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Elimination of Fluoride Ions from Water of Wells and Tyikomiyne Sources by The Hydroxyapatite Phosphocalcic, Talssint (Eastern Morocco)

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Abstract: Two sources and five wells Tyikomiyne area, Talssint region on the eastern coast of Morocco were analyzed for fluoride ion. In all the wells studied, fluoride contents exceed the standard set by the WHO (1.5 mg/L), probably due to the geological nature of the terrain traversed. Thus, our work aims more specifically on the treatment of water from these wells containing fluoride using support apatite. The results obtained show that the apatite is suitable to obtain a better performance of the elimination of the fluoride ion. **Keywords:** Elimination, Fluoride ions, Water, Talssint region, Morocco.

I. Introduction

Groundwater is a very important part of the hydraulic heritage. They have compared to surface water clear advantages in terms of coverage of needs. In Marrakech, groundwater plays an important role in the development of irrigation and drinking and industrial water, whether in urban or rural centers [1-3]. In Tyikomiyne area (Figure 1), using the waters of springs and wells for drinking and irrigation, but the geological nature of the soil in the region likely cause contamination of these waters by fluoride ions, which can migrate and reach groundwater, accumulate in the food chain and pose risks to human health.

Interest in contamination of groundwater, aquifers of water and soil by fluoride ions from natural rocks is increasingly increased. This is because of the adverse effect this has on the human health. That is why it is considered a major environmental problem and removal of this pollutant is becoming increasingly important. Thus the study of the quality of water Tiykomiyne well physicochemistry water Tyikomiyne wells and evaluation of the water quality of the river Tislit-Talssint was recently reported by our group [4-7]. In this work, we analyzed the fluoride ion content of the water wells and sources Tyikomiyne then we do the treatment of water from these wells and springs containing fluoride using an apatite support.



Figure 1 Study area location in the watershed of the river Guir.

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The center of Talssint belongs to the south side of the High Atlas, it is the Guir Basin (Figure 2), which contains numerous discrete groundwater and deep aquifers whose recognition remains to be done [8]. The center of Talsint is the capital of the rural district of Talsint, caïdat under the same name and the circle of Beni-Tadjit, part of the province of figuig, eastern region of Morocco[8]. Our study concerns among the wells and sources of Tyikomiyne area Talssint region which, to our knowledge, has been no prior academic study and is limited by the village Ezzaouia the south, Affia area to the north, the regional road RP601 to 'Beni-Tadjit west and east Jbal Alaajra. Thus two sources and five wells have been retained on the study area (Figure 2):



Figure 2. Location of wells and sources that are considered from left to right: Faryat (W1), El Masjid (W2), Hadi (W3), Hilla (W4), Deppiz (W5), Annakhla (S1), Aghram (S2),

The region is characterized by pre-Saharan and Saharan environments. Temperatures are high in summer and very cold in winter. The average minimums of the coldest month (January) is -5 $^{\circ}$ C and maxima of the hottest month (July) 47 $^{\circ}$ C. The average annual rainfall was around 244.9 mm for the period 1983/2007 and 500 mm for the period 2008/2010, , With important interannual variations, with extremes of 61 mm in 1998/99 and 684.5 mm in 2009/2010 [8].

II. Expérimental

2.1 Materials used

In the field of radioactive waste, apatite phosphosilicates whose composition is close to that of natural apatite, confined in their wombs of radioactive elements [9]. The apatite phosphates belong to a large family of biomaterials applied in dentistry and Otorhinolaryngology [10-12]. And other studies have shown that the importance of these materials is their ability to set a large number of metal species in aqueous solution diluted with a great performance[13]. For our part, the hydroxyapatite calcium phosphate was used as extractant matrix fluoride in our water treatment of the five wells and two sources. Its chemical formula is: Ca_{10} (PO 4)₆ (OH)₂.

The calcium phosphate hydroxyapatite of formula Ca10 (PO4) 6 (OH) 2 belong to the crystallographic family of apatites, isomorphic compounds having the same hexagonal structure. This compound is the calcium phosphate most commonly used as a biomaterial. The main uses of hydroxyapatite in the medical sector are:

- Coatings for prostheses.

- For the development of bone substitutes (types of calcium phosphate ceramics, types,

ionic cements ...).

