Available online at www.ilcpa.pl

International Letters of Chemistry, Physics and Astronomy

10(1) (2013) 48-60 ISSN 2299-3843

Defluoridation of drinkable water ″Comparative study and parameter influent″

Djamel Atia, Abdelghani Hoggui, Bebba Ahmed Abdelhafidh*

Laboratoire de Valorisation et Technologie des Ressources Sahariennes, Département Sciences de la Matière, Institut des Sciences et Technologie Centre, Universitaire Ouargla, Algérie

*E-mail address: Atia.sahan1@gmail.com

ABSTRACT

El-Oued is known for some diseases caused by fluoride concentration in drinkable water. To reduce it , a sample with the biggest content among many sources was chosen. A comparative study between the precipitation with calcium salts [$Ca(OH)_2$, $CaCl_2$, $CaSO_4$] and the coagulation with the following salts [$Al_2(SO_4)_2 \cdot 18H_2O$, $Fe_2(SO_4)_2 \cdot H_2O$, $FeSO_4$] was done. Finely we studied the parameters influencing (the mass , pH, temperature) to choose the best conditions in order to get better reduction yield.

***Keywords*:** fluorine, defluoridation, drinkable water, coagulation, precipitation.

1. INTRODUCTION

The concentration of fluoride in drinkable water depends on the geological characteristics, and chemical properties of rocks and climate of the region. Fluoride content in the groundwater of northern Algerian desert often exceeds the world Health Organization standards, which indicated that the consumption of high fluoride water for long periods causes health complications from discolored teeth to fluoride poisoning bone. When concentration between (0.5-1.5 mg / l), it gives good protection against tooth decay, and if it exceeds 1.5 mg / l, defect occurs in teeth enamel but at a concentration between 4 and 8 mg / l, it leads to the risk of fluorosis skeletal [1]. The water of El Oued is characterized by high concentrations of fluoride, associated with severely high and excessive total mineralization. This water is the only source of drinking. The hot and dry climate has forced people to consume a lot of water which leads to raise the daily consumption rate of fluoride, in addition the large consumption of dates and tea leads to the spread of fluorosis disease which is characterized by the yellowish of tooth enamel according to the classification of the national program of school health [2,3]. To prevent these diseases from happening or reduce them, many defluoridation techniques are used such as: membrane technologies, precipitation and adsorption. A comparative study between precipitation and coagulation has been done with different salts, then determination of optimal conditions of factors affecting the reduction of fluoride in the studied water.

2. EXPERIMENTAL SECTION

2. 1. Preparation of curve witness fluoride

To determine the concentration of fluoride in Various samples, a potentiometer method was used (Rodier2005) [4]. Different standard concentration solutions were prepared from NaF salt in cups of plastic. Then their potential are measured by using specific fluoride pole (ISE15381/1) and a pH-meter model (pH211), using a solution of TISAB [(12)]. The graph E = f (log C_F) is presented in Figure 1.

