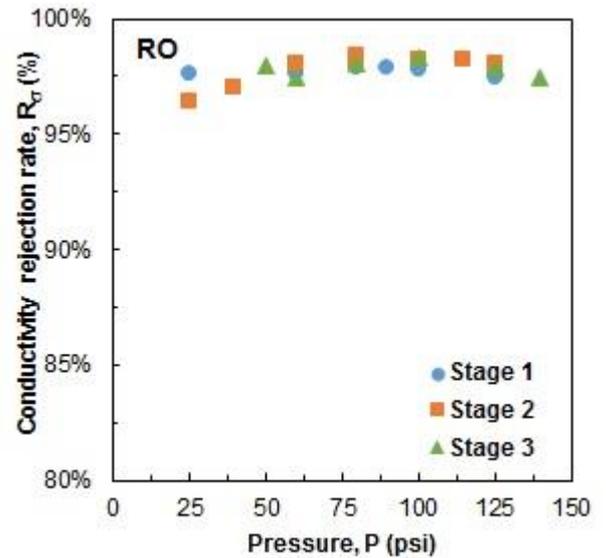


Fig. 15 RO conductivity rejection rate vs. transmembrane pressure

treatment process (see Fig. 14). This is not the case of the permeate conductivity, at least for the optimal transmembrane pressure, as clearly shown on Fig. 13. The equivalent ‘conductivity’ balance was holding for all stages within a relative deviation below 4 %. This allowed us to define a kind of ‘conductivity’ rejection rates similar to species rejections given by Eq. (2). For RO, they are shown on Fig. 15 with almost a clear maximum of 98.3 ± 0.5 % at the optimal previously indicated transmembrane pressure.

The NF results are not as good as those of RO as both permeate and retentate conductivities were increasing from batch 1 to 3 (see Figs. 16 and 17). Thus, probably there is a need of more batch treatments to reach a pseudo-continuous hybrid process in the case of NF.

Similarly to RO, the conductivity balance was holding for all batch treatments within a relative error below 3% giving an equivalent ‘conductivity’ rejection rates of about 84.6 ± 3.2 % in the vicinity of the optimal trans-membrane pressure (Fig. 18).

The solutions handled in this fluoride hybrid removal process were supersaturated with respect to calcium fluoride. Supersaturation values were estimated for all water streams. Ionic activity coefficients, were roughly assessed using extended Debye-Hukel model. All solutions’ Ionic Strengths (IS) were calculated. For RO and NF membrane separations, although, the focus was on Ca and F solutions’ contents, retentates IS were coarsely assessed using adequate rejection rates for other chemical species

(Hchaichi *et al.* 2014). IS of raw, diluted and neutralized industrial wastewater are given in Table 2. The feed calcium fluoride supersaturation evolved from 1.6 to 2.6 for consecutive batches in the RO process and from 1.1 and 5.8 for the NF batches. Figs. 19 and 20 show supersaturation ranges for various transmembrane pressures for RO and NF membrane separations. Supersaturations increase for higher transmembrane pressures, i.e. greater recovery rates. Compared to RO, NF recovery rates are higher for similar transmembrane pressures yielding more supersaturated concentrates.

Table 2 Calculated solutions' ionic strengths

	industrial wastewater	After dilution	After Neutralization
Ionic strength (mol/L)	0.16-0.23	0.06-0.08	0.01-0.02

