Desalination and Water Treatment
www.deswater.com

doi: 10.1080/19443994.2014.899515

54 (2015) 2280–2292
May

Taylor & Francis
Taylor & Francis Group

Removal of fluoride from aluminum fluoride manufacturing wastewater by precipitation and adsorption processes

Abdessalem Ezzeddine[a], Ahmed Bedoui[b], Ahmed Hannachi[a], Nasr Bensalah[c,*]

[a]*Department of Chemical-Process Engineering, National School of Engineering of Gabes, University of Gabes, Omar Ibn Elkhattab Street, 6072 Zrig, Gabes, Tunisia*
[b]*Faculty of Sciences of Gabes, Department of Chemistry, University of Gabes, Erriadh City, 6072 Zrig, Gabes, Tunisia*
[c]*Department of Chemistry and Earth Sciences, College of Arts and Sciences, Qatar University, Doha 2713, Qatar, Tel. +974 44036540; Fax: +974 44034651; email: nasr.bensalah@qu.edu.qa*

Received 18 April 2013; Accepted 8 February 2014

ABSTRACT

In this study, the treatment of aluminum fluoride manufacturing Wastewaters (AFMW) by precipitation–neutralization using calcium hydroxide (lime) or calcium carbonate (limestone) and adsorption using activated clay has been investigated. Effects of experimental conditions such as lime or limestone dose, clay mass, initial fluoride concentration and initial pH on the fluoride removal efficiency and the final pH have been evaluated. Results of this study indicated that precipitation–neutralization processes can be successfully used to remove more than 90% of fluoride from AFMW. The treatment of AFMW containing different fluoride concentrations ranging from 167 to 5295 mg/L by precipitation with lime using $[Ca^{2+}]/[F^-]$ molar ratio of 0.8 led to fluoride removal higher than 95% with a final pH within the range 6.5 ± 0.1 to 8.5 ± 0.1. Precipitation with $CaCO_3$ needed higher $[Ca^{2+}]/[F^-]$ molar ratio of 2 to reach 90% of fluoride removal and obtain a final pH in the range from 6.5 ± 0.1 to 8.5 ± 0.1. The results of the treatment of AFMW by adsorption on activated bentonite clay indicated that using $[clay]/[F^-]$ mass ratio of 60 under different pH varying from pH 2 ± 0.1 to pH 12 ± 0.1 can lead to 80% fluoride removal. Synthetic calcium fluoride (SCFL) generated by precipitation–neutralization with lime SCFL contains 77.9% of CaF_2; however, only 48.3% of CaF_2 are contained in solids generated from precipitation–neutralization with limestone SCFLS.

Keywords: Fluoride; Precipitation–neutralization; Adsorption; Lime; Limestone; Synthetic calcium fluoride; Aluminum fluoride manufacturing; Activated clay

1. Introduction

Fluoride is a common element in the earth's crust and is highly soluble in water. Intake of fluoride is mainly through consuming drinking water containing fluoride. Fluoride intake at 0.5–1.5 mg/day will benefit teeth and bone development [1]. However, excessive fluoride intake can lead to dental and skeletal fluorosis, a chronic endemic disease. Fluorosis is a worldwide health problem and is endemic in certain areas in Tunisia, Algeria, Senegal, China, India, etc. In addition, exposure to excessive fluoride can also cause metabolic, structural and functional damages in such organs as nervous system [2], endocrine glands [3],

---

*Corresponding author.

reproductive system [4], hypertension [5], kidney, and liver [6].

Fluoride pollution occurs through two different sources including natural and artificial sources. In groundwater sources, the natural concentration of fluoride depends on the geological, chemical, and physical characteristics of the aquifer. Fluoride ions can also found in wastewater from the fluoride chemical industries, such as aluminum fluoride manufacturing, semiconductor, fertilizer and glass-manufacturing industries. Some of these wastewaters were discharged into natural environment without any treatment. In Tunisia during manufacturing of aluminum fluoride, large quantities of hydrofluoric acid (HF) are used. Hence, effluents from this process contain high levels of fluoride. Typical fluoride concentrations are from 100 to 6,500 mg/L. The international legal requirement for effluent discharge needs an efficient treatment to remove fluoride ions contained in this effluent prior its discharge into the environment.

Several research efforts aiming to the development of efficient technologies for the reduction of the fluoride anions in industrial effluents have been reported in the literature and several methods such as coagulation [7], adsorption [8,9], reverse osmosis [10,11], nanofiltration [12], electrodialysis [13], Donnan dialysis [14], ion-exchange [15], and electrolytic methods [16,17] have been employed or tested for defluoridation. These studies have shown that several methods are successful to remove fluoride contained in industrial wastewaters but their feasibility is case specific. The disadvantages of most of these methods are high operational and maintenance costs and complicated procedure involved in the treatment. For example, the coagulation methods have generally been found effective in defluoridation, but they are unsuccessful in bringing fluoride to desired concentration levels. Furthermore, membrane processes do not require additives, but these are relatively expensive to install and operate and prone to fouling, scaling, or membrane degradation. Also, the electrochemical techniques, in general, suffer due to the high cost factor, during installation and maintenance [18].

For high fluoride concentration, chemical precipitation–neutralization technique is one of the common techniques widely used to remove fluoride from industrial wastewaters, which offers a low cost to many fluoride wastewaters treatment [19]. This process produces calcium fluoride (CaF_2) particles through the addition of lime or any other calcium salt, such as, $CaCO_3$, $CaSO_4$, and $CaCl_2$ according to Eq. (1):

$$Ca(OH)_{2\,(s)} + 2F^-_{(aq)} \rightarrow CaF_{2(s)} + 2OH^- \quad (1)$$

The adsorption process is widely used offering satisfactory results and seems to be a more attractive method for the removal of fluoride in terms of cost, simplicity of design and operation [20,21]. More than 100 adsorbents for fluoride adsorption are presented in the literature [22], e.g. clayey soils [23], magnesium incorporated bentonite clay [24], Algerian clay montmorillonite with and without calcium [25], granular acid-treated bentonite GHB [26], bentonite-based [27], organically modified clays [28], and more. High fluoride removal efficiency can be realized by adsorption on natural clays especially after optimization of operating conditions.

The present work aims to (i) evaluate the feasibility of precipitation process using $Ca(OH)_2$ or $CaCO_3$ and adsorption on Tunisian activated bentonite clay to treat high fluoride-content wastewater generated from aluminum fluoride plant, (ii) evaluate the ability of these processes to reduce fluoride load and to adjust medium pH, (iii) investigate the influence of different experimental parameters such as initial pH, initial fluoride concentration, calcium/fluoride molar ratio on the effectiveness of fluoride treatment contained in aluminum fluoride-manufacturing wastewaters (AFMW), (iv) determine the optimal conditions allowing the highest removal efficiency with these process in order to fulfill the normative requirements, and (v) compare quantitatively the performance of these processes: neutralization-precipitation by lime and limestone and adsorption on Tunisian activated clay, to decrease fluoride concentration to desirable values in accordance with international environmental regulations [29].

2. Materials and methods

2.1. Chemicals and reagents

All chemicals used in the present study were of analytical reagent grade. Sodium hydroxide (NaOH), sodium fluoride (NaF), silver chloride (AgCl), sodium chloride (NaCl), cyclohexane diamino-tetra-acetic acid (CDTA), hydrochloric acid (HCl), and sulfuric acid (H_2SO_4) were purchased from Fluka chemical. Calcium hydroxide $Ca(OH)_2$ (see characteristics in Table 1), procured by a local suppliers' (Interchaux) and calcium carbonate $CaCO_3$ witch specification are presented in Table 2 is purchased from SOFAP company located nearly the aluminum fluoride manufacturing plant. Double-distilled water was used in all the experimental runs.

