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Defluoridation of water by precipitation with lime and calcium Sulfate

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ABSTRACT

El-Oued is known for some diseases caused by fluoride concentration in drinkable water. To reduce it, we have chosen a sample with the highest content of fluoride among many sources in order to precipitate it with $\text{Ca}(\text{OH})_2$ and CaSO_4 . In order to get better reduction yield of fluoride, a study has been done on the influencing parameters (concentration, pH, temperature) to choose the best conditions. The removal of fluoride is favorable at low concentration of $\text{Ca}(\text{OH})_2$, at room temperature and normal acidity.

Keywords: fluorine, defluoridation, drinkable water, precipitation.



INTRODUCTION

The concentration of fluoride in groundwater depends on the geological characteristics, and chemical properties of rocks and climate of the region. Fluoride content in the groundwater of the major classes of northern Algerian desert often exceed 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 raised 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 of precipitation has been done with different salts of calcium and determination of optimal conditions of factors affecting the reduction of fluoride in drinking water.

Experimental section

Preparation of curve witness fluoride

To determine the concentration of fluoride in various samples, a potentiometer method was used (Rodier 2005) [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⁽⁸⁾. The graph $E=f(\log C_F)$ is presented in Figure (1).

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.

Determination of the predominant concentration of ions in the studied water:

The study was done according to (Rodier 2005) [4] on cold water of Shuhada as follows:

Nitrates and sulfates: Spectroscopy method (UV) ray using (spectrophotometer DR 2400).

Total hardness: By complexity with EDTA⁽¹⁾ in the presence of *Eriochrome Black T* at buffer solution of pH=10.



Sodium and potassium: Using flame atomic absorption analysis. Results of Predominant ions are presented in table (2).

Alkalinity: Determining ⁽⁶⁾ and TAC⁽⁷⁾ using PhPh⁽⁵⁾ and MO⁽⁴⁾ indicators respectively.

Chlorides: Volumetric method for Mohr.

Calcium concentration: By complexity with EDTA⁽¹⁾ in the presence of murexide in a solution of pH=12.

Magnesium concentration: Calculated from the difference Total hardness and Calcium concentration.

Treatment: The factors affecting (mass, pH, and temperature T) were studied by the Precipitation method using CaSO₄.2H₂O and Ca(OH)₂ at a purity of 98% and 97% respectively.

Effect of calcium concentration:

Based on the precipitation of fluoride in the form of CaF₂, low soluble according to equilibrium (1). 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 3 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) and figure(2).

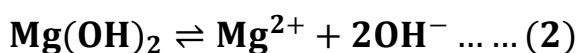
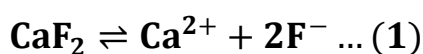
Effect of pH :

Based on displacing the equilibrium towards the precipitation of fluoride in the form of CaF₂ 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 CaSO₄ and Ca(OH)₂ but changing the pH by buffer solutions. The results are presented in table (4) and figure (3).

Effect of temperature T:

The same steps of the experiment are repeated as mentioned in (2.4.2) by fixing the added optimal concentration of CaSO₄ and the optimal pH, but changing the temperature in a first step and fixing the added optimal concentration of Ca(OH)₂ and the optimal pH, but changing the temperature in a second step. The results were presented in table (5) and figure (4) [5].

Equations and equilibriums:



$$[F^-] = \sqrt[3]{2K_{sp} \left(1 + \frac{[H^+]}{K_a}\right)^2} \dots \dots (1)$$

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

Sources of water	19]mars city	Sidimastur city	400 city	Tugurt city	8may city	1Nov City	Nezla city	Shuhada
[F⁻] (mg/l)	1.87	1.90	1.92	0.44	1.84	1.94	0.46	2.61

Table 2: physico-chemistry 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	54.93	2.41	5.9	0	105	402

Table3: Relation between the added calcium and the residual fluoride at

(pH=7.30 and T= 21.7 °C)

[Ca²⁺](g/l)	[F⁻]⁽²⁾Ca(OH)₂(mg/l)	[F⁻]⁽³⁾ CaSO₄ (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
0.93		1.56
1.44	0.43	1.46
3.6	0.31	1.32
10.82	0.19	1.15