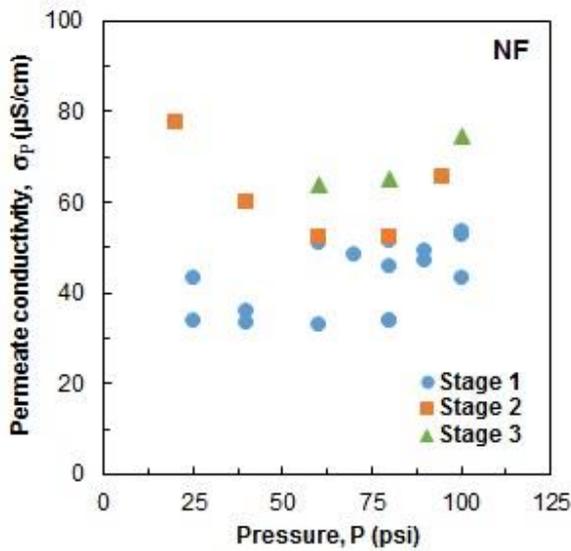


Fig. 16 NF Permeate conductivity vs. transmembrane pressure

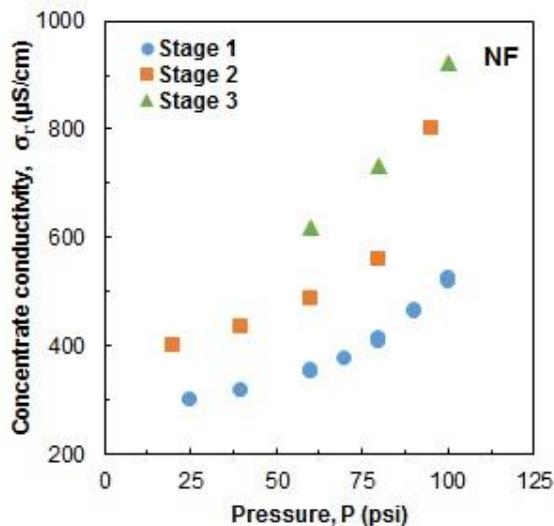


Fig. 17 NF Concentrate conductivity vs. transmembrane pressure

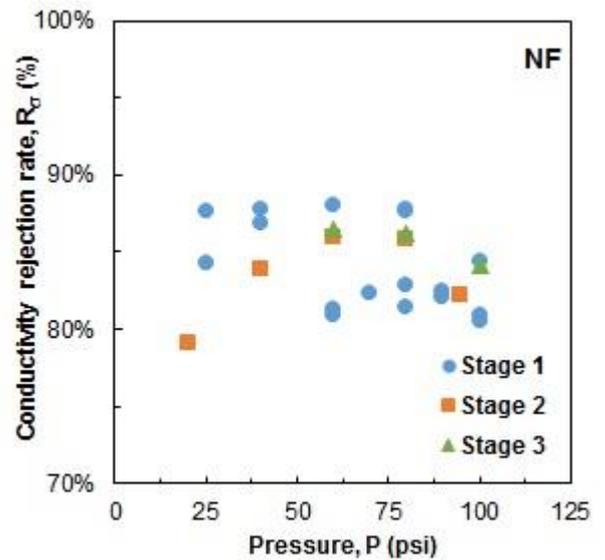


Fig. 18 NF conductivity rejection rate vs. transmembrane pressure

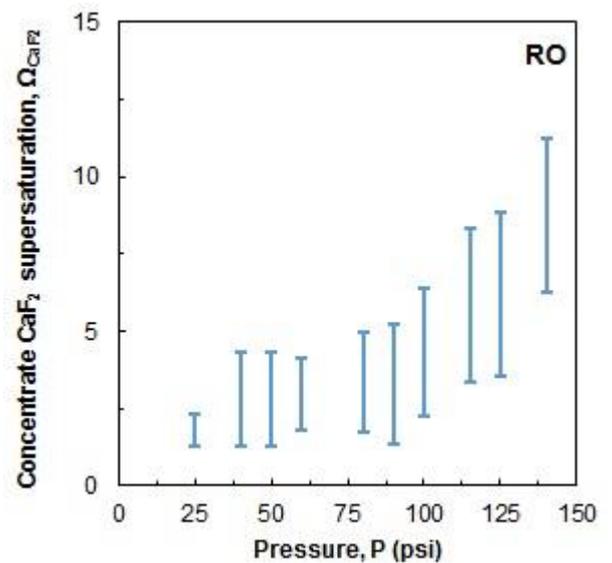


Fig. 19 RO concentrate calcium fluoride supersaturation vs. transmembrane pressure

4. Conclusions

The treatment of an industrial wastewater, having an excessive fluoride concentration (2900 - 5700 mg/L) was considered in this study. The treatment consisted of a hybrid process combining a neutralization step with lime and a NanoFiltration (NF) or Reverse Osmosis (RO) membrane separation. In order to simulate a continuous treatment process 3 consecutive batch treatments were performed with full recirculation of brines in the neutralization step.

The optimal neutralization step allowed reducing fluoride concentration by 99.1±0.4 %. The optimally neutralized effluents were further batch wise treated using

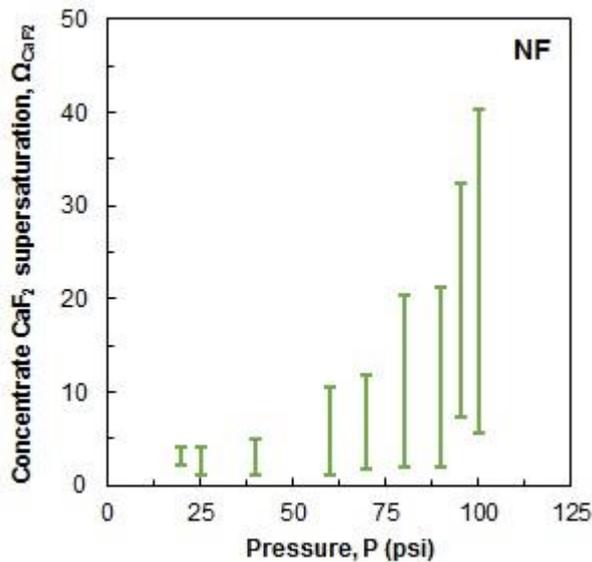


Fig. 20 NF concentrate calcium fluoride supersaturation vs. transmembrane pressure

membrane processes. The optimized RO polishing treatment allowed attaining fluoride permeate concentrations and rejection rates of 0.9 ± 0.3 mg/L and 93 ± 2 %, respectively. This was obtained for an optimal trans-membrane pressure of around 100 psi. The corresponding results for NF membrane polishing treatment, at the optimal trans-membrane pressure of around 80, were 1.1 ± 0.4 mg/L and 88 ± 5 % for fluorides' permeate contents and rejection rates, respectively. Thus, with respect to RO, NF allowed decreasing the driving force by 20% at the expense of only 5% drop of rejection rates. The overall rejection rate for the hybrid processes was exceeding 99.99% for both NF and RO with permeates at optimal operating trans-membrane pressures respecting the Tunisian environmental regulations for reject streams discharge into the environment.

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