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Removal of fluoride from an industrial wastewater by a hybrid process combining precipitation and reverse osmosis

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ABSTRACT

The purpose of this study is to apply a hybrid process that combines the precipitation with hydrate lime along with reverse osmosis (RO) treatment to deal with a real industrial wastewater having an excessive fluoride concentration of 3,200 mg/L. The effluent is discharged from an aluminum fluoride manufacturing unit. Neutralization with hydrated lime using excesses above 50% at pH 7–8 led to fluoride removal rates higher than 98%. The industrial effluent neutralized under optimal conditions underwent an RO treatment that allowed to reduce the fluoride content to about 8 mg/L giving an overall removal of 99.9% F^-. This study demonstrated that the hybrid precipitation–RO process could effectively remove fluoride from wastewater, and produce permeate and precipitates for potential recovery and reuse.

Keywords: Aluminum fluoride manufacturing; Industrial wastewater; Fluoride removal; Precipitation; Reverse osmosis

1. Introduction

Aluminum fluoride production is performed through the following process:

Acid grade fluorspar (CaF_2) reacts with sulfuric acid (H_2SO_4) in externally heated rotary kilns, generating hydrofluoric acid (HF) gas and calcium sulfate ($CaSO_4$) according to the equation:

$$CaF_2 + H_2SO_4 \Leftrightarrow 2HF + CaSO_4 \quad \text{(R.1)}$$

HF reacts with dry aluminum hydrate ($Al(OH)_3$) in fluidized bed reactor to produce aluminum fluoride (AlF_3).

$$Al(OH)_3 + 3HF \Leftrightarrow AlF_3 + 3H_2O \quad \text{(R.2)}$$

This process generates large amounts of hazardous waste, including fine dust particles, acid, liquid effluent, and solid waste. The management of these wastes has become one of the critical environmental challenges for this industry.

Aluminum fluoride manufacturing wastewaters (AFMW) generated from the process operations have low pH and contain high levels of fluoride. In the aluminum fluoride plant, the source of fluoride in the aqueous effluent is HF absorbed by washing of the unit flue gas as shown in Fig. 1. Typical fluoride concentrations in the effluent lay between 100 and 6,500 mg/L [1]. The discharge of such wastewater into

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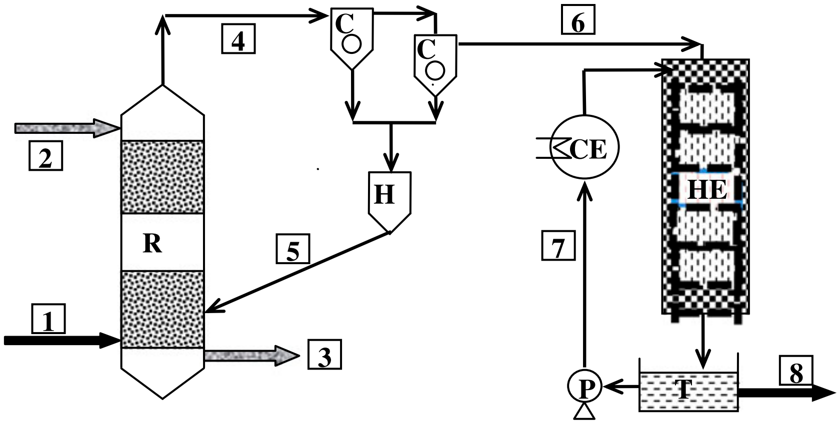

	Equipment	*Stream n°*	*Medium*
TK	*Waste water storage tank*	*1*	*Hydrofluoric acid (HF) gas*
C	*Cyclone*	*2*	*Dry aluminum hydrate*
HE	*Heat exchanger (condenseur)*	*3*	*Aluminium fluoride*
CE	*Cooling exchanger*	*4*	*HF + steam + dust*
P	*Wastewater pump*	*5*	*Aluminium fluoride*
R	*Fluidized bed reactor*	*6*	*HF + steam*
H	*Hopper*	*7 & 8*	*AFMW*

Fig. 1. Flowsheet of the AFMW generation process.

the sea would lead to the pollution of the marine environment. Fluoride is essential in small quantities for mineralization of bone and protection against dental caries; higher intake causes metabolic activity, structural and functional damages in organs such as nervous system, hypertension, kidney, and liver [2–4]. Due to its high toxicity, industrial wastewater containing fluoride is strictly regulated. The current discharge standards for wastewater containing fluoride vary from country to country. For instance, the recommended values for some countries are reflected in the Table 1. Examination of this table shows that Tunisia is among the most stringent countries with respect to fluoride contents.