Table 1
Chemical and physical specifications of lime

Chemical characteristic (weight %)		Physical characteristics	
$Ca(OH)_2$	94.1	Grading	Undersize 90 μm > 92%
CO_2 residual	2.1		Undersize 200 μm > 98%
SiO_2	1.9	Apparent density	1.5
MgO	0.4		
Fe_2O_3	0.4		
Al_2O_3	0.3		

Table 2
Chemical and physical proprieties of limestone

Chemical characteristic (weight %)		Physical characteristics	
H_2O	0.6		
$CaCO_3$	98.6		Cut 3 mm
SiO_2	0.3	Grain size	Lower than 1 mm 82%
MgO	0.08		Lower than 0.1 mm 20%
Fe_2O_3	0.04		
Al_2O_3	0.1		
K_2O	0.02		

2.2. Clay

2.2.1. Crude clay

We used a clay collected from the deposit of “Djebel Aïdoudi” from the region of “Gabes”, located in south Tunisia near the aluminum fluoride manufacturing factory.

2.2.2. Purified clay

The content of impurities was decreased or removed completely by applying a purification protocol proposed by van Olphen [30]. This was achieved by dispersing the crude lumps in hydrochloric acid solution (0.1 M) to facilitate elimination of carbonates by controlled acid attack but not to destroy the structure of the clay. This argillaceous suspension was agitated mechanically during 4 h and then centrifuged at 3,500 rpm during 15 min. Supernatant was removed; the remaining argillaceous fraction is mixed with 400 mL of NaCl solution (1 M). The clay suspension was shaken for 12 h. Then, it was centrifuged 3,000 rpm for 5 min. The clay phase was recovered and the NaCl solution was rejected. This cycle of agitation–centrifugation was carried out seven times under the same conditions in order to exchange the interfoliaceous cations against those of sodium and to eliminate impurities by sedimentation. After these exchanges, clay was washed three times with distilled water. The suspension obtained was put in dialysis membranes to remove the chloride ions adsorbed onto the surface from the layers. The dialysis water was renewed until what the test with silver nitrate indicates the absence of chloride ions. Then, the purified clay suspension was dried in an oven at a temperature not exceeding 60 ± 1˚C in order to be activated later.

2.2.3. Activated clay

Acid activation [31] was carried out with sulfuric acid (1.5 M) in a jacketed glass reactor equipped with a reflux condenser, a thermometer, and a stirrer. At the end of each experiment, the solid content was immediately filtered, washed free of sulfate with hot water until the washing water was neutral, and dried at 110 ± 1˚C for a few hours, in order to obtain dehydrated samples and a constant weight. The chemical analyses of the raw material and solids regenerated during the treatment were performed by atomic absorption spectrometry and X-ray fluorescence (see Table 3). The specific surface area was measured by the BET/N_2 adsorption and was found as 69 m^2/g [31,32]. The samples were dried at 110 ± 1˚C for a minimum of 24 h before usage.

2.3. Industrial fluoride effluent

Real effluents from Tunisian aluminum fluoride industry were used in this study. For all fluoride-con-

Table 3
Chemical analyses of clay and acid-activated clay (weight %) [32]

Clay	MgO	Fe_2O_3	Al_2O_3	SiO_2	SO_3	CaO	K_2O	Na_2O	P_2O_5	TiO_2	ZnO	L.O.I[a]
Natural	1.46	6.07	14.27	49.87	0.77	7.00	1.09	0.53	0.19	1.41	0.18	17.62
Acid activated	0.36	1.58	7.94	66.94	2.19	0.14	0.61	0.11	0.01	2.32	0.24	14.13

[a] Loss on ignition at 975˚C.

taining solutions, only polypropylene (PP) vessels were used for sample preparation and storage.

2.4. Treatment

2.4.1. Precipitation process

The treatment experiments were performed in a batch thermostated polypropylene reactor of 0.5 L capacity. All measurements were made at room temperature (25 ± 1˚C) and atmospheric pressure under stirring conditions. A specific quantity of reagents lime or limestone was added at the beginning of the treatment to a desired volume of fluoride solution under vigorous magnetic stirring. The mixed solution was stirred for 120 min to allow the precipitation reaction. Sample was taken at certain time intervals (every 10 min), followed by immediate analysis to determine pH and fluoride concentration.

2.4.2. Adsorption process

In the experiments, a desired amount of clay was added to a desired volume of the fluoride solution (pH between 2.5–12 and F^- concentration of 167 mg/L) in PP bottles equipped with magnetic stirring the mixture is maintained at vigorous agitation for 3 h at 25 ± 1˚C. Periodically, 2 mL of the sample is taken to determine fluoride concentration and pH value.

2.5. Analytical methods

The fluoride concentration was determined using the potentiometric standard method with Metrohm 781 pH/Ion Meter equipped by an ion-selective electrode (Metrohm 6.0502.150) and Ag/AgCl reference electrode (Metrohm 6.0726.100). Total Ionic Strength Adjustment Buffer (TISAB) solution was added to samples and standards to adjust the ionic strength and the pH (5.5) and to suppress complexation of fluoride ions by polyvalent cations, essentially Al^{3+} and Fe^{3+} [33]. The TISAB solution was obtained by dissolving 57 mL glacial acetic acid, 58 g sodium chloride, and 4 g cyclohexane diamino-tetra-acetic acid (CDTA) in one liter of double–distilled water. The pH of the solution was adjusted to 5.3 with sodium hydroxide solution (5 M). The conductivity was measured using Metrohm 856 Conductivity Module at 25 ± 1˚C. The precipitated solids were filtered using a membrane filter (0.45 μm) and dried at 110 ± 0.2 ˚C overnight.

X-ray fluorescence (XRF) spectrometer (PANalytical model AXIOS) was used to characterize the obtained precipitates. The samples were used in briquettes form containing 10 g of precipitate and pressed with 2.5 g of binder. The pH of the wastewater was measured by Metrohm 780 pH meter equipped by a HF-resistant glass electrode (Metrohm 6.0421.100). The instrument was calibrated each time the analysis was done. The metallic species concentrations were determined by atomic absorption spectrometry (Polarized Zeeman spectrophotometer HITACHI Z-6100). 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. General characterization

AFMW were known by important fluctuations for the content of the element fluoride, so 10 samples which cover the range of variation of contents in this element were taken. Table 4 represents compositions of a representative industrial effluent AFMW. The major anions are fluoride and sulfate; their concentrations are 3,300 and 345 mg/L, respectively. The major cation is aluminum (789 mg/L). The values of pH and conductivity make this effluent clearly different from those reported in similar published studies [34]. All these physicochemical characteristics confirm its toxicity and shows that it is mandatory to be treated before it is discharged into the environment.

