Homemade bone charcoal adsorbent for defluoridation of groundwater in Thailand

Sunisa Smittakorn, Nithat Jirawongboonrod, Surat Mongkolnchai-arunya and Deanna Durnford

ABSTRACT

High levels of fluoride in groundwater are a significant environmental and health problem in Thailand, as in many parts of the world. Small household defluoridators have several advantages over centralized treatment systems. In Thailand, however, use of bone char for water treatment has met resistance because of objectionable taste and odours of the water produced and the social resistance to handling fresh bone. This paper presents a method that uses bone charcoal as an absorbent for removing fluoride from groundwater. The commercially provided boiled bone is burned in a simple homemade furnace that can be constructed, operated and maintained easily by small rural householders. The method to produce the Thai bone char eliminates the odour and objectionable taste and also does not require the user to handle fresh bone, thus eliminating the social resistance. To evaluate the efficacy of the absorbent, batch experiments compare Thai and Indian bone char. Sorption isotherms are fit to the Freundlich and Langmuir equations and the kinetics are modelled using the pseudo first-order Lagergren equation. Results show that the sorption characteristics of Thai bone char compare favourably with the Indian bone char, with approximately 80% of the fluoride removed in both cases.

Key words | bone char, fluoride, groundwater

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NOMENCLATURE

C	constant related to thickness of the boundary layer (mg g^{-1})
C_e	fluoride concentration at equilibrium (mg l^{-1})
C_0	initial concentration of fluoride (mg l^{-1})
C_t	fluoride concentration at any time (mg l^{-1})
k_1	rate constant of pseudo-first-order equation (h^{-1})
K_A	Langmuir isotherm constant
K_d	constant which is a measure of the adsorption capacity
k_p	intra-particle diffusion rate constant (mg g^{-1} h$^{-1/2}$)
n	constant related to the adsorption capacity
q	weight of sorbed fluoride at any time per unit weight of bone char (mg g^{-1})
q_e	weight of sorbed fluoride at equilibrium per unit weight of bone char (mg g^{-1})
q_m	weight of sorbed fluoride at saturation per unit weight of bone char (mg g^{-1})
t	Time (h)

doi: 10.2166/wh.2010.131

INTRODUCTION

Groundwater is a major source of water in rural Thailand. However, fluoride concentrations of 1 to 10 mg l^{-1} are common in groundwaters in Thailand (Fawell *et al.* 2006). According to a UNICEF report, Thailand is not alone. High concentrations of fluoride in groundwater are ubiquitous in at least 25 countries. The maximum limit for fluoride in drinking water recommended by the World Health Organization is 1.5 mg l^{-1} (WHO 2006). Intake of fluoride higher than the allowable drinking water standard can cause dental, or even crippling skeletal, fluorosis (Fawell *et al.* 2006).

Recent studies also suggest the potential for other serious health problems besides fluorosis caused by high fluoride concentrations. Liver and kidney damage have been documented (Xiong *et al.* 2007) and a correlation between high fluoride intake and a bone cancer called osteosarcoma (Bassin *et al.* 2006) has been found in young boys. In Thailand, dental fluorosis has been recorded since 1960 (Leatherwood *et al.* 1965).

There are several methods available to remove fluoride from drinking water, including reverse osmosis (Schneiter & Middlebrooks 1983), membrane technology (Kettunen & Keskitalo 2000) and activated alumina (Lounici *et al.* 2004). These methods, though effective, come with high installation costs and the need for specific technical skills, parts, chemicals and maintenance (Dahi 1996) that may not be available. For developing countries, successful treatment procedures should be simple and use locally available materials. Examples are methods based on the adsorption of fluoride by animal bone char, local soil, mixed rare earth, laterite, hydrated cement (Bhargava & Killedar 1992; Raichur & Basu 2001; Wang & Reardon 2001; Sarkar *et al.* 2006; Medellin-Castillo *et al.* 2007; Kagne *et al.* 2008) or precipitation (Saha 1993). The effectiveness of the adsorption methods is dependent on the quality of the adsorbent. When precipitation is used as a treatment method, large amounts of sludge at the end of the process reduce the effectiveness of the method in many cases (Onyango *et al.* 2004). Another method that has been successfully applied in villages in India, Kenya, Senegal and Tanzania is called the 'Nalgonda' method. In this method, alum and lime are mixed with fluoride-contaminated water (Dahi *et al.* 1996).

Removal of fluoride by adsorption onto bone char has been used successfully in several countries, including India and Tanzania (Mjengera & Mkongo 2003; Kaseva 2006). Mwaniki (1992), Abe *et al.* (2004) and Medellin-Castillo *et al.* (2007) studied the effects of pH and temperature on the adsorption capacity of bone char. In these papers, commercial bone char is used. In Thailand, however, previous attempts to use locally produced bone char to treat fluoride-contaminated groundwater have not been successful, primarily because of a societal aversion to handling fresh bone, as well as the odour and offensive taste of the produced water and poor quality of the bone char. To produce better quality char, an expensive furnace could be used but there is still social resistance to handling the fresh bone and an odour associated with the final water. Because of these issues, attempts to use bone char for fluoride treatment in rural areas of Thailand have been abandoned (Dental Health Division 2000).