Thus the AFMW needs to undergo an adequate treatment prior to its discharge. The only way to circumvent this problem is defluoridation. A review of several defluoridation methods was reported by Mohapatra et al. [11]. Defluoridation techniques include adsorption, ion-exchange, fluidized bed precipitation, electrodialysis, and electrolytic defluoridation [12–18]. Membrane processes such as reverse osmosis (RO), nanofiltration, and Donnan dialysis were also investigated to reduce fluoride concentrations in water and wastewater [19–22].

Among the wastewater treatment techniques, adding excess of lime to form calcium fluoride (CaF_2) is the most commonly used way to remove fluoride ions from industrial effluent containing high concentration of this element [23]. However, achieving low fluoride concentration within the environmental standards using precipitation technique is difficult and requires large amounts of lime.

In practice, the precipitation can only reduce the fluoride concentration to a range of 20–100 mg/L. Consequently, another defluoridation process must be performed. This is often carried out by chemical coagulation. Although it is simple and effective, it induces a secondary pollution by increasing water hardness and generating water effluents containing very small particles and sludge volumes of that poses disposal problems. RO is an alternative technology for post-lime neutralization of water and wastewater defluoridation systems. Compared to conventional chemical coagulation, it has proved to be more effective in removing inorganic contaminants. Meenakshi and Maheshwari [24] reported a comparative analysis of

Table 1
Discharge standards of fluoride in wastewater

Country	USA	Tunisia	Japan	China	France	Poland
Norms (mg/L)	4	5–3	5–15	10	15	25
Reference	[5]	[6]	[7]	[8]	[9]	[10]

various techniques for fluoride removal, and they showed that RO has the highest removal (90–92%) as compared to adsorption and coagulation.

In a previous work, removal of fluoride from AFMW by precipitation and adsorption processes was studied [1]. Treatment of AFMW by precipitation–neutralization using calcium hydroxide (lime) or calcium carbonate (limestone), and adsorption using Tunisian activated clay has been investigated.

In the present work, the RO was used for polishing treatment after neutralizing step. The objective of this investigation is to find the optimal operating conditions for the hybrid AFMW neutralization in the first step.

2. Materials and methods

2.1. Industrial waste effluent

Studies were carried out using raw wastewater generated during the manufacturing of aluminum fluoride (AFMW) using HF and aluminum hydrate. The effluent was collected from Tunisian AlF_3 plant. The physico-chemical compositions of this industrial wastewater are given in Table 2.

As shown in this table, this acidic effluent to be treated has a very elevated conductivity and high fluoride content. In contrast, silica, calcium, iron, and magnesium levels were low. For all fluoride-containing solutions, only polyethylene (PE) vessels were used for sample preparation and storage. Prior to treatment, the AFMW was diluted to obtain an effluent containing about 300 mg/L of fluoride.

2.2. Chemicals and reagents

In the experiments, analytical grade chemicals were used. They include: sodium hydroxide (NaOH), aluminum sulfate ($Al_2(SO_4)_3 \cdot 18H_2O$), sodium fluoride (NaF), silver chloride (AgCl), silver nitrate ($AgNO_3$), sodium chloride (NaCl), cyclohexane diamino-tetraacetic acid (CDTA), and hydrochloric acid (HCl).

Several studies showed that hydrated lime is an adequate source of calcium to neutralize fluoride containing wastewater [1,25]. In addition, $Ca(OH)_2$ is cheap and available in Tunisia and elsewhere. Local-grade hydrated lime, whose specifications were reported in a previous work [1] was used for neutralization.

