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In vitro inhibitory effect of drinking water from south Algeria on the dissolution of dental hydroxyapatite

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Abstract: Epidemiological surveys in Algeria conducted in the school health program show that the dental carious prevalence is about 67%. Water is the main source of fluorine, recognized as the essential chemical element to prevent carious dental For this purpose, the objective of this study is to test, in vitro, the inhibitory effect of Saharan fluoridated water for the dissolution of hydroxyapatite $Ca_5(PO_4)_3OH$, under physiological conditions: acid (HNO_3) at pH = 5.1 and T = 37 ° C. Thence, the fluoride content of drinking water of some Saharan region was measured, it varies from 0.48 to 3.87 ± 0.05 mg / L.

The Inhibitory effect of waters is between 54.28 and 83.1%, VC <5%. In addition, a low concentration of fluorine [F-] = 0.25 mg / L reduced the solubility (S) of hydroxyapatite by a factor of 2. Thus, the studied Sahara waters inhibit 'in vitro' the dissolution of hydroxyapatite $Ca_5(PO_4)_3OH$.

Keywords: Fluorine, Saharan Drinking Water, Dental hydroxyapatite, Inhibition.

Introduction

Fluoride is an essential element to prevent carious dental[1-2]. Incorporated into the teeth, fluoride decreases the solubility of enamel in acid medium which is consists mainly of hydroxyapatite and favorize the remineralization of initial carious lesions of enamel[3-6].
Water is the main source of fluoride ions[7-8].

Similarly, all foods contain at least a small amount of fluorine ions and those containing the highest levels, like tea[9], are the most consumed drink in sahara. Indeed, in this region, water used to make tea has a high fluoride content, so the amount ingested could be higher by several times level than permitted dose[10].

In southern Algeria, the drinking water supply is provided exclusively by groundwater from the aquifers of the Terminal Complex and Continental Intercalary (Albian water), characterized by high level of fluor. However, excessive consumption of this oligo-element becomes toxic. Thus, in 2001, endemic areas of fluorosis were detected in Algerian sahara (El-Oued, Touggourt, Biskra, Timimoun, Ouargla and Ghardaïa), constituting a public health problem caused by the ingestion of an excess of fluoride[11]. In this respect, may be these regions are not concerned by the program of oral-dental health in schools[12].

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The aim of our study is, firstly, to quantify the fluoride in the water consumed by inhabitants of different regions from south Algeria, of fact that, the consumption of water becomes more important in these regions of high temperatures. Secondly, to measure the impact of fluoridated water on the dissolution of dental hydroxyapatite.

Results and Discussion

Physico-chemical quality of drinking water from South Algeria

In southern areas, where temperatures are high, the daily intake of water becomes more important. In this respect, the standards of the World Health Organization (WHO) set at 0.8 mg/L the maximum concentration of fluorine permissible for public distribution water in these warm regions[13]. In fact, the fluorine content in these samples ranged from 0.48 to 3.87 mg /L (Figure 1). The highest contents of this element was found in the public distribution waters from the Wilaya (district) of Biskra, Adrar, Ouargla and Oued Souf.