After abandoning bone char as an absorbent, the Thai government began installing reverse osmosis systems in problem areas. From 2004 to 2008, about 1,250 villages in Chiang Rai, Kamphaeng Phet, Sukhothai, Uthai Thani, Kanchanaburi, Lumpang, Payao, Nakhon Pathom, Prachuap Kiri Khan and Lamphun provinces received reverse osmosis systems (Department of Groundwater Resources 2008). The reverse osmosis systems are installed in the centre of each village. In outlying areas where the population density is low, there is typically no water pipeline available and each household has its own groundwater well. In order to have safe water, people have to travel into the town centre to buy treated groundwater for domestic use and carry it back home. Reverse osmosis also comes with a high cost of installation, operation and maintenance. Finally, the water remaining on the intake side of the treatment membrane has a very high concentration of fluoride. Disposal of this high concentration by-product water creates another potential environmental problem.

The costs of reverse osmosis suggest that a household defluoridator would be an advantage in rural Thailand, assuming objections to the handling of fresh bone could be overcome and the process removed sufficient fluoride. An acceptable defluoridator in Thailand would have the following characteristics: (1) the bone char would be produced with an inexpensive, easily operated, homemade furnace; (2) the user would not handle fresh bone because of the social objections to this in Thailand; (3) chemicals would not be needed to control pH; and (4) the bone char would not require sieving or grinding prior to use to minimize handling of the bone char and keep the production of the bone char straightforward. This paper presents a method that meets all of these requirements. The paper summarizes the method proposed and presents the results of batch experiments which characterize the sorption properties. The sorption characteristics of the Thai bone char are compared with those for Indian bone char which is successfully used in villages in Nalgonda district, Andhra Pradesh, India.

MATERIALS AND METHODS

Production of the bone char

In our study, boiled cow bone was obtained courtesy of the Bone Industry, Ltd in Pathum Thani, Thailand. In the production of gelatin, cow skeleton is used as the raw product. Cow bone is boiled before the gelatin extraction process. Boiled cow bone has no smell and the need to handle fresh bone is eliminated so the social objections to using the bone char are eliminated. We propose that the government of Thailand supply rural areas with boiled cow bone if there is not enough production from commercial gelatin factories. This would be less expensive than providing central reverse osmosis systems to each village.

The homemade furnace used to produce the charcoal was a 20-litre recycled steel container. Rice husks were placed on the bottom and along the sides of the container. Boiled cow bone was put into the middle of the container. More rice husks were then added to cover the bone. The lid was closed and the bone was burned for about 8 h. The temperature measured during the burning was between 500 and 600°C. After 8 h, burning was stopped but the bone char was left in the container for 24 h to cool down before being removed. The bone char produced was greyish black and brittle with no odour. The size was about 1 to 3 cm in length. It should be noted that rice leaves were first used as a fuel but the quality of the bone char produced was poor. Therefore, rice husks, which are well-known in Thailand as an alternative fuel, were used.

The adsorption batch experiment

Batch sorption experiments were conducted to investigate the potential for the Thai bone char (THA BC) to remove excess fluoride from aqueous solutions and quantify its sorption characteristics. The same batch experiments were performed with Indian bone char (IND BC) for comparison, since bone char is used successfully in India. The Indian bone char was provided by the Sai Oral Health Foundation. The batch tests were performed with both adsorbents and two types of fluoride-contaminated aqueous solution.

The first aqueous solution used for the batch tests, called the synthetic water in this paper, was produced by mixing sodium fluoride with distilled, deionized water. Initial concentrations of the fluoride ranged from 1 to 6 mg l^{-1}. In these tests, 10 g of Thai bone char were added to 100 ml of the synthetic water at fluoride concentrations of 1, 2, 3, 4, 5 and 6 mg l^{-1} in a polyethylene bottle. In a similar set of batch experiments, 10 g of Indian bone char were added to solutions with the same six concentrations. The bottles were shaken in a water bath at room temperature. The solutions were sampled at 10, 60, 240, 420, 480, 540, 600, 960 and 1,440 min.

The second type of water was a field groundwater sample collected from a well in the Nakorn Patum province in Thailand. This field groundwater had a fluoride concentration of 3.5 mg l^{-1}. The constituent chemistry of the field groundwater was tested prior to the experiment. In addition to the fluoride, groundwater samples contained, on average, 20 mg l^{-1} of sulfate, 50 mg l^{-1} of chloride, 3.36 mg l^{-1} of nitrate, 0.008 mg l^{-1} of manganese, and a coliform bacteria concentration of approximately 4.5 MPN/100 ml. The pH was 7.6. Medellin-Castillo *et al.* (2007) showed that adsorption capacity of bone char is independent of the presence of other anions.

The field groundwater batch tests were run in a slightly different manner from the synthetic water tests. In these tests, 100 ml of the field groundwater sample, with a fluoride concentration of 3.5 mg l^{-1}, was placed in a polyethylene bottle with 2, 4, 6, 8, 10 and 12 g of either the Thai bone char or, in another set of tests, the Indian bone char. The bottles were shaken in a water bath at room temperature. The solutions were sampled at 10, 60, 240, 420, 480, 540, 600 and 720 min.

