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Removal of Fluorine from Water by the Aluminum-Modified Bone Char

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[1]***Abstract:*** **The bone char was modified by $AlCl_3$ and was used to remove the fluorine in the drinking water. The factors of influencing the fluorine removal rate, including the types of the alumium salt, the initial fluorine ion concentration, the mass of the adsorbent and the adsorption time, was studied in the research. The fluorine removal percentage was 97% by 10 g/L modified bone char in the 10 mg/L fluorine solution at pH7, 25±2℃. The results suggest that is an ideal candidate for the treatment of fluorine contaminated drinking water.**

Keywords: fluorine, bone char, modified, adsorption, removal rate

I. INTRODUCTION

Fluorine is one of the necessary microelements that body requires. However, long-term intake of excess fluorine through drinking water can cause many bone diseases [1]. The maximum contaminant level (MCL) for fluorine in drinking water which established by the World Health Organization (WHO) is 1.5 mg/L and is also the China recommended limit [2]. It was estimated that more than 260 million people worldwide consume drinking water with a fluorine content of >1.0 mg/L from all over the world including China, India, Pakistan and Thailand [3, 4].

Various technologies are currently available to remove fluorine from water, such as precipitation [5], membrane processes [6], electrolytic treatment [7], ion-exchange [8], and adsorption [9]. In contrast with these methods, sorption processes are simple to perform, usually inexpensive, and applicable for decentralized water treatment facilities and on-site decontamination [10]. A wide variety of different materials has been proposed for the sorption of pollutants. It has recently been suggested that poorly crystallized apatite, such as bone char (BC) apatite, might represent a low-cost and readily available phosphate source that could be used to as an adsorbent [11]. Bone char, a mixed adsorbent containing around 10% carbon and 90% calcium phosphate, is mainly produced by the carbonization of bones. Its potential as a defluorinating agent and to remove heavy metals from solution has also been reported in the literature [12]. In the present study, BC is used as an inexpensive adsorbent to investigate the effectiveness of using BC for fluorine removal from aqueous solution.

This study is to modify the BC using $AlCl_3$ for substantially enhancing the BC adsorptive capacity for aqueous fluorine ions. The effects of several reaction variables such as the types of the alumium salt, the initial fluorine ion concentration, the mass of the adsorbent and adsorption kinetics on the fluorine removal were evaluated. The removal efficacy of aqueous fluorine ions was determined by batch experiments of adsorptive.

II. EXPERIMENTAL

A. Preparation of the aluminum moified bone char (MBC)

In the present study, the BC (20×40 mesh) was produced from cattle bone (Henan Luohe bone char Ltd.).

The BC was washed with distilled water. One gram of dry based BC was equilibrated with 30mL 1.0 M $AlCl_3$, $AlNO_3$, $NaAlO_2$, $Al_2(SO_4)_3$ solution for 2 h. The slurry was diluted by 3 times using deionized water. After 6 h of agitation, aluminum modified bone char was separated from the mixture, dried at 120℃ and washed with deionized water for 3 times. Then they were dried at 120℃ and stored in a desiccator.

B. Adsorption experiments

Series of experiments were carried out using 100 ml solution of NaF of initial concentration of 10 mg/L using 8 g/L aluminum modified BC to define the factors influencing the sorption process. In this concern, the following conditions were tested: the types of the alumium salt ($AlCl_3$, $Al(NO_3)_3$, $NaAlO_2$, $Al_2(SO_4)_3$), the initial fluorine ion concentration, the adsorbent dosages (0-40 g/L) and adsorption kinetics. The pH of the solutions were adjusted to neutral by dilute NaOH or HCl solutions after the addition of MBC to the solution. After equilibration in a shaker (150rpm) for 72 h at pH 7, 25±2℃, the solution was filtered through 0.2μm membrane filter for aqueous fluorine analysis.

C. Methods of analysis

Fluorine analysis was done by ion selective electrode method using ion meter (Shanghai precise science instrument Co. PRC) coupled with fluorine ion selective electrode (Model pF-1). Blank experiments were conducted throughout the studies and majority of the experiments were re-

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peated twice and it was observed that the experimental error was within ±2%.

III. RESULTS AND DISCUSSION

A. *Effect of alumium salts*

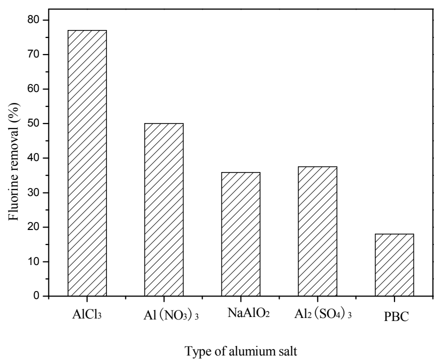

Figure 1. The effect of different alumium salts on the fluorine removal. ($AlCl_3$: $AlCl_3$ modified plain bone char ;PBC: plain bone char)

Batch studies were performed for a total of 4 commercially available alumium salts. Fig.1 gives the results of fluorine by the different alumium salts modified bone char. The $AlCl_3$ modified bone char showed significant fluorine removal rate while $Al_2(SO_4)_3$, $NaAlO_2$ modified bone char exhibited least of four alumium salts. Therefore, The $AlCl_3$ modified bone char was considered as the optimum adsorbent for further adsorption studies. The diversity in the efficiency of fluorine removal may be attributed to their own different anions.