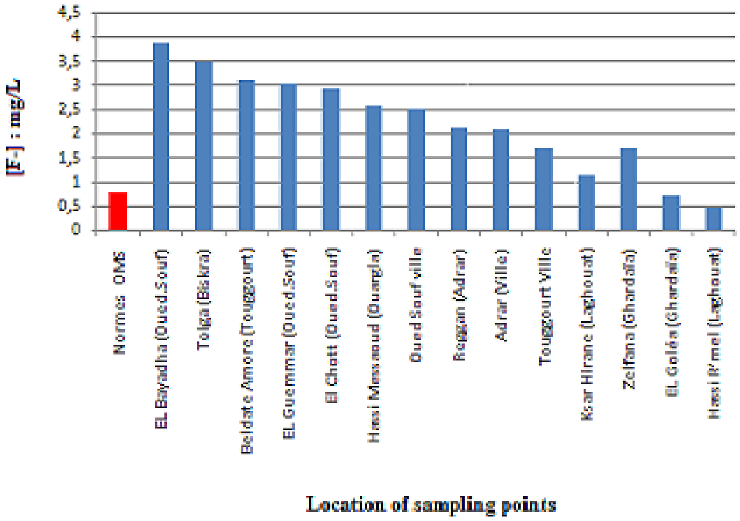

Fig. 1: Fluoride levels in drinking water from South Algeria

Dissolution Kinetic of hydroxyapatite in the presence of demineralized water

Figure 2 shows the reference curve of the dissolution of HAP that connects the volume of nitric acid used HNO_3 (0.01 N) versus time. This curve is a half-parabola increasing, its asymptote represents the equilibrium state (stationary) of the reaction and its value is the total volume of nitric acid used (VE).

The equilibrium solubility of HAP is realised as follows:

$$Ca_5(PO_4)_3OH \longrightarrow 5\,Ca^{2+} + 3\,PO_4^{3-} + OH^- \quad (1)$$

The variation coefficient (VC) is less than 5%, which proves that our experimental model is reproducible.

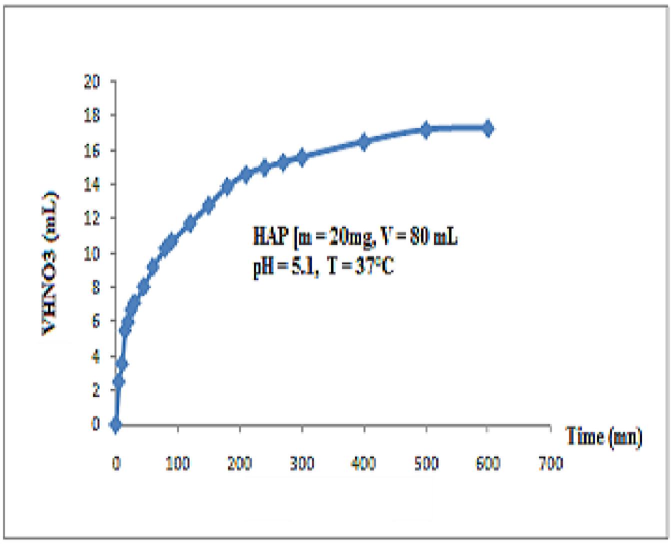

Fig. 2: Dissolution Kinetic of hydroxyapatite in the presence of demineralized water [F$^-$] = 0

Dissolution Kinetic of hydroxyapatite in the presence of synthetic fluorinated water

The kinetic of dissolution of HAP in the synthetic solutions is shown in Figure 3. The study of all the curves allowed us to determine the volume at equilibrium (EV) for each kinetics dissolution of the HAP, from which the solubility (S), the dissolution coefficient (α) and the rate of inhibition (I %) were calculated.

