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Fluoride removal from drinking water by adsorption using bone char as a biosorbent

Wei Ma[1,2], Feiqun Ya[1], Ren Wang[1], Yaqian Zhao[2]

[1,2]Department of Chemistry, Dalian University of Technology, Dalian, 116024, P. R. China

[2]Centre for Water Resources Research, School of Architecture, Landscape and Civil Engineering, University College Dublin, Earlsfort Terrace, Dublin 2, Ireland

Tel. +86(411)8470-6303; mawei@dlut.edu.cn

Abstract:

As a biomass material, bone char was investigated for the feasibility to be used as a cost-effective biosorbent for fluoride removal from drinking water in groundwater environment. Based on the batch tests with natural tourmalin and active alumina being the reference adsorbents, BF (referring to bone char) has demonstrated a higher fluoride adsorption capacity. This capacity was found being increased with the increase of fluoride concentration. Furthermore, BF based column adsorption experiments indicated that the fluoride removal could be significantly affected by flow rate and bed height. A mass transfer model developed in this study can be used to optimize the bed configuration and operation parameters. Experimental results and predicted data by the model have shown a good consistent. A full-scale BF fixed-bed to treat fluoride-containing groundwater in Northeast China has been successfully operated since 2002.

Key words: Adsorption; Bio-adsorbent; Drinking water; Fluoride; Batch tests; Column

Introduction

The removal of fluoride from drinking water is one of the most important environmental issues in the world. As a necessary dilute element in human body, fluoride in drinking water may be beneficial or detrimental depending on its concentration (Srimurali et al., 1998). Excess fluorides can cause skeletal and dental fluorosis. The optimum fluoride level in drinking water for general good health set by WHO is considered to be between 0.5 and 1.0 mg/l (Srimurali et al., 1998; Yan et al., 2001; Fan et al., 2003; Ghorai et al., 2004). Fluoride concentrations in groundwater of some places in the world exceed the acceptable value; for example, in some area of Northeast China the fluoride concentration is about 4mg/l. Fluoride removal from drinking water is presently a common practice worldwide.

To date, various methods to remove fluoride from groundwater have been proposed and applied in decades. Sedimentation with calcium and aluminum salts is one of the commonly used processes to eliminate fluoride. It can reduce the fluoride concentration to about 2mg/l and can be used for fluoride-rich industrial wastewater treatment as well (Huang et al. 1999). However, the process generates large amounts of fluoride-containing sludge and causes an unavoidable sludge treatment and disposal problem with increased costs (Aldaco and Irabien, 2005). Other methods, which include ion exchange, membrane (including reverse osmosis and nano-filtration), Donnan dialysis and integrated physiochemical and biological adsorption on active alumina, fly ash, and carbon nano-tubbe etc, have all been used for fluoride removal practice (Lounici et al., 1997; 2004; David and Herbet, 1998; Kettunen et al., 2000; Li et al., 2001; 2003; Garmes et al., 2002, Ruiz et al., 2003; Hu et al., 2005; Subhashini et al., 2005). Among the various methods, it has been accepted that the ion exchange,

electro-dialysis and membrane processes are effective and can remove the fluoride to a suitable level. But they are expensive and require frequent regeneration of ion exchange beds or cleaning of the scaling and fouling on the membrane (Aldaco and Irabien, 2005). Although adsorption of defluoridation from drink water by activated alumina was successfully demonstrated, the fluoride removal capacity changed significantly with pH value of water. In addition, it was found that the Al^{3+} ions released during the treatment process. Therefore, searching for cost-effective adsorbents remains an active theme in the research and practice of fluoride removal.

In recent years, a lot of efforts have been devoted and some new cost-effective fluoride adsorbents, such as, zeolites (Onyango et al., 2004) and biomass material, like fishbone charcoal (Bhargava and Killerdar, l991; Christoffersen et al., 1991) as well as other novel adsorbents (Das et al., 2003; Mjengera et al., 2003) have been identified/investigated. More significantly, biosorption was studied as a property of certain types of biomass to adsorb cations and anions, like heavy metal ion, from even very dilute aqueous solutions. It has been demonstrated that biosorption is good at affinity and selectivity for ion removal (Volesky et al., 1994; Dividl and Herbert, 2000).

