CHAPTER 5

A Study of Ion Exchange Process Involving Defluoridation by Bone Char Using Spectrophotometric Flow Injection Analysis

5.1 Introduction

Fluoride plays a significant role for human. An appropriate fluoride content in food or drinking water has a potential to reduce dental caries. An acute intake or chronic ingestion of fluoride, however, results in adverse effects, for example, dental fluorosis and bone disorders. In many parts of the world, an important source of water supply, i.e. ground water, containing high level of fluoride, which causes the problem of endemic dental fluorosis, has been reported [1]. Therefore, fluoridated water supply must be frequently treated to remove excessive fluoride content.

The industrial water treatment processes for fluoride removal are usually expensive and require skill operation. Some methods have inadequate efficiency and are not appropriate for defluoridation especially in a small community or household level. The preferable processes should be able to remove substantial quantity of fluoride, they should be relatively simple, cost effective and based on local or obtainable resources and skill. Sorption or ion exchange by locally available sorption media [2-5] represents all of the above advantages. The widely used sorption matrix in Thailand is the bone char [6] which normally is cattle bone charred at high temperature.

Although the defluoridation processes by bone char are more intricate and dependent mainly on experimental conditions, three fluoride uptake reactions in which the major component, hydroxyapatite $Ca_{10}(PO_4)_6(OH)_2$, principally participate have been proposed [7]. These are the ion exchange of fluoride for hydroxide with the fluorapatite formation in low concentration of fluoride, fluorapatite recrystallization using Ca^{2+} and PO_4^{3-} from the dissolution of hydroxyapatite, and calcium fluoride precipitation in higher concentration if its solubility product is favoured. These reactions can be written as follows :

$$Ca_{10}(PO_4)_6(OH)_2 + 2F^- \rightarrow Ca_{10}(PO_4)_6F_2 + 2OH^- \quad (5\text{-}1)$$

$$10Ca^{2+} + 6PO_4^{3-} + 2F^- \rightarrow Ca_{10}(PO_4)_6F_2 \quad (5\text{-}2)$$

$$Ca_{10}(PO_4)_6(OH)_2 + 20F^- \rightarrow 10CaF_2 + 6PO_4^{3-} + 2OH^- \quad (5\text{-}3)$$

At neutral pH, the ion exchange according to equation (5-1) is predominant but the non-stoichiometric interchange is observed possibly owing to fluoride replacement with H_2O at surface rather than OH^- at OH^- site. No exact mechanisms reveal. Therefore the aim of this work is to investigate the ion exchange process previously involving defluoridation by bone char. Hence, a spectrophotometric flow injection system for simultaneous determination of fluoride and hydroxide have been developed to study the relationship between both ions during fluoride removal process.

5.2 Experimental

5.2.1 Apparatus and chemicals

All equipment and chemicals were used as previous described. Deionized water was used throughout.

5.2.2 Bone char

Bone char, 2-5 mm granule, was obtained from Intercountry Center for Oral Health, Thailand. It was made from cattle bone charred at 600°C for 20 minutes with partial presence of oxygen. Its BET surface area and pore volume are 82.7 $m^2 g^{-1}$ and 0.324 $cm^3 g^{-1}$ respectively. A column, Tygon tube with an inner diameter of 9.5 mm and a bed length of approximately 15 cm, contains 7.71 g of bone char.