3.2. Removal of fluoride by precipitation with lime

3.2.1. Effect of lime dose

$Ca(OH)_2$ dose is an important factor to determine the performance of precipitation–neutralization

Table 4
Composition of a representative sample of AFMW effluent

Parameters	Unity	Value
Conductivity at 25˚C	mS/cm	33.5
pH	–	2.5
F^-	mg/L	3,300
Cl^-	mg/L	295
Na^+	mg/L	141
K^+	mg/L	10.0
Ca^{2+}	mg/L	5.91
Al^{3+}	mg/L	789
Mg^{2+}	mg/L	0.24
Fe^{3+}	mg/L	1.20
Si	mg/L	4,340
SO_4^{2-}	mg/L	345
PO_4^{3-}	mg/L	7.0
Suspended solids	mg/L	470

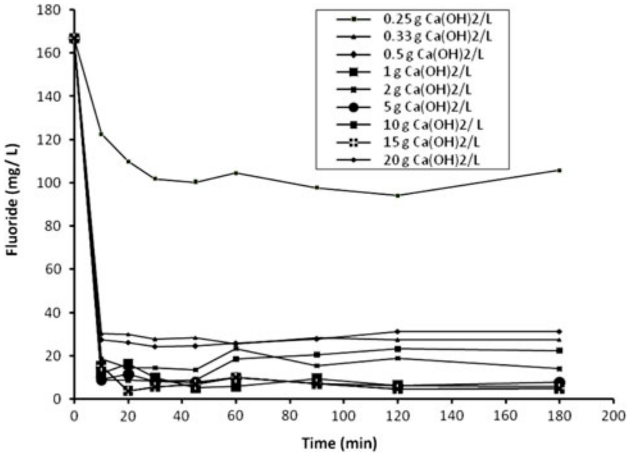

Fig. 1. Effect of lime dose on the changes in fluoride concentration with time (initial pH 2.5 ± 0.1, initial fluoride concentration 167 mg/L and temperature 25 ± 1 ℃).

process using lime [35]. Fig. 1 shows changes in fluoride concentration with time during the treatment of AFMW containing 167 mg F/L with different doses of lime. The results of Fig. 1 show that fluoride removal is largely affected by lime dose in the range from 0.25 to 20 g/L. As it can be seen, the increase in $Ca(OH)_2$ dose from 0.25 to 1 g/L decreases fluoride concentration from 167 to 105 and 9 mg/L, respectively, after 30 min. However, increasing lime dose higher than 1.0 g/L does not enhance fluoride removal.

Furthermore, Fig. 2 present the changes in pH with time during the treatment of AFMW using different doses of lime. This figure shows that the pH increased with the increase in the $Ca(OH)_2$ dose from initial pH 2.5 ± 0.1 to 3.5 ± 0.1, 5.5 ± 0.1, 8.0 ± 0.1, 10.5 ± 0.1, and 11.6 ± 0.1 for $Ca(OH)_2$ doses of 0.25, 0.33, 0.5, 1.0, 2, and 5 g/L, respectively, after 30 min contact time. For higher lime dose than 5.0 g/L, pH values higher than 11.6 ± 0.1 were obtained at the end of the treatment. For low doses of lime (0.25 g/L) corresponding to $[Ca^{2+}]/[F^-]$ molar ratio of 0.4, the final pH of treated AFMW was acidic (pH ≤3.5 ± 0.1). However, increasing lime dose from 0.25 to 0.33 and 0.5 g/L (corresponding to $[Ca^{2+}]/[F^-]$ molar ratios of 0.5 and 0.8, respectively), pH increased rapidly with time and reached a final pH of 5.7 ± 0.1 and 8.0 ± 0.1, respectively. A rapid increase in pH from initial pH 2.5 ± 0.1 to pH 10.5 ± 0.1, 11.0 ± 0.1, and 11.6 ± 0.1 was observed for lime doses of 1, 2, and 5 g/L ($[Ca^{2+}]/[F^-]$) molar ratios of 1.5, 3, and 7.5), after 30 min, and then pH remains constant till the end of treatment.

Considering both fluoride removal efficiency and final pH of treated AFMW, dose of lime of 0.5 g/L corresponding to molar ratio equal to 0.8 is optimal to leading to more than 90% fluoride removal with dischargeable pH conditions (pH ranged from 6.5 to 8.5). This result of pH is consistent with those of Chang and Liu [36], who observed maximum fluoride removal at pH 6.5–8.5. While for the parameter ratio of calcium to fluoride, $[Ca^{2+}]/[F^-]$ obtained in this study (0.8) is higher than the ratio of 0.5 find by these authors. These results can be interpreted as follows:

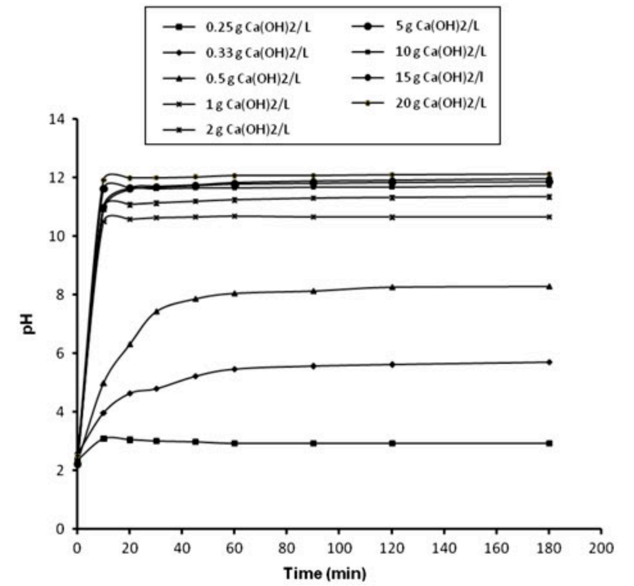

Fig. 2. Effect of lime dose on the changes in pH with time (initial pH 2.5 ± 0.1, initial fluoride concentration 167 mg/L and temperature 25 ± 1 ℃).

- For low lime doses (<0.5 g/L), calcium cation Ca^{2+} are not enough to totally precipitate fluoride ions and to attain desired environmental pH.
- Increasing progressively lime dose to 0.5 g/L, increases Ca^{2+} in the medium, and then precipitates further fluoride ions and neutralizes pH.
- For lime doses higher than 0.5 g/L, the solubility of calcium fluoride ($K = 3.46 \times 10^{-11}$) is exceeded and fluoride is converted from AFMW into solid crystal. Mechanism includes the following reactions:

$$HF \rightarrow H^+_{(aq)} + F^-_{(aq)} \tag{2}$$

$$Ca(OH)_{2(s)} \rightarrow Ca^{2+}_{(aq)} + 2OH^-_{(aq)} \tag{3}$$

$$Ca^{2+}_{(aq)} + 2F^-_{(aq)} \rightarrow CaF_{2(s)} \tag{4}$$

An excess of hydroxyl anions (OH^-) is also generated, which explain highly alkaline conditions obtained at the end of the treatment (pH 8.5 ± 0.1).

3.2.2. Effect of the initial fluoride concentration

Due to the variability of fluoride concentration in AFMW and taking into account that fluoride content plays a crucial role in the precipitation–neutralization treatment, it is necessary to examine the effect of fluoride content on the efficiency of the treatment [37]. To study the influence of fluoride content, some experiments were performed at different initial fluoride concentrations maintaining $[Ca^{2+}]/[F^-]$ molar ratio constant and equal to 0.8. Fig. 3 present the changes in fluoride concentration with time during treatment of AFMW containing different initial concentrations of fluoride. It is obvious that fluoride content affects fluoride removal during the treatment of AFMW by precipitation–neutralization using lime. Increasing initial fluoride concentration from 167 to 420 and 1,324 mg/L leads to fluoride removal of 90–97 and 92%, respectively. However, increasing fluoride content from 1,324 to 5,295 mg/L decreases fluoride removal from 92 to 67%, respectively. From these results, it can be concluded that fluoride removals higher than 90% were obtained for fluoride content in the range from 1,670 to 1,324 mg/L. Also, residual fluoride concentrations are 19, 13, and 106 mg/L for initial concentrations of 167, 420, and 1,324 mg/L, respectively. Consequently, optimal initial concentrations must be in the range from 167 to 420 mg/L. To verify the accountability of pH with environmental regulations, the changes in pH with time was monitored. The pH measured at different fluoride concentrations maintaining $[Ca^{2+}]/[F^-]$ molar ratio equal to 0.8 increased at the beginning and then reached a plateau between 8 ± 0.1 and 8.5 ± 0.1 by the end of the treatment.