After mixing the groundwater with the bone char, there was no change in colour, taste or odour of the groundwater. There was no grinding or sieving of the bone char before the adsorption test. Thai bone char size was 1 to 3 cm in length, while Indian bone char size was 1 to 3 mm. The pH was measured before and after the batch tests in all experiments. The pH of the groundwater was about 7.6 prior to shaking and about 7.8 after 10 h of contact time. Therefore, the pH was within the drinking water standard.

Fluoride concentrations were measured using the ion-specific selective method (electrode) using Orion research expandable ion analyzer EA 940 at the analytical laboratory of the Dental Health Division, Department of Health, Ministry of Public Health, Nonthaburi, Thailand.

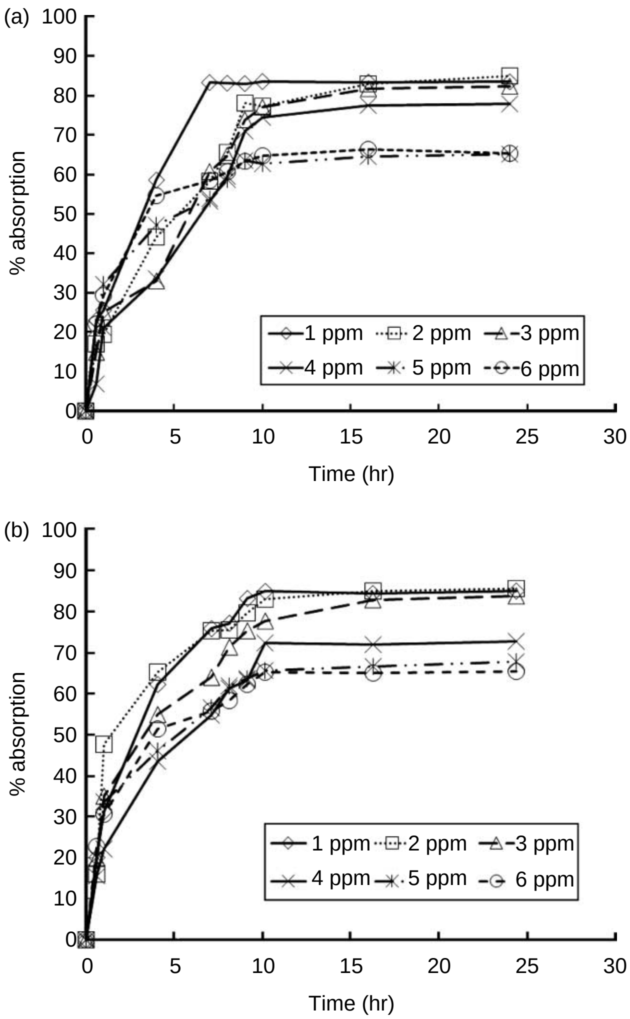

Figure 1 | Adsorption percentage for different initial concentrations of fluoride in a synthetic solution with (a) 10 g of Thai bone char and (b) 10 g of Indian bone char.

RESULTS AND DISCUSSION

Sorption capacity

The percentage of fluoride in the original solution sorbed to the bone char at any time, t, can be expressed as a percentage of the initial concentration by the following equation:

$$\%\ \text{Adsorption} = \frac{C_0 - C_t}{C_0} \times 100 \tag{1}$$

where C_0 and C_t are the initial concentration and concentration at time t in mg l^{-1}, respectively. Figure 1 shows the adsorption percentage for the synthetic fluoride solution for both Thai and Indian bone char. Figure 2 shows results for the batch tests using the field groundwater.

The percentage sorbed was approximately the same for the Thai and Indian bone chars, 60 to 80%, using the synthetic solution in the batch tests. Similar results were obtained for the field contaminated groundwater and the two adsorbents. Adding more bone char to the system resulted in higher adsorption percentages. The percentage of fluoride adsorption increased with time until about 10 h, after which the adsorption percentage remained constant. The time when the percentage of adsorption reached this constant is the equilibrium time. The adsorption percentage for the field groundwater was about 80% for both the Thai and the Indian