His interest results from its perfect biocompatibility and bioactivity[14]. The hydroxyapatite calcium phosphate crystallises in the hexagonal system (space group = $P_{6,3/m}$) with the following crystallographic parameters [15]:

a = 9,418 Å, c = 6,881 Å, $b = 120^{\circ}$. Hydroxyapatite the solubility equilibrium is generalized in the form: $Ca_{10}(PO_4)_6(OH)_2 \longrightarrow 10 Ca^{2+} + 6 PO_4^{3-} + 2 OH^{-}$

2. 2. Extraction Technique and Method of Analysis

We used an extraction technique based on: glass electrode, thermometer, magnetic stirrer and pH meter (Figure 3).



Figure 3. Technique Extraction and Analysis Method

Each support phosphate 0.1g sample mass is placed in a cell thermostated at room temperature, containing 100 ml of water to be analyzed; and these waters are initial known concentrations of fluoride ion. Each cell is provided with a control thermometer with a combined glass electrode and a magnetic stirrer. The initial pH is adjusted by the first pH meter. To promote better contact between the support and the pollutant fluoride to remove the samples are stirred at room temperature for 4 hours. When the extraction equilibrium is attained, the loaded carrier is separated from the fluoride supernatant solution by filtration.

So Fluoride was assayed by ion chromatography at the National Center of Scientific and Technical Research (CNRST).

The extraction yield is given by the following relationship:

$$R = \frac{(C_i - C_f) \, 100}{C_i}$$

Ci: Initial concentration of fluoride in water studied. Cf: Concentration of fluoride, to the extraction balance.

III. Results

The addition of small amounts of fluoride is necessary to significantly reduce dental caries. However, its excessive accumulation in the body causes fluorosis, dental and musculoskeletal essentially reached [16]. The comparison of the levels of fluoride ion, recorded in the waters of the well studied and those set by the World Health Organization, shows that these waters are contaminated by this element which creates a risk for the dental health of populations in the region [16].

The results of reachent with hadde fons Hydroxyupatte calefulli phosphate are given in rable 1.					
	[F ⁻] _i	$[F]_{f}$	pH i	$pH_{\rm f}$	R%
Well 1	2.09	0.12	8.17	9.78	94.25
Well 2	1.76	0.19	8.10	9.62	89.20
Well 3	1.70	0.30	8.04	9.41	82.35
Well 4	1.75	0.47	7.52	8.85	73.14
Well 5	2.08	0.19	8.12	9.63	90.86
Source 1	1.44	0.33	8.00	8.95	77.08
Source 2	1.52	0.27	7.06	9.47	82.23

The results of treatment with fluoride ions Hydroxyapatite calcium phosphate are given in Table 1:

Table 1. Treatment of fluoride ions by hydroxyapatite calcium phosphate

Thus we simultaneously plot the histogram of fluoride ion concentrations according to the study sites before and after the extraction of a portion and the histogram of the initial pH (pHi: pH before extraction) and final pH (pHf: pH after extraction) on the other (figure 4).

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Figure 4: Comparison of average levels of fluoride ions and water wells Tyikomiyne of sources before and after extraction.



Figure 5: Water pH Comparisons wells and Tyikomiyne sources before and after extraction.

According to Figures 4 and 5 it is seen that for water puts 1 for example, the initial amount of fluoride is about 2.09 mg / l, and the remaining amount after extraction, is around 0.12 mg / l, other hand, the initial pH is of the order of 8.17 while the final pH is about 9.78. It is noted that in all the wells and springs investigated, the concentrations of fluoride ion decrease after extraction, while the final pH increases. Increasing the pH is essentially due to the release of hydroxide ions OH- dropped by the phosphate carrier.

The balance sheet anion exchange between the support and the phosphate of fluoridated water sample is as follows:

 $F^{-}(\text{liquid}) + OH^{-}(\text{solid}) \longrightarrow F^{-}(\text{solid}) + OH^{-}(\text{liquid})$ The OH- dropped by the support hydroxide is released into the solution at the end of the reaction, while the fluoride ion F- is consumed by the calcium phosphate carrier. Then we plotted the ion extraction yield histogram fluorides based on plants studied (Figure 6).





Assay results of figure 6 show that the maximum yield has been obtained at the well1, is of the order of 94.25. While the minimum yield was obtained at the well 4 which is of the order of 73.14. These results suggest that the apatite is suitable for a better performance of the elimination of the fluoride ion.

IV. Conclusion

The extraction of fluoride ion by hydroxyapatite $Ca_{10}(PO4)_6OH_2$ was studied. The results obtained in this study show that:

In all water wells and studied sources of Tyikomiyne area Talssint region, the fluoride ion concentrations decrease after extraction and the pH of the supernatant solution increases during extraction due to the release of the OH- ions in the apatite support. So the extraction equilibrium is effected by anion exchange: OH- ions forming the solid support are substituted with F- ions contained in the water sample to be analyzed.

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