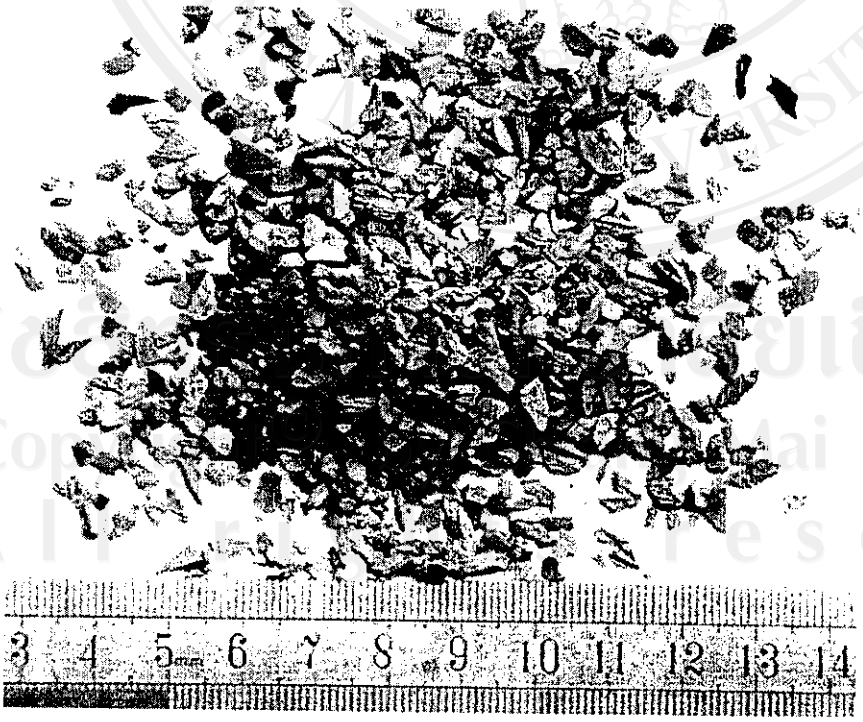


Figure 5.1 Bone char appearance.

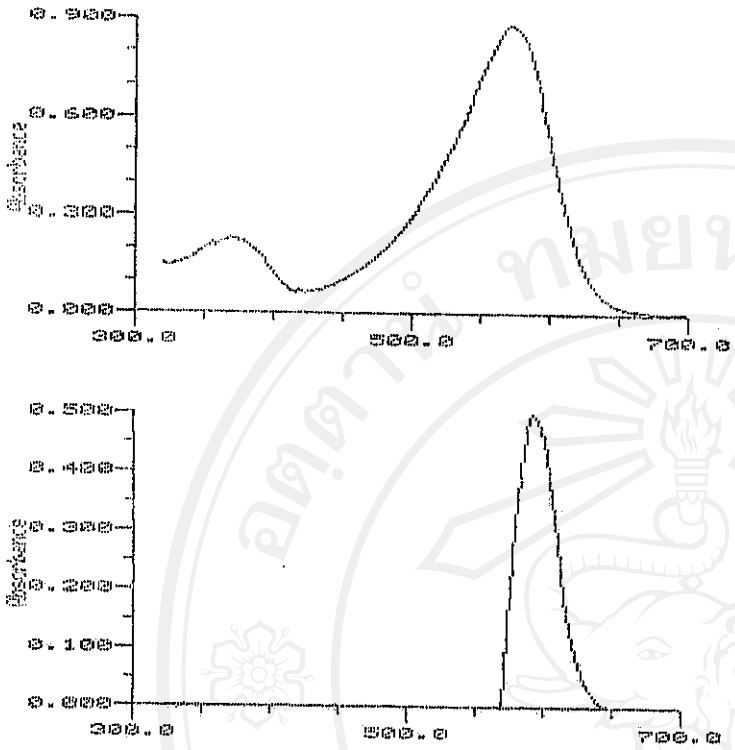
5.3 Results and discussion

5.3.1 Simultaneous determination of fluoride and hydroxide by flow injection spectrophotometry

Once the spectrophotometric methods for fluoride and hydroxide determinations were developed, the system for simultaneous detection of both ions was subsequently constructed. However, due to the obvious fact that maximum absorption wavelengths used in the spectrophotometric determinations of fluoride and hydroxide were different. An analytical wavelength suitable for the determination of both ions must be appropriately selected.

Analytical wavelength

One advantage of *m*-cresol purple for pH measurement is that its maximum absorption wavelength is close to that of ternary aluminium complex for fluoride determination, i.e. 576 and 590 nm respectively, as depicted in Figure 5.2. The wavelength between these values could be used for simultaneous spectrophotometric determination of both ions. In the present work, the one at 583 nm was selected and the obtained results were satisfactory. No attempt was made to optimize the analytical wavelength.