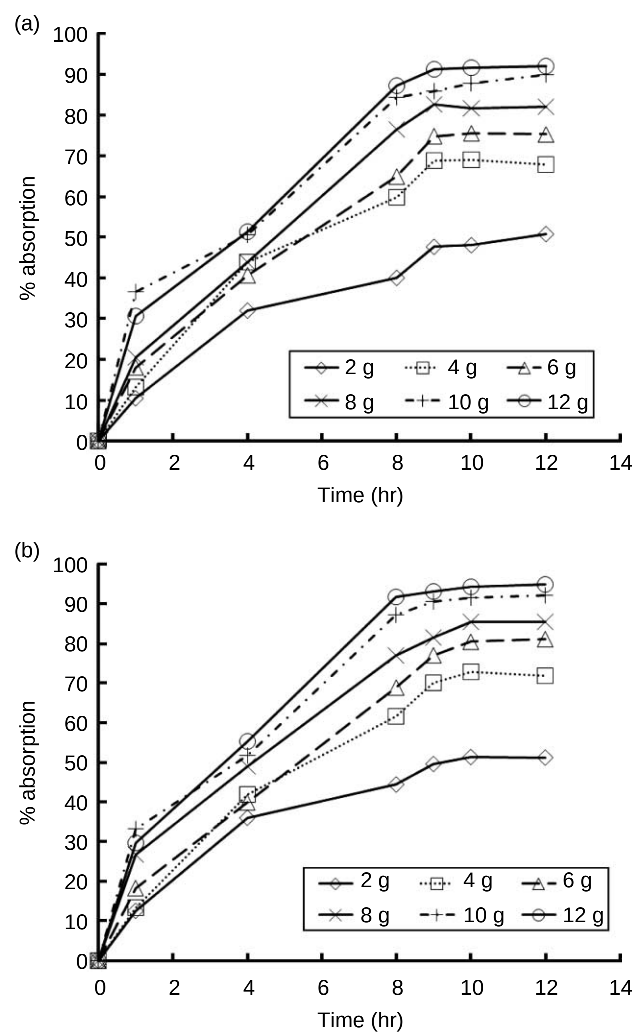

Figure 2 | Adsorption percentage for the field groundwater containing 3.5 mg l^{-1} F^- with varying amounts of (a) Thai bone char and (b) Indian bone char.

Table 1 | Lagergren pseudo-first-order reaction rate constants, k_1, with measured and fitted equilibrium concentrations, q_e, for the batch tests using the synthetic groundwater

	THA BC				IND BC			
		Lagergren Equation (3) fits				Lagergren Equation (3) fits		
Initial conc. ($mg\,l^{-1}$)	Measured q_e ($mg\,g^{-1}$)	q_e ($mg\,g^{-1}$)	k_1 (h^{-1})	R^2 fit to Equation (3)	Measured q_e ($mg\,g^{-1}$)	q_e ($mg\,g^{-1}$)	k_1 (h^{-1})	R^2 fit to Equation (3)
1	0.009	0.012	0.667	0.908	0.009	0.009	0.357	0.938
2	0.018	0.018	0.229	0.913	0.018	0.015	0.295	0.949
3	0.029	0.032	0.271	0.853	0.029	0.026	0.234	0.971
4	0.032	0.038	0.262	0.867	0.030	0.036	0.336	0.714
5	0.036	0.032	0.318	0.917	0.037	0.033	0.299	0.961
6	0.043	0.035	0.305	0.969	0.042	0.045	0.414	0.758

bone chars and an initial concentration of $3.5\,mg\,l^{-1}\,F^-$. When comparing 10 g of Thai bone char with 10 g of Indian bone char, both with an initial fluoride concentration of $3\,mg\,l^{-1}$, the adsorption percentages using the synthetic solution were slightly less, between 70 and 80%.

Adsorption kinetics

The pseudo-first-order equation of Lagergren (Lagergren 1898) is used to quantify the rate of adsorption to the bone char. This equation is:

$$\frac{dq}{dt} = k_1(q_e - q) \quad (2)$$

where $q =$ the weight of the adsorbate at any time t per unit weight of adsorbent ($mg\,g^{-1}$), $q_e =$ the weight of fluoride sorbed at equilibrium per unit weight of the adsorbent ($mg\,g^{-1}$), and k_1 = a rate constant for pseudo-first-order sorption (h^{-1}).

Integrating Equation (2) from $t = 0$ to $t = t$ and $q = 0$ to $q = q_e$ gives:

$$\log(q_e - q) = \log(q_e) - \frac{k_1}{2.303}t \quad (3)$$

The rate constant, k_1, and the amount of sorbed fluoride per weight of bone char at equilibrium, q_e, for the synthetic solution using Thai and Indian bone char derived from Equation (3), the pseudo-first-order equation, are shown in Table 1. Most of the data fit the pseudo-first-order equation well (see R^2 values in Table 1) and the fit to Equation (3) predicted the amount of sorbed fluoride per weight of bone char at equilibrium well (compare measured and fitted q_e in Table 1).

For the field groundwater, again, the rate constant, k_1, and the amount of sorbed fluoride per weight of bone char

Table 2 | Lagergren pseudo-first-order reaction rate constants, k_1, with measured and fitted equilibrium concentrations, q_e, for the batch tests using the field groundwater

	THA BC				IND BC			
		Lagergren Equation (3) fits				Lagergren Equation (3) fits		
Bone char weight (g)	Measured q_e ($mg\,g^{-1}$)	q_e ($mg\,g^{-1}$)	k_1 (h^{-1})	R^2 fit to Equation (3)	Measured q_e ($mg\,g^{-1}$)	q_e ($mg\,g^{-1}$)	k_1 (h^{-1})	R^2 fit to Equation (3)
2	0.093	0.102	0.281	0.930	0.095	0.101	0.327	0.927
4	0.063	0.065	0.255	0.996	0.067	0.079	0.319	0.904
6	0.046	0.047	0.239	0.985	0.049	0.058	0.313	0.911
8	0.037	0.043	0.328	0.946	0.039	0.043	0.319	0.964
10	0.033	0.039	0.366	0.973	0.034	0.047	0.478	0.931
12	0.028	0.031	0.355	0.936	0.029	0.039	0.479	0.959

