

## Research Article

# Defluoridation with Locally Produced Thai Bone Char

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The fluoride sorption ability of a locally available bone char is quantified. Both a synthetic solution and natural groundwater samples from several sites are studied and compared to Indian bone char, which is widely accepted and used successfully in India and elsewhere. The Freundlich and Langmuir sorption isotherms were used to quantify sorption properties. Results show that the Thai bone char is as effective as the Indian bone char for removing fluoride from contaminated water, despite the more rigid physical and social constraints found in rural Thailand. Sorption studies with fluoride-contaminated natural groundwater samples also show that chlorides, nitrates, and sulfates had little effect on the removal of fluoride by the homemade bone char.

## 1. Introduction

Fluoride contamination of groundwater is a common environmental problem worldwide. The allowable drinking water standard for fluoride is  $1.5 \text{ mg L}^{-1}$  [1]. Concentrations of fluoride higher than this level affect both teeth and bone, resulting in dental or skeletal fluorosis. In rural Thailand, fluoride concentrations in groundwater range from 1 to  $20 \text{ mg L}^{-1}$  and dental fluorosis has been recorded since 1960 [2]. Studies have also documented liver and kidney damage [3] and a bone cancer called osteosarcoma found in young boys exposed to high levels of fluoride [4]. Continuous intake of fluoride may also cause damage to the nervous system [5].

Fluoride removal at point of use is still an ongoing research area since the major water source in most rural areas around the world is groundwater. Rural areas use groundwater for drinking and household use. Centralized methods, such as the village-centered reverse osmosis systems installed in about 1250 villages in Thailand between 2004 and 2008 for fluoride removal, are costly, require high maintenance, and are simply not available to many rural areas.

Effective fluoride removal methods such as reverse osmosis [6, 7] and membrane technology [8–10] are applied in

many countries; however the high installation and maintenance costs of these methods generally preclude their use in poor countries. Low cost fluoride removal technologies, such as coagulation [11] and adsorption [12], are more acceptable in developing countries. Adsorption is a very popular method because of its simplicity in preparation, operation, and maintenance. Recently, many attempts have been made to use waste or low cost materials as the absorbent. The materials studied include bauxite [13], montmorillonite [14], activated water treatment sludge [15], waste mud [16], red mud [17], granular ceramic [18], hydrous iron (III)-tin (IV) mixed oxide [19], and schwertmannite [20].

Bone charcoal or bone char has been successfully used for fluoride removal in India and Tanzania [24, 25]. The effectiveness of bone char as an adsorbent has been studied using batch experiments with synthetic fluoride solutions under different conditions, for example, variable pH, temperature, chemical and thermal activation, adsorbent dosage, initial fluoride concentration, and coexisting anions [26]. Activated alumina sorbed less fluoride in high pH ( $>8$ ) conditions [27]. Fluoride adsorption by granular ceramic [18], activated alumina [27], granular ferric hydroxide [26], and schwertmannite [20] was found to decrease in the presence

of phosphate. Competing ions were found to have no effect on fluoride adsorption by other absorbents such as hydrous iron (III)-tin (IV) mixed oxide [19], polymer composites [28], and disposed earthenware [29]. However, sulfate and phosphate ions were found to compete with fluoride sorption on materials with iron and aluminum bases [13]. Chloride and sulfate interfered with fluoride removal by mixed-phase nano iron oxides [30]. All these experiments on the influence of other ions on sorption were done with synthetic fluoride solutions mixed with only single ion. Actual groundwater, however, contains multiple ions. The interactions of these ions on fluoride sorption of bone char have not been well tested.

There is a clear need in Thailand to develop a point-of-use defluoridator that will be successful in rural areas of Thailand that are experiencing high fluoride levels. In a previous paper by the authors [31], a simple method of producing bone char for a point-of-use defluoridator in rural areas of Thailand is described. The boiled cow bone from a gelatin production factory is the raw material. The homemade furnace consists of a 20-liter recycled steel tank. The boiled bone is placed in the middle of the tank surrounded by rice husks. After closing the lid of the tank, the burning process takes about 8 hours, at which time the temperature reaches 500°C to 600°C. The bone char is left in the container to cool down for 24 hours. The advantages of the method, compared to previous methods, include elimination of the need for the user to handle fresh bone, the use of small homemade furnaces, no offensive smell during the burning process, no need for chemical additives during the process, and no requirement for crushing or sieving of the bone at the local level. These differences address societal and physical constraints in rural areas of Thailand.

