

MECHANISMS OF DEFLUORIDATION OF DRINKING WATER BY TRICALCIUM PHOSPHATE

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SUMMARY: Hydroxyapatite (HAP) is a natural material that is strong in fixing fluoride. An X-ray diffraction analysis proved that the densitometric tracings of tricalcium phosphate (TCP) are similar to those of HAP. The present work examines and compares the efficiency of defluoridation from drinking water by TCP under various pH level, temperature and contact time conditions. Its defluoridation mechanisms are discussed in detail. The results showed that there was a close negative correlation between the defluoridation efficiency of TCP and the pH levels of raw water, $r^2 \in [-0.8934 ; -0.9915]$, as well as evident positive correlation between defluoridation efficiency and both the temperature and the contact time, $r^2 \in [0.6420 ; 0.9207]$ and $r^2 \in [0.1956 ; 0.9839]$, respectively. This suggested that the defluoridation mechanism of TCP could be a complex chemical reaction needing energy.

Key words: defluoridation, mechanism, tricalcium phosphate, endemic fluorosis

INTRODUCTION

China is severely affected by endemic fluorosis. Excess fluoride intake has recently been estimated to affect some 100 million people. Fluorosis districts, where fluoride occurs in drinking water in concentrations higher than 4 mg-F/L, account for about 20 % of the affected population, and maximum fluoride concentrations in drinking water reach 40 mg-F/L. Most of endemic fluorosis are found in the arid or semi-arid regions where it is difficult to find drinking water with low fluoride concentrations, and there is no piped supply. Therefore, physical or chemical methods of removing fluoride from drinking water are important measures to prevent endemic fluorosis.

In recent years, considerable attention has been paid to develop effective defluoridation materials with steady qualities and a wide range of applications as well as development of new techniques. Extensive studies on different sorts of calcium phosphate have been performed. Simple methods have been reported for home water treatment based on co-precipitation of fluoride with calcium and phosphate, forming fluorapatite and fluorhydroxyapatite¹⁻⁴. However, no quantitative data for practical application were given. Tricalcium phosphate has been used to remove fluoride from drinking water since the 1930's. Nevertheless, limited information exists on the fluoride removal efficiency from different water qualities and under different conditions. The mechanism of defluoridation is not yet clear.

This present study examines in detail the effects of various water quality parameters: different pH levels, temperatures and contact periods, on the fluoride removal efficiency of TCP, and discusses the possible mechanism of its defluoridation. Finally, a home-based defluoridation method is established.

TABLE 1. Effects of pH, temperature and contact time on defluoridation efficiency of $\text{Ca}_3(\text{PO}_4)_2$.

Raw Water			Treated Water					
pH	Fluoride	Temp	Fluoride, mg/L				Phosphate	pH
	mg/L	°C	9 h	23 h	30 h	46 h	mg P/L	
5.52	10.23	6	1.63	0.97	0.85	0.62	0.88	6.64
		15	1.04	0.6	0.52	0.46	0.49	6.7
		25	0.86	0.46	0.42	0.35	0.56	7.4
		35	0.75	0.5	0.39	0.3	0.53	7.13
6.51	10.33	6	2.17	1.6	1.42	1.18	0.6	7.4
		15	1.58	0.8	1.24	1.19	0.49	7.47
		25	1.37	1	0.98	0.87	0.34	8.06
		35	1.34	0.98	0.96	0.9	0.45	7.85
7.6	10.31	6	2.47	1.9	1.78	1.6	0.6	7.88
		15	1.89	1.45	1.49	1.27	0	8.31
		25	1.8	1.34	1.4	1.21	0.49	7.89
		35	1.66	1.41	1.46	1.47	0.67	8.35
8.49	10.29	6	½	2.25	2.17	1.9	1.53	7.97
		15	1.85	1.46	1.43	1.26	2.07	8.05
		25	1.84	1.39	1.34	1.26	0	8.36
		35	1.6	1.39	1.5	1.43	1.46	8.32
9.42	9.4	6	3.42	2.88	2.6	2.53	1.24	8.28
		15	2.94	2.41	2.44	2.15	0.41	8.75
		25	2.93	2.35	2.36	2.19	0	8.66
		35	2.69	2.4	2.42	2.37	0.45	8.53

pH levels and phosphate concentrations in treated water were determined after 23 h.

