



# Adsorption capacity of bone char for removing fluoride from water solution. Role of hydroxyapatite content, adsorption mechanism and competing anions



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## ABSTRACT

The adsorption of fluoride from water on bone char (BC) was investigated in this work, and the fluoride adsorption capacity of BC was compared to that of hydroxyapatite (HAP). The adsorption capacity of BC and HAP drastically increased while decreasing the pH from 7.0 to 5.0. Furthermore, the fluoride adsorption on BC was due to its HAP content and was not considerably affected by the presence of the anions  $\text{Cl}^-$ ,  $\text{HCO}_3^-$ ,  $\text{CO}_3^{2-}$ ,  $\text{SO}_4^{2-}$ ,  $\text{NO}_3^-$  and  $\text{NO}_2^-$ . The mechanism of fluoride adsorption on BC was attributed to electrostatic interactions between surface charge of BC and fluoride ions in solution.

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## 1. Introduction

The impact of fluoride concentration in drinking water onto human health has been extensively studied and reviewed in various works [1,2]. A concentration of fluoride between 0.5 and 1.5 mg/L is essential for the human body, especially in preventing the incidence of dental caries; however, long term ingestion of water with excess amount of fluoride, above 2 mg/L, can cause diseases such as dental and skeletal fluorosis, masculine infertility and cancer [2].

Several treatment processes have been applied to remove excess fluoride from drinking water. Some of the common processes are chemical precipitation [3], ion exchange [4], adsorption [5,6], reverse osmosis [4], electrodialysis [7] and nanofiltration [8]. Adsorption is the most suitable process for drinking water treatment because it is relatively simple, economic, and appropriate for small communities [9,10].

During the past 10 years, extensive research has been carried out to find both low-cost and high capacity adsorbents for the removal of fluoride from drinking water. A wide range of

adsorbents have been developed and tested, including activated alumina [11], natural minerals such as laterite, zeolite, and caolinite [12–14], nanomaterials [15], carbonaceous materials [7,16], bone char (BC) and hydroxyapatite (HAP) [5,17,18].

BC is manufactured by the carbonization of cattle bones and contains around 10% carbon and 90% HAP [19]. The adsorption of fluoride on BC has been investigated in various works [5,6,18,20]. In a previous work [5], it was shown that the capacity of BC for adsorbing fluoride was higher than those of activated alumina and activated carbon. Furthermore, the effect of solution pH and temperature on the adsorption capacity of fluoride onto BC was investigated and it was found that the maximum adsorption took place at pH 3 and decreased nearly 20 times by increasing the pH from 3 to 12. This behavior was attributed to the electrostatic interactions between the surface of BC and fluoride ions in solution. The adsorption capacity was not influenced by temperature in the range from 15 to 35 °C.

The anions  $\text{HCO}_3^-$ ,  $\text{CO}_3^{2-}$ ,  $\text{Cl}^-$ ,  $\text{NO}_3^-$ ,  $\text{NO}_2^-$ , and  $\text{SO}_4^{2-}$  are commonly found in drinking water and these anions can compete with the fluoride for the adsorption sites of BC, affecting the adsorption capacity of BC toward fluoride. The competing effect of these anions on the capacity of BC for adsorbing fluoride has not been investigated in detail. Due to the high toxicity of As(V), the competitive adsorption of As(V) and fluoride from aqueous

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solution on BC has been studied because it is well documented that fluoride and As(V) may be co-occurring in drinking waters in several countries of Latin America [21]. Mlilo et al. [22] determined the adsorption isotherm of fluoride on BC with and without As(V) and concluded that the As(V) did not affect the fluoride adsorption capacity of BC for an initial concentration of As(V) of 0.250 mg/L.

Calcium hydroxyapatite,  $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$ , is an important inorganic material in biology and chemistry [23–25]. Its structure, ion exchange capacity, adsorption affinity, and its capacity to bond with organic molecules of different sizes, have attracted much attention in the last two decades. The adsorption of heavy metals,  $\text{Pb}^{2+}$ ,  $\text{Cu}^{2+}$  and  $\text{Cd}^{2+}$ , from aqueous solutions on HAP has been attributed to the ion exchange of  $\text{Ca}^{2+}$  on the HAP by the metal cation in solution [26,27]. Adsorption of fluoride on this adsorbent has been studied in several works [17,27] and it has been found that the mechanism of fluoride adsorption is due to electrostatic attractions and ion exchange processes.

BC is mainly composed of HAP and it is essential to evaluate the contribution of this mineral to the adsorption of fluoride on BC. Thus, the main objective of this research was to evaluate the role of HAP on the capacity of BC for adsorbing fluoride from aqueous solution. Furthermore, the mechanism of fluoride adsorption on BC would be elucidated, and the effect of the presence of anions, commonly found in natural waters, on the fluoride adsorption capacity of BC would be analyzed in detail.

## 2. Materials and methods

### 2.1. Bone char and hydroxyapatite

In this work, the granular BC used is commercially known as *Fija Fluor* and is manufactured from cattle bones by APELSA, Guadalajara, Mexico. The BC was sieved to an average particle diameter of 0.79 mm, washed repeatedly with deionized water, dried in an oven at 100 °C for 24 h, and stored in plastic containers. Analytical grade hydroxyapatite (purity < 99% according to the manufacturer, Sigma–Aldrich, CAS Number: 1306-06-5) was also used in this study.