The purpose of this paper is to report the results of a study of the adsorption properties of the Thai homemade bone char, referred to as THAI BC in this paper. The kinetics of the adsorption process are investigated. The effect of the size of the homemade bone char is studied to insure that the simple production of homemade bone char will yield reasonable results for fluoride removal, without further crushing of the bone. Results are compared to those of Indian bone char (IND BC), which is widely accepted and effectively used as an adsorbent in the removal of fluoride in India and other areas worldwide. The sorption ability of the Thai homemade bone char was also evaluated using natural groundwater. Natural groundwater contains multiple component ions. The research presented here addresses the influence of these other ions on fluoride removal. In addition, fluoride-contaminated groundwater samples were collected from several sites in Chachengsao, Phetchaburi, and Nakorn Pathom provinces of Thailand.

## 2. Materials and Methods

Boiled cow bone, courtesy of the Thai Bone Industry in Pathum Thani province, Thailand, was the raw material. Two advantages of using boiled bone instead of fresh bone are the hygienic handling of the bone and the lack of an offensive

odor during the charring process. A homemade furnace is made from a 200-litre steel container. It should be noted that the size of the steel container has been increased from the previous work so that more bone char can be produced. Rice husks are used as fuel. Dried rice leaves were initially tested; however the heat generated from the leaves was less than 500°C resulting in a poorer quality of bone char. Rice husks are well known as an alternative renewable fuel. A stainless steel pot is filled with about 7 kg of the boiled bone and placed on top of the rice husk. The lid is closed and rice husks are added until the pot is covered. The fire is lit and rice husks fill the whole container. Typically, heat is applied for about 8 hours with bone char being left to cool for about 24 hours before it is removed. About 5 kg of bone char is left from the process. In this paper, this bone char is referred to as THAI BC. The length of the bone char produced is about 1 to 3 cm. As discussed by Smittakorn et al. [31], for acceptance in Thailand, the production of the homemade bone char has to be simple and to require no added chemicals, no sieving or crushing during the process, readily available local raw materials, and no need for small households to handle the fresh bone.

A series of batch experiments were conducted to assess the effect of bone char size on the fluoride removal ability. The bone char was crushed with a mortar and pestle and then sieved into four different sizes which were less than 0.841 mm, 0.841–1.18 mm, 1.19–2.37 mm, and 2.38–4.74 mm. In these tests, 200 mL of a synthetic fluoride aqueous solution with a concentration of 3.9 mg/L was mixed with 10 g of the homemade bone char in a plastic bottle and then shaken in a water bath at room temperature. Samples were collected and analyzed at 2, 4, 6, 8, 10, 12, 16, 20, and 24 hours. Sorption kinetics and isotherms for each size of bone char were then analyzed.

The fluoride sorption capacity of the Thai bone char (THAI BC) was then compared to that of Indian bone char. Indian bone char (IND BC) was set as a benchmark since it is successfully used in India and elsewhere. For these tests, six groundwater samples were collected from wells at sites in Chachengsao, Phetchaburi, and Nakorn Pathom provinces of Thailand. The groundwater was stored in plastic containers and kept refrigerated prior to the sorption tests. The fluoride concentrations of the groundwater samples (designated as GW1 to GW6) ranged from 3 to 19 mg/L while the synthetic fluoride concentration was again 3.9 mg/L. Procedures for the batch experiments are as described above.

The final tests presented in this paper investigate the effect of multiple ions on the sorption ability of bone char. The Thai and Indian bone chars were compared for sorption capacity using a synthetic solution and a second set of groundwater samples from six locations in Chachengsao, Phetchaburi, and Nakorn Pathom provinces of Thailand. These were collected from different wells from the isotherm experiment and are designated as Sites 1 through 6. Samples were taken at the time to equilibrium assumed to be 12 hours. Again, batch tests procedures are described above.

Fluoride and other ion concentrations were measured using the ion analyzer EA 940 at the analytical laboratory of the Dental Health Division, Department of Health,

TABLE 1: Constants and goodness of fit for size ranges of Thai BC using linear, first order, and second order kinetic equations.