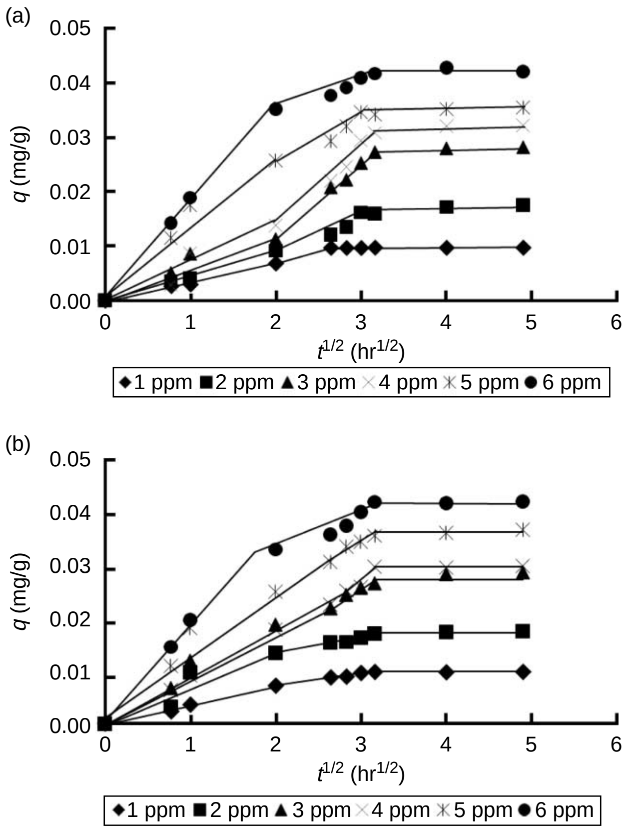

Figure 3 | Adsorbed fluoride per unit weight of bone char vs. $t^{1/2}$ for the synthetic solution with (a) Thai bone char and (b) Indian bone char.

at equilibrium, q_e, for the synthetic solution using Thai and Indian bone char derived from Equation (3), the pseudo-first-order equation, are shown in Table 2. The rate constants for both Thai and Indian bone char were similar. The amount of sorbed fluoride per weight of bone char calculated from the fit of Equation (3) is compared in Table 2 with the value measured from the batch test. The predicted and measured values compare well.

Time-dependent sorption typically involves three consecutive steps: bulk transport, film diffusion and pore diffusion (Weber 1972). First, mass transfer occurs due to mixing and advective flow. The second step involves the diffusion of the solute through the hypothetical film boundary layer. Then the solute must diffuse within the pore of the adsorbent. Several studies have focused on the importance of intra-particle diffusion in the adsorption of fluoride (Yadav *et al.* 2006; Ayoob *et al.* 2008) or adsorption of arsenate and acid dye (Badruzzaman *et al.* 2004; Cheung *et al.* 2007) during the pore diffusion step. Table 1 clearly shows that the rate constant, k_1, is not a linear function of the initial concentration. It can be concluded that the sorption process is not strict surface adsorption but, in fact, also includes intra-particle diffusion (Ghorai & Pant 2005; Kagne *et al.* 2008). Intra-particle diffusion describes the mass transfer within the adsorbent.

The importance of intra-particle diffusion can be investigated by plotting the amount of sorbed fluoride per weight of bone char versus the square root of time:

$$q = k_p t^{1/2} + C \tag{4}$$

where $k_p =$ the intra-particle diffusion rate constant ($\text{mg}\,\text{g}^{-1}\,\text{h}^{-1/2}$) and C = a constant related to thickness of the boundary layer ($\text{mg}\,\text{g}^{-1}$).

Figures 3 and 4 show the amount of sorbed fluoride per weight of bone char versus square root of time for all cases studied. If intra-particle diffusion is significant in the adsorption process, the relationship between the adsorbed