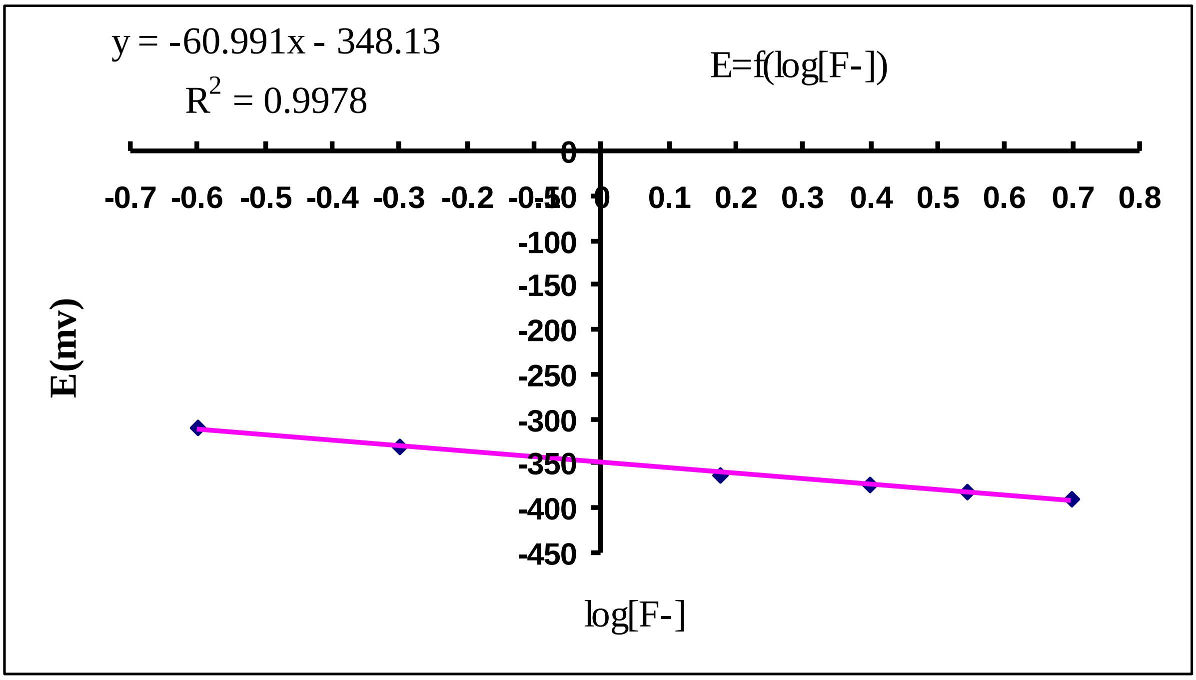

Figure 1. The witness graph for fluoride.

2. 2. Determination of fluoride concentration in some samples of the study area

The concentration of fluoride has been determined in some water sources of the study area in order to determine and treat the largest content of fluoride. The results are presented in Table 1. The selected sample (cold water of Shuhada) has a concentration of fluoride 2.61 mg / l.

Table 1. Fluoride concentration for some water in the study areas at T = 19.3 °C

Sources of water	**mars city**	**mastur city**	**400 city**	**8 may city**	**1 Nov City**	**Nezla city**	**Shuhada**
$[F^-]$ (mg/l)	1.87	1.90	1.92	1.84	1.94	0.46	2.61

2. 3. Determination of the predominant concentration of ions in the studied water

The study was done according to (Rodier2005) [4] on cold water of Shuhada as follows:

2. 3. 1. Nitrates and sulfates

Spectroscopy method (UV) ray using (spectrophotometer DR 2400).

2. 3. 2. Total hardness

By complexity with EDTA[1] in the presence of *Eriochrome BlackT* at buffer solution of pH = 10.

2. 3. 3. Sodium and potassium

Using flame atomic absorption analysis.

2. 3. 4. Alkalinity

Determining TA[10] and TAC[11] using PhPh[9] and MO[8] indicators respectively.

2. 3. 5. Chlorides

Volumetric method for Mohr.

2. 3. 6. Calcium concentration

By complexity with EDTA[1] in the presence of murexide at a solution of pH = 12.

2. 3. 7. Magnesium concentration

Calculated from the difference Total hardness and Calcium concentration.
The results are presented in Table 2.

Table 2. Physics-chemical properties of Shuhada water.

Property	SO_4^{2-}	Ca^{2+}	Mg^{2+}	Na^+	K^+	NO_3^-	TA	TAC	Cl^-
C (mg/l)	544	492	140	55	2.4	5.9	0	105	402

2. 4. Treatment

2. 4. 1. Coagulation

The factors affecting (mass, pH, and temperature T) were studied by the Coagulation method using $Al_2(SO_4)_3\cdot 18H_2O$, $Fe_2(SO_4)_3\cdot H_2O$ and $FeSO_4$ at a purity of (98-100) %, 100 % and 84 % respectively.

2. 4. 1. 1. Effect of cathion concentration

Based on the adsorption of F^- on both $Al(OH)_3$ and $Fe(OH)_3$ according to equilibriums (1), (2), (3) and (4) [8-10]. 100 ml of Shuhada water was put in each cup of plastic then the pH and temperature T were measured, after that different amount of the same salt was added to each cup. After stirring for three minutes, they are left for a while then filtered, finally the amount of fluoride in the filtrate was measured. The results were presented in Table 3.

Table 3. Relation between the added cathion and the residual fluoride.

$[M^{n+}]$ (g/l)	$[F^-](Al^{3+})^{(2)}$ (mg/l)	$[F^-](Fe^{3+})^{(6)}$ (mg/l)	$[F^-](Fe^{2+})^{(7)}$ (mg/l)
0.0020	1.79		
0.0024	1.57		
0.0028	1.41		
0.0032	1.28		
0.0040	1.09		
0.0048	0.96		
0.01		2.48	
0.03		2.08	
0.05		1.67	
0.06			1.63
0.08		1.49	
0.11		1.25	
0.13		1.2	
0.31			1.61
1.55			1.57
3.10			1.63
6.19			1.97

4. 2. 1. 2. Effect of pH

Based on the adsorption of fluoride ion on cathion hydroxides [$Al(OH)_3$ and $Fe(OH)_3$] which is related to the pH of the studied water according to equilibriums (5) and (6) for Al^{3+} [8], equilibriums (7) and (8) for Fe^{3+} [9] and equilibrium (9) for Fe^{2+} [10]. We repeat the same steps of the previous experiment as mentioned in (2.4.1) by fixing the temperature and the added optimal concentration of each cathion separately but changing the pH by buffer solutions. The results are presented in Figure 2 and Table 4.