Size of BC (mm)	$q_e$ (mg/g) (experiment)	Zero order equation			First order equation			Second order equation		
		$k_0$ (h <sup>-1</sup> )	$q_e$ (mg/g)	$R^2$	$k_1$ (h <sup>-1</sup> )	$q_e$ (mg/g)	$R^2$	$k_2$ (g·mg <sup>-1</sup> ·h <sup>-1</sup> )	$q_e$ (mg/g)	$R^2$
2.38–4.74	0.067	0.0025	0.048	0.875	0.143	0.070	0.967	1.235	0.094	0.959
1.19–2.37	0.069	0.0023	0.041	0.783	0.187	0.070	0.942	2.154	0.086	0.965
0.841–1.18	0.062	0.0019	0.034	0.700	0.127	0.042	0.954	2.833	0.074	0.987
<0.841	0.073	0.0023	0.048	0.880	0.105	0.061	0.985	1.421	0.092	0.988
$P$ value		$1.52 * 10^{-3}$			0.28			$9.29 * 10^{-3}$		

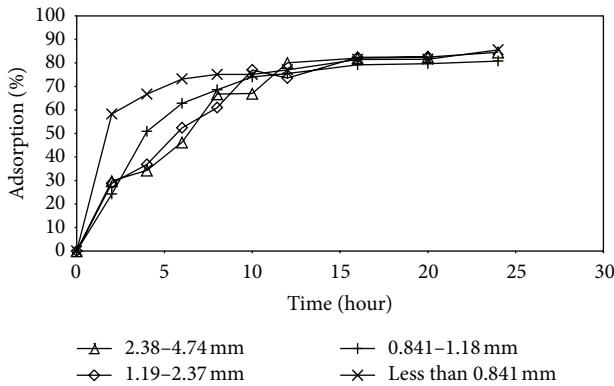


FIGURE 1: Adsorption percentage at different times for each range of bone char size.

Ministry of Public Health, Nonthaburi, Thailand. The Sai Oral Health foundation in Hyderabad, India (<http://www.saioralhealthfoundation.org>), supplied the Indian bone char (IND BC) used throughout this work.

### 3. Results and Discussions

**3.1. Contact Time or Time to Equilibrium as a Function of Bone Char Size.** One criterion for the Thai bone char is that the local user need not crush the bone. To determine if the size of the Thai bone char produced by the homemade furnace affects sorption, the bone char was crushed and sieved into four size ranges. Batch experiments were performed for each size range of bone char. A synthetic solution with a concentration of 3.9 mg/L was used in these tests.

The relationship between contact time and the adsorption percentage is shown in Figure 1. The percent sorbed increased with time for the first 12 hours, after which data reached an asymptote at about 80% (Figure 1). Thus, it can be assumed that the contact time or time to equilibrium for all size ranges of the homemade bone char, THAI BC, is 12 hours. Time to equilibrium for other sorbates has been found to range from one hour to 72 hours [12].

The smallest size of bone char had a more rapid adsorption rate at earlier time. This result agrees with Mjengera and Mkongo [25], who concluded that fine particles would remove fluoride faster because there is more available surface area. However, clogging will likely occur more easily with fine

particles and handling of these finer particles will complicate production of the bone char.

#### 3.2. The Effect of Thai Bone Char Sizes on the Sorption Capacity in the Synthetic Fluoride Solution

**3.2.1. Adsorption Kinetics.** To evaluate the efficacy of the homemade bone char, another set of batch experiments was performed. The procedure was similar to those earlier experiments in that 200 mL of a synthetic fluoride solution with the concentration of 3.9 mg/L was shaken with 10 g of homemade bone char. Samples were collected until 12 hours. The data were fit to pseudo zero, first, and second order adsorption models to quantify the adsorption kinetics of Thai bone char to the synthetic fluoride solution.

The pseudo zero order kinetic equation is given by

$$q_e - q_t = q_e - k_0 t, \quad (1)$$

where  $q_e$  and  $q_t$  are the mass of sorbed fluoride per unit mass of the adsorbent (mg g<sup>-1</sup>) at equilibrium and at any time  $t$  (h), respectively. The rate constant  $k_0$  was assumed constant, computed from the best-fit slope of a linear plot of  $(q_e - q_t)$  versus time.

The pseudo first order kinetic equation of Lagergren [32] is given by

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303} t. \quad (2)$$

The rate constant,  $k_1$ , is determined from the slope of the linear relationship described by (2).

A pseudo second order kinetic equation [33] is given as

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e}, \quad (3)$$

where the rate constant is  $k_2$ . A linear relationship between  $(t/q_t)$  and time was constructed to determine the rate constant for this equation.