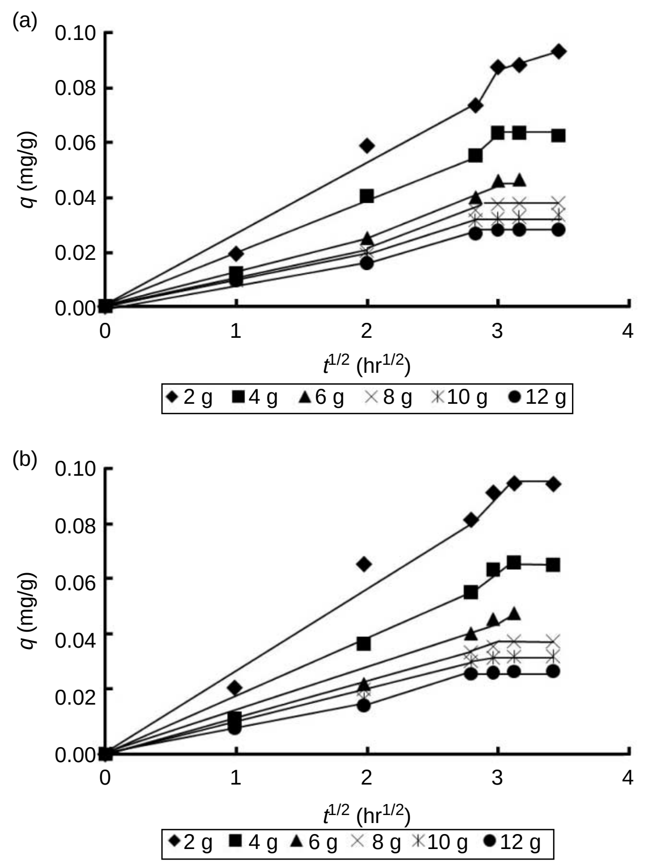

Figure 4 | Adsorbed fluoride per unit weight of bone char vs. $t^{1/2}$ for the field groundwater with (a) Thai bone char and (b) Indian bone char.

Table 3 | Parameters for Freundlich sorption isotherm

	From Equation (6)			95% confidence interval		
Type of bone char	**1/*n***	**log K_d**	***P*-value**	**Lower**	**Upper**	**R^2**
Field groundwater						
THA BC	0.618		6.87×10^{-4}	0.437	0.798	0.958
		−1.262	3.27×10^{-7}	−1.315	−1.208	
IND BC	0.535		8.49×10^{-4}	0.369	0.699	0.953
		−1.192	9.39×10^{-7}	−1.257	−1.125	
Synthetic solution						
THA BC	0.569		3.46×10^{-5}	0.491	0.647	0.990
		−1.597	1.16×10^{-8}	−1.627	−1.568	
IND BC	0.535		2.19×10^{-4}	0.418	0.652	0.976
		−1.558	8.74×10^{-8}	−1.606	−1.510	

fluoride and the square root of time should be linear (Weber & Morris 1963; McKay *et al.* 1987). Further, if the relationship between q vs. $t^{1/2}$ passes through the origin with C equal to zero, then it can be concluded that the intra-particle diffusion is the rate-controlling step (Ayoob & Gupta 2007). There appear to be three sections on the plots shown in Figures 3 and 4. The first period might indicate a boundary layer diffusion effect. If the second part is linear, intra-particle diffusion is indicated (Yadav *et al.* 2006) and the third part of the curve appears to be a constant, q, indicating equilibrium has been reached. While not conclusive, the results in this study are similar to those for other fluoride adsorbents such as brick powder and hydrated cement (Yadav *et al.* 2006; Kagne *et al.* 2008).

Adsorption isotherms

Adsorption isotherms are commonly used to quantify the distributions of the absorbent between the liquid and solid phases at equilibrium. By fitting adsorption data from the batch tests to standard isotherm equations, the effectiveness of different adsorbents can be compared.

The Freundlich sorption isotherm (Freundlich 1926) has been widely applied and is given by:

$$q_e = K_d C_e^{1/n} \quad (5)$$

where q_e = the weight of the solute adsorbed at equilibrium per unit weight of adsorbent (mg g^{-1}), C_e = the fluoride concentration at equilibrium (mg l^{-1}), K_d = a

Table 4 | Parameters for Langmuir sorption isotherm

	From Equation (8)			95% Confidence Interval			
	$1/q_m$	**$1/(K_a q_m)$**	***P*-value**	**Lower**	**Upper**	**R^2**	**q_m**
Field groundwater							
THA BC	6.381		2.02×10^{-2}	1.636	11.126	0.777	0.157
		11.097	3.45×10^{-3}	6.127	16.068		
IND BC	7.007		1.11×10^{-2}	2.649	11.365	0.833	0.142
		7.525	6.48×10^{-3}	3.513	11.538		
Synthetic solution							
THA BC	17.752		1.82×10^{-4}	14.062	21.441	0.978	0.056
		18.928	5.41×10^{-4}	13.724	24.132		
IND BC	18.471		1.57×10^{-4}	14.769	22.172	0.979	0.054
		14.990	1.06×10^{-3}	10.083	19.897		

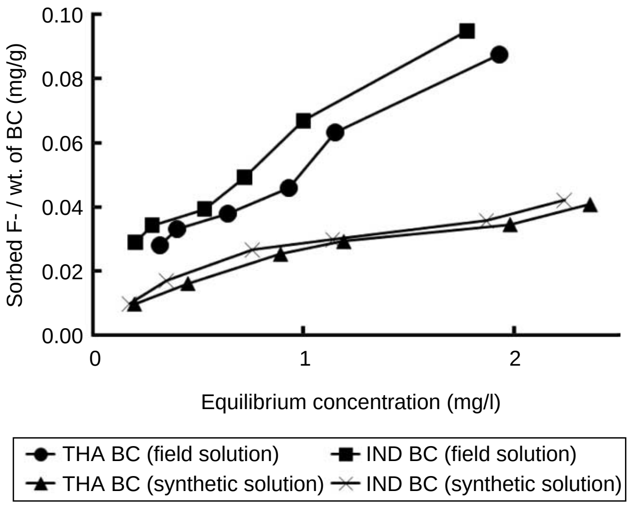

Figure 5 | Sorbed fluoride per unit weight of bone char for the synthetic and field groundwater.

constant which is a measure of the adsorption capacity, and $1/n$ = a constant which is a measure of the adsorption intensity. The linearized form of the equation is:

$$\log(q_e) = \log K_d + \frac{1}{n}\log C_e \tag{6}$$

The linearized Freundlich sorption isotherm is written for the synthetic and field groundwater as in Equation (6) for both the Thai and Indian bone char. Statistical analysis was performed on the data indicating, by a P-value less than 0.05, that the constants from Equation (6), are within the 95% confidence interval. The constants for the Freundlich sorption isotherm for the field and synthetic groundwater are shown in Table 3. The constant $1/n$, a measure of the adsorption intensity, was found to be less than one for all cases. The higher K_d values found for the field groundwater indicate that more fluoride adsorbed onto the bone char for the synthetic solution.