In present study, bone char was used as a bio-adsorbent, which is a disintegrative product of animal bones. The batch adsorption tests were conducted using NaF as fluoride model source. The efficiencies of fluoride removal were compared with that obtained from the natural materials named tourmaline and active alumina. Langmuir and Freundlich isotherms were employed to evaluate the batch adsorption tests. Thereafter, a bone char column test was performed and a mass transfer model was developed to describe the adsorption behaviour. Finally, an example of the industrial application of this study is briefly described.

Methods

Theoretical backgrounds
Adsorption values were calculated from the change in solution concentration using the equation:
$$q = V(C_0 - C_f) / W \qquad (1)$$
where q is the adsorption (mgl/g), C_0 and C_f the initial and final concentrations (mg/l), V the volume of solution (l)and W the mass of biosorbent used (g).
The most commonly used equations for modeling biosorption equilibrium data are the Langmuir and Freundlisch adsorption isotherms which may be expressed in Eq. (2) and (3), respectively:

$$q_{eq} = \frac{q_{max} b C_{eq}}{1 + b C_{eq}} \qquad (2)$$

$$q = k C_{eq}^{1/n} \qquad (3)$$

where $q(q_{eq})$ is the amount of adsorbed ion per unit weight of biosorbent, q_{max} is the maximum amount of adsorbate per unit weight of biosorbent forming a complete monolayer on the surface and C_{eq} is the remaining or equilibrium ion concentration in bulk solution. The magnitude of b reflects the slope of the adsorption isotherm which is a measure of whether adsorption is favourable or unfavourable. k and 1/n are adsorption constants of Freundlich isotherm.
Estimation of the key design parameters to characterize the performance of the biosorbent in a column system was based on the classical early work described by Bohart and Adams (1920). The residual

capacity (N) of the biosorbent can be written as:

$$\frac{\delta N}{\delta t} = -KNC \qquad (4)$$

and the solute concentration (C) which diminishes in the solvent at a rate given by

$$\frac{\delta C}{\delta D} = -KNC/\upsilon \qquad (5)$$

where D is the bed height of the column (cm); υ is the linear flow rate through the bed; N is residual capacity of the biosorbent (mg/g); and K is kinetic constant (min^{-1}). Solution of the two partial differential equations for a set of two boundary conditions (at $t=0$, $N=N_0$, initial capacity of the biosorbent, and at $D=0$, $C=C_0$, inlet concentration) results in the following expression (Hutchins 1973; Ghorai et al., 2005):

$$\ln[(C_0/C_{eq})-1] = \ln(e^{DnoK/\upsilon}-1) - KC_0t \qquad (6)$$

Following expression for t was given:

$$t = (N_0/C_0\upsilon)D - \ln[(C_0/C_e)-1]/KC_0 \qquad (7)$$

when given value of Ce at the time t=0 and solving for D:

$$D_{min} = (\upsilon/kN_0)\ln[(C_0/C_e)-1] \qquad (8)$$

where D_{min} is theoretical minimum height of the adsorbent in the column (cm). It can be apply to the design process.

Experimental

Raw material of biosorption bone char samples were obtained from animal bones provided by Dalian Greenstar Environmental Limit Company. After heat treatment they were initially purified and sieved into different size of fractions. Distilled water was then added to obtained biomass to remove suspended impurities. This was followed by drying process, and finally the dried samples were kept in airtight containers for using as biosorbent, referring to BF. The size of BF used in this study is 0.2mm. The surface property of prepared BF was examined by scanning electron microscope (SEM). Other sorbents of tourmaline and activated alumina used as reference soebents in present study with particle size of 0.2mm were also supplied by Dalian Greenstar Environmental Limit Company. Chemical of NaF is an analytical degree agent.

Batch adsorption studies were conducted by contacting ca. 0.1 g quantities of adsorbent with 100 ml of solution at varying fluoride concentrations (3–100 ppm) in 250 ml Erlenmeyer flasks shaking for ca. 120min, which had been shown in preliminary study to ensure equilibration to be reached. Temperature of the adsorption tests was 22–25℃ while the pH of the distilled water was in the range of 6.8-7.1 (similar with groundwater). After shaking, the suspension was subjected for centrifugation and the final fluoride ions concentration of the supernatant was determined using fluoride ions selective electrode. The same adsorption test procedures were applied for the tests with sorbents of tourmaline and activated alumina.