The constants determined for (1), (2), and (3) are shown in Table 1 for each size range of Thai BC investigated, along with correlation coefficients. The correlation coefficients,  $R^2$ , for the pseudo first order and second order equations were found to be closer to 1 than those obtained from the zero order equation. Comparing the amount of fluoride sorbed at equilibrium per unit mass of bone char ( $q_e$ ) from the experimental results with the best fit for  $q_e$  using the equations, the  $P$  value from zero order and second order kinetic

equations was less than 0.05. This indicates that the values of  $q_e$  using these two equations were significantly different from the experimental values. The  $P$  values from the first order kinetic equation by Lagergren [32] were greater than 0.05 meaning that equilibrium concentrations,  $q_e$ , predicted by this equation were good fits to the experimental values. Since both the  $R^2$  and  $P$  values are high for the Lagergren equation, it can be concluded that this first order kinetic model best describes the rate of adsorption of fluoride onto Thai bone char.

**3.2.2. The Sorption Isotherm.** Freundlich [34] presented a sorption isotherm that is widely used for fitting results of sorption experiments. The Freundlich equation is given by

$$q_e = K_d C_e^{1/n}, \quad (4)$$

where  $q_e$  is the mass of the solute adsorbed at equilibrium per unit mass of adsorbent ( $\text{mg g}^{-1}$ ),  $C_e$  is the fluoride concentration at equilibrium ( $\text{mg L}^{-1}$ ),  $K_d$  is a constant which is a measure of the adsorption capacity, and  $1/n$  is a constant which is a measure of the adsorption intensity. The Freundlich sorption isotherm is linearized as

$$\log(q_e) = \log(K_d) + \frac{1}{n} \log(C_e). \quad (5)$$

A limitation of the Freundlich sorption isotherm is that there is no maximum limit to the sorbed solute.

The Langmuir sorption isotherm [35] is also commonly used in sorption studies. The Langmuir sorption isotherm is given by

$$q_e = \frac{q_m K_A C_e}{1 + K_A C_e}, \quad (6)$$

where  $C_e$  is the fluoride concentration at equilibrium ( $\text{mg L}^{-1}$ ),  $q_e$  is the mass of sorbed fluoride per unit mass of bone char at equilibrium ( $\text{mg g}^{-1}$ ),  $q_m$  is the mass of sorbed fluoride per unit mass of bone char at saturation ( $\text{mg g}^{-1}$ ), and  $K_A$  is an isotherm constant. To evaluate parameters from the Langmuir sorption isotherm, (6) is rearranged resulting in a linear relationship between  $C_e$  and  $(C_e/q_e)$ :

$$\frac{C_e}{q_e} = \frac{C_e}{q_m} + \frac{1}{K_A q_m}. \quad (7)$$

Results of fitting the data from the batch tests to the Freundlich and Langmuir sorption isotherms are shown in Table 2.

A low  $1/n$  in the Freundlich equation implies that there is a strong bond between the adsorbent and the adsorbate. In this case, the values of  $1/n$  for all sizes of bone char were similar, with an average of 0.69. Similar values of  $K_d$  mean that the sorption capacities for different sizes of bone char are similar. This is the case for all size except for the smallest size (less than 0.8 mm), where the greater surface area likely affects the isotherm as mentioned previously.

Other researchers have computed Freundlich parameters for bone char of various sizes from 0.5 to 1.29 mm. Results

TABLE 2: Freundlich and Langmuir sorption isotherms parameters for different size ranges of the Thai BC using synthetic solution (3.9 mg/L).

Range of BC size (mm)	Freundlich isotherm			Langmuir isotherm		
	$K_d$	$1/n$	$R^2$	$q_e$	$K_A$	$R^2$
2.38–4.74	0.053	0.728	0.901	0.279	0.241	0.973
1.19–2.37	0.059	0.792	0.940	0.597	0.109	0.946
0.841–1.18	0.050	0.610	0.934	0.214	0.309	0.984
<0.841	0.136	0.633	0.781	0.243	1.206	0.928

are summarized in Table 3 and compared to parameters in this study. Differences can be explained, in part, because the initial fluoride concentration in the batch tests in this paper had a concentration of 3.9 mg/L, whereas the range was larger in the other papers, from 1 to 20 mg/L. In addition, Thai bone char was manufactured from a homemade furnace while bone char from other works was commercially produced. The homemade furnace would produce a less consistent product. This could be another reason for the lower sorption capacity found for the Thai bone char.

**3.3. Comparison of Sorption Isotherms for Thai and Indian Bone Char for Natural Groundwater Samples.** Groundwater samples were collected from wells at six sites in Chachengsao, Phetchaburi, and Nakorn Pathom provinces of Thailand. These water samples will be used to compare sorption isotherms for the Thai bone char with those for Indian bone char. Indian bone char does not address all of the societal issues required for small scale defluoridators in Thailand but it is widely accepted and successfully used in many areas worldwide. Because of its wide acceptance, it is used here as a benchmark. The Indian bone char was supplied by the Sai Oral Health foundation in Hyderabad, India (<http://www.saioralhealthfoundation.org>).