Table 4. Relation between the pH and the residual fluoride
$[Al^{3+}] = 0.0024 g/l$, $[Fe^{3+}] = 0.08 g/l$, $[Fe^{2+}] = 1.55 g/l$

pH	$[F^-](Al^{3+})^{(2)}$ (mg/l)	$[F^-](Fe^{3+})^{(6)}$ (mg/l)	$[F^-](Fe^{2+})^{(7)}$ (mg/l)
4			2.61
4.02	1.8		

4.3		1.64	
5		1.36	2.2
5.07	1.46		
6	1.23	1.26	2.06
7			1.66
7.02	1.27		
7.4		1.35	
7.5			1.49
8	1.5		1.45
8.1		1.66	

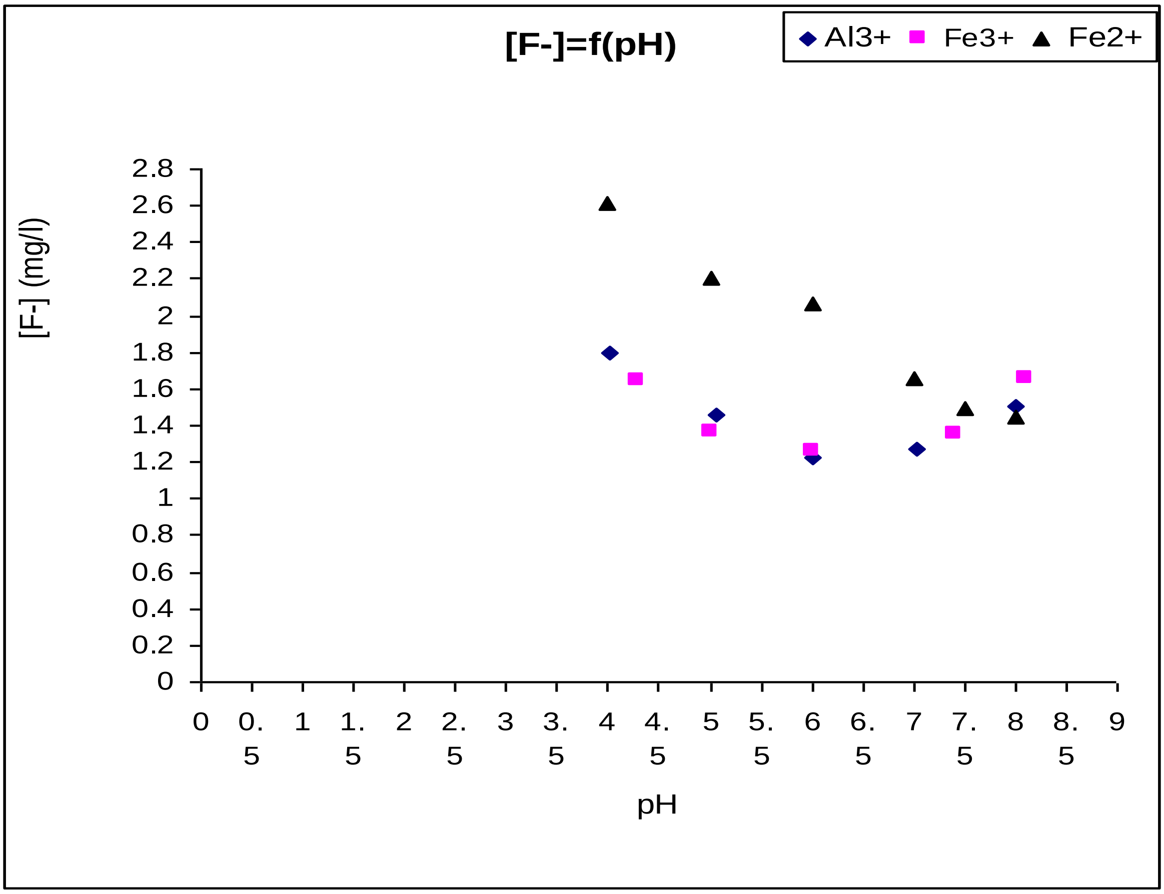

Figure 2. variation of residual fluoride against pH.

