Sorption Study for Defluoridation by Bone Char

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SUMMARY: The sorption of fluoride by bone char for defluoridation purpose was studied in laboratory batch experiments. The sorption isotherm at a low concentration range of fluoride tended to be a momentarily sorption type. In addition, the sorption of fluoride was found not to increase significantly with the increase in temperature. Some ions such as halide and alkali posed only no or slight effect on the sorption of fluoride but calcium ion did probably due to precipitation of calcium fluoride. The defluoridation of 10-13 mg fluoride/L water samples from the districts of San Kamphaeng and Fang in Chiang Mai, was attempted by single batch equilibration treatment. The fluoride level could be reduced with the efficiency of about 65 % after equilibrating with 0.100 g of bone char at pH 7 for 9 hours.

Key words: Bone char, defluoridation, fluoride sorption, batch experiment, Thailand.

INTRODUCTION

Bone char has been widely used for various purposes in many industries i.e. the discoloration and refining of sugar, making pottery and glass and also in cleaning jewellery. Due to the porous structure of bone char with specific area of about 600-1,000 m^2 g^{-1}, this characteristic makes bone char be a good sorbent. In Thailand and elsewhere also, bone char has been used to reduce the level of fluoride in drinking water. Defluoridation of water has also been investigated by various methods such as electrocoagulation[1], dialysis[2], coprecipitation[3], *etc*. The characteristics of bone char related to the efficacy of fluoride removal was also carried out by x-ray diffraction and infrared absorption spectroscopy[4].

In this work, sorption study of fluoride on bone char was reconfirmed and the effects of temperature and coexisting ions on the sorption were investigated. Single batch equilibration treatment for defluoridation of highly fluoridated water from some natural sources in Chiang Mai Province was then followed at the optimum sorption condition.

MATERIALS AND METHODS

All chemicals used were of analytical grade. Stock solution of 1000 mg/L NaF was prepared in de-ionised water. Bone char, obtained from the Intercountry Centre of Oral Health, ICOH, Chiang Mai, Thailand, was crushed and sieved to the range of 20-50 mesh (0.3 – 1 mm).

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The sorption study of fluoride on acid washed bone char was carried out. Firstly, the determination of the optimum equilibration time for fluoride was done by shaking 0.100 g of bone char with 25.00 mL of 25.0 mg/L fluoride solution at pH 7 for 1, 2, 3, 6, 9 and 12 hours, respectively. Then the temperature effect was studied by equilibrating 0.100 g of bone char with 25.00 mL of fluoride solution at different (initial) concentrations ranging from 5-100 mg/L. The bone char was allowed to equilibrate for 9 hours at different temperatures of 25, 35 and 45 ^{O}C. Additionally, the equilibration of bone char with the solution of mixed fluoride with other ions; namely, Cl^{-}, I^{-}, Na^{+}, K^{+} and Ca^{2+} at different mass ratios of 1 : 1 up to 1 : 300 was investigated under the same equilibrating condition as done for the temperature study. Finally, the defluoridation of water samples collected from the districts of San Kamphaeng and Fang in Chiang Mai was attempted by single batch equilibration at the same experimental condition used previously. The fluoride content throughout the investigation was measured by using an Orion fluoride ion selective electrode model 9409.

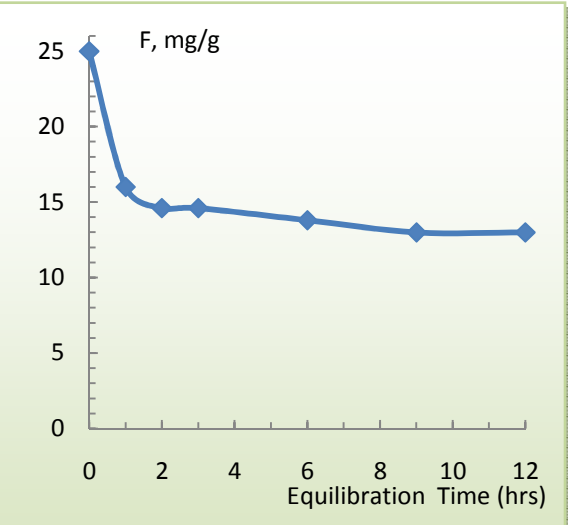

Figure1. The concentration of fluoride remaining in the solution after being sorbed on the bone char at various equilibration times. (contact time, mg/g).

RESULTS

Equilibration time. The equilibration time of fluoride sorption by bone char was obtained potentiometrically using fluoride ion selective electrode. As depicted in Figure 1, the concentration of fluoride left unsorbed in the solution tends to decrease drastically in the first hour of equilibration, then the remaining fluoride decreases slightly afterward.

Sorption isotherms. When the dependence of fluoride sorption on the temperature was studied, its sorption behaviour are revealed in Figure 2 and Figure 3. Both figures show the increase of fluoride sorption as the temperatures of the sorption processes are raised.

Effect of coexisting ions. The influence of the presence of other ions in the fluoride solution on the sorption of fluoride on bone char was also investigated. Figure 4 indicates that other ions impose no effect on the fluoride sorption, except the calcium ion.

Single batch test for defluoridation. The optimum sorption condition obtained from the start of the study was applied on trial in order to remove fluoride in natural potable water. After treating these water samples which contained fluoride in the range of 275-325 µg with 0.100 g of bone char, its fluoride contents was lowered down to 104-110 µg only in one batch of equilibration.