The Freundlich model suffers from the problem that there is theoretically no upper limit to the amount of solute that can be adsorbed. In the Langmuir model (Langmuir 1918), however, a single layer of adsorption sites is assumed. When all the sorption sites are filled, the surface will no longer sorb solute from solution. The Langmuir isotherm is given by:

$$q_e = \frac{q_m K_A C_e}{1 + K_A C_e} \tag{7}$$

where C_e is the fluoride concentration at equilibrium ($\mathrm{mg\,l^{-1}}$), q_e is the weight of sorbed fluoride per unit weight of bone char at equilibrium ($\mathrm{mg\,g^{-1}}$), q_m is the weight of sorbed fluoride per unit weight of bone char at saturation ($\mathrm{mg\,g^{-1}}$), and K_A is an isotherm constant. Rearranging Equation (7) gives:

$$\frac{C_e}{q_e} = \frac{C_e}{q_m} + \frac{1}{K_A q_m} \tag{8}$$

A linear relationship between (C_e/q_e) and C_e for the synthetic and field contaminated groundwater can be written in the form of Equation (8). From the isotherm, the saturated amount of sorbed fluoride per unit weight of the bone char and the isotherm constant can be estimated for the field and synthetic groundwater, as shown in Table 4. The Langmuir sorption isotherm shows that the saturation capacities of the Thai and Indian bone char were about the same for the synthetic groundwater solution, at 0.056 and 0.054 $\mathrm{mg\,g^{-1}}$, respectively. The sorption isotherm showed higher saturation capacities with the field contaminated groundwater at 0.157 and 0.142 $\mathrm{mg\,g^{-1}}$ for Thai and Indian bone char, respectively. The R^2 value for the field contaminated groundwater was less than that for synthetic contaminated groundwater. The results are within the 95%

Table 5 | Freundlich sorption isotherm constants for the field water and a synthetic solution with 3.5 $\mathrm{mg\,l^{-1}}$ F^- using Thai bone char

				95% Confidence Interval		
Solution	**1/n**	**log K_d**	**P-value**	**Lower**	**Upper**	**R^2**
Field	0.618		6.87×10^{-4}	0.437	0.798	0.958
(From Table 3)		−1.262	3.27×10^{-7}	−1.315	−1.208	
Synthetic	0.638		4.88×10^{-3}	0.368	0.908	0.949
		−1.299	7.62×10^{-6}	−1.362	−1.237	

Table 6 | Langmuir sorption isotherm constants for the field water and a synthetic solution with 3.5 mg l^{-1} F^{-} using Thai bone char

				95% Confidence interval			
Solution	$1/q_m$	$1/(K_a q_m)$	P-value	Lower	Upper	R^2	q_m
Field	6.381		2.02×10^{-2}	1.636	11.126	0.777	0.157
(From Table 4)		11.097	3.45×10^{-3}	6.127	16.068		
Synthetic	7.665		4.94×10^{-3}	4.406	10.924	0.949	0.130
		11.732	1.81×10^{-3}	8.198	15.266		

confidence interval as shown from the statistical analysis, with P-value less than 0.05.

The two types of bone char, Thai and Indian, had similar adsorption capacities. However, results showed that both bone chars sorb more fluoride from the field groundwater, compared with the synthetic solution. Figure 5 plots sorbed fluoride per weight of bone char and the concentration at equilibrium for all cases. The amount of sorbed fluoride per unit weight of bone char was higher at equilibrium for the field groundwater sample compared with the synthetic groundwater. For the field groundwater, there was only one concentration of 3.5 mg l^{-1} in the experiment. To obtain the sorption isotherm, the weight of the bone char was varied. With more bone char in the system, there was relatively more adsorption sites available for the fluoride, resulting in the higher fluoride sorbed per gram of bone char. For the case of synthetic water, the concentration was varied and the weight of bone char was kept constant. It is hypothesized that the number of adsorption sites was limiting in the case of the synthetic solution, when concentrations were higher.