MATERIALS AND METHODS

All chemicals used for analysis were of analytical grade. Fluoride water of various concentrations was prepared from distilled- and tap water. The experiments were performed in 250 ml cone glass bottles containing 100 ml of fluoride solution at five pH levels and four ranges of temperature by static coagulation.

300 mg of TCP, 40 meshes, was suspended in 100 ml of fluoride-containing water under magnetic stirring. After continuous mixing for 1-2 minutes, the glass bottles were left for static reaction at different temperatures, and supernatant was sampled after different contact times for determination of pH, fluoride, phosphate and calcium using standard methods. For the adsorption equilibrium experiments, the added amounts of TCP were varied. Batch experiments with 2 and 30 litres of fluoride-containing water respectively were carried out at neutral pH level (pH = 7-8) and at room temperature (T = 20-25 °C). 3 g of TCP was added per litre in order to examine the feasibility of the method.

RESULTS AND DISCUSSION

The results of defluoridation using TCP at different pH, temperatures and contact times are presented in Table 1. Within the ranges of temperature and contact time tested in this study, there are close negative correlations between the removal efficiency and the pH of raw water. The removal efficiency at pH 5.52 is 19.7-21.4 %

higher than at pH 9.42. The removal efficiency decreased by approximately 3-7 % per pH unit in the pH range 5.5-7.6; 0-3 % in the pH range 7.6-8.5 and 11-13 % at pH range 8.5-9.5. This indicates that the removal efficiency of fluoride by TCP decreases considerably when pH exceeds 8.5. The pH levels of the treated water in all experiments ranged from 6.64 to 8.35, which proved that there is a phenomenon of pH neutralisation.

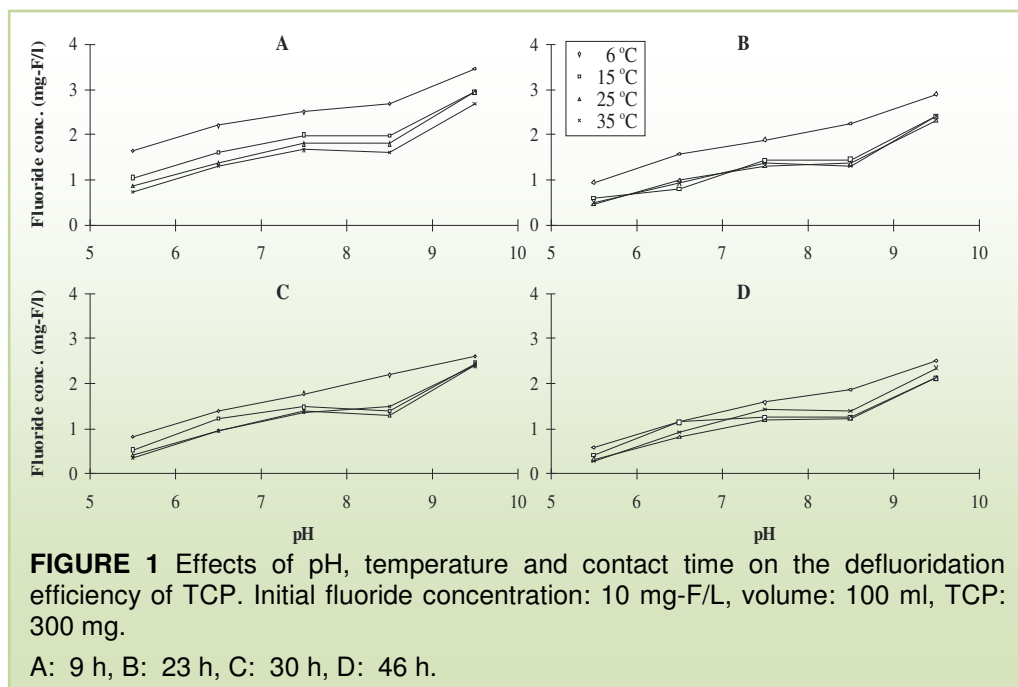


TABLE 2. Relationship between coagulant and defluoridation amount and contact time.