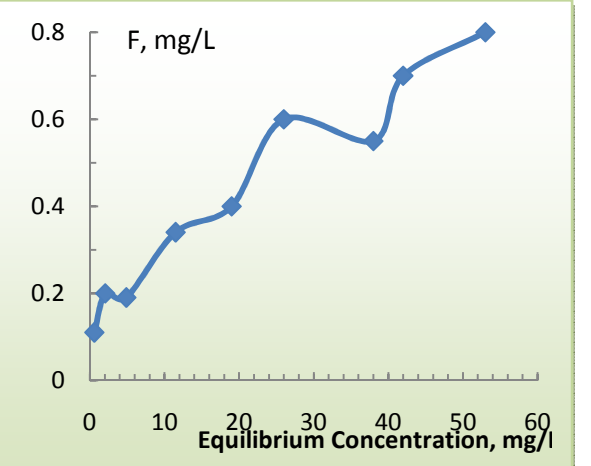

FIGURE 2. Sorption isotherm of fluoride on bone char at 25 ^{O}C.

CONCLUSION

In order to confirm the equilibration time with the previous study [5], which was done colourimetrically, Figure 1 again indicates that 5 hours of equilibration time is sufficient for the fluoride sorption study, which is agreeable for both potentiometric and colorimetric measurements. However, the equilibration time of 9 hours was selected and used throughout the entire study to ensure the equilibrium maximum sorption. The decrease of sorption rate reveals in this Figure indicates slow sorption kinetics of the fluoride, even though ones believe that fluoride sorption on bone char is based on ion exchange phenomenon[6] which supposes to occur very fast. The fast sorption kinetics through the ion exchange process might be noticeable in this experiment during the first hour of equilibration. This process is believed to occur at the surface of bone char, but inversely the rest of fluoride in the bulk solution is forced to diffuse slowly into the pores of the bone char due to the repulsion that is created by the exchanged fluoride. Therefore longer time is needed for the sorption to approach equilibrium.

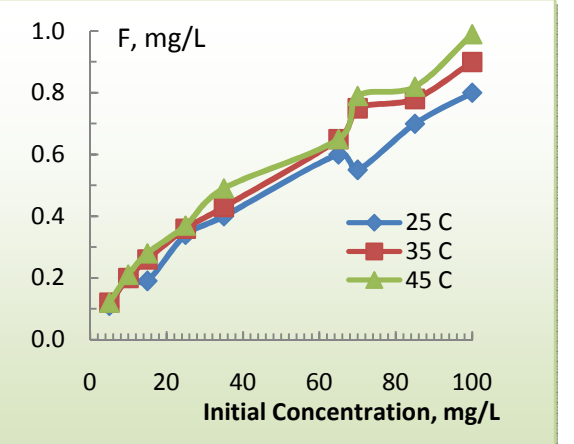

FIGURE 3. Sorption isotherm of fluoride on bone char at selected temperatures.

The sorption of fluoride on bone char is often referred to as an ion exchange process, therefore a sorption isotherm with a saturation of the uptaken fluoride should be obtained. Figure 2 briefly shows such a sorption behaviour only at a low concentration range of fluoride (10-20 mg/L) with the maximum sorption as a monolayer of about 399 µg/g.

When the influence of temperature on the fluoride sorption on bone char at three different temperatures i.e. 25, 35 and 45 ^{O}C was investigated as depicted as the isotherms in Figure 3. It is seen from the isotherms that more sorption occurs at higher temperature and the monolayer sorption at 35 and 45 ^{O}C are obtained with the amounts of 427 and 546 µg of fluoride per gram of bone char, respectively. This nature of sorption which is dependent on temperature is due to the kinetic effects. At higher temperature, the fluoride ions move faster and more fluorides can penetrate into the cavities of the porous bone char' s structure. Hence, this results in more exchange of fluoride with the hydroxyl ion of the bone char's hydroxyapatite.

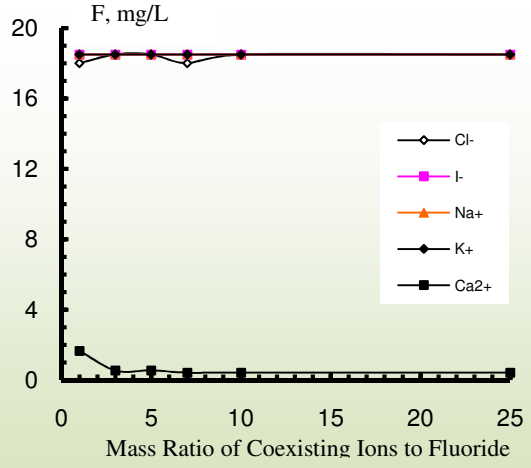

FIGURE 4 Concentration of fluoride remaining in solution at various mass ratios of coexisting ions and fluoride.

Due to the nature of being ion exchange process for fluoride sorption, the evaluation on the effect of the presence of other ions other than fluoride on the sorption behaviour is displayed in Figure 4. It indicates that Cl^- and I^- pose little effect on the fluoride sorption, eventhough the mass ratio of fluoride to imposing ion was increased up to 1: 300. The same observation was also noticed for cations such as Na^+ and K^+ except Ca^{2+}, which had pronounce effect on fluoride sorption. This is probably because Ca^{2+} can precipitate out fluoride as CaF_2 if the concentration of Ca^{2+} is high enough. Even if the Ca^{2+} concentration is relatively low, the ion-interaction between fluoride and calcium still prevents the exchange of fluoride with hydroxide of the apatite.

For the defluoridation test by single batch equilibration, the removal efficiency with the average of 65 % was obtained when water samples from both districts were treated. This indicates clearly that the bone char is feasible to be used as the medium in the form of packed column to remove fluoride from the water that would be used in the household.

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