It was shown in the previous section that the size of bone char does not affect the adsorption capacity. Therefore, Thai bone char produced without crushing will be tested in this section. The fluoride concentrations in the groundwater sampled, designated as water samples GW1–GW6 in this paper, range from 3 to 19 mg/L. The synthetic fluoride concentration is again 3.9 mg/L. The Thai and Indian bone chars are compared using the Freundlich and Langmuir sorption isotherms (Tables 4 and 5).

From Table 4, the  $P$  values for  $K_d$  and  $1/n$  were greater than 0.05 which indicates that there was no significant difference in means between Thai and Indian bone char for either parameter. The Langmuir sorption isotherm (Table 5) shows that the equilibrium capacities,  $q_e$ , and values of  $K_A$  for the Thai and Indian bone char were similar, with  $P$  values for  $q_e$  and  $K_A$  greater than 0.05. From both sorption isotherms, the  $R^2$  values are quite comparable, although the  $R^2$  from the Freundlich isotherms showed a slightly better fit than those from the Langmuir sorption isotherm. From these results, it is concluded that Thai bone char is as effective in removing fluoride as the widely accepted Indian bone char and that either the Freundlich or the Langmuir sorption isotherm can

TABLE 3: Comparison of fitted Freundlich sorption isotherm parameters for different sizes of bone char found in this study with parameters from other publications.

Bone char size (mm)	$K_d$	1/n	pH	Type of bone char	Reference
2.38–4.74	0.053	0.728	8	Charred by homemade furnace	This work
1.19–2.37	0.059	0.792	8	Charred by homemade furnace	This work
0.841–1.18	0.050	0.610	8	Charred by homemade furnace	This work
<0.841	0.136	0.633	8	Charred by homemade furnace	This work
0.79	2.710	0.284	7	Commercial BC	Medellin-Castillo et al. 2007 [21]
0.79	0.870	0.339	10	Commercial BC	Medellin-Castillo et al. 2007 [21]
0.5–1.0	0.549	0.510	N/A	Charred by electric furnace	Kawasaki et al. 2009 [22]
0.65	2.840	0.328	7	Commercial BC	Leyva-Ramos et al. 2010 [23]
0.79	2.720	0.289	7	Commercial BC	Leyva-Ramos et al. 2010 [23]
1.29	1.950	0.435	7	Commercial BC	Leyva-Ramos et al. 2010 [23]

\*A synthetic solution was used in these tests.

N/A: pH condition was not reported.

TABLE 4: Parameters for the Freundlich sorption isotherm comparing Thai and Indian bone char.

Sample	$K_d$		1/n		$R^2$	
	THAI BC	IND BC	THAI BC	IND BC	THAI BC	IND BC
GW1	0.053	0.064	0.634	0.664	0.965	0.947
GW2	0.057	0.079	0.634	0.792	0.953	0.932
GW3	0.060	0.051	0.654	0.812	0.943	0.987
GW4	0.049	0.069	0.936	0.679	0.925	0.932
GW5	0.056	0.066	0.705	0.499	0.862	0.805
GW6	0.072	0.099	0.757	0.766	0.987	0.957
Syn.	0.063	0.081	0.595	0.671	0.941	0.950
P value	0.063		0.940			

be used to describe the process. This finding agrees with Abe et al. [36] and Medellin-Castillo et al. [21].

**3.4. The Effect of Multiple Ions on the Sorption Capacity.** Thai and Indian bone char sorption capacities are compared in this section to determine the effects of multiple ions on the sorption capacity. The tests again used the synthetic solution (initial concentration of  $3.9 \text{ mg L}^{-1}$ ) and an additional set of groundwater samples taken from wells in six locations in Chachengsao, Phetchaburi, and Nakorn Pathom provinces of Thailand. The chemical constituencies of the groundwater samples are shown in Table 6. Samples were taken for analysis at a time to equilibrium assumed to be 12 hours. Figure 2 shows the amount of fluoride sorbed per unit mass comparing Thai and Indian bone char when the solution contains different concentrations of (a) chloride, (b) nitrate, (c) sulfate, and (d) fluoride.