(a). *m*-cresol purple

λ_{max} 576 nm

(a). ternary aluminium complex (Al-ECR-CTA)

λ_{max} 590 nm

Figure 5.2 Absorption spectra of (a) *m*-cresol purple and (b) ternary aluminium complex.

Manifold design

The flow configuration for contemporaneous quantification of fluoride and hydroxide was absolutely the combination of those for both ions. Figure 5.3 represented the flow injection manifold of the combined system for spectrophotometric determinations of fluoride and hydroxide simultaneously. R1 and R2 were the reagents for fluoride determination (aluminium solution and its chromogenic reagents), C was a carrier (water), while R3 was an indicator solution for pH detection (*m*-cresol purple). The samples which were effluent from a bone char column were introduced to the system at the injection valve1 (I1). The obtained sample zone was then split into two lines for

fluoride (MC1 line) and hydroxide quantification. Normally the hydroxide line was propelled to a spectrophotometer, however, when the line switching valve or the injection valve 2 (I2) was switched, the fluoride line was flowed to the detector instead.

In the combined system, the previous conditions were employed without further optimization. Note that the mixing coil 3 (MC3) was inserted in order to overcome back pressure which forced the sample zone flow in one direction.

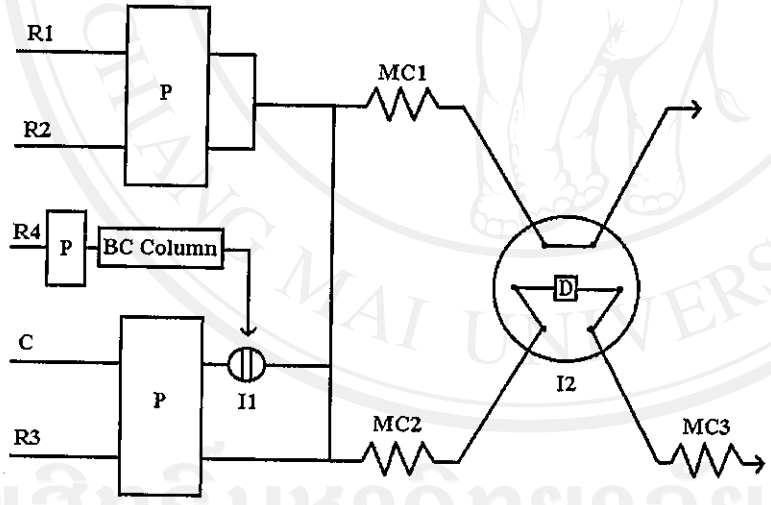


Figure 5.3 Manifold configuration for simultaneous determination of fluoride and hydroxide. P: peristaltic pump, I: injection valve, MC: mixing coil, D: spectrophotometer, C: carrier (water), R1: aluminium solution, R2: ECR/CTA reagent, R3: *m*-cresol purple, R4: synthetic fluoride solution, BC: bone char column.

5.3.2 Fluoride removal by bone char in a fixed bed column

Defluoridation in a fixed bed column containing bone char was performed in order to investigate the relationship between the sorbed amount of fluoride and the released quantity of hydroxide. The breakthrough curve for fluoride removal as well as the desorption graph were depicted in Figure 5.4. Deionized water was firstly pumped at a constant rate (1.05 mL/min) into the bone char column to carry out a blank test. It