Raw water Fluoride (mg-F/L)	Time of adding coagulant (min)	Total experimental time (min)	Treated water fluoride (mg-F/L)
4.0	0	30	1.25
	30	60	1.08
	60	90	0.95
	120	150	0.94
3.33 (Natural water sample)	Not added	14 hr	1.02
	4 hr	5 hr	0.71

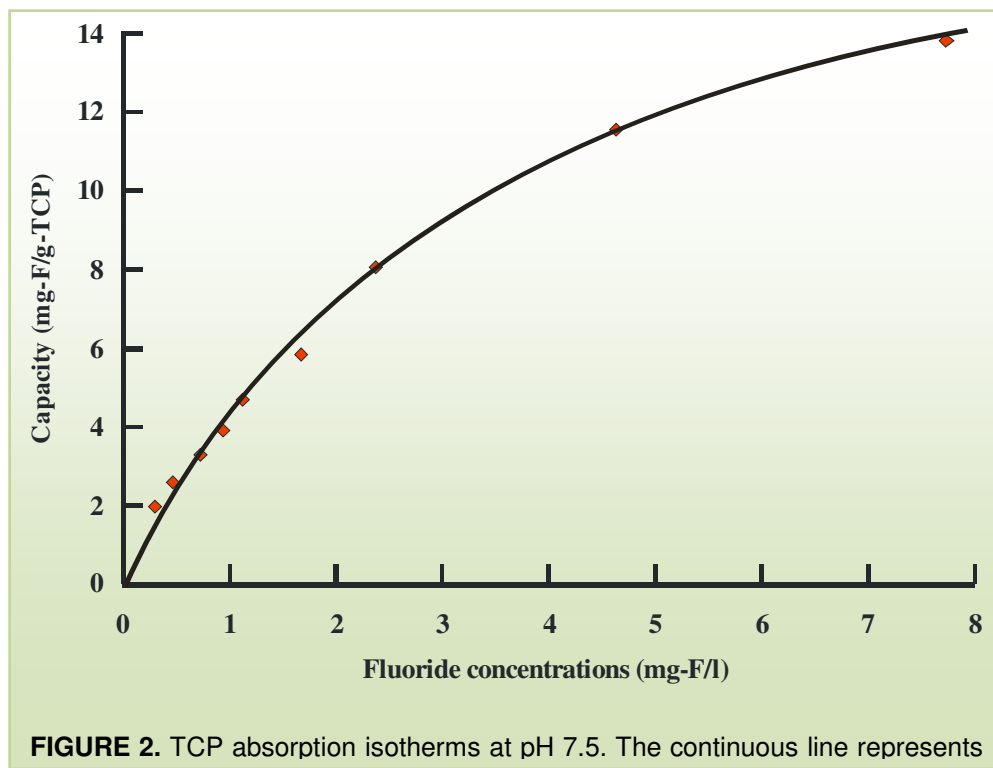
Conditions: 2 litres of fluoride-containing water at neutral pH (pH = 7-8) and at room temperature (T = 20-25 °C); 3 g/L TCP is added at t=0; polyacrylamide concentration 0.2 mg/L.

The effects of the water temperature on the defluoridation efficiency of TCP generally show positive correlation. However, the positive correlation became less significant with longer contact times.

At given pH and temperature, a close positive correlation existed between the contact time and the defluoridation efficiency, $r^2 \in [0.6201 ; 0.9839]$. The effects of pH, temperature and contact time on the defluoridation efficiency of TCP are presented in Figure 1. Most defluoridation takes place during the first 10 hours (64 - 92 % removal of fluoride), whereas lesser defluoridation occurs after this time. When polyacrylamide was used as coagulant, the fluoride concentration was e.g. reduced to 0.95 mg/L from 4.0 mg/L in 1.5 hours (Table 2). The defluoridation capacity of TCP is presented in Figure 2. The adsorption isotherm indicates the defluoridation capacity as a function of the TCP amount.

Many methods of defluoridation are based on one of two principles; ion adsorption and ion exchange. In case of ion adsorption, fluoride is attracted to the surface of an inert substance, usually an insoluble aluminium salt, while ion exchange involves the uptake of fluoride in exchange for some other anion. Maier (1947) reported that synthetic calcium phosphate most often has been used in ion exchange⁵. However, TCP has no anion group which can be exchanged by fluoride.