Table 7 shows Pearson correlation coefficients between fluoride and both the Thai and Indian bone chars that are close to one (0.942 and 0.831, resp.), indicating a high positive linear relationship between those two parameters. Thus, the amount of fluoride sorbed onto bone char tends to increase with the increasing initial fluoride concentration (see Figure 2(d)). This agrees with results by Eskandarpour et al. [20]. On the other hand, the correlation coefficients between chloride, nitrate, and sulfate to either Thai or Indian

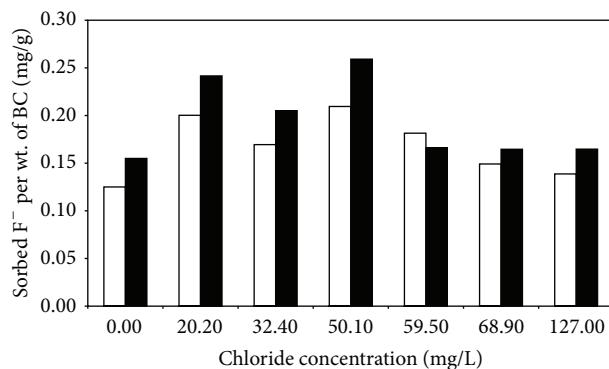
bone char approach zero (except for the case of sulfate and Thai bone char) implying that there is less of the relationship or an uncorrelated relationship between ion concentrations and the sorbed fluoride per weight of bone char. Even though the chloride and nitrate contain mono anions as well as fluoride, the adsorption mechanisms of chloride and nitrate are totally different than fluoride. While fluoride adsorbs with strong bonds by active sites at the inner Helmholtz plane, chloride and nitrate adsorb with weaker bonds at active sites on the outer Helmholtz plane. The presence of sulfate showed no obvious effect on fluoride adsorption. The adsorption mechanism of sulfate is only partially inner Helmholtz plane but it might interfere with the fluoride adsorption slightly [20].

Abe et al. [36] report that the amount of sorbed fluoride increased with increased concentration of chloride in the solution. The difference between Abe et al. [36] and this study is type of fluoride-contaminated solution. In Abe et al's study, synthetic fluoride solution with only sodium chloride added into the fluoride solution, while in this study multiple ions presented in the actual groundwater. Other ions might have been the contribution to such different result.

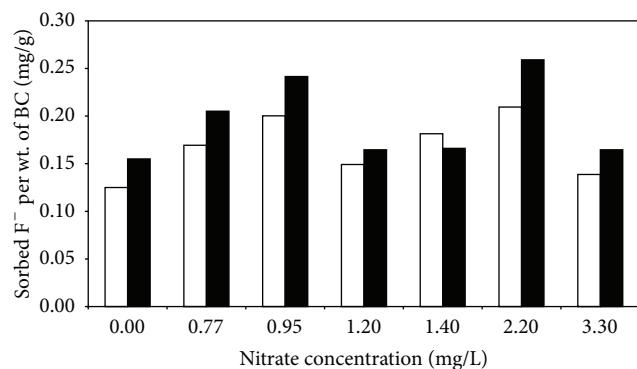
The concentrations of chloride, nitrate, sulfate, and phosphate were also evaluated after the batch test. There was no significant change in the concentration of any ions except for phosphate. Chloride, nitrate, and sulfate do not compete

TABLE 5: Parameters for the Langmuir sorption isotherm comparing Thai and Indian bone char.

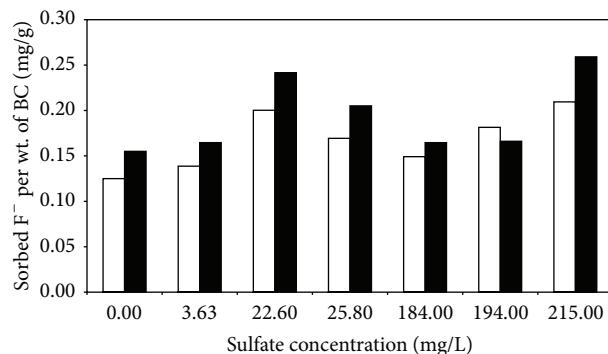
Sample	$q_e$	$K_A$	$R^2$			
	THAI BC	IND BC	THAI BC	IND BC	THAI BC	IND BC
GW1	0.191	0.217	0.409	0.455	0.913	0.858
GW2	0.209	0.391	0.408	0.262	0.952	0.506
GW3	0.196	0.362	0.478	0.167	0.848	0.747
GW4	0.644	0.364	0.092	0.229	0.912	0.415
GW5	0.204	0.134	0.389	1.049	0.543	0.878
GW6	0.321	0.457	0.306	0.289	0.893	0.399
Syn.	0.188	0.264	0.556	0.480	0.957	0.819
<i>P</i> value		0.668		0.751		