2.3. Neutralization test

The experiments were performed in a closed batch polyethylene reactor of 1 L capacity. All experiments were performed at room temperature (25 ± 1˚C) and atmospheric pressure under stirring conditions. Specific quantities of lime were added at the beginning of the treatment to the desired volume of AFMW and allowed to react for a period exceeding 50 min under vigorous stirring. The mixed solution was stirred for 120 min to allow the precipitation reaction. Samples were taken at regular time intervals (every 10 min), to monitor the pH, conductivity, and fluoride concentration. A flocculent, aluminum sulfate, was added to speed up settling of suspended matters. A jar test was performed to determinate the adequate flocculent amount. The same flocculent amount was added for all precipitation batches.

After the neutralization, the formed CaF_2 and the remaining unreacted lime have to be separated from the liquid. This was performed by filtration using 0.45 μm membrane filter. The obtained cake was dried at 110 ± 0.2˚C overnight before being analyzed. The filtrate will be further treated by RO.

2.4. RO unit

A low-pressure RO pilot unit was used in the experiment. The unit is designed for a maximum operating pressure of 6 bar. An antiscalent was used to prevent membrane fouling. Membrane permeability was checked before and after RO treatment of neutralized effluent using pure water. Several operating parameters such as flow rates, conductivities, and applied pressure were monitored. All water steams, in RO unit, were occasionally subject to chemical analysis. Intermittently fluoride concentration, conductivity, and pH were determined for feed water before and after the pretreatment process.

2.5. RO treatment efficiency

To assess the RO treatment efficiency some useful equations and parameters need to be introduced:

The recovery rate (τ) is defined as the ratio of the permeate flow rate and that of the feed water to the unit:

$$\tau = 100\frac{Q_p}{Q_f} \tag{1}$$

where Q_f and Q_p are the feed and permeate flow rates, respectively.

Table 2
Wastewater physico-chemical parameters

Parameter		Units	Value
Conductivity at 25 ± 1˚C		mS/cm	198.4
pH			1.7
Silt density index	(SDI)	mL/g	0.01
Turbidity		NTU	94.3
Total suspended solids	(TSS)	mg/L	267
Total organic carbon	(TOC)	mg/L	36.16
Biochemical oxygen demand	(BOD)	mg/L	104
Chemical oxygen demand	(COD)	mg/L	124
Total Kjeldahl nitrogen	(TKN)	mg/L	1.75
Total phosphorus as P	(TP)	mg/L	4.5
Oil, fat, and grease	(FOG)	mg/L	<0.5
Cations	Ca^{2+}	mg/L	59.3
	Mg^{2+}	mg/L	29.5
	Na^{+}	mg/L	163
	K^{+}	mg/L	1.54
	Al^{3+}	mg/L	375
	Sr^{2-}	mg/L	0.66
	Ba^{2+}	mg/L	0.69
	Fe^{3+}	mg/L	10.09
	Mn^{2+}	mg/L	<0.05
Anions	HCO_3	mg/L	<1
	NO_3	mg/L	<1
	Cl	mg/L	416.9
	SO_4	mg/L	86
	F	mg/L	3,200
Other	SiO_2	mg/L	1,501
	Free chlorine	mg/L	<0.5
	Alkalinity as $CaCO_3$	mg/L	148.1
	TDS	g/L	90.8

The fluoride rejection rate (F_R) is given by the following relation:

$$F_R = 100\frac{[F^-]_f - [F^-]_p}{[F^-]_f} \tag{2}$$

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

In all RO polishing treatment experiments, a balance on fluoride was performed. It is expressed as:

$$Q_f[F^-]_f = Q_p[F^-]_p + Q_r[F^-]_r \tag{3}$$

where Q_r and $[F^-]_r$ are the retentate flow rate and retentate fluoride concentration (mg/L), respectively.

2.6. Analytical methods

A conductivity meter (Metrohm 856 Conductivity Module) and pH meter (Metrohm 780 pH meter equipped by a HF-resistant glass electrode Metrohm 6.0421.100) were used to measure the conductivity at 25 ± 1˚C and the pH of the applied samples.