B. *Effect of the initial fluorine ion concentration*

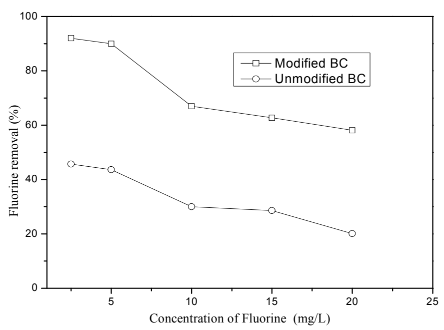

Figure 2. The effect of initial fluorine concentration on the fluorine removal by MBC.

The effect of initial fluorine concentration on the percent removal of fluorine of MBC was studied and is shown in Fig. 2. It was observed that with increase in the initial fluorine concentration, percent removal of fluorine decreases, while the fluorine adsorption capacity increases. This decrease in the percent fluorine removal is obviously due to the availability of more fluorine ions in solution at higher fluorine concentration, which also indicates that the fluorine binding capacity of MBC was almost exhausted. However, at low fluorine concentration, the ratio of surface active sites to total fluorine is high and therefore the interaction of fluorine with the active sites on adsorbent surface was sufficient for efficient fluorine removal.

C. *Effect of adsorbent dosage.*

The minimum amount of adsorbent required to bring down the fluorine concentration below 1.5 mg/L (WHO prescribed limit) was determined by studying the effect of variation in adsorbent dose (0-40 g/L) on fluorine removal efficiency (Fig. 3). It was observed that, fluorine removal efficiency increased from 21% to 95.8% with increase in adsorbent dose of 0-40 g/L of MBC, while it was only half of it in case of plain BC. This increase in the fluorine removal efficiency of MBC with increase in adsorbent dose was obviously due to the enhancement in the number of active sites available for adsorption of fluorine ions. Dilip Thakre et al. have reported maximum of 95.5% fluorine removal for magnesium incorporated bentonite at an initial fluorine concentration of 5mg/L and pH of 2-3 [13]. This pH is very low and cannot be maintained during drinking water defluoridation. The pH of MBC was therefore maintained at 7. In the present study, the fluorine concentration below 1.5 mg/L was achieved at an adsorbent dose of 10 g/L and hence considered as the optimum adsorbent dose for further adsorption studies.

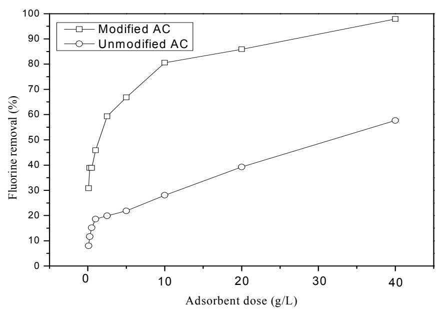

Figure 3. The effect of adsorbent dosage on the fluorine adsorption on MBC

D. Adsorption Kinetics.

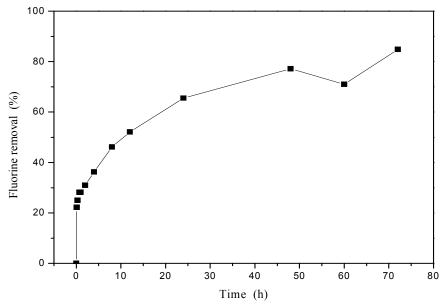

Figure 4. Kinetic of fluorine sorption from aqueous solution by MBC

As shown in Fig.4, the kinetic of fluorine adsorption by MBC included two steps: a fast initial sorption followed by a much slower sorption process. At pH7, approximately 65.5% and 84.9% of fluorine was removed in the first 24 h and 72 h from fluorine solution and adsorption equilibrium was reached in 72 h (~97%). Therefore, 72 h duration was considered as the optimum equilibrium contact time for further adsorption studies. Similar phenomena was also observed for the adsorption of cations (e.g. As^{3+}, As^{5+}, Pb^{2+} and Cd^{2+}) on activated carbon (or peat) and the fast initial sorption was attributed to fast transfer of ions to the surface of adsorbent particles, while the following slow sorption was as a result of the slow diffusion of metal ions into the intra-particle pores of adsorbents [14].

IV. CONCLUSIONS

The MBC was prepared by loading Al^{3+} onto/into bone char and its performance for fluorine removal from drinking water was investigated by batch adsorption experiments. The results showed that the synthesized adsorbent was effective for the removal of fluorine with relatively fast kinetics. In conclusion, there are good prospects for MBC in practical applications for the removal of fluorine from contaminated drinking water.

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