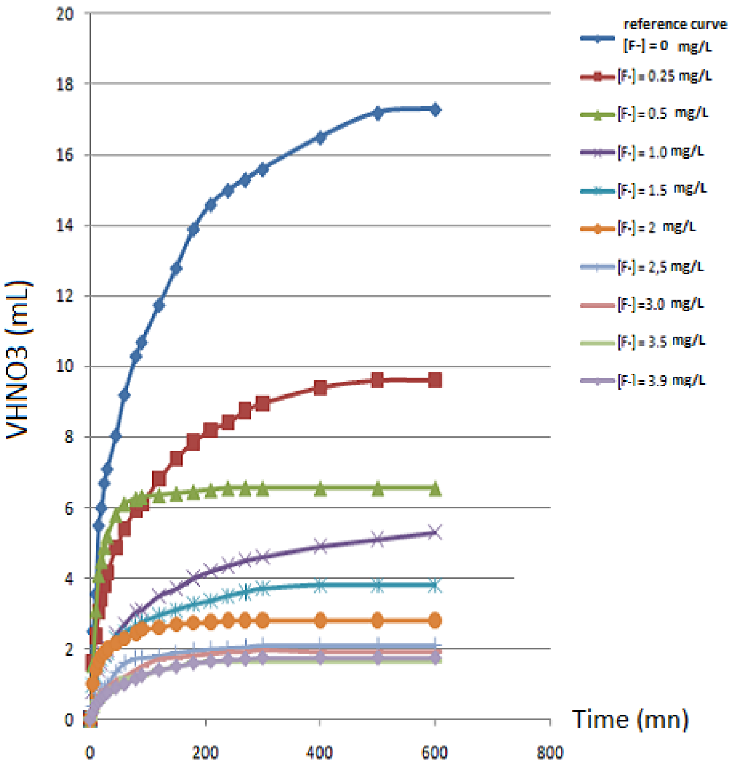

Fig. 3: Dissolution Kinetic of hydroxyapatite in the presence of synthetic fluorinated water

The solubility was obtained as follows:

$$S = [OH^-] = [H_3O^+] = N_{HNO3}*VE_{HNO3} \qquad (2)$$

The dissolution coefficient of the HAP was calculated by the following formula:

$$\alpha = S/C_0 \qquad (3)$$

With $C_0 = 4.98 \times 10^{-4}$ mol/l, corresponds to the initial concentration of HAP in each experiment.

The inhibition rate (I) was evaluated by the following relation:

$$I = (\alpha_x - \alpha_0) / \alpha_0 \qquad (4)$$

with:

α_0 : The coefficient of dissolution of the HAP at the concentration $[F^-]=0$

α_x : The coefficient of dissolution of HAP at the concentration $[F^-]$ different to zero.

All these parameters are summarized in Table 1. The form of the curves represents that dissolution kinetic of this mineral in the synthetic fluorinated solutions (from 0.25 to 3.9 mg /L) is always below the curve representing the dissolution in the standard reference water.

This results in an asymptotic slope corresponding to the EV value (total volume of acid used to neutralize the OH^- ions) which is strictly less than EV value for demineralised water (reference).

In addition, it was found that EV value decreases with increasing concentration of fluoride (Figure 3). However, the increase of fluoride concentration decreases the solubility of HAP (Figure 3 and Table 1). This would confirm that the OH^- substitution by F^- is carried out in acid medium. Indeed, the following reaction shows the formation of fluorapatite (FAP) $Ca_5(PO_4)_3F$:

$$Ca_5(PO_4)_3OH + F^- \rightarrow Ca_5(PO_4)_3F + OH^- \qquad (5)$$

On the other hand, the results found show that fluorine concentration increases with the rate of inhibition, (Figure 3). Thus, it appears from these results, that a low concentration of fluoride in the range of 0.25 mg/L reduced the solubility and the coefficient of HAP dissociation by a factor of 02 and increased the inhibitory factor I from the value 0% to 45%.

However, the variation of inhibitory effect becomes less significant when the fluorine concentration is superior to 2.5 mg/L.

Similarly, previous in vitro studies have shown that very low concentrations of fluoride (less than 0.1 ppm) had the ability to inhibit the progression of carious lesions[14,15].

Dissolution Kinetic of hydroxyapatite in the presence of water from public supplies in the South Algerian

Under the chosen experimental conditions which are similar to those of the oral medium (temperature and pH), the action of some waters containing different concentrations of fluoride (an element considered as an inhibitor on dissolution of the hydroxyapatite) was studied.

All the curves of the variation of nitric acid volume with time (Figure 3) have the same form as the reference curve indicated in Figure 2.

Table 2 summarise the set of parameters (EV, Inhibition rate and efficacy E) of different curves in the absence and presence of drinking water.

The efficacy of fluoride ions contained in the tested waters was evaluated according to the ratio of inhibition rate in presence of the drinking water and synthetic water. For all tested waters, the total acid volume used to neutralize OH^- ions was lower than that of the demineralized water (reference). As indicated in Table 2, the inhibitory effects of Saharan waters are located within a range of 54.28 and 83.1%.