### 2.2. Characterization of bone char and hydroxyapatite

The contents of carbon, hydrogen and nitrogen on BC were determined using an Elemental Analyzer, Fisons Carlo Erba, EA-1108. The phosphorus weight percentage of BC was evaluated by Inductively Coupled Plasma (ICP) Atomic Emission Spectroscopy using a Thermo Jarrel Ash, model IRIS/AP, instrument. The sample was prepared for ICP analysis using the method described by Medellín-Castillo [28].

The surface charge and point of zero charge (PZC) of BC and HAP were determined by a titration method [5]. The acid stability of BC was determined by a procedure similar to that recommended by Wingenfelder et al. [29]. A BC mass of 0.5 g and 40 mL of solution with an initial pH varying from 0.8 to 12.0 were added to a plastic bottle. The solutions were prepared by mixing proper volumes of 0.1 N  $\text{HNO}_3$  and NaOH solutions. The BC and acid solution were left in contact for 7 days and periodically mixed in an orbital shaker, and the final pH of the acid solution was measured. Moreover, the concentration of  $\text{Ca}^{2+}$  and  $\text{PO}_4^{3-}$  dissolved in the acid solutions were determined by atomic absorption spectroscopy and atomic emission spectroscopy.

The morphology of BC and HAP particles were observed by means of a scanning electron microscope (SEM), Philips, model XL-30. The microscope was equipped with an energy dispersive Si(Li) detector EDAX DX4 for microanalysis.

X-ray diffraction (XRD) analysis was used to identify the crystalline species present in both adsorbents employing an X-ray

diffractometer, Rigaku, model DMAX 2000. The textural properties of both materials (specific area, pore volume and average pore diameter) were determined by the  $\text{N}_2$ -BET method using a surface area and porosimetry analyzer, Micromeritics, model ASAP 2010.

### 2.3. Determination of the concentrations of the anions in water solution

The fluoride concentration in an aqueous solution was determined by a potentiometric method using a potentiometer, Orion, model SA720, and a selective electrode for fluoride ion. This method allowed the determination of fluoride concentrations in the range from 0.1 to 10 mg/L. The fluoride calibration curves were prepared with standard solutions of fluoride. Further details of the analytical method can be found elsewhere [28,30].

The concentrations of bicarbonate ( $\text{HCO}_3^-$ ), carbonate ( $\text{CO}_3^{2-}$ ), chloride ( $\text{Cl}^-$ ), nitrate ( $\text{NO}_3^-$ ), nitrite ( $\text{NO}_2^-$ ), phosphate ( $\text{PO}_4^{3-}$ ), and sulfate ( $\text{SO}_4^{2-}$ ) in water solutions were determined using the methods recommended by APHA [30].

### 2.4. Adsorption equilibrium data

Experimental adsorption equilibrium data were obtained as follows. A portion of 490 mL of an aqueous solution of a known initial concentration of fluoride or  $\text{HCO}_3^-$ ,  $\text{CO}_3^{2-}$ ,  $\text{Cl}^-$ ,  $\text{NO}_3^-$ ,  $\text{NO}_2^-$ , and  $\text{SO}_4^{2-}$  was added to the batch adsorber. A given mass of BC or HAP was added to a Nylon basket and placed inside the adsorber. The mass of BC or HAP was 0.5 or 1.0 g, and the initial concentrations of fluoride varied from 1 to 20 mg/L. The adsorber was placed in a constant temperature water bath and the solution was continuously mixed by a magnetic stirrer located just below the water bath. The solution was left in contact with the BC or HAP until equilibrium was reached, which took between 5 and 7 days. The solution pH was measured periodically with a pH-meter and kept constant by adding few drops of 0.01 and 0.05  $\text{HNO}_3$  or NaOH solutions as required. The total volume added of  $\text{HNO}_3$  or NaOH solutions was recorded and considered in the mass balance. The solution was sampled at specific time intervals and the concentration of fluoride was determined for each sample. Equilibrium was reached when the concentrations of two consecutive samples did not change over time. The mass of fluoride or  $\text{HCO}_3^-$ ,  $\text{CO}_3^{2-}$ ,  $\text{Cl}^-$ ,  $\text{NO}_3^-$ ,  $\text{NO}_2^-$ , and  $\text{SO}_4^{2-}$  adsorbed at equilibrium was calculated by performing a mass balance of fluoride or other anions.

The effect of coexisting or competing anions such as chloride on the fluoride adsorption capacity of BC was carried out by determining the adsorption equilibrium data of fluoride at pH = 7.0 and  $T = 25$  °C, and varying the initial concentration of chloride from 20 to 80 mg/L during the adsorption of fluoride.

## 3. Results and discussion

### 3.1. Morphology of BC and HAP

As seen in Fig. 1(a), the forms and shapes of the BC particles are very irregular and its surface is fractured, rough and porous. The distribution of the particle sizes is not uniform. The morphology of the HAP particles is shown in Fig. 1(b), and the particles presented a layered shape that is typical of HAP.

### 3.2. Chemical composition

The elemental analysis of BC showed that the weight percentages of nitrogen, hydrogen and carbon were 0.95, 0.52 and 6.31%, correspondingly. The carbon content is very similar to the value reported by Wilson et al. [31] for a BC manufactured from cattle bones.

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