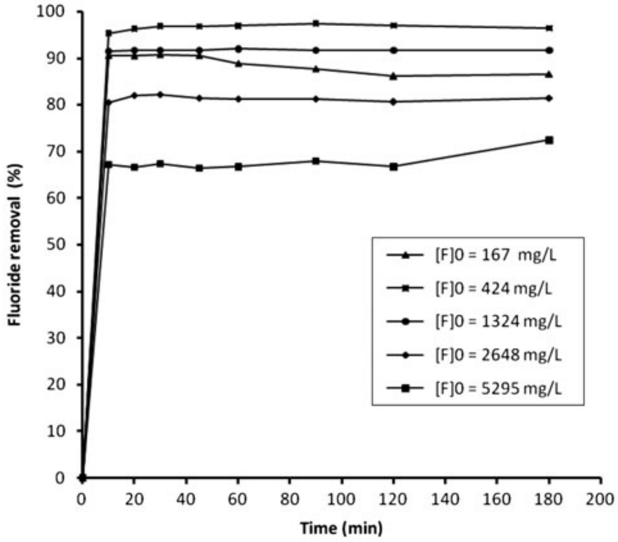

Fig. 3. Effect of fluoride content on the changes in fluoride removal with time (initial pH 2.5 ± 0.1, $[Ca^{2+}]/[F^-]$ 0.8 and temperature 25 ± 1˚C).

The main advantage of precipitation with lime is the reuse of precipitated solid wastes, which are to be recycled back as raw material or additive in several industrial applications. Consequently, success of this process is related to ability to produce residual solids rich in CaF_2 synthetic calcium fluoride (SCFL). For this reason, treated AFMW were filtered and SCFL was dried at 105 ± 0.2˚C. The qualitative characterization of

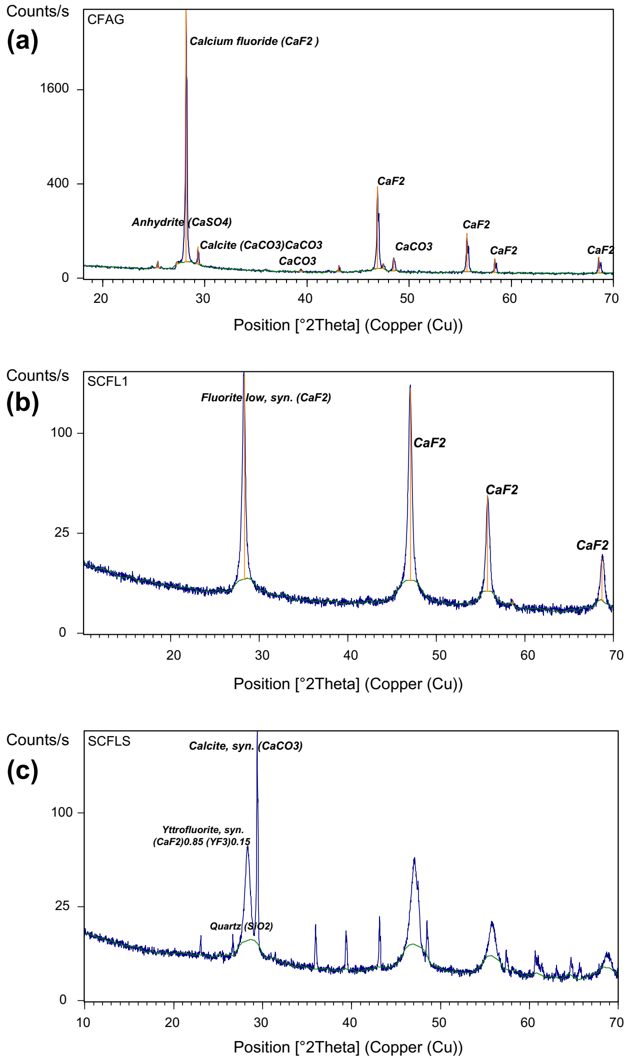

Fig. 4. XRD pattern: (a) Calcium fluoride acid grade (CaF_2>97%); (b) SCFL generated by precipitation–neutralization with lime (SCFL); (c) SCFL generated by lime stone treatment of AFMW (SCFLS).

Table 5
Commercial fluorspar grades

Weight (%)	Calcium fluoride commercial grades		
	Metallurgical grade	Ceramic grade	Acid grade
CaF_2	60–85	85–97	>97
SiO_2		>3	<1
$CaCO_3$		>1.5	<1.5
Fe_2O_3		<0.14	<0.5
P_2O_5		<0.1	<0.03
S (sulfur)		Traces	Traces
Zn		Traces	Traces

Table 6
Chemical analyses of SCFL

Composition	CaF_2	CaO	SiO_2	Fe_2O_3	Al_2O_3	P_2O_5
Weight (%)	77.9	18.1	1.9	0.62	0.35	0.048

this product was carried out by Philips Panalytical X’Pert PRO X-ray powder diffractometer (XRD) using cobalt radiation with a step angle of 0.017˚C. Fig. 4(a) and (b) shows X-ray diffraction diagrams of the Calcium Fluoride Acid Grade (CFAG) ($CaF_2 > 97\%$, Morocco quality) and the SCFL quality, respectively. It can be seen that data of the acid grade are very close of the SCFL, indicating that the products from the precipitation process with lime are mainly calcium fluoride. Table 5 shows the composition of CFAG. The results of the chemical analyses of SCFL were presented in the Table 6. The examination of this table shows that SCFL are a metallurgical grade containing small amounts of silica. This material is preferred by the manufacturers because a high grade in silica causes losses in the yield of hydrofluoric acid (HF). So, this quality validates the possible reuse like an additive of these solids generated from AFMW treatment by precipitation with lime in the HF production as is shown in Fig. 5.

3.3. Removal of fluoride by precipitation with limestone

To examine the influence of different type calcium salts on the efficiency of the precipitation–neutralization process, the treatment of fluoride effluent with $CaCO_3$ was studied and the influence of different experimental parameters on the effectiveness of the treatment of fluoride in wastewater was investigated. The main motivation toward the use of limestone is to utilize a more cost-effective calcium source reagent that can lead to the formation calcium fluoride which to be recycled as raw material.

3.3.1. Effect of limestone dose

It has been pointed out that $CaCO_3$ dose is one of the most important parameters in the precipitation process [38]. To study the effect of limestone on the efficiency of precipitation–neutralization process, the initial concentration of fluoride was maintained constant at 167 mg/L, at initial pH 2.5 ± 0.1 and precipitation time of 180 min. The dose of $CaCO_3$ was varied in the range from 0.45–20 g/L. The effect of limestone dose was evaluated by determining the evolution of pH and fluoride concentration in aqueous medium. Effect of limestone dose on the efficiency of fluoride removal is illustrated in Fig. 6. This figure shows that when limestone concentrations is increased from 0.45 to 1.8 g/L, the fluoride concentration decreases from 167 to 137 and 15 mg/L, respectively, after 20 min. Higher doses of limestone than 1.8 g/L did not improve the removal efficiency. From these results, it can be concluded that the effective removal of fluoride (>90%) can be achieved by precipitation–neutralization process for limestone equal to or greater than 1.8 g/L for an initial fluoride concentration of 167 mg/L. The calcium carbonate dose of 1.8 g/L was able to adjust the pH to be within the range of 7 ± 0.1 to 8 ± 0.1 at the end of the treatment. A calcium carbonate dose of 1.8–167 mg/L of fluoride corresponds to $[Ca^{2+}]/[F^-]$ molar ratio of 2 was found to be very effective for removal of fluoride as well as medium neutralization, and as result, the molar ratio of $[Ca^{2+}]/[F^-]$ was kept at 2 for the successive experiments. This optimal value is four times higher than the theoretical $[Ca^{2+}]/[F^-]$ molar ratio of 0.5. To explain these results, it should be considered that the efficiency of fluoride removal depends to large extent on the solubility of calcium carbonate in aqueous medium. For low calcium carbonate doses, the more calcium carbonate added; the more calcium ions are dissolved in aqueous solution, and hence, the more fluoride is removed as calcium fluoride precipitate. On the other hand, at high calcium carbonate doses, the low solubility of limestone and the increase in medium pH limit the generation of calcium ions in aqueous medium. The evolution of medium pH to neutral values only for high quantity of $CaCO_3$ is mainly due to the absorption of significant amounts of H^+ ions by carbonate anions (CO_3^{2-}) to generate CO_2 and H_2O in these conditions as represented by the following chemical equations:

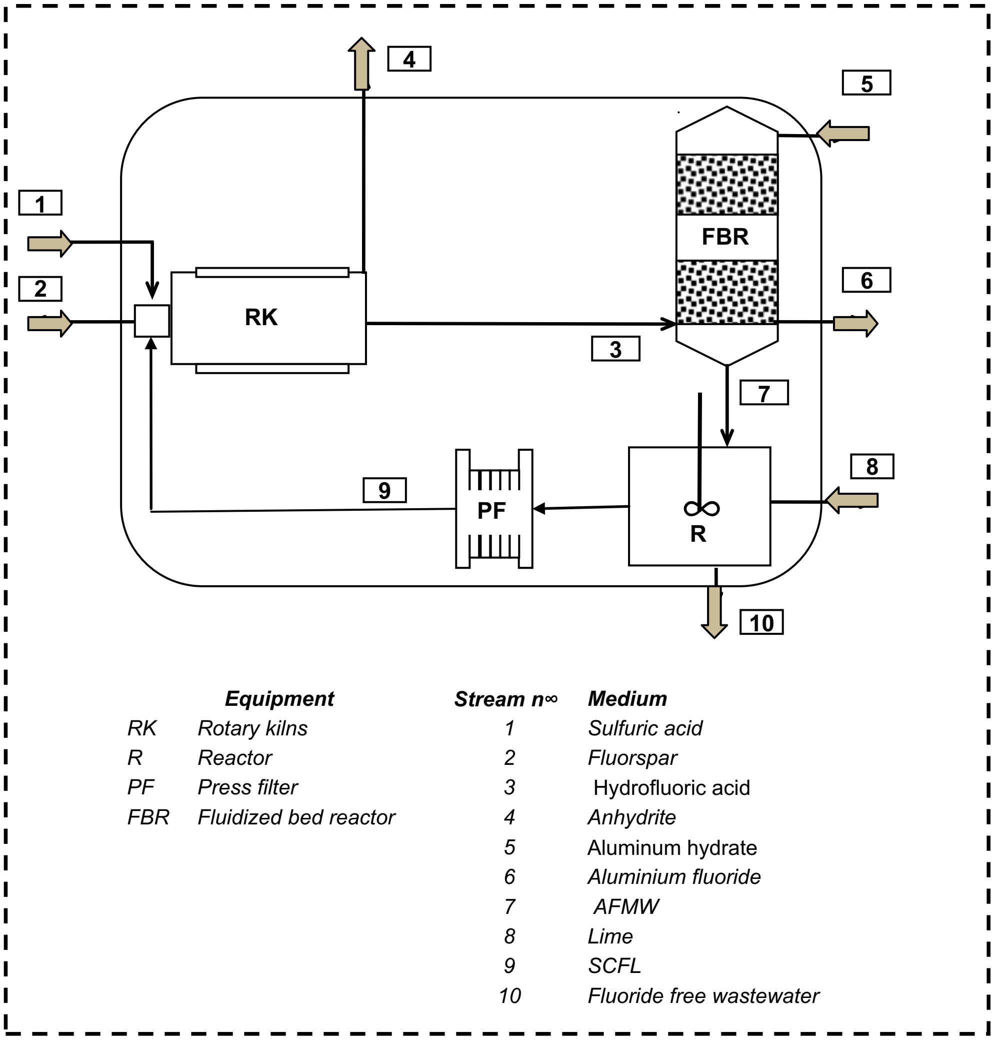

Fig. 5. Scheme of HF and AlF_3 production with integration of SCFL.

$$CaCO_{3(s)} \leftrightarrows Ca^{2+} + CO_3^{2-} \tag{5}$$

$$CO^{2-}_{3(s)}H_3O^+ \leftrightarrows 2H_2O + CO_2 \tag{6}$$

3.3.2. Effect of fluoride concentration

It was indicated that precipitation process was significantly affected by variation of the fluoride concentration [35]. It is interesting to examine how the initial fluoride concentration affects the performance of precipitation process. This requires that the molar ratio of calcium to fluoride $[Ca^{2+}]/[F^-]$ must be maintained constant and equal to 2 as found to be optimum for fluoride removal as well as medium neutralization from preceding experiments examined the effect of limestone dose of fluoride removal. A series of experiments were conducted in which initial fluoride concentration was varied in the range from 167 mg/L to 6,100 mg/L at $[Ca^{2+}]/[F^-]$ molar ratio of 2. Fig. 7 indicates that removal efficiency is not significantly varied when the initial concentration of fluoride was increased from 167 to 1870 mg/L giving removal efficiency of 80–90%. Meanwhile, the removal efficiency decreased notably from 80 to 65 and 55%, as initial fluoride concentration increased from 1870 to 2,200 and 6,100 mg/L, respectively, after 60 min. However, Fig. 8 represents the evolution with time of pH for different initial fluoride concentrations in the range from 167–6,100 mg/L at $[Ca^{2+}]/[F^-]$ molar ratio of 2. This figure indicates that as fluoride concentration increases from 167.0 to 855 mg/L, no significant difference in

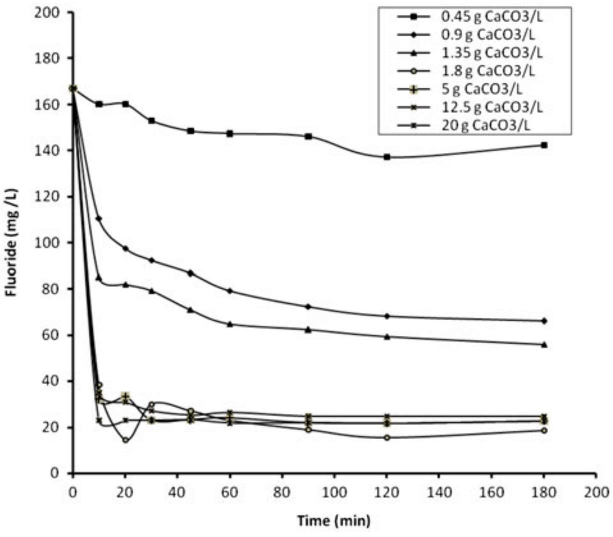

Fig. 6. Effect of limestone dose on the changes in fluoride concentration with time (initial pH 2.5 ± 0.1, initial fluoride concentration 167 mg/L and temperature 25 ± 1˚C).

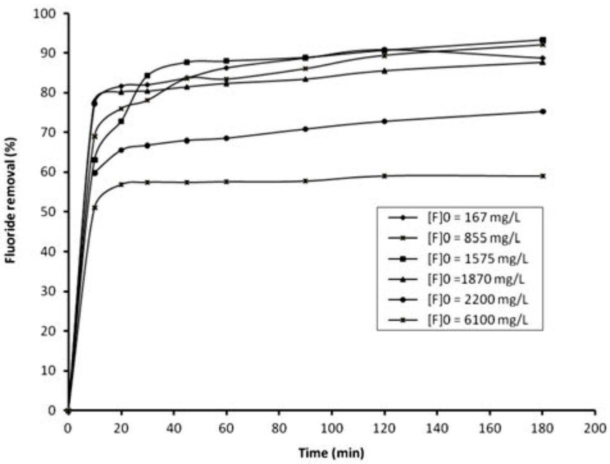

Fig. 7. Effect of fluoride concentration on the changes in fluoride removal with time (initial pH 2.5 ± 0.1, $[Ca^{2+}]/[F^{-}]$ 2, and temperature 25 ± 1˚C).