Column operations of a fixed-bed absorber system were conducted in this study to reveal the effects of process parameters such as inlet flow rate, initial fluoride concentration and bed height on fluoride removal capacity. BF was added in a series of three experimental columns with 14mm in diameter and 2.3 and 2.8mm in height. The analytic relation between of breakthrough point (time t_b) and minimum height of bed (D_{min}) will be identified by the mass transfer model. Breakthrough curves derived from the experimental data were correlated with that predicted by model.

Results and discussion

Fig. 1 presents the SEM observation. It is seen that the BF powders are irregular clumps in the surface. By using the energy spectroscopy equipped on SEM the atomic ratio of Ca:P:O:C of BF is measured and the result is about 2.4:2:6:1, showing low ratio of carbon. Further examination of using X-ray diffraction (XRD) spectrum has demonstrated (data not shown) that there were no peaks to indicate the crystallization structure, suggesting that the BF power is amorphous.
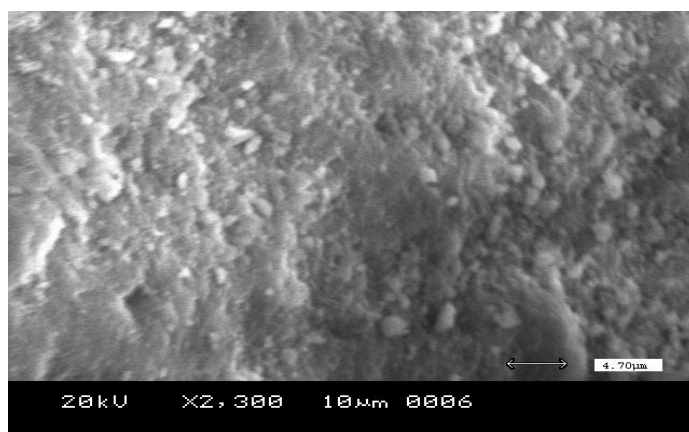

Fig1: ESEM photograph of bone char before adsorption

Fig. 2 shows the removal capacity of fluoride by BF, tourmaline and activated aluminum under different concentrations of fluoride. It appears that adsorption process of fluoride on those three materials depends obviously on initial concentrations of fluoride. As concentration increases, adsorption capacity also increases, but a plateau is gradually reached for all the three materials when the concentration of fluoride is beyond 40 mg/l as shown in Fig. 2.
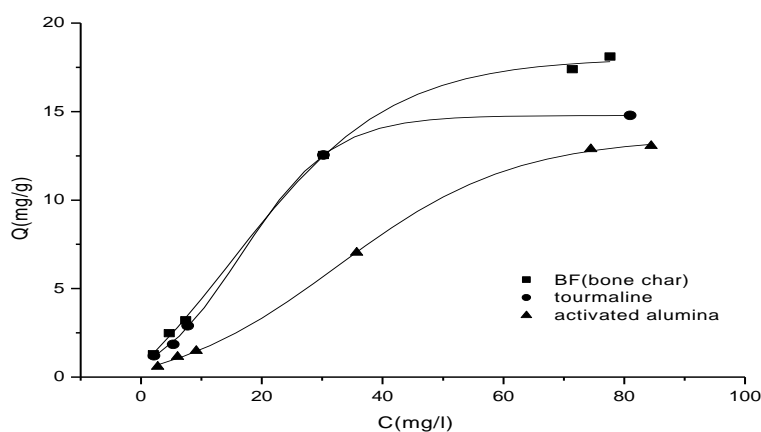
The Freundlich model, which is an indicative of surface heterogeneity of the adsorbent, was used to explain the observed phenomena. The model equations of BF, tourmaline and activated aluminum fit Frendlich model are respectively $q=0.76C^{\frac{1}{1.33}}$, $q=0.62C^{\frac{1}{1.31}}$ and $q=0.21C^{\frac{1}{1.05}}$ and average percent deviations (%) are 3.60, 5.34 and 3.54, respectively. Fig. 3 plotted in the linearity of $\lg q$ versus $\lg c$ predicts the fluoride biosorption data at various initial fluorides with correlative coefficient R^2 of 0.98 ,0.97, 0.98. respectively.
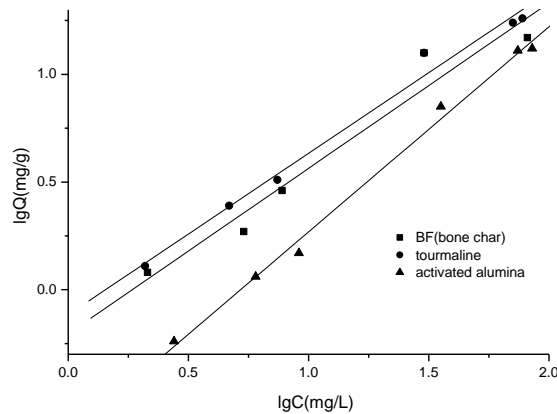