Table 1: Calculated parameters: Solubility, Dissociation coefficient and inhibition rate of HAP dissolution

Fluorine Concentration $[F^-]$ (mg/L) (Synthetic Water)	VE (mL)	Dissociation Coefficient	Solubility S (mol /L)	Inhibition rate I (%)
0	17.5	0,03501	1.75×10^{-4}	0
0.25	9.6	0,1920	9.6×10^{-5}	45,16
0.48	6.7	0,1340	$6.7.\ 10^{-5}$	61,72
0.70	6.1	0,1220	$6.1.\ 10^{-5}$	65,15
0.5	6.7	0,1340	6.7×10^{-5}	61,72
0.85	6.1	0,1220	$6.1.\ 10^{-5}$	65,15
1.0	5.3	0,1060	5.3×10^{-5}	69,72
1.38	3.9	0,0780	$3.9.\ 10^{-5}$	77,72
1,5	3,8	7,63	$3,8.\ 10^{-5}$	78,21
1.71	2.5	0,0500	$2.5.\ 10^{-5}$	85,79
2.0	2.8	0,05601	2.8×10^{-5}	84,00
2.08	2.8	0,0560	$2.8.\ 10^{-5}$	84,00
2.13	2.85	0,0570	$2.85.\ 10^{-5}$	83,72
2.5	2.1	0,0420	2.1×10^{-5}	88,00
2.51	2.1	0,0420	$2.\ 1.\ 10^{-5}$	88,00
2.58	2.1	0,0420	$2.1.\ 10^{-5}$	88,00
2.94	1.9	0,0380	$1.9.\ 10^{-5}$	89,15
3.0	1.85	0,0370	1.85×10^{-5}	89,43
3.03	1.85	0,0370	$1.85.\ 10^{-5}$	89,43
3.11	1.83	0,0366	$1.83.\ 10^{-5}$	89,55
3.50	1.75	0,0350	$1.75.\ 10^{-5}$	90,00
3.87	1.65	0,0330	$1.65.\ 10^{-5}$	90,57
3.9	1.65	0,0330	1.65×10^{-5}	90,57

On the other hand, the calculation of the efficacy E for each fluoridated water showed that fluoride in water has a great inhibitory effect on the dissolution of hydroxyapatite (Table 2). So, our results are in accordance with other studies which showed that fluoride in the water natural mineral WATTWILLER have an inhibitory effect on the dissolution of this mineral[16].

Table 2: Inhibitory effect of Saharan water on the dissolution of hydroxyapatite

Water samples	VE (mL)	I %	I ref %	E = I/Iref %
Reference [F $^-$] = 0 mg/L	17.50	0	-	0
1-EL BAYADHA (O.SOUF)	5.25	70	90.57	77.77
2-TOLGA (BISKRA)	4.80	72.5	90	80.55
3- BELDATE AMORE (TOUGGOURT)	3.90	77.71	89.54	86.78
4- EL GUEMMAR (O.SOUF)	5.10	70.8	89.42	79.17
5- EL CHOTT (O.SOUF)	2.95	83.1	89.14	93.22
6-HASSI -MESSAOUD (OUARGLA)	3.20	81.7	88	92.84
7- OUED SOUF (ville)	4.10	76.57	88	87.01
8- REGGANE (ADRAR)	4.60	73.71	83.71	88.05
9- ADRAR (Ville)	5.30	69.71	84	82.98
10- TOUGGOURT (Ville)	8.0	54.28	85	63.85
11- KSAR HIRANE (LAGHOUAT)	4.80	72.57	77.71	93.38
12- ZELFANA (GHARDAIA)	6.80	61.14	61.71	99.07
13- HASSI R'MEL (LAGHOUAT)	7.80	55.43	65.14	85.09
14- EL GOLEA	6.50	62.85	61.71	101.80

Moreover, Dissananyake[17], showed that dental carious occurs in region where drinking water is less fluoridated, while it is absent in areas with fluorine rich water. Other studies have indicated that fluoridation of water is very important to maintain the bucco-dental health[14, 18,19]. In contrary, according to the World Health Organization[20], the fluoride rich water causes a risk of dental fluorosis. Indeed, the amount of fluorine called "optimal dose of fluoride in drinking water" which decreases the prevalence of dental carious with the absence of a significant fluorosis varies between 0.7 and 1.2 mg/L[8].