The fluoride concentrations were measured with a fluoride-selective electrode (Orion, 9609BNWP) connected to an ion meter (Orion, 4-Star) according to the standard method given by American Public Health Association [26]. To prevent the interference from other ions (Fe^{3+}, Al^{3+}, Cu^{2+}, and Ca^{2+}), a total ionic strength adjustment buffer solution containing cyclohexane diamino-tetra-acetic acid (CDTA) was added to the samples.

X-ray fluorescence spectrometer PANalytical model AXIOS was used to characterize the obtained precipitates. All quantitative analyses were run in triplicate for reproducibility of data and results in the figures, and tables were the average ones.

3. Results and discussion

3.1. Chemical precipitation

Fig. 2 shows the pH evolution as a function of lime excess used for neutralization of the AFMW. Three stages of pH variation were obtained: pH increased slowly up to 40% lime excess; afterwards a steep pH increase from 4 to 10 for 70% lime excess; finally a pseudo plateau for high lime excess was reached.

The effect of lime excess on the extent of fluoride removal was studied. Lime excess was varied from 10 to 90% for a neutralization time of two hours. Fig. 3 presents the changes in fluoride concentration with lime excess. It can be seen that the fluoride concentration is largely affected by lime excess. Increasing lime excess drastically decreases fluoride concentration in the effluent up to 60% excess. Beyond this excess the fluoride removal rate reaches a pseudo plateau giving a removal rate of 98.1%. This result is consistent with what was reported in the literature [1,27] i.e. there is an optimal lime excess.

The fluoride concentration after neutralization is still high requiring a polishing treatment. Since RO was chosen to further decrease fluoride concentration, effluent conductivity was monitored. Fig. 4 summarizes the effect of lime excess on the conductivity at 25 ± 1°C of the medium during the AFMW treatment.

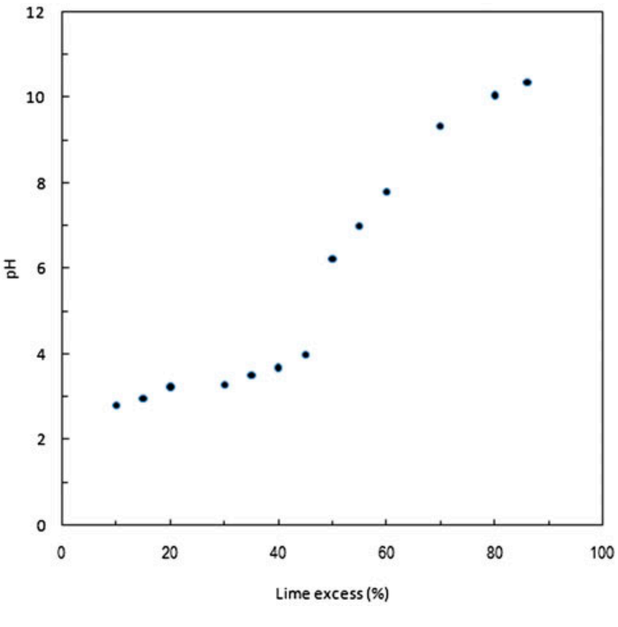

Fig. 2. pH vs. lime excess.

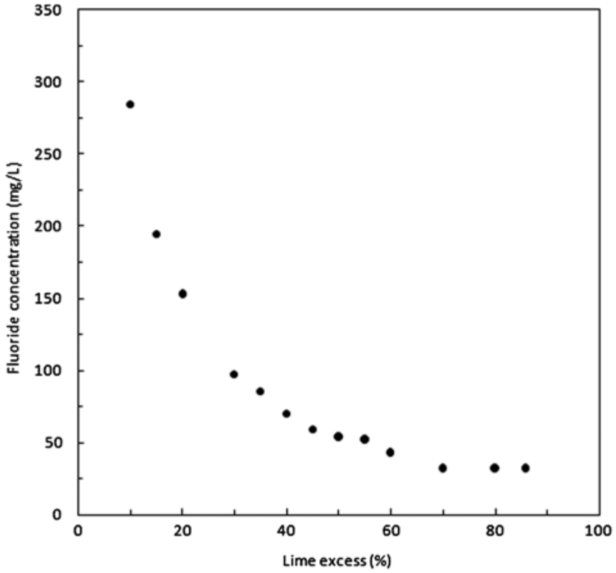

Fig. 3. Effect of lime excess on fluoride concentration.