Fig.3. Effect of concentration on removal of fluoride fits on Frendlich model

Three fit equations of Langmuir model for BF, tourmaline and activated aluminum are in turn qe=0.58Ce/(0.02Ce+1), qe=0.49Ce/(0.02Ce+1) and qe=0.19Ce/(0.002Ce+1) with average percent deviations (%) of 12.60, 55.34 and 3.54, respectively. The relation of linearity by plotting C/q versus C is show in the Fig. 4 with correlative coefficient R^2 being 0.98 ,0.97, 0.98 for BF, tourmaline and activated aluminum, respectively.
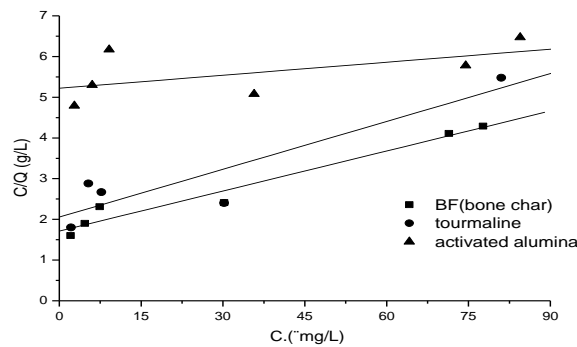

Fig.4. Effect of concentration on removal of fluoride fits on Langmuir model

Comparison of adsorption isotherms between BF and tourmaline as well as activated aluminum shows that the adsorption capacity of BF is better than that of tourmaline and activated aluminum. Considering the BF adsorption mechanism, it is inferred that the active sites of calcium in BF surface can bind fluoride ions. In addition, some anions in BF may function the ion exchange with fluoride ions.

Keeping these in mind, the following reaction mechanism may be supposed:

$$\underline{Ca\text{-}(W)_M} + F^- \longrightarrow \underline{Ca(X+F)_n} + Y^- \qquad (9)$$
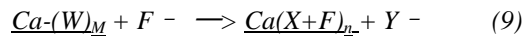
According to the results of the batch tests associated with the consideration of the economical viewpoint, it is fair to conclude that BF exhibits higher removal capacity and is inexpensive. Therefore, three columns, which were packed with BF, were tested for the removal ability of fluoride solution. The fluoride-bearing solution of concentration 9.2mg/l (C_0) was passed through three columns operated simultaneously with samples taken periodically at the end of each column. The operation strategy adopted in this investigation is based on the theoretical description reported by Bohart and Adams (1920) for determining the optimal configuration and operation parameters such as bed height and several flow rate etc.

During the column experiments, constant flow rates were set at υ_1=0.078 L/h•cm^2, υ_2=0.0975 L/h•cm^2 and υ_3=0.156 L/h•cm^2. Experiments were also conducted at different bed height of D_1=2.3cm and D_2=2.8cm. The maximum outlet effluent concentration was specified as not to exceed 1.0mg/l, which is the potable water quality standard for fluoride. When the effluent concentration at each sampling point exceeded this value, i.e. breakthrough point, the operation time was noted as the best service time (t_b). The breakthrough curves developed from the column experiments with different flow rates and bed height are presented in Fig. 5. The relationships between D and t_b for each flow rate are computed and shown as follows:

flow rate	0.078 L/h•cm^2	t_b=102.15D-134.54	(10)
flow rate	0.0975 L/h•cm^2	t_b=62.34D-84.71	(11)
flow rate	0.156 L/h•cm^2	t_b=28.05D-50.82	(12)