Table4: Relation between the pH and the residual fluoride

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

pH	$[F^-]^{(2)}_{Ca(OH)_2}(mg/l)$	$[F^-]^{(3)}_{CaSO_4}(mg/l)$
4		1.82
4.06	1.73	
5	1.67	
5.1		1.73
6	1.61	
6.1		1.68
7	1.53	1.62
7.4	1.51	
8	1.47	1.56

Table5: Relation between the temperature and the residual fluoride

$pH_{Ca(OH)_2} = 7.40$, $pH_{CaSO_4} = 8.00$

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

T(°C)	$[F^-]^{(2)}_{Ca(OH)_2}(mg/l)$	$[F^-]^{(3)}_{CaSO_4}(mg/l)$
20	1.57	1.59
22	1.5	
22.4		1.50
30	1.27	1.24
40	0.97	0.99
45	0.87	0.87

Figure1: The witness graph for fluoride

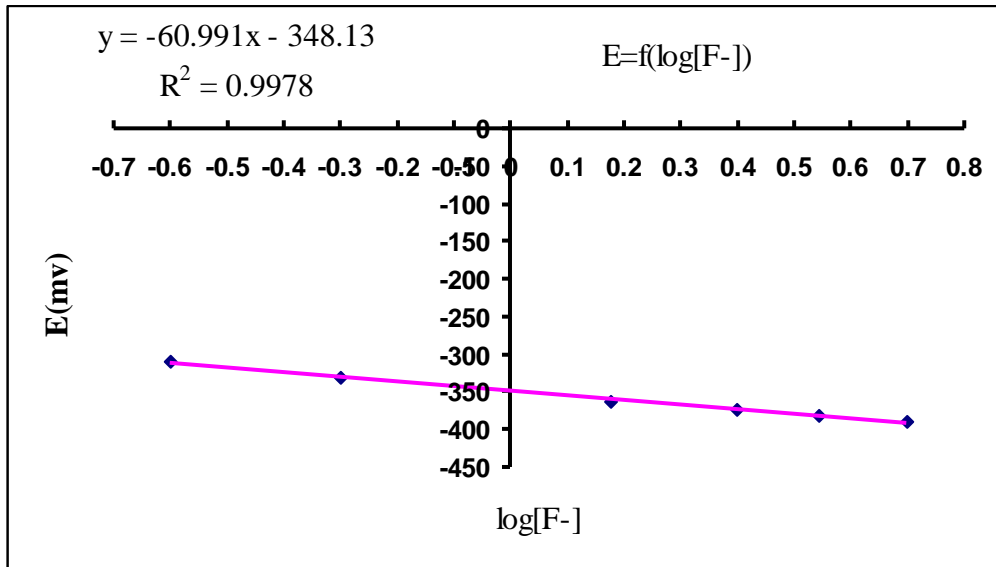


Figure2: variation of residual fluoride against added calcium concentration

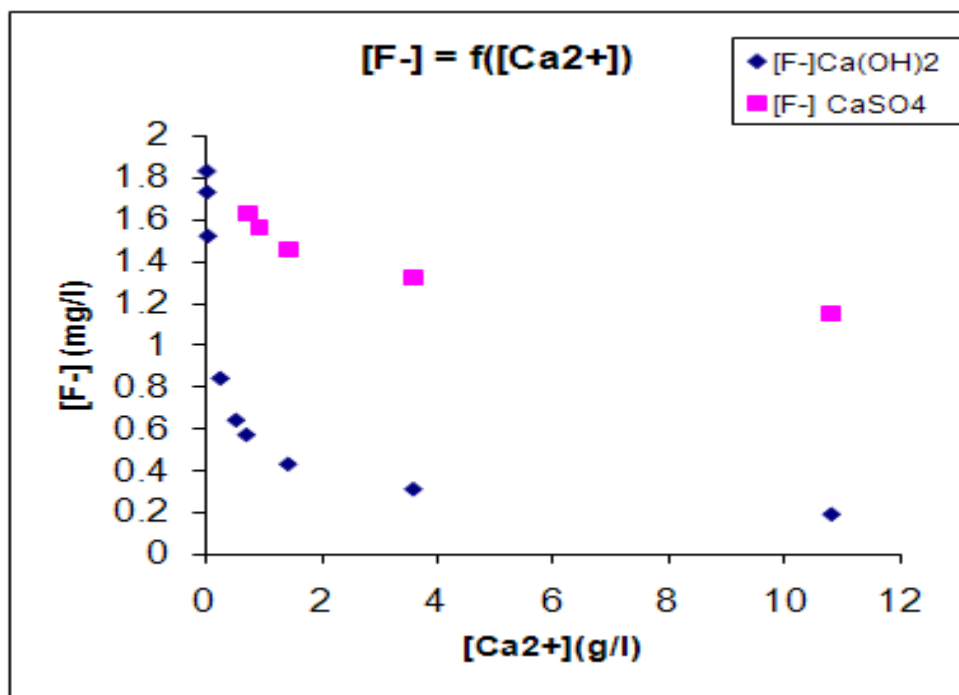


Figure3: variation of residual fluoride against pH

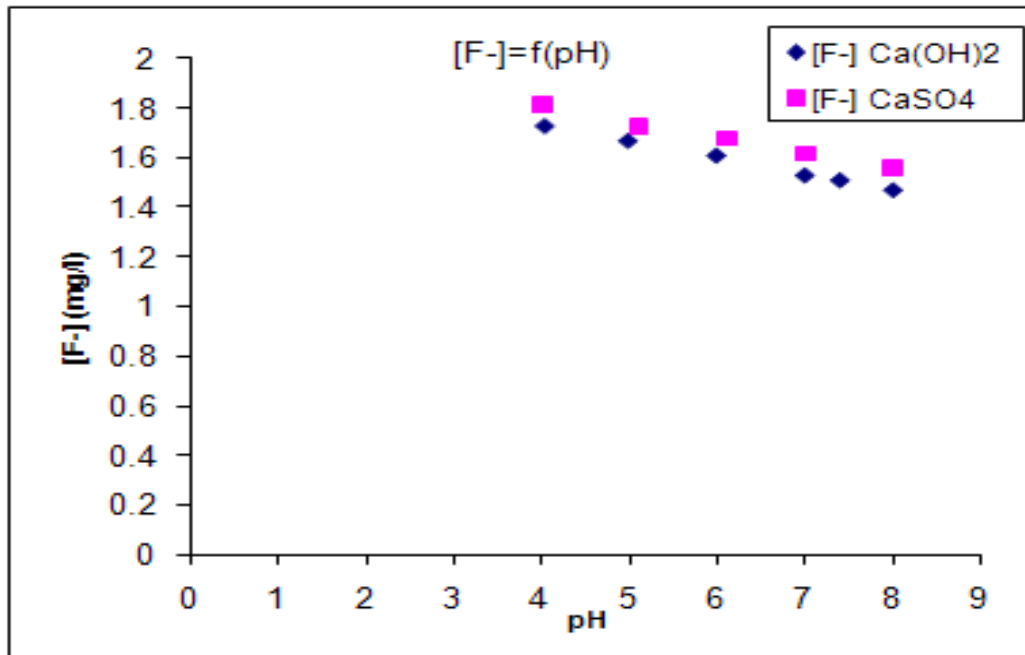
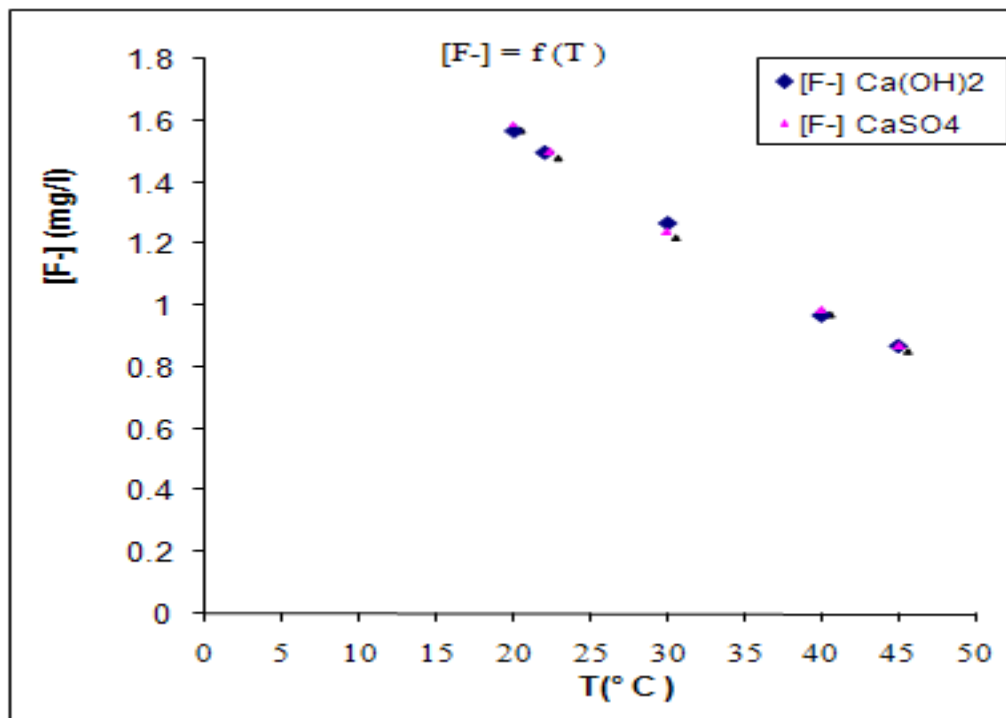