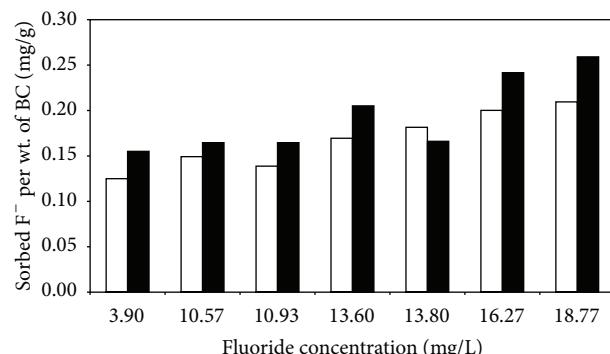
(a) Chloride: the water samples (from left) are the synthetic solution, and sites 1, 2, 3, 5, 4, and 6 are in Table 1, shown in increasing concentrations



(b) Nitrate: the water samples (from left) are the synthetic solution, and sites 2, 1, 4, 5, 3, and 6 are in Table 1, shown in increasing concentrations



(c) Sulfate: the water samples (from left) are the synthetic solution, and sites 6, 1, 2, 4, 5, and 3 are in Table 1, shown in increasing concentration



(d) Fluoride: the water samples (from left) are the synthetic solution, and sites 4, 6, 2, 5, 1, and 3 are in Table 1, shown in increasing concentration

FIGURE 2: Comparisons of the mass of fluoride sorbed per unit mass of Thai and Indian bone char with the increasing concentrations of (a) chloride, (b) nitrate, (c) sulfate, and (d) fluoride in the groundwater samples.

with the fluoride ion on bone char. Prior to the batch test, the concentration of phosphate was less than 0.01 mg/L, while the final concentration of phosphate was 0.8 mg/L. The increasing concentration of phosphate associated with the fluoride removal by bone char is similar to two previous works [22, 37]. He et al. [37] note that tricalcium phosphate is partially broken off in water which can occur in three different possible pH states: acidic, neutral, and alkaline.

These are shown in (8), (9), and (10), respectively. Consider the following:

*acidic pH:*

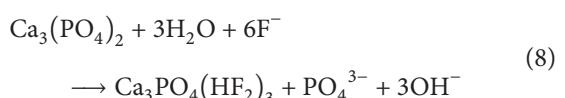


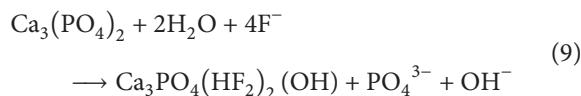
TABLE 6: Ion concentrations in the groundwater samples.

Number	Concentration (mg/L)				
	F <sup>-</sup>	Cl <sup>-</sup>	NO <sub>3</sub> <sup>-</sup>	SO <sub>4</sub> <sup>2-</sup>	PO <sub>4</sub> <sup>3-</sup>
Site 1	16.27	20.20	0.95	22.60	<0.1
Site 2	13.60	32.40	0.77	25.80	<0.1
Site 3	18.77	50.10	2.20	215.00	0.43
Site 4	10.57	68.90	1.20	184.00	<0.1
Site 5	13.80	59.50	1.40	194.00	<0.1
Site 6	10.93	127.00	3.30	3.63	<0.1
Syn.	3.9	—	—	—	—

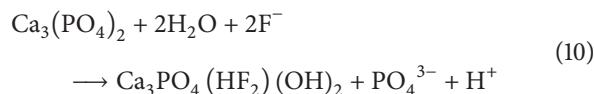
TABLE 7: The Pearson correlation coefficient between sorbed fluoride per mass of bone char and each ion.

Ion	Thai bone char	Indian bone char
Chloride	-0.168	-0.264
Nitrate	0.129	0.105
Sulfate	0.474	0.183
Fluoride	0.942	0.831

*neutral pH:*



*alkaline pH:*



From all three possible reactions, the phosphate ion appears as a product of the reaction. From (10), after the reaction, the H<sup>+</sup> ion is released at an alkaline condition resulting in the decreasing pH. The final pH of groundwater in our batch tests was 8.2, which was slightly more acidic when compared to the initial pH of solutions which was 8.3. There was relatively no change in the pH, smell, and color of the treated groundwater.