Consistently with the pH variation, the optimal lime excess is about 50% giving the lowest conductivity, i.e. lower mineral contents in the effluent. For lower lime excesses, dissolved lime is matched by CaF_2 precipitation giving a net conductivity decrease. Beyond 50% lime excess, dissolved lime increases in the effluent hindering fluoride removal.

Furthermore, Fig. 5 presents conductivity variations along neutralization for three limes excess: 50, 67, and 85%. For 50% lime excess, conductivity monotonously decreases before reaching a plateau of 0.14 mS/cm after 25 min. However, for higher lime excesses, conductivity decreases even faster in the first 5 min of neutralization period; a jump of conductivity was then observed reflecting higher mineral content of the effluent. The limiting conductivity value increases with increasing lime excess. Despite the fact that the literature is relatively rich in reporting fluoride removal using calcium salts, none has given an interest in conductivity variations and its kinetics [1,25].

Table 3 shows the differences in composition between the supernatant after precipitation and the raw water before precipitation. The removal rate of fluoride after precipitation exceeded 98.1%, but the concentration of fluoride ions did not fall below 60 mg/L. Although Al^{3+}, SO_4^{2-}, Ca^{2+}, and Mg^{2+} ions

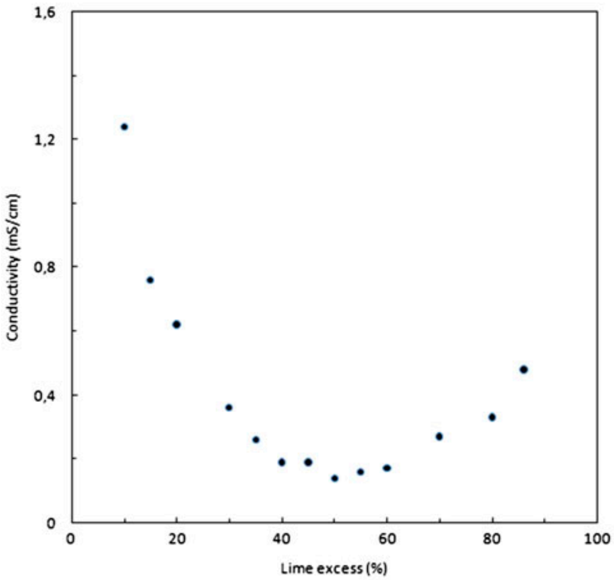

Fig. 4. Effect of lime excess on conductivity.

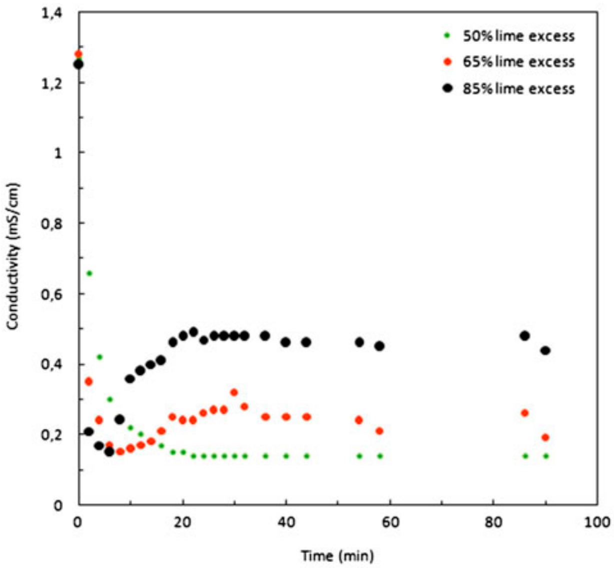

Fig. 5. Wastewater conductivity variation with time at different lime excesses.

could be removed, the concentrations of Si rose after precipitation.

Now the optimal conditions for neutralization were determinate and the final fluoride effluent content is not satisfactory. An additional RO treatment will be applied.