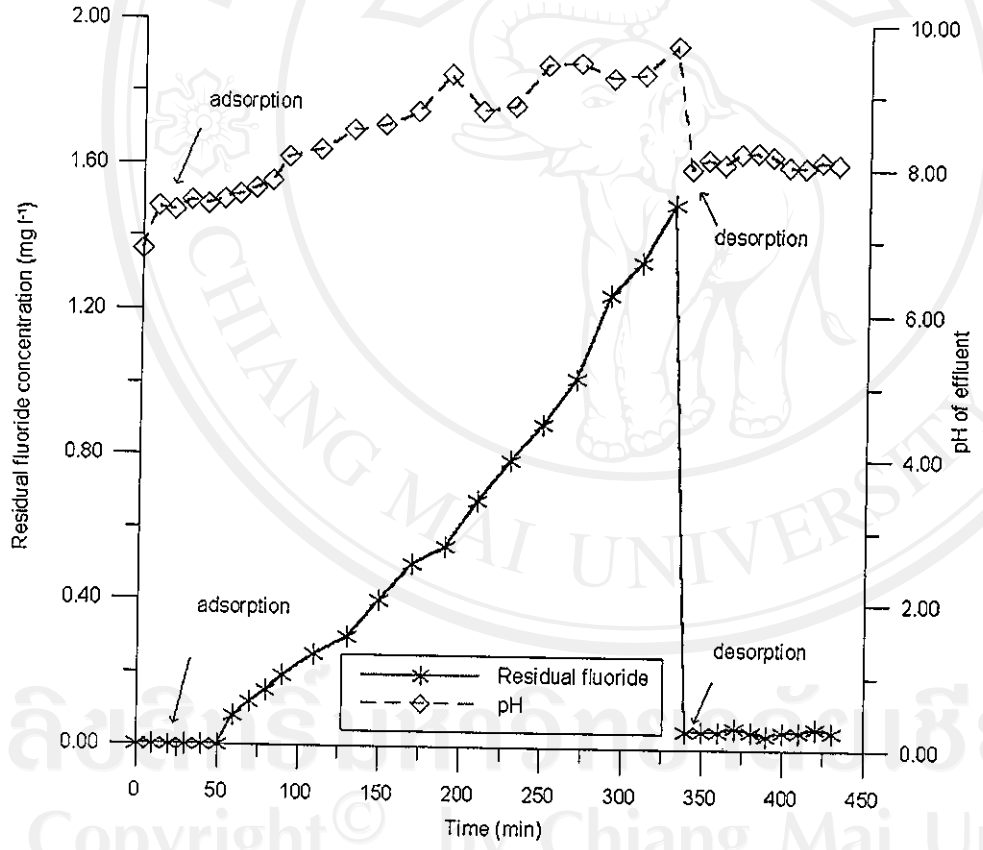


Figure 5.4 Breakthrough curve and desorption graph for fluoride removal in a fixed bed column containing bone char. 0-20 min deionized water for blank study, 21-330 min 6-ppm synthetic fluoride solution, 331-430 min deionized water for desorption study.

revealed that no fluoride liberated from the column while the effluent pH was increased owing to dissolution of hydroxyapatite which was the major component of bone char. An artificial fluoride solution was subsequently treated instead of water caused further increase of the pH. In other words, the rise in pH in the presence of fluoride indicated that fluoride sorption by bone char occurred.

Sorption characteristic of fluoride and released magnitude of hydroxide were calculated by integrating the area above (for fluoride) and below (for hydroxide) the corresponding curve using the computer program ORIGIN and illustrated in Figure 5.5 and 5.6 respectively. Sorption behavior of fluoride against time was linear demonstrating that fluoride was depleted at a constant rate under experimental conditions. On the other hand, no hydroxide released from the column in the beginning, until 150 min later the drastic increase of liberated hydroxide was exhibited. Moreover, it was obvious that the fluoride exhaustion was much more than the hydroxide liberated.