4. 2. 1. 3. Effect of temperature T

The same steps of the experiment are repeated as mentioned in (2.4.2) by fixing the concerned added salt and the optimal pH, but changing the temperature. The results were presented in Table 5 and Figure 3 [5].

Table 5. Relation between the temperature and the residual fluoride
$pH_{Al_2(SO4)_3} = pH_{Fe_2(SO_4)_3} = 7.60, pH_{FeSO_4} = 7.51$
$[Al^{3+}] = 0.0024 g/l$, $[Fe^{3+}] = 0.08 g/l$, $[Fe^{2+}] = 1.55 g/l$

T (°C)	**$[F^-](Al^{3+})^{(2)}$ (mg/l)**	**$[F^-](Fe^{3+})^{(6)}$ (mg/l)**	**$[F^-](Fe^{2+})^{(7)}$ (mg/l)**
16.4			1.41
17		2	
20	1.67		
25			1.15
25.4		1.62	
26.5	1.5		
30	1.41		1.02
35			0.83
35.2		1.05	
40	1.21		0.69
45	1.1	0.73	0.56

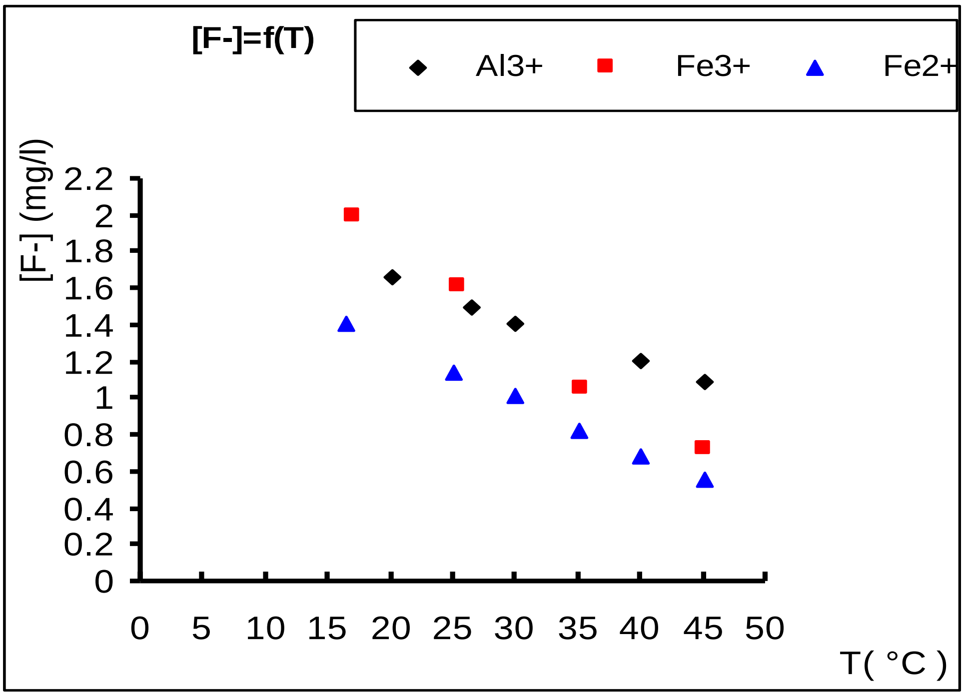

Figure 3. variation of residual fluoride against temperature.

2. 4. 2. precipitation

The factors affecting (mass, pH, and temperature T) were studied by the Precipitation method using$CaSO_4 \cdot 2H_2O$, $CaCl_2$ (98 %) and $Ca(OH)_2$ (97 %).

2. 4. 2. 1. Effect of calcium concentration

Based on the precipitation of fluoride in the form of CaF_2,low soluble according to equilibrium (10). 100 ml of Shuhada water was put in each cup of plastic then the pH and temperature T were measured, after that different amount of the same salt was added to each cup. After stirring for three minutes, they are left for a while then filtered, finally the amount of fluoride in the filtrate was measured. The results were presented in Table 6 and Figure 4.

Table 6. Relation between the added calcium and the residual fluoride at (pH = 7.30 and T = 21.7 °C).