Table 3
Ions in AFMW before and after neutralization with lime

Species	Before precipitation (mg/L)	After precipitation (mg/L)	Removal rate (%)
F^-	3,200	60.13	98.1
Ca^{2+}	59.3	24.8	58.2
Mg^{2+}	29.5	6.72	77.2
SO_4^{2-}	86	38	55.8
Al^{3+}	375	180	52.0
SiO_2	1,501	2,410	–

3.2. RO polishing treatment

Lab-scale experiments were conducted to investigate the performance of RO polishing treatment of the overall fluoride removal. A low pressure RO unit fed with neutralized AFMW effluent was used for the experiments. After each RO experiment, the membrane permeability is assessed with distilled water to spot any membrane fouling occurrence. No fouling was observed in the study. The recovery rate (τ) was used to evaluate the RO unit performances. Several experiments were conducted to investigate the pressure effects on the unit recovery rate. These runs were conducted at variable transmembrane pressure in the interval 30–60 psi. The results of this set of experiments are summarized in Fig. 6. The recovery rate ranged between 8 and 30%. As expected, the conversion rate steadily increases with cross-membrane pressure difference.

Furthermore, Fig. 7 presents the changes of fluoride concentration in the permeate. From this figure, it can be seen that the fluoride concentration in the permeate decreases with the increase of pressure from 10.8 to 8 mg/L for pressure range of 30–60 psi. This is also demonstrated by the fluoride rejection rate given by Eq. (2). Fig. 8 gives the variation of the fluoride rejection rate with the pressure. This figure clearly shows that the fluoride rejection rate increased with pressure from 85 to 88% for transmembrane pressure between 30 and 60 psi. However, when operating at high pressures, rejection rate is expected to decrease as reported by Li et al. [28]. Therefore, there should be an optimal operating pressure for the RO treatment.

Considering both recovery rate and permeate fluoride concentration within the covered operating range, it is better to operate at high pressure.

In all experiments, mass balance was cheeked with respect to fluoride. The error did not exceed 2% in most experiments.

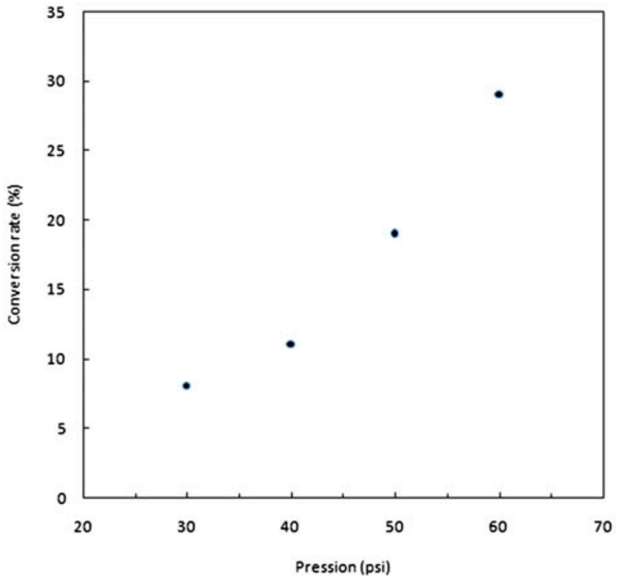

Fig. 6. Conversion rate vs. cross-membrane pressure difference.

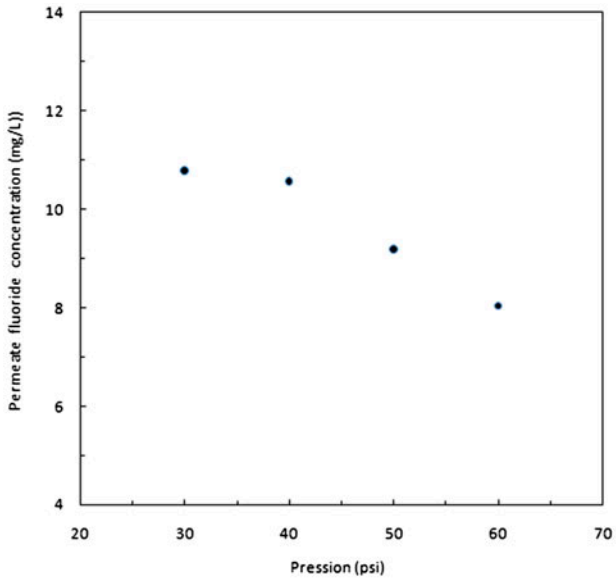

Fig. 7. Permeate fluoride concentration vs. pressure.