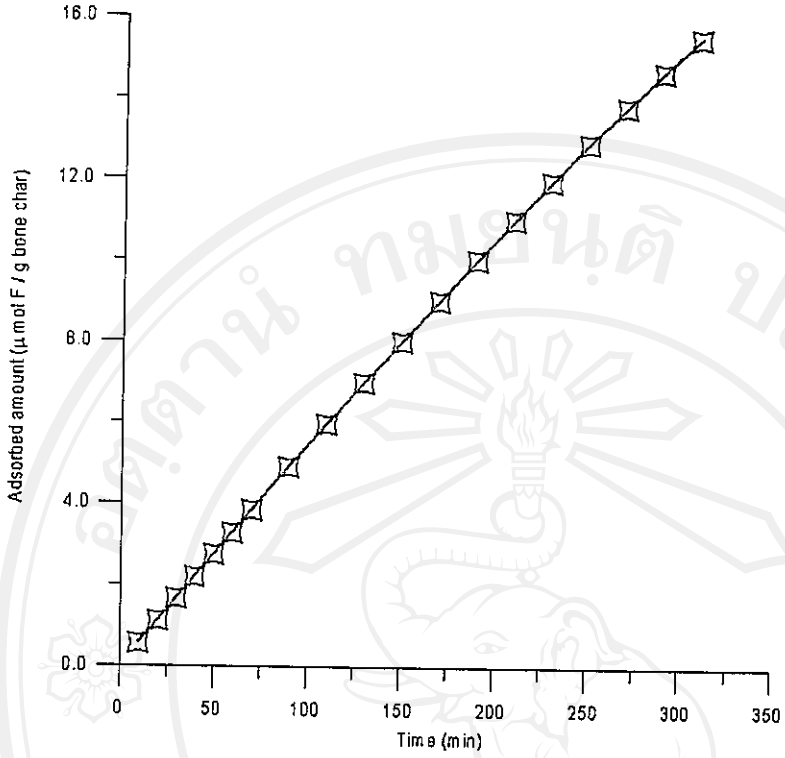


Figure 5.5 Sorption feature of fluoride in a fixed bed column containing bone char.

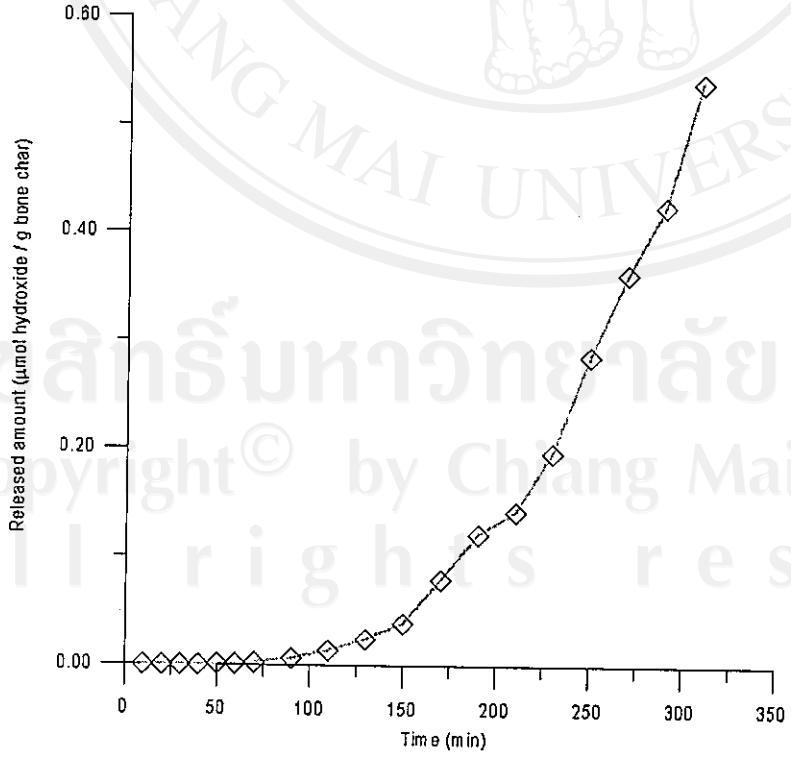


Figure 5.6 Liberated behavior of hydroxide from the bone char column.

Another experiment with a specially designed FI manifold as shown in Figure 5.7 was conducted to confirm these facts. The bone char column was placed after the injection valve (I1) and any signal change after various concentrations of fluoride solution were injected at the constant volume was observed. The results were tabulated in Table 5.1. At low fluoride concentration or amount of fluoride, no signal change due to hydroxide liberated from the column was detected while that due to fluoride was significantly observed. Higher dose of fluoride injection resulted in the considerable change in the signal of the two ions.