$[Ca^{2+}]$ (g/l)	$[F^-]^{(4)}$ $Ca(OH)_2$ (mg/l)	$[F^-]^{(5)}$ $CaSO_4$ (mg/l)	$[F^-]^{(3)}$ $CaCl_2$ (mg/l)
0.037	1.83		
0.043	1.73		
0.054	1.52		
0.27	0.84		
0.54	0.64		
0.72	0.57	1.63	2.42
0.93		1.56	
1.0 8			2.28
1.44	0.43	1.46	2.15
1.8			1.98
3.6	0.31	1.32	1.57
9.01			1.026
10.82	0.19	1.15	0.98
12.61			0.92
14.41			0.85
16.22			0.71

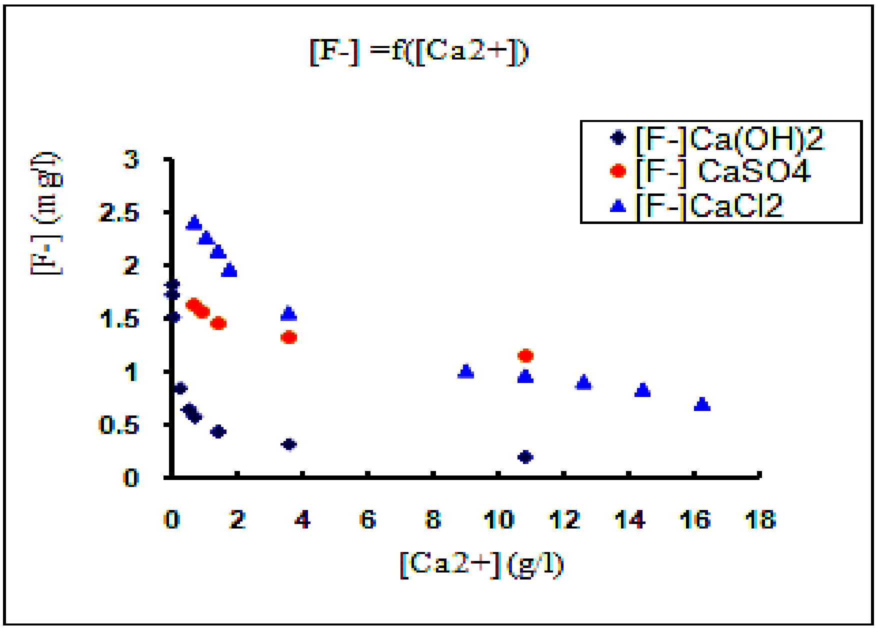

Figure 4. Variation of residual fluoride against added calcium concentration.

2. 4. 2. 2.Effect of pH

Based on displacing the equilibrium towards the precipitation of fluoride in the form of CaF_2 according to the relation (1). We repeat the same steps of the previous experiment as mentioned in (2.4.1) by fixing the temperature and the added optimal concentration of either $CaSO_4$, $CaCl_2$ and $Ca(OH)_2$,but changing the pH by buffer solutions. The results are presented in Table 7 and Figure 5.

Table 7. Relation between the pH and the residual fluoride

$[Ca^{2+}]CaSO_4 = 0.93 g/l$, $[Ca^{2+}]Ca(OH)_2 = 0.054 g/l$, $[Ca^{2+}]CaCl_2 = 3.6 g/l$, $T = 21.7\ °C$

pH	$[F^-]^{(4)}$ $Ca(OH)_2$ (mg/l)	$[F^-]^{(5)}$ $CaSO_4$ (mg/l)	$[F^-]^{(3)}$ $CaCl_2$ (mg/l)
4		1.82	1.87
4.06	1.73		
5	1.67		1.78
5.1		1.73	
6	1.61		1.69
6.1		1.68	
7	1.53	1.62	1.61
7.4	1.51		
7.5			1.56
8	1.47	1.56	1.52