Some experiments for the hybrid process were performed. In these runs, the retentate was used for diluting the AFMW prior to neutralization. The results were promising with permeate fluoride concentration levels below Tunisian standard (5 mg/L), so that permeate stream can be reused or discharged into the sea.

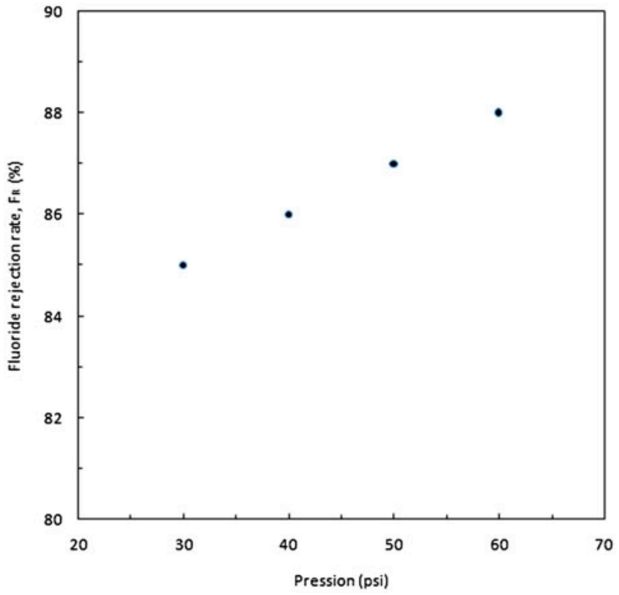

Fig. 8. Variation of the rejection rate vs. the cross-membrane pressure difference.

4. Conclusion

A lab-scale experimental investigation was performed for treating fluoride rich wastewater. The effluent was generated by aluminum fluoride manufacturing unit with fluoride contents of 3,200 mg/L. The treatment process combined a neutralization step using lime and a polishing treatment by RO. Precipitation using lime alone was efficient and reduces the fluoride concentration to 60 mg/L. The optimal lime excess for precipitation test was determined. This allowed obtaining a fluoride removal rate of 98%. The neutralized effluent was further treated using a low-pressure RO unit. This polishing treatment allowed to decrease the permeate fluoride concentration to 8 mg/L, allowing to reach an overall fluoride removal rate of 99.7%.

References

[1] A. Ezzeddine, A. Bedoui, A. Hannachi, N. Bensalah, Removal of fluoride from aluminum fluoride manufacturing wastewater by precipitation and adsorption processes, Desalin. Water Treat. 11 (2014) 1–13.

[2] L. Valdez-Jiménez, C. Soria Fregozo, M.L. Miranda Beltran, O. Gutierrez Coronado, M.I. Perez Vega, Effects of the fluoride on the central nervous system, Neurologia 26 (2011) 297–300.

[3] L. Sun, Y. Gao, H. Liu, W. Zhang, Y. Ding, B. Li, M. Li, D. Sun, An assessment of the relationship between excess fluoride intake from drinking water and essential hypertension in adults residing in fluoride endemic areas, Sci. Total Environ. 443 (2013) 864–869.

[4] A. Chattopadhyay, S. Podder, S. Agarwal, S. Bhattacharya, Fluoride-induced histopathology and synthesis of stress protein in liver and kidney of mice, Arch. Toxicol. 85 (2011) 327–335.

[5] EPA, Federal Water Pollution Control Act (Clean Water Act), Semiconductor Best Practicable Control Technology Currently Available (BPT) Effluent Limitations, May 2, 2014. Available from: http://www.epa.gov/dfe/pubs/pwb/tech_rep/fedregs/regsectb.htm.

[6] Tunisian standard NT.106.002 relative to wastewaters (Environmental protection), Off. J. Tunisian Repub. 59 (1989) 1332–1338.

[7] M. Yang, T. Hashimito, N. Hoshi, H. Myoga, Fluoride removal in a fixed bed packed with granular calcite, Water Res. 33 (1999) 3395–3402.