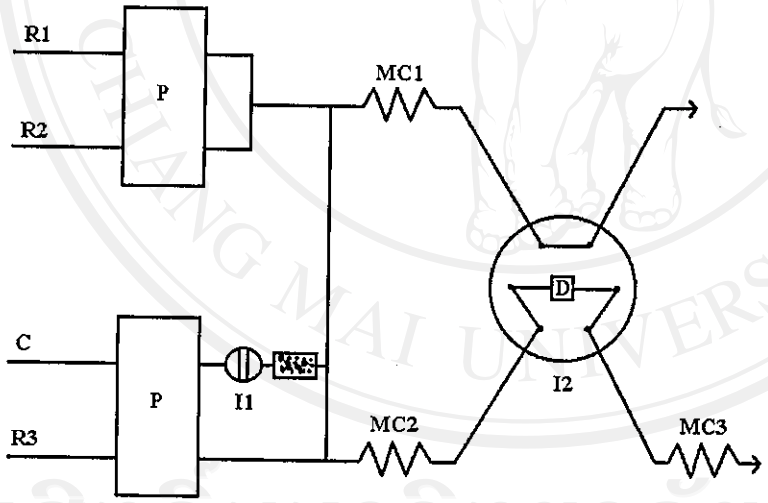


Figure 5.7 Flow injection manifold for the study of an ion-exchange process during defluoridation in bone char column (see figure 5.3 for explanation of abbreviation).

Table 5.1 Signal change of fluoride and hydroxide in the effluent of a bone char column.

Fluoride concentration (mg L^{-1})*	Peak height or signal change (mV)	
	OH^-	F^-
6.00	ND**	ND
15.0	ND	4.9
25.0	ND	9.0
50.0	ND	57.4
75.0	5.1	82.2
100.0	9.5	133.8
125.0	13.5	194.6

*Injection volume = 600 µl

** ND = not detected

5.3.3 Continuous desorption by water

Figure 5.3 also represents the desorption study of fluoride by water. Small amount of fluoride released from the bone char column when deionized water was used as an eluent. This suggests that under the experimental conditions one of the fluoride uptake processes that occurs in the fixed bed column containing bone char is physical adsorption in which the adsorbate-adsorbent interaction is relatively weak, compared to that in the chemical adsorption mode. Another process mainly involves

chemisorption owing to the fact that partially adsorbed fluoride could not be eluted by water. Similar result was also obtained by Lin [8].

Defluoridation on the bone char column at low fluoride concentration raises the hydroxide level but the fluoride consumed is much more than the hydroxide liberated. In the early stage no hydroxide releases from the column while the fluoride uptake appears. Fluoride is therefore used up by a certain process before it is depleted by the process that releases hydroxide, i.e. ion exchange of fluoride and hydroxide. Later fluoride exhaustion accompanies hydroxide released. Desorption studies reveal that both physical adsorption and chemisorption undergo in the fluoride removal process due to the adsorbed fluoride partially desorbed. Defluoridation process at low level of fluoride may therefore be proposed as adsorption on bone char followed by adsorption together with ion exchange at higher fluoride content.

5.4 Conclusion

The use of a fixed bed column packed with bone char for removal of fluoride has been proven to be possible. The developed FI method for simultaneous determination of fluoride and hydroxide is very sensitive with the detection limits of 0.02 mg L^{-1} and 7.41×10^{-8} mol L^{-1} for fluoride and hydroxide respectively, and very reproducible with the relative standard deviation of not greater than 4% for both ions. The method can be used as a tool for investigation of the fluoride removal process in a fixed bed column containing bone char. The process may be proposed as adsorption followed by adsorption accompanying with ion exchange.

5.5 The relevancy of the research work to Thailand

Endemic dental fluorosis due to the intake of fluoridated drinking water has been reported in many parts of Thailand especially in the north. Removal of fluoride from water is therefore considerably important. The present work is aimed to investigated the process of defluoridation by low cost adsorbent widely used in Thailand, i.e. bone char, using a flow injection technique with the emphasis on an ion exchange.

The developed flow injection technique can be used as a tool for investigation of defluoridation process by bone char. The process may be proposed as an adsorption followed by adsorption accompanying with an ion exchange. Application of bone char to remove fluoride in a small community or household level should be carried out in the way that conditions for fluoride adsorption are mainly obtained to maximized the removal efficiency.