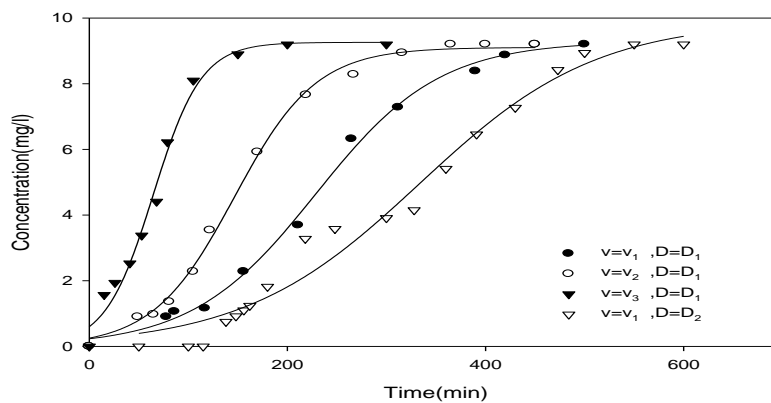
Fig.5.Breakthrough curves for BF biosorption columns fed with fluoride of C_0=9.2mg/l.

As can be expected, both increasing flow rates and decreasing bed height can result in shortening of the breakthrough time and flattening of the breakthrough curve. Respective values of parameter D_{min} were determined from the above equations by solving each equation for D with t_b=0. Respective values of parameters are determined from Equation (5). The fitting curve was close to the experimental one and the trend in residuals is presented in Fig. 6, it shows that average residual less than 4%.
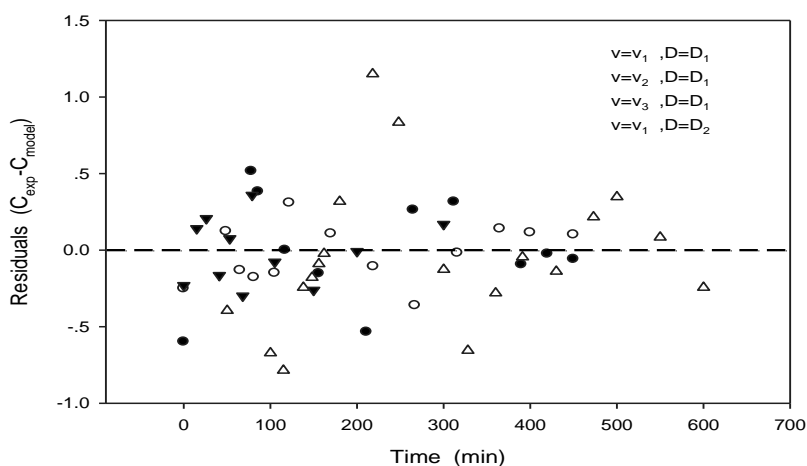
Fig.6. Residuals of the experimental and the mass transfer model calculated fluoride breakthrough curve.

Regeneration of BF was also considered and tested during this study. Regeneration of BF could be achieved by using only one wash step with 0.5% NaOH, followed by water washing under the pH of adjusted less than 9. It had been found that there was no obvious loss of binding capacity of fluoride after BF regeneration.

According to the results from this study, BF is suitable to immobilize fluoride with concentration under 9ml/l. A full-scale application of this research had been carried out in Northeast China, where a concentration of fluoride of about 4mg/l was found in groundwater. A fixed bed of 1T/h had been installed in 2003 for the removal of fluoride by BF, with effluent concentration of fluorides less than 0.8mg/l.

Conclusions

The amorphous biosorbent BF powder can be prepared mainly by heating the biomass-bone, which contains the elements O, Ca and P. The adsorption capacity of BF has been demonstrated to be better than that of tourmaline and activated aluminum. Compared with traditional fluoride removal methods, the BF could be used as a cost-effective biosorbent for efficient fluoride removal in groundwater. Removal of fluoride could be attributed to the processes of ion binding and ion exchange between BF and fluoride. The static and kinetic models were developed, providing a satisfactory prediction on fluoride concentration after adsorption. Experiments have shown that the fixed-bed adsorption capacity depends strongly on the flow rate, inlet fluoride ion, and adsorbent filling height. In addition, the BF can be regenerated by 0.5% NaOH, making it a very potential and promising material for purifying drinking water.

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