#### 4. Conclusions

The groundwater in many rural areas of Thailand has fluoride concentrations that are as high as 20 mg/L, much higher than the drinking water standard of 1.5 mg/L. However, attempts to provide centralized treatment systems to remove the fluoride have failed. Small point-of-use defluoridators face limitations that are unique to Thailand. This study evaluated the sorption properties of a bone char produced using a method introduced in an earlier paper to address a number of societal and physical constraints that the authors found in rural Thailand. These constraints included elimination of the need for the small household user to handle fresh bone

and the use of small homemade furnaces and elimination of the need for chemical additives during the process, requiring readily available local materials and no crushing or sieving of the bone at the local level. Boiled bone as raw material for the defluoridator is available through the bone factory in each province. However, the government should provide the information such as the location of such factory in the area or even set up a distribution center of the boiled bone.

This paper presents the results of batch tests which compare the sorption properties of the homemade Thai bone char with Indian bone char. Indian bone char was used as a benchmark because it is used effectively in India and elsewhere and is well accepted as an effective sorbent for fluoride. Our results showed that, for both synthetic fluoride solution and natural fluoride-contaminated groundwater, the Thai bone char was as effective as the Indian bone char. We also found that there was no advantage or need to further crush the bone provided by the gelatin factory. The paper presents coefficients for common isotherms for Thai bone char sorption and we found that coexisting ions such as chloride, nitrate, and sulfate have little effect on the sorption properties of the Thai bone char. The sorption capability of homemade bone char is less than other expensive commercial sorbents. However, even though the coefficients derived from sorption isotherms for Thai BC were less than those found in others' work, the defluoridator meets the goal of a sustainable household device that removes fluoride at low levels. In this application, the Thai homemade bone char shows high potential to remove fluoride in remote areas of Thailand where groundwater is essential for household consumption. Lastly, it is possible to regenerate the bone char using the burning process. Further researches can be done to evaluate the optimum conditions to regenerate the exhausted bone char such as the temperature and the duration of the heating process. It is also necessary to consider the longevity and the fluoride removal effectiveness of the regenerated bone char.

#### Notations

- C: Constant related to thickness of the boundary layer (mg g<sup>-1</sup>)
- C<sub>B</sub>: Desired concentration of solute (mg L<sup>-1</sup>)
- C<sub>e</sub>: Fluoride concentration at equilibrium (mg L<sup>-1</sup>)
- C<sub>0</sub>: Initial concentration of fluoride (mg L<sup>-1</sup>)
- C<sub>t</sub>: Fluoride concentration at any time (mg L<sup>-1</sup>)
- k<sub>0</sub>: Rate constant of pseudo zero order equation (h<sup>-1</sup>)
- k<sub>1</sub>: Rate constant of pseudo first order equation (h<sup>-1</sup>)
- k<sub>2</sub>: Rate constant of pseudo second order equation (g mg<sup>-1</sup> h<sup>-1</sup>)
- K: Adsorption rate constant (mg L<sup>-1</sup> min<sup>-1</sup>)
- K<sub>A</sub>: Langmuir isotherm constant
- K<sub>d</sub>: Constant which is a measure of the adsorption capacity
- k<sub>p</sub>: Intraparticle diffusion rate constant (mg g<sup>-1</sup> h<sup>-1/2</sup>)
- n: Constant related to the adsorption capacity

- $q$ : Weight of sorbed fluoride at any time per unit weight of bone char ( $\text{mg g}^{-1}$ )  
 $q_e$ : Weight of sorbed fluoride at equilibrium per unit weight of bone char ( $\text{mg g}^{-1}$ )  
 $q_m$ : Weight of sorbed fluoride at saturation per unit weight of bone char ( $\text{mg g}^{-1}$ )  
 $q_t$ : Weight of sorbed fluoride at any time per unit weight of bone char ( $\text{mg g}^{-1}$ )  
 $t$ : Time (h).

## Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

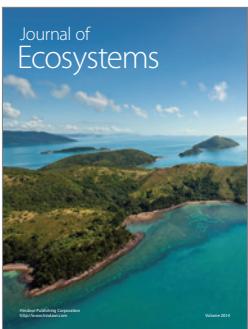
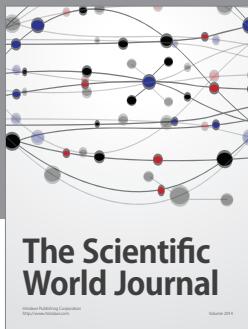
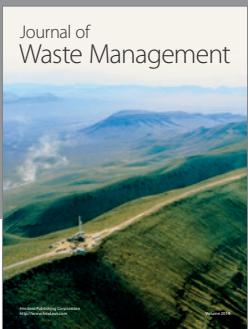
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