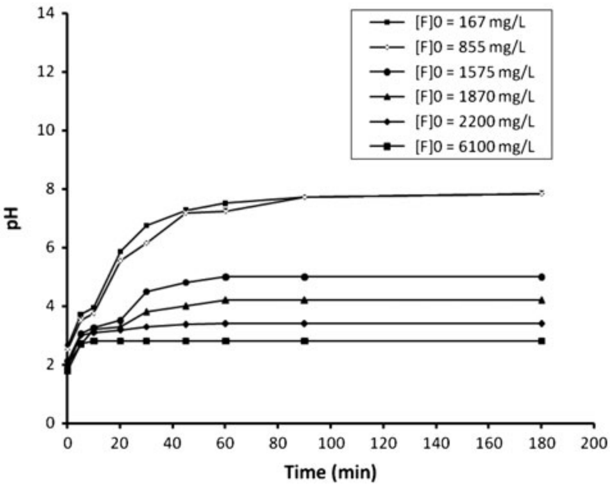

Fig. 8. Effect of fluoride concentration on the evolution with time of pH medium (pH 2.5 ± 0.1, $[Ca^{2+}]/[F^{-}]$ 2 and temperature 25 ± 1˚C).

Table 7
Chemical analyses of SCFLS

Composition	CaF_2	$CaCO_3$	SiO_2	Fe_2O_3	Al_2O_3	MgO
Weight (%)	48.3	47.9	1.6	0.4	0.3	0.3

pH behavior with time was observed and that the medium pH increases to about 7.5 ± 0.1 after 60.0 min and remains constant to the end of experimentation time of three hours. From these results, it can be concluded that the fluoride removal efficiency is high in the range of fluoride concentration of 167 to 1870 mg/L. However, for fluoride concentrations higher than 855 mg/L, the neutralization process efficiency was deceased.

These results may be due to the fact that increasing fluoride concentration increases the limestone dose required, but due to its low solubility; $CaCO_3$ is not totally dissolved in aqueous solution to generate sufficient calcium ions. Consequently, fluoride ions cannot completely be precipitated as CaF_2. In addition, at these conditions of low pH (lower then 5), the solubility of CaF_2 is increased causing incomplete precipitation of CaF_2 and hydrolysis of F^{-} to form HF [39].

The precipitation process discharges large quantity of residual solids, Fig. 4(a) and (c) shows X-ray diffraction pattern of CFAG ($CaF_2 > 97\%$, Morocco quality) and the SCFLS quality, respectively. It can be seen that data of the acid grade are close to those of SCFLS's, indicating that the products from the precipitation process with limestone are mainly calcium fluoride. Table 7 shows the chemical composition of SCFLS. This table has indicated that residual solid contains 48.3% of CaF_2, which can be recycled back in small quantity as raw material during the production of HF gas; however, it indicated as well that about 48% of the precipitate is calcium carbonate, which means that there is under utilization of calcium carbonate used and that it is wasted in the residual precipitate.

3.4. Removal of fluoride by adsorption using activated clay

The abundance of clay in south Tunisia and its low cost make it very attractive to be applied for treatment of AFMW. Furthermore, the chemical treatment of the clay substrates with acidic or basic solutions was found to enhance significantly the adsorption capacities of some clay by increasing the porosity and surface area [40]. As a result, it was decided to investigate the removal of fluoride from AFMW utilizing locally available clay and to evaluate the influence of certain experimental parameters (initial pH, activated clay mass, initial fluoride concentration) on the ability of the activated clay to adsorb the fluoride ions and to compare the efficiency of this adsorption process with the results obtained from precipitation–neutralization process.

3.4.1. Effect of activated clay dose

The effect of adsorbent dose (ranging from 1 to 20 g/L) on the fluoride removal was studied at pH 2.5 ± 0.1, room temperature and 167 mg/L of fluoride. The results obtained are shown as fluoride concentration and time in Fig. 9. It was observed that an increase in clay dose from 1 to 10 g/L decreases the fluoride concentration from 167 to 143 and 30 mg/L, respectively, after 60 min of treatment. However, an increase in clay dose to 20 g/L decreases the fluoride concentration only to 21 mg/L. From this result, it can be deduced that the dose of activated clay affects largely the efficiency of fluoride adsorption but up to certain level at which higher applied doses will not affect the removal efficiency. The optimal clay dose necessary to eliminate the maximum of fluorides from aqueous solution having a concentration equal to 167 mg/L was found to be 10 g/L. This result can be interpreted as the following:

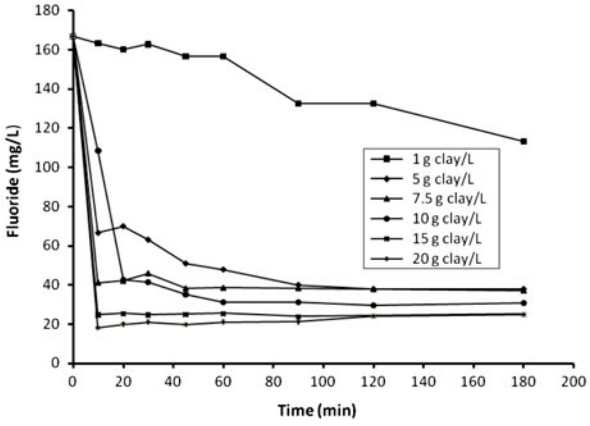

Fig. 9. Effect of clay quantity on the changes in fluoride concentration with time (initial pH 2.5 ± 0.1, initial fluoride concentration 167 mg/L, and temperature 25 ± 1˚C).

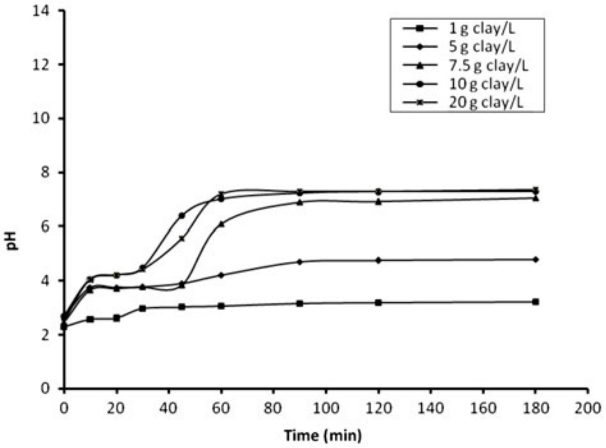

Fig. 10. Effect of clay quantity on the changes in pH with time (initial pH 2.5 ± 0.1, initial fluoride concentration 167 mg/L and temperature 25 ± 1˚C).

- For low doses of activated clay, the number of activated sites of clay is limited. Consequently, there are not sufficient active sites to retain fluoride ions and the majority remains in solution.
- An increase in clay amount increases the number of active sites and promotes the adsorption of fluoride ions.
- As excess clay amount exceeds 10 g/L, the physical equilibrium adsorption-desorption is increased. This phenomenon limits the retention of fluorides on activated sites of adsorbent.

Fig. 10 presents the evolution with time of pH during the treatment of this industrial aqueous wastewater at different clay doses. This figure shows that in all cases, the pH increases gradually during the first 60 min of treatment and then it remains constant. Furthermore, this figure shows that increasing clay quantity from 1 to 10 g/L increases the pH medium from 2.5 ± 0.1 to 3.2 ± 0.1 and 7.2 ± 0.1, respectively, after 60 min, while higher clay dose was found to have no significant affect on pH changes. These results indicated that a clay dose of 10 g/L is optimal to neutralize AFMW and to obtain high fluoride removal than 80%. An increase in clay dose from 1 to 10 g/L increases the number of adsorption sites and then more fluoride ions can be adsorbed on the activated clay. However, for higher activated clay doses than 10 g/L, adsorption equilibrium is obtained and a saturation state is established.