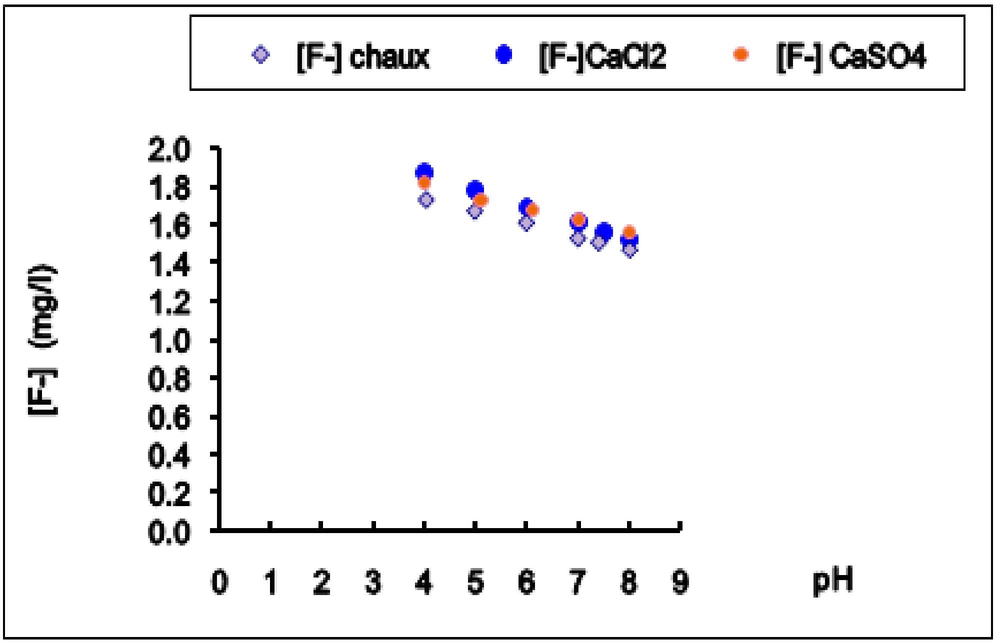

Figure 5. Variation of residual fluoride against pH.

2. 4. 2. 3. Effect of temperature T

Based on displacing the equilibrium towards the precipitation of fluoride in the form of CaF_2 according to the relation (1). We repeat the same steps of the previous experiment as mentioned in (2.4.1) by fixing the pH and the added optimal concentration of either $CaSO_4$,$CaCl_2$ and $Ca(OH)_2$,but changing the temperature by buffer solutions. The results are presented in Table 8 and Figure 6 [5].

Table 8. Relation between the temperature and the residual fluoride

$$\mathrm{pH}_{\mathrm{Ca(OH)_2}} = 7.40, \mathrm{pH}_{CaSO_4} = \mathrm{pH}_{CaCl_2} = 8$$

$$[\mathrm{Ca}^{2+}]_{\mathrm{Ca(OH)_2}} = 0.054\mathrm{g/l}, [\mathrm{Ca}^{2+}]_{\mathrm{CaCl_2}} = 3.6\mathrm{g/l}, [\mathrm{Ca}^{2+}]_{\mathrm{CaSO_4}} = 0.93\mathrm{g/l}$$

T (°C)	$[F^-]^{(4)}$ $Ca(OH)_2$ (mg/l)	$[F^-]^{(5)}$ $CaCl_2$ (mg/l)	$[F^-]^{(3)}$ $CaSO_4$ (mg/l)
20	1.57	2.04	1.59
22	1.5		
22.4			1.50
29		1.5	
30	1.27	1.41	1.24
40	0.97	1.08	0.99
45	0.87	0.91	0.87

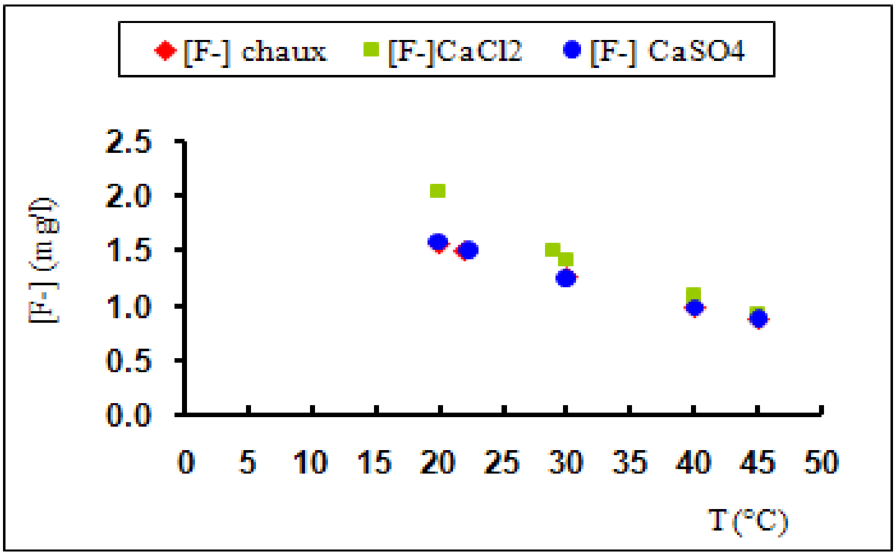

Figure 6. Variation of residual fluoride against temperature.