[8] F. Shen, X. Chen, P. Gao, G. Chen, Electrochemical removal of fluoride ions from industrial wastewater, Chem. Eng. Sci. 58 (2003) 987–993.

[9] JORF, Decree of September 26 1985 regarding surface finishing units (in French). Available 2 May 2014 from: http://www.legifrance.gouv.fr/affichTexte.do.

[10] B. Grzmil, J. Wronkowski, Removal of phosphates and fluorides from industrial wastewater, Desalination 189 (2006) 261–268.

[11] M. Mohapatra, S. Anand, B.K. Mishra, D.E. Giles, P. Singh, Review of fluoride removal from drinking water, J. Environ. Manage. 91 (2009) 67–77.

[12] P. Koilraj, S. Kannan, Aqueous fluoride removal using ZnCr layered double hydroxides and their polymeric composites: Batch and column studies, Chem. Eng. J. 234 (2013) 406–415.

[13] V. Tomar, S. Prasad, D. Kumar, Adsorptive removal of fluoride from aqueous media using *Citrus limoum* (Lemon) leaf, Microshem. J. 112 (2014) 97–103.

[14] N. Viswanathan, S. Meenakshi, Role of metal ion incorporation in ion exchange resin on the selectivity of fluoride, J. Hazard. Mater. 162 (2009) 920–930.

[15] D.B. Bhatt, P.R. Bhatt, H. Hari Prasad, K.M. Popat, P.S. Anand, Removal of fluoride ion from aqueous bodies by aluminium complexed amino phosphonic acid type resins, Indian J. Chem. Technol. 11 (2004) 299–303.

[16] R. Aldaco, A. Irabien, P. Luis, Fluidized bed reactor for fluoride removal, Chem. Eng. J. 107 (2005) 113–117.

[17] M.A. Menkouchi Sahli, S. Annouar, M. Tahaikt, M. Mountadar, A. Soufiane, A. Elmidaoui, Fluoride removal for underground brackish water by adsorption on the natural chitosan and by electrodialysis, Desalination 212 (2007) 37–45.

[18] E. Ergun, A. Tor, Y. Cengeloglu, I. Kocak, Electrodialytic removal of fluoride from water: Effects of process parameters and accompanying anions, Sep. Purif. Technol. 64 (2008) 147–153.

[19] L.A. Richards, M. Vuachère, A.I. Schäfer, Impact of pH on the removal of fluoride, nitrate and boron by nanofiltration/reverse osmosis, Desalination 261 (2010) 331–337.

[20] P. Sehn, Fluoride removal with extra low energy reverse osmosis membranes: Three years of large scale field experience in Finland, Desalination 223 (2008) 73–84.

[21] K. Hu, J.M. Dickson, Nanofiltration membrane performance on fluoride removal from water, J. Membr. Sci. 279 (2006) 529–538.

[22] A. Tor, Removal of fluoride from water using anion-exchange membrane under Donnan dialysis condition, J. Hazard. Mater. 141 (2007) 814–818.

[23] S. Vasudevan, B.S. Kannan, J. Lakshmi, S. Mohanraj, G. Sozhan, Effects of alternating and direct current in electrocoagulation process on the removal of fluoride from water, J. Chem. Technol. Biotechnol. 86 (2011) 428–436.

[24] M. Arora, R.C. Maheshwari, Fluoride in drinking water and its removal, J. Hazard. Mater. 137 (2006) 456–463.

[25] S. Saha, Treatment of aqueous effluent for fluoride removal, Water Res. 27(8) (1993) 1347–1350.

[26] APHA, Standard Methods for the Examination of Water and Wastewater, twentieth ed., American Public Health Association/American Water Works Association/Water Environment Federation, Washington, DC, 1998.

[27] D.F. Lawer, D.H. Williams, Equalization/neutralization modeling, Water Res. 18(11) (1984) 411–419.

[28] S.J. Li, Y.F. Wang, T.Y. Wang, D.Z. Tian, L.J. Zheng, Q.X. Luo, Removal of fluorions from trifluoroacetic acid by reverse osmosis, Desalin. Water Treat. 20 (2010) 66–71.