Figure4: variation of residual fluoride against temperature



RESULTS AND DISCUSSION

- ✓ 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 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 $\text{Ca}(\text{OH})_2$ is better than the use of CaSO_4 . This can be explained by the precipitation of CaF_2 (equilibrium 1) and the adsorption of fluoride on the flocks of $\text{Mg}(\text{OH})_2$ which is formed according the equilibrium (2) [6]. The optimal concentrations of Ca^{2+} resulting from both $\text{Ca}(\text{OH})_2$ and CaSO_4 are 0.054g/l and 0.93g/l respectively.
- ✓ The results of table 4 indicate that the concentration of residual fluoride are decreased when the values of pH are increased. This can be explained according to equation (1). The use of $\text{Ca}(\text{OH})_2$ is better 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 (1). The optimal pH resulting from both $\text{Ca}(\text{OH})_2$ and CaSO_4 are 7.40 and 8.00 respectively.
- ✓ The results of table 5 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 $\text{Ca}(\text{OH})_2$ and CaSO_4 are 22°C and 22.4°C respectively.

CONCLUSION

- According to the quantity of fluoride in the water of some region of El-Oued, it appears that most of them contain surplus exceeds the standard value of (WHO)⁽⁹⁾ with a high total hardness.
- The present investigation indicates that reducing fluoride from water by using $\text{Ca}(\text{OH})_2$ is an economic method 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 $\text{Ca}(\text{OH})_2$ by adding an amount at a concentration of 0.1g / l, pH=7 and a temperature of 22°C.

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ABRIVIATIONS

EDTA⁽¹⁾: Complexon III (Ethylene diamine tetra acetic acid disodium salt).

[F] $\text{Ca}(\text{OH})_2$ ⁽²⁾: concentration of fluoride residual after adding CaCl_2 to water.

[F] CaSO_4 ⁽³⁾: concentration of fluoride residual after adding $\text{Ca}(\text{OH})_2$ to water.

MO⁽⁴⁾: methyl orange

Ph.Ph⁽⁵⁾: phenolphthalein

TA⁽⁶⁾: alkalimetric title.

TAC⁽⁷⁾: The complete alkalimetric title.

TISAB⁽⁸⁾: total ionic strength adjustment buffer



WHO⁽⁹⁾: World Health Organization.

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