3. EQUATIONS AND EQUILIBRIUMS

$$6HCO_3{}^- + Al_2(SO_4)_3 \rightleftharpoons 3SO_4{}^{2-} + 2Al(OH)_{3(S)} + 6CO_2 \ldots..(1)$$

$$Fe^{3+} + 3OH^- \leftrightharpoons Fe(OH)_{3(S)} \ldots..(2)$$

$$Fe^{2+} + 2HCO_3{}^- \leftrightharpoons Fe(HCO_3)_{2(S)} \ldots \ldots (3)$$

$$4Fe(HCO_3)_2 + 10H_2O + O_2 \rightleftharpoons 4Fe(OH)_{3(S)} + 8H_2CO_3..(4)$$

$$Al(OH)_{3(S)} + 3H_3O^+ \rightleftharpoons Al^{3+} + 6H_2O \ldots \ldots..(5)$$

$$Al(OH)_{3(S)} + OH^- \rightleftharpoons Al(OH)_4{}^- \ldots \ldots..(6)$$

$$Fe(OH)_{3(S)} + 3H_3O^+ \rightleftharpoons Fe^{3+} + 6H_2O \ldots \ldots..(7)$$

$$Fe(OH)_{3(S)} + OH^- \rightleftharpoons Fe(OH)_4{}^- \ldots \ldots..(8)$$

$$Fe^{3+} + 3OH^- \rightleftharpoons Fe(OH)_{3(S)} \ldots \ldots \ldots.(9)$$

$$CaF_2 \rightleftharpoons Ca^{2+} + 2F^- \ldots (10)$$

$$Mg(OH)_2 \rightleftharpoons Mg^{2+} + 2OH^- \ldots \ldots (11)$$

$$\eta = Ae^{B/T} \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots.(1)$$

$$V = \frac{Z.D.E}{4\pi\eta} \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots..(2)$$

$$V_{mob} = {}^{V}/_{E} \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots (3)$$

$$[F^-] = \sqrt[3]{2K_{sp}\left(1 + \frac{[H^+]}{Ka}\right)^2} \ldots \ldots.(4)$$

4. RESULTS AND DISCUSSION

4. 1. Coagulation

- ✓ According to the results of Table 2 we observe that the high concentrations of (Ca^{2+}, Mg^{2+}, SO_4^{2-}, Cl^-) exceed the WHO[(10)] standards of water . This related to the geological characteristics and the structure of rocks .
- ✓ According to the results of Table 3 , defluoridation by the use of $Al_2(SO_4)_3$ is the best. This can be explained by the adsorption of fluoride on the flocks of $Al(OH)_3$ (equilibrium 1). The optimal concentrations of cathions resulting from both $Al_2(SO_4)_3{\cdot}18H_2O$, $Fe_2(SO_4)_3{\cdot}H_2O$ and $FeSO_4$ are 0.0024 g/l , 0.08 g/l and 1.55 g/l respectively.
- ✓ According to the results of Table 4, the optimal pH resulting by the addition of both $Al_2(SO_4)_3{\cdot}18H_2O$, $Fe_2(SO_4)_3{\cdot}H_2O$ and $FeSO_4$ are 8.0, 7.6 and 7.5 respectively.
- ✓ According to the results of Table 5 we observe that residual [F^-] is decreased whenT is increased, this can be proved by the following:
  Increasing T leads to the decrease of [equation of Guzman-andrad] (1), so V is increased [equation (2)]. As a result V mob is increased [equation (3)] [6,7]. The optimal temperatures resulting from both $Al_2(SO_4)_3{\cdot}18H_2O$, $Fe_2(SO_4)_3{\cdot}H_2O$ and $FeSO_4$ are 26.5 °C, 25.4 °C and 16.4° crespectively.
  The optimal conditions for coagulation by the previous salts are presented in Table 9.

Table 9. Optimal values of factors affecting by coagulation treatment.

Added salt	Factors influencing				[F^-] residual (mg/l)
	Added salt concentration (g/l)	Added [M^{n+}] (g/l)	pH	T (°C)	
$Al_2(SO_4)_3{\cdot}18H_2O$	0.03	0.0024	8.00	26.5	1.50
$Fe_2(SO_4)_3$	0.3	0.08	7.60	25.4	1.62
$FeSO_4$	5	1.55	7.51	16.4	1.41

4. 2. Precipitation

- ✓ According to the results of Table 7, defluoridation by the use of $Ca(OH)_2$ is the best. This can be explained by the precipitation of CaF_2 (equilibrium 10) and the adsorption of fluoride on the flocks of $Mg(OH)_2$ which is formed according to the equilibrium (11) [6]. The optimal concentrations of Ca^{2+} resulting from both $Ca(OH)_2$, $CaCl_2$ and $CaSO_4$ are 0.054 g/l, 3.6 g/l and 0.93 g/l respectively.
- ✓ The results of Table 8 indicate that the concentrations of residual fluoride are decreased when the values of pH are increased. The use of $Ca(OH)_2$ is the best because it has a basic nature which rise the pH of the solution. As a result, the concentration of residual fluoride is decreased which is fitted to equation (4).
  The optimal pH resulting from both $Ca(OH)_2$, $CaCl_2$ and $CaSO_4$ are 7.40, 8.00 and 8.00 respectively.