Our results show that the fluoride removal efficiency of TCP increased with decreasing pH levels of the raw water under given temperature and contact time conditions.



The concentration of phosphate in the treated water in all experiments increased by 0.5-1.5 mg-P/L, independent of initial pH levels. This indicates that the higher defluoridation activity of TCP at lower pH is not due to a higher degree of dissolution of TCP at lower pH. The results from experiments with distilled water and tap water (containing 85 mg-Ca²⁺/L), showed that the defluoridation efficiency of TCP was not affected by the existence of Ca²⁺ in the raw water. Therefore, precipitation of CaF₂ is not likely to play any major role in this defluoridation system. During the process of defluoridation, the results were obviously affected by water temperature. Under given pH levels and contact time conditions, the higher the water temperature, the higher removal. This phenomenon indicates that defluoridation using TCP can be a chemical reaction needing energy rather than a physical surface adsorption. Physical adsorption usually declines with higher temperatures. Furthermore, there is a positive correlation between the defluoridation rate and the contact time, and equilibrium does not appear within 46 hours. Therefore, the defluoridation process of TCP expresses typical characteristics of a chemical reaction: Higher reaction rate with higher temperature and higher H⁺ ion concentration.

One of the defluoridation mechanisms may be: H⁺ ion concentration is higher than OH⁻ ion under weak acidic conditions (pH = 5.5-6.5). H⁺ combines with fluoride to form HF₂⁻. TCP (K_{sp}^{*} = 10⁻²³) can be partially dissociated in water, forming the positive ion Ca₃PO₄³⁺, which can combine with HF₂⁻ to produce Ca₃PO₄·(HF₂)₃. Thus six fluoride ions and three hydrogen ions are fixed in this reaction. This is in accordance with our experiments where pH increased with 0.66-1.64 units during the defluoridation process when the raw water was acidic (Table 1). At neutral pH range (pH = 7.6-8.5), the concentration of H⁺ ions in the solution is approximately equal to the concentration of OH⁻ ions. In this case, OH⁻ can compete with HF₂⁻ in the reaction with Ca₃PO₄³⁺, to form Ca₃PO₄·(HF₂)₂(OH). At neutral pH, the rate of defluoridation was lower than at acidic pH. Also the consumption of H⁺ ions decreases so that the pH levels are only increased by 0.07-0.52 during the process (Table 1). In a weak alkalinity solution (pH = 8.5-9.5), the concentration of OH⁻ ions is higher than the concentration of H⁺ ions, and thus, higher than the concentration of HF₂⁻. In this case Ca₃PO₄·(HF₂)(OH)₂ may be formed, in which less fluoride is fixed and OH⁻ is consumed so that the pH levels of treated water decrease. This is in accordance with our experiments where pH decreased by 0.32-1.24 units, based on the raw water.

The possible reactions are:

Acidic pH:



Neutral pH:



Alkaline pH:



These chemical reactions will predict that the removal activity of TCP will decrease with increasing pH, that the concentration of phosphate in the treated water is independent of pH, and that pH will move towards neutral pH. These predictions are identical with our findings.

Wang Liangfang et al. (1993)⁶ reported that defluoridation of water using TCP can be a mechanism which needs Ca^{2+} . That fluoride combines with Ca^{2+} forming CaF_2 which then links with $[\text{Ca}_3(\text{PO}_4)_2]_n$ forming $[\text{Ca}_3(\text{PO}_4)_2]_n \cdot \text{CaF}_2$. However, this reaction mechanism cannot explain such phenomenon as the pH movement towards neutral pH. Further studies and demonstrations are required on the effects of Ca^{2+} containing raw water on the defluoridation mechanism of TCP and interaction conditions.

CONCLUSIONS

Based on the results presented above, the following conclusions can be drawn:

There is a negative correlation between the defluoridation efficiency of TCP and the pH levels of raw water, and a positive correlation between the defluoridation efficiency and the temperature as well as the contact time.

The defluoridation contact time is practically cut down when polyacrylamide is used as coagulant.

The defluoridation of TCP may be a complex chemical reaction mechanism which needs energy.

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