Conclusion

If we consider the influence of temperature, all public supply waters of the south Algeria are excessively fluoridated. On the other hand, the experimental approach, in vitro, shows the importance of fluoride of drinking water from southern Algeria in preventing dental carious.

Indeed, the extremely high temperature of the South is a major factor contributing to the increase in demand for drinking water and, consequently, the increase in dental fluorosis.

Therefore, to reduce this risk in these region, consumers need to correct their food habits, not exceeded the needs of the body in fluorine. Thus, 0.05 to 1 mg of fluoride are considered as not toxic daily dose on the health of the adult population.

Experimental Section

Evaluation of the fluoride levels in drinking water from South Algeria

Fluoride was dosed by the potentiometric method (NF T 90-004) with a specific electrode to fluoride ions (lanthanum fluoride crystal)[21].

Potential measurement was carried out compared to a calomel reference electrode ($Hg/Hg_2Cl_2/KCl$ satured) using a millivoltmeter for measuring the potential difference at 0.1 mV approximately.

The determination of fluoride concentration was done under experimental conditions defined in ion concentrations, pH and complexion. It was noted that, we must used the electrode in a pH range of about 5-6 to avoid the interference of the hydroxide ion[22]. The detection limit is 0.05 mg /L.

The establishment of calibration curve between the logarithms of fluoride ion concentration to potentials measured is needed.

All analysis were performed at room temperature not exceeding 20 ° C.

Kinetic of hydroxyapatite dissolution

It is well known that the hydroxyapatite is the essential mineral compound of the dental enamel. For this purpose, the in vitro study of fluoride ions effect of contained in the waters from southern Algeria on oral-dental health was performed by monitoring the dissolution of this mineral in the absence and presence of fluoride ions. So, the volumetric method was chosen for continuous monitoring of the, in vitro, dissolution process of hydroxyapatite $Ca_5(PO4)_3OH$ (HAP). This experimental model is characterized by its simplicity of implementation and good reproducibility.

The experimental conditions were chosen to reproduce the oral environment: pH equal to 5.1, fixed temperature to 37°C and a continuous and constant agitation.

On the other hand, we note that when the HAP is contacted with an aqueous solution, it is capable of releasing a large amount of calcium ions, phosphate and hydroxide, before reaching the dissolution equilibrium.

The evaluation of the solubility product or the determination of dissolution effect goes through the quantification of these species when equilibrium is reached.

In fact, evolution of the pH over time is a good indicator of the progress state of equilibrium[23].

First, the dissolution of the HAP was studied with demineralized water (reference). A mass of 20 mg of HAP was introduced into a 100 mL reactor. To maintain a constant temperature, the reactor is placed in a thermostatic bath at 37 ° C, which correspond to the human physiological temperature. The measurement of pH and agitation begins at the moment when the demineralized water (80 mL) is introduced into the reactor. As soon as setting in the solution, the HAP dissolves and the value of pH increases. The pH of the solution was rapidly adjusted to pH 5.1 by adding a solution of nitric acid HNO_3 (0.01 N).

The volume of acid used was recorded for metering the amount of OH^- ions released during the dissolution of the mineral, until the stationary phase of equilibrium which extends to 10 hours.

For identical initial conditions, all our tests were repeated three times, which allows us to determine the variation coefficient (VC%).

Then, the effect of fluorinated synthetic solutions was studied as well as those of drinking water from the Sahara on the dissolution of the HAP. The same protocol was followed as that used with demineralized water.

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