✓ The results of Table 9 indicate that the concentration of residual fluoride are decreased when the values of temperature are increased which is not expected theoretically, but fits to the results reached by (SAOUD 2009) [5]. The optimal temperatures resulting from both $Ca(OH)_2$, $CaCl_2$ and $CaSO_4$ are 22 °C, 29 °C and 22.4° crespectively.
The optimal conditions for precipitation by the previous salts are presented in Table 10.

Table 10. Optimal values of factors affecting by precipitation treatment.

Added calcium salt	Factors influencing				$[F^-]$ residual (mg / l)
	Added salt concentration (g / l)	Added $[Ca^{2+}]$ (g/l)	pH	T (°C)	
$Ca(OH)_2$	0.1	0.054	7.4	22	1.50
$CaCl_2$	10	3.6	8	29	1.50
$CaSO_4$	4	0.93	8	22.4	1.50

5. CONCLUSIONS

- According to this study on the water of some region of El-Oued, it appear that most of them Contain a high quantity of fluoride exceeds the standard value of (WHO)[10] with a high total hardness.
- This lead us to look for the best way to reduce the amount of fluoride by comparative study between precipitation and coagulation treatments suit the characteristics of the studied water .
- Through this research, it appear that the precipitation is better the coagulation for the defluoridation of water.
- The present investigation indicates that reducing fluoride from water by using $Ca(OH)_2$ is economic and decreases the hardness of the treated water .
- Through the study of factors affecting (concentration, pH, temperature) it is possible to choose the best conditions for a reduction process with $Ca(OH)_2$by adding an amount at a concentration of 0.1 g/l, pH = 7 and a temperature of 22 °C.

ABBREVIATIONS

EDTA(1): ComplexonIII (Ethylene diamine tetra acetic acid disodium salt).
$[F^-]$ Al^{3+} (2): concentration of fluoride residual after adding $Al_2(SO_4)_3$ to water.
$[F^-]$ $CaCl_2$ (3): concentration of fluoride residual after adding $CaCl_2$ to water.
$[F^-]$ $Ca(OH)_2$ (4): concentration of fluoride residual after adding $Ca(OH)_2$ to water.
$[F^-]$ $CaSO_4$ (5): concentration of fluoride residual after adding $CaSO_4$ to water.

$[F^-]$ Fe^{3+} (6): concentration of fluoride residual after adding $Fe_2(SO_4)_3$ to water.
$[F^-]$ Fe^{2+} (7): concentration of fluoride residual after adding $FeSO_4$ to water.
MO(8): methyl orange
Ph.Ph(9): phenolphthalein
TA(10): alkalimetric title
TAC(11): The complete alkalimetric title.
TISAB(12): *total ionic strength adjustment buffer*
WHO(13): World Health Organization.

REFERENCES

[1] WHO, *Fluoride in drinking water,* IWA Publishing, London, 2006.

[2] Ministère de la santé et de la population et OMS, Programme National de Santé Bucco-dentaire en milieu scolaire, Mai 2001.

[3] Circulaire interministérielle du 07 Mai 2001 relative au Programme National de Santé Bucco-dentaire en milieu scolaire.

[4] Rodier et Coll., *L'analyse de l'eau : eaux naturelles, eaux résiduaires, eau de mer.* 8e édition; Paris, 2005, pp 299 à 310 et pp 219 à 221.

[5] Saoud D, *Etude de l'effet des dérives organiques sur la formation de lithiase urinaire dans la région du Sud-Est Algérienne.* Thèse de Magister, Université de Ouargla 2009, pp. 71.

[6] Brodsky A., Zdenek V., *Possibilités de décarbonatation des eaux à la chaux, la technique de l'eau et de l'assainissement,* 3 (1973) 33-40.

[7] M. G. Sujana, G. Soma, N. Vasumathi, S. Anand, *Journal of Fluorine Chemistry* 130(8) (2009) 749-754.

[8] Djamel Atia, Abdelghani Hoggui, *International Letters of Chemistry, Physics and Astronomy* 5 (2013) 39-46.

[9] Djamel Atia, Abdelghani Hoggui, *International Letters of Chemistry, Physics and Astronomy* 5 (2013) 57-65.

[10] Djamel Atia, Abdelghani Hoggui, *International Letters of Chemistry, Physics and Astronomy* 7(1) (2013) 39-46.

(Received 16 May 2013; accepted 21 May 2013)