3.4.2. Effect of initial pH

Several previous studies [23] demonstrate that the pH is an important variable affecting defluoridation at

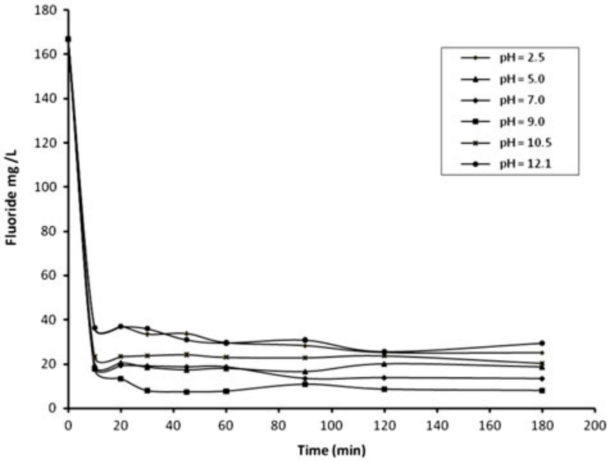

Fig. 11. Effect of initial pH on the changes in fluoride concentration with time (initial pH 2.5 ± 0.1, initial fluoride concentration 167 mg/L, clay mass 10 g/L, and temperature 25 ± 1˚C).

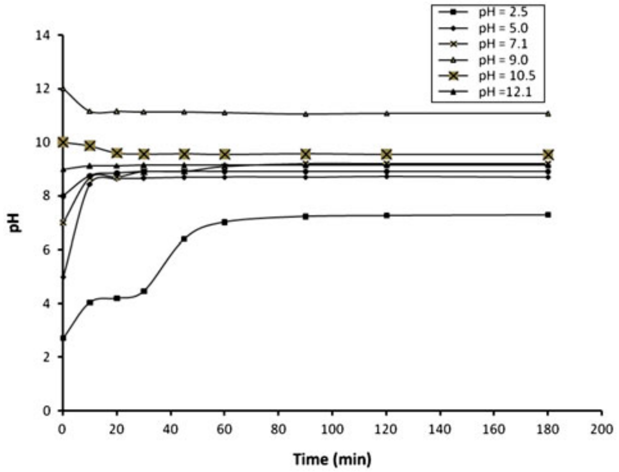

Fig. 12. Changes in pH with time at different pH conditions (initial pH 2.5 ± 0.1, initial fluoride concentration 167 mg/L, clay mass 10 g/L, and temperature 25 ± 1˚C).

water-adsorbent interfaces. To study the effect of initial pH on fluoride adsorption efficiency on activated clay adsorbent, some experiments are carried out keeping constant clay dose of 10 g/L and initial concentration fluoride of 167 mg/L at initial pH values varying from 2.5 ± 0.1 to 12 ± 0.1 at room temperature of 25 ± 1˚C over 3 h. Fig. 11 shows the evolution with time of fluoride ion concentration at different initial pH values. It can be observed that the rate of elimination of fluorides ions does not depend on initial pH of aqueous solutions at the initial stage and maximum fluoride elimination was obtained after 30 min of the treatment. However, it was found that increasing the initial pH from 2.5 ± 0.1 to 5 ± 0.1, 7 ± 0.1 and 9 ± 0.1 lead to decrease in the equilibrium concentration of fluorides to 30, 18, 15, and 7.5 mg/L, respectively. In the mean time, it was found that increasing the initial pH to 10.5 and 12.1 lead to an increase in equilibrium fluoride concentration to 25 and 30 mg/L, respectively, which in turn indicates that initial pH has strong influence on fluoride removal efficiency by adsorption. Fig. 12 presents the changes in pH with time during the treatment of AFMW by adsorption on activated clay at different initial pH. It can be observed, increasing initial pH from 2.5 ± 0.1 to pH 5 ± 0.1, and 7.1 ± 0.1 increases equilibrium pH to 6.2 ± 0.1, 8.5 ± 0.1 and 8.7 ± 0.1, respectively. Contrary, for high initial pH of 10.5 ± 0.1 and 12.1 ± 0.1, a decrease in equilibrium pH to 9.2 ± 0.1 and 11.1 ± 0.1, respectively, was observed. In the mean time at pH 9 ± 0.1, no significant change in pH was observed.

In acidic conditions, the decrease in fluoride removal can be attributed to the stability of hydrofluoric acid HF (pKa = 3.18), which is a weak acid in the form ions pair (H^+, F^-) in water. Hydrofluoric acid (H^+, F^-) is weakly dissociated in acid pH, which prevents fixing fluoride ions on the active surface of activated clay [41]. Furthermore, high acid conditions facilitate the dissolution of metal cations (Al^{3+} and Fe^{3+}) contained in the clay layers, which decreases active sites on the surface of activated clay. In alkaline conditions, the decrease in fluoride removal when pH is increased from 9 ± 0.1 to 12 ± 0.1 may be due to competition between hydroxide and fluoride ions to be adsorbed on the surface of activated clay. Such types of adsorption behavior of fluoride had been reported for waste residue from alum manufacturing process [42] but at pH from 10 to 12. In addition, the adsorbent surface becomes negatively charged due to the formation of SiO_3^{2-} and AlO_2^-as shown in Eqs. (7) and (8). Consequently, fluoride adsorption becomes difficult due to electrostatic repulsion between active surface and fluoride anions.

$$SiO_2(s) + 2NaOH \leftrightarrows 2Na^+ + SiO_3^{2-} + H_2O \tag{7}$$

$$Al_2O_3(s) + NaOH \leftrightarrows Na^+ + AlO_2^- + H_2O \tag{8}$$

For pH ranging from 7 ± 0.1 to 9 ± 0.1, higher adsorption efficiency may be due to much more free active sites on the surface of activated clay capable to interact with fluoride ions in water. Similar trend was observed by Liang et al. [43] in an adsorption system involving fluoride and MgAl-CO_3 layered double hydroxides.

It is known that clay minerals possess attractive properties as solid acids [44,45]. Their acidities are due to active centers on the surface that exhibit

Bronsted and Lewis acidities and govern most of the clay's interactions in so many application areas. Acid-activated clays exhibit significantly different physicochemical characteristics compared to their non-activated counterparts and one of these physicochemical properties is surface acidity, which is a combination of its Bronsted and Lewis acidities [46].

4. Conclusion

The results found in this work demonstrate that the precipitation–neutralization and adsorption processes are very efficient to reduce the concentration of fluoride anions contained in industrial wastewater of aluminum fluoride manufacturing in order to meet environmental regulation for wastewater discharge in terms of residual fluoride concentration and medium pH. Chemical precipitation–neutralization using $Ca(OH)_2$ has the advantage to obtain SCFL to be reused in the hydrofluoric acid manufacture, making the process more technically and economically feasible. The use of limestone as precipitation–neutralization agent allows obtaining SCFL contain small amounts of silica, and therefore, it also acceptable for HF manufacture but in small quantity. It was found that lower $[Ca^{2+}]/[F^-]$ molar ratio of 0.8 was required for precipitation using lime, compared to 2 required for precipitation using lime stone. Furthermore, more calcium fluoride of about 80% was found in the precipitate using lime as reagent, compared to only 48% when using lime stone, making precipitation–neutralization using lime more attractive and contributes to an environmental friendly production; however, more detailed techno-economical analysis is need as limestone present more cost-effective reagent compared to lime. The adsorption process offers satisfactory results in terms of fluoride removals, and in addition, clay is obtained from natural raw source and is an environmental friendly material of low cost; however, discharge of large quantity of residual solid and difficulty in regeneration of clay should be considered.