To investigate the hypothesis that the number of adsorption sites was limiting in the case of the higher concentrations in synthetic water, another series of batch experiments were conducted. The concentration of fluoride was held constant at 3.5 mg l^{-1} so that results could be compared with the field contaminated groundwater, which had this concentration. These experiments were done with various weights of Thai bone char. Results of fits to the Freundlich and Langmuir sorption isotherms for the various weights of bone char and a synthetic solution concentration of 3.5 mg l^{-1} are shown in Tables 5 and 6 compared with the previous batch test results of field solution with the fluoride concentration of 3.5 mg l^{-1}. Tables 5 and 6 show that the Freundlich and Langmuir sorption isotherm constants from both field water and a synthetic solution are similar. Again, from the statistical analysis, all parameters are within the 95% confidence interval. This confirms the results of Medellin-Castillo *et al.* (2007), who found that other anions in the water did not interfere with the sorption process. It also indicates that, when concentrations are high, the number of adsorption sites may be a limiting factor.

Comparison of Thai bone char sorption capacity with other bone chars

The weight of sorbed fluoride at saturation was found to be about 0.157 mg of fluoride per gram of bone char with the initial concentration of 3 mg l^{-1} (from Table 6). Medellin-Castillo *et al.* (2007) found that commercial bone char, with a particle diameter of 0.79 mm, has an adsorption capacity of 2.71 mg g^{-1} when the fluoride concentration was 1 to 20 mg l^{-1}. Mwaniki (1992) studied three grades of bone char, designated black, grey and white grey bone char. He found the adsorption capacity was 11.4 mg g^{-1}, 2.4 mg g^{-1} and less than 0.3 mg g^{-1} for these three grades, respectively. The particle size by sieving of these bone chars was less than 0.25 mm. The initial fluoride concentration was between 25 and 1,300 mg l^{-1}. The adsorption capacity of Thai bone char is one to two orders of magnitude lower than these commercial bone chars. This is probably due to the difference in the particle size. Thai bone char had an average particle size of 1 to 3 cm compared with less than 0.25 mm (Mwaniki 1992) to 0.79 mm (Medellin-Castillo *et al.* 2007). Even though it is known that smaller particle sizes are more effective in fluoride removal (Mjengera & Mkongo 2003), it was the goal of our research to keep production of the bone char as uncomplicated as possible. Therefore, we did not grind the bone char used. Our results show that the initial concentration of fluoride is another factor to be considered. Typically, higher influent concentrations result in higher adsorption capacities of the adsorbent, until the saturation capacity is reached (Ayoob & Gupta 2008). The maximum initial concentration in our research was 6 mg l^{-1} compared with 1,300 mg l^{-1} in Mwaniki (1992) and 20 mg l^{-1} in Medellin-Castillo *et al.* (2007).

CONCLUSIONS

The goals of the research presented in this paper were to design and evaluate a household defluoridator that could be used in Thailand. The requirements of the system are that the bone char be produced with an inexpensive homemade furnace, the user should not handle fresh bone because of social objections to this in Thailand, defluoridation should be accomplished without adding chemicals, and the bone char should not require sieving or grinding prior to use to minimize handling of the bone char and keep the production of the bone char straightforward. These requirements were all met in the design presented in this paper. Good quality Thai bone char was successfully produced with a simple homemade furnace. There was no need to handle fresh bone during the bone char production. Treated water did not have any colour, offensive smell or taste. The pH was not changed during fluoride treatment so chemicals to control pH were not needed. Our defluoridator used boiled bone provided by a commercial gelatin factory. However, the government could provide villages with boiled bone at lower cost than the current programme of providing reverse osmosis systems to each village, with the burning step using an easily constructed household furnace.

Results of batch tests presented in this paper show that the adsorption characteristics and capacity of the Thai bone char are similar to those for Indian bone char. Bone char is successfully used in India for fluoride treatment at a local scale. The aqueous solutions used in the batch test were a synthetic solution, as well as a field groundwater. The Thai bone char has a grain size that is about an order of magnitude larger than the Indian bone char. However, the adsorption capability of the two chars is in the same range so it can be concluded that the Thai bone char does not need the further step of grinding before use.

The batch tests show that Thai bone char has potential as an adsorbent for removing fluoride in a household apparatus in Thailand. However, batch experiments are just a first step in evaluating an adsorbent. The violent shaking which is part of the procedure used in batch tests accelerates the adsorption process, compared with the slower flow conditions in defluoridators. Future research should include column tests conducted at flow rates matched to low influent rates. Column studies are also generally more useful in evaluating factors that might lower the effectiveness of the defluoridator, such as clogging of the pores in the bone char with time or bypassing of the solution due to side-wall leakage.

In conclusion, good bone char was produced using a household defluoridator that meets the social restrictions of Thailand and uses readily available materials. Adsorption characteristics of the produced bone char were studied using batch experiments and results were found to be similar to those for Indian bone char, which is successfully used in rural India. Results of this study show that bone char has great potential as an adsorbent in an effective household defluoridator in rural areas of Thailand.

ACKNOWLEDGEMENTS

The authors would like to thank the Bone Industry, Ltd in Pathum Thani, Thailand, for the boiled bone char and Dr A. S. Narayana, MDS, from the Sai Oral Health Foundation, India, for the donation of the Indian bone char. This paper was written while the first author (Smittakorn) was on leave at Colorado State University. Funding for this leave was provided by the American Association of University Women (AAUW) and is gratefully acknowledged. Helpful comments from the reviewers are appreciated.

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First received 29 October 2009; accepted in revised form 17 February 2010. Available online 22 April 2010