References

[1] E. Varol, S. Akcay, I.H. Ersoy, M. Ozaydin, B.K. Koroglu, S. Varol, Aortic elasticity is impaired in patients with endemic fluorosis, Biol. Trace Elem. Res. 133 (2010) 121–127.

[2] L. Valdez-Jimenez, 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] E.A. García-Montalvo, H. Reyes-Pérez, L.M. Del Razo, Fluoride exposure impairs glucose tolerance via decreased insulin expression and oxidative stress, Toxicology 263 (2009) 75–83.

[4] P. Hao, X. Ma, X. Cheng, Y. Ba, J. Zhu, L. Cui, Effect of fluoride on human hypothalamus-hypophysis-testis axis hormones (in Chinese), Wei Sheng Yan Jiu 39 (2010) 53–55.

[5] 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.

[6] 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.

[7] W.X. Gong, J.H. Qu, R.P. Liu, H.C. Lan, Effect of aluminum fluoride complexation on fluoride removal by coagulation, Colloids Surf., A 395 (2012) 88–93.

[8] 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.

[9] V. Tomar, S. Prasad, D. Kumar, Adsorptive removal of fluoride from aqueous media using Citrus limonum (lemon) leaf, Microchem. J. 112 (2014) 97–103.

[10] S. Nicolas, L. Guihard, A. Marchand, B. Bariou, A. Amrane, A. Mazighi, N. Mameri, A. El Midaoui, Defluoridation of brackish northern Sahara groundwater—Activity product calculations in order to optimize pretreatment before reverse osmosis, Desalination 256 (2010) 9–15.

[11] 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.

[12] 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.

[13] N. Kabay, Özgür Arar, S. Samatya, Ümran Yüksel, M. Yüksel, Separation of fluoride from aqueous solution by electrodialysis: Effect of process parameters and other ionic species, J. Hazard. Mater. 153 (2008) 107–113.

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

[15] E. Alkan, E. Kır, L. Oksuz, Plasma modification of the anion-exchange membrane and its influence on fluoride removal from water, Sep. Purif. Technol. 61(3) (2008) 455–460.

[16] J. Zhu, H. Zhao, J. Ni, Fluoride distribution in electrocoagulation defluoridation process, Sep. Purif. Technol. 56 (2007) 184–191.

[17] 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.

[18] S. Ayoob, A.K. Gupta, V.T. Bhat, A conceptual overview on sustainable technologies for the defluoridation of drinking water, Crit. Rev. Environ. Sci. Technol. 38 (2008) 401–470.

[19] N.C. Lu, J.C. Liu, Removal of phosphate and fluoride from wastewater by a hybrid precipitation–microfiltration process, Sep. Purif. Technol. 74(3) (2010) 329–335.

[20] 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.
[21] P. Miretzky, A.F. Cirelli, Fluoride removal from water by chitosan derivatives and composites: A review, J. Fluorine Chem. 132 (2011) 231–240.
[22] A. Bhatnagar, E. Kumar, M. Sillanpää, Fluoride removal from water by adsorption — A review, Chem. Eng. J. 171 (2011) 811–840.
[23] N. Hamdi, E. Sarasra, Retention of fluoride from acidic wastewater and NaF solution by three Tunisian clayely soils, Fluoride 42 (2009) 39–45.
[24] D. Thakre, S. Rayalu, R. Kawade, S. Meshram, J. Subrt, N. Labhsetwar, Magnesium incorporated bentonite clay for defluoridation of drinking water, J. Hazard. Mater. 180 (2010) 122–130.
[25] A. Ramdani, S. Taleb, A. Benghalem, N. Ghaffour, Removal of excess fluoride ions from Saharan brackish water by adsorption on natural materials, Desalination 250 (2010) 408–413.
[26] Y. Ma, F. Shi, X. Zheng, J. Ma, C. Gao, Removal of fluoride from aqueous solution using granular acid-treated bentonite (GHB): Batch and column studies, J. Hazard. Mater. 185 (2011) 1073–1080.
[27] J. Ma, J. Qi, Ch Yao, B. Cui, T. Zhang, D. Li, A novel bentonite-based adsorbent for anionic pollutant removal from water, Chem. Eng. J. 200–202 (2012) 97–103.
[28] S. Gammoudi, N. Frini-Srasra, E. Srasra, Preparation, characterization of organosmectites and fluoride ion removal, Int. J. Miner. Process. 125 (2013) 10–17.
[29] US EPA, Federal Water Pollution Control Act (Clean Water Act), Semiconductor Best Practicable Control Technology Currently Available (BPT) Effluent Limitations. Available 5 Feb 2014 from: http://www.epa.gov/dfe/pubs/pwb/tech_rep/fedregs/regsectb.htm.
[30] H. Van Olphen, Introduction to Clay Colloid Chemistry, 2nd ed., Wiley and Sons, New York, NY, 1976.
[31] A. Amari, M. Chlendi, A. Gannouni, A. Bellagi, Optimised activation of bentonite for toluene adsorption, Appl. Clay Sci. 47 (2010) 457–461.
[32] A. Amari, A. Gannouni, M. Chlendi, A. Bellagi, Optimization by response surface methodology (RSM) for toluene adsorption onto prepared acid activated clay, Can. J. Chem. Eng. 86 (2008) 1093–1102.
[33] APHA, Standard Methods for the Examination of Water and Wastewater, 20th ed., American Public Health Association/American Water Works Association/Water Environment Federation, Washington, DC, 1998.
[34] S. Saha, Treatment of aqueous effluent for fluoride removal, Water Res. 27(8) (1993) 1347–1350.
[35] A. Toyoda, T. Taira, A new method for treating fluorine wastewater to reduce sludge and running costs, IEEE Trans. Semicond. Manuf. 13 (2000) 305–309.
[36] M.F. Chang, J.C. Liu, Precipitation removal of fluoride from semiconductor wastewater, J. Environ. Eng. 133 (2007) 419–425.
[37] T.C. Chuang, C.J. Huang, J.C. Liu, Treatment of semiconductor wastewater by dissolved air flotation, J. Environ. Eng. 128 (2002) 974–980.
[38] E.J. Reardon, Y. Wang, A limestone reactor for fluoride removal from wastewaters, Environ. Sci. Technol. 34 (2000) 3247–3253.
[39] C.J. Huang, J.C. Liu, Precipitate flotation of fluoride-containing wastewater from a semiconductor manufacturer, Water Res. 33 (1999) 3403–3412.
[40] P. Komadel, Chemically modified smectites, Clay Miner. 38 (2003) 127–138.
[41] M.G. Sujana, R.S. Thakur, S.b. Rao, Removal of fluoride from aqueous solution by using alum sludge, J. Colloid Interface Sci. 206 (1998) 94–101.
[42] W. Nigussie, F. Zewge, B.S. Chandravanshi, Removal of excess fluoride from water using waste residue from alum manufacturing process, J. Hazard. Mater. 147 (2007) 954–963.
[43] L. Liang, H. Jing, W. Min, D.G. Evans, Z. Zhaoliang, Treatment of high fluoride concentration water by MgAl-CO_3 layered double hydroxides: Kinetic and equilibrium studies, Water Res. 41 (2007) 1534–1542.
[44] K. Tanabe, Solid Acids and Bases, Academic Press, New York, NY, 1970.
[45] J. Ravichandran, B. Sivasankar, Properties and catalytic activity of acid-modified montmorillonite and vermiculite, Clay Miner. 45 (1997) 854–858.
[46] T. Alemdaroglu, G. Akkus, M. Onal, Y. Sarikaya, Investigation of the surface acidity of a bentonite modified by acid activation and thermal treatment, Turk. J. Chem. 27 (2003) 675–681.