Adsorptıon of Arsenıc (V) from Drınkıng Water onto Bone Char

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Abstract. The adsorption of As(V) onto the bone char (BC) was investigated in this work as an alternative for removing As(V) from drinking water. This work was aimed at studying the contribution of the hydroxyapatite (HAP) contained in the BC to the adsorption capacity of BC. The adsorption isotherms of As(V) on BC and HAP were determined in a batch adsorber. The effects of temperature and pH on the adsorption capacity were studied in detail. The XRD analysis of BC showed that the main components of BC were HAP $[Ca_{10}(PO_4)_6(OH)_2]$ and calcite $(CaCO_3)$. Besides, the BC surface was examined by TEM analysis and the sheets of HAP were observed in the BC. The adsorption capacity was raised by decreasing the solution pH due to electrostatic interactions between the arsenate anions and the surface of the adsorbents. The adsorption of As(V) was endothermic because the adsorption capacity increased with temperature. The adsorption capacity of HAP towards As(V) was greater than that of BC, and the capacity of BC was dependent on the HAP contained in the BC. The adsorption of As(V) from drinking water samples was carried out and the results showed that the As(V) could be efficiently removed from drinking water.

Keywords: Adsorption, Arsenic, Bone Char, Hydroxyapatite

1. Introduction

Arsenic is an ubiquitous nonmetallic element in the earth's crust, and it can be present in organic or inorganic forms. The concentration of the arsenic in natural waters is very variable, and it depends on the presence of arsenic species in the soil (Mandal and Suzuki, 2012). In the aquatic systems, the arsenic could be present in its four oxidation states (+5, +3, 0, -3). In natural waters, trivalent (arsenites) and pentavalent (arsenates) states are the most common species.

Diverse epidemiological studies have found that the exposure to arsenic via the consumption of drinking water can cause the illness hyperkeratosis and cancer in bladder, lungs, skin, kidneys, liver and prostate. Besides, arsenic exposure has been associated to cardiovascular, pulmonary, immunological, neurological, peripheral vascular and endocrine diseases. The Agency of Environmental Protection of the United States of North America (USEPA) has classified arsenic as cancerogenic in the group A due to the evidence of its adverse effects to human health.

It is very documented in the technical literature that one of the main exposure routes to arsenic is the ingestion of water contaminated with arsenic from natural sources. The removal of arsenic from drinking water can be accomplished by several separation processes such as adsorption, ion exchange, precipitation, filtration and coagulation, reverse osmosis and electrodialysis (Garelick *et al.*, 2005). Adsorption is the preferential accumulation of a pollutant on the surface of a porous solid due to interactions between the surface of the adsorbent and the pollutant. Nowadays, adsorption is considered one of the best methods available to eliminate arsenic from drinking water becuase it can reduce the arsenic concentration to trace leves and its easeness of operation (Leyva-Ramos, 2010). However, it is necessary to investigate and find novel adsorbent materials, which have a high capacity for adsorbing arsenic and adsorbents are inexpensive and efficient.

The cations and anions contaminating water solutions can be eliminated by adsorption on BC. The main constituent of BC is hydroxyapatite (HAP) $[Ca_{10}(PO_4)_6(OH)_2]$, and the adsorption capacity of BC can be attributed to the hydroxyapatite present in the BC (Medellin-Castillo *et al.*, 2014; Wilson *et al.*, 2003).

In recent years, several studies have demonstrated that the removal of fluoride from drinking water can be effectively carried out by adsorption on BC and the adsorption capacity of BC towards fluoride was shown to be dependent on HAP contained in BC. The adsorption of As(V) on BC has been investigated in previous works, but the adsorption mechanism has not been argued in detail (Sneddon *et al.*, 2005). The main objective of this work was to elucidate the adsorption mechanism and to find out the contribution of HAP to the adsorption capacity of BC.

2. Materials and Methods

2.1. Bone Char and Hydroxyapatite

The granular bone char used in this work is commercially known as Fija Fluor and is manufactured from cattle bones by APELSA, Guadalajara, Mexico. Analytical grade

hydroxyapatite (purity < 99 %), CAS Number: 1306-06-5), was supplied by Sigma-Aldrich.

2.2. Characterization of Bone Char

The morphology of the BC particles was examined using a scanning electron microscope (SEM), Philips, model XL-30, while the HAP particles were analyzed with an SEM, JEOL, model JSM-6610LV.

The textural properties such as surface area, pore volume and average pore diameter were determined by the N_2-BET method using a surface area and porosimetry analyzer, Micromeritics, model ASAP 2020.

X-ray diffraction (XRD) analysis was used to identify the crystalline species present in both adsorbents employing an X-ray diffractometer Bruker, model D8 Advance.

The concentrations of acidic and basic sites in BC and HAP were determined by the acid-base titration method proposed by Boehm (1994). The surface charge and point zero charge (pH_{PZC}) were quantified by a titration method. The surface charge was calculated from the potentiometric curves of the solutions with and without adsorbent, and the procedure and equation were described elsewhere (Medellin-Castillo *et al*., 2014), and the surface charge versus pH was graphed to obtain the surface charge distribution.

2.3. Determination of the concentration of the As(V) in water solution

The concentration of As(V) in an aqueous solution was quantified by an Atomic Fluorescence Spectrophotometric method. The emission intensity of a sample was determined in an atomic fluorescence spectrophotometer, Millenium Excalibur PSA, and As(V) concentration in a sample was calculated from a calibration curve, which was prepared with standard solutions of As(V) with concentrations ranging from 2 and 60 µg/L.

2.4. Adsorption equilibrium data

A solution of known initial concentration of As(V) was prepared in a 50 mL volumetric flask, and a sample of 10 mL was taken to corroborate its initial concentration. The remaining 40 mL of the solution and a particular mass of the BC or HAP were added to a batch adsorber, which consisted of a 50 mL plastic centrifuge vial. The adsorber was placed in a constant temperature water bath, and the solution in the adsorber was stirred by placing the adsorber in an orbital shaker for 20 minutes three times daily. The solution pH was periodically measured and kept constant by adding few drops of 0.01 N HNO_3 or NaOH solutions, as needed. The adsorber solution was left in contact with the adsorbent until equilibrium was reached. In preliminary runs, it was found that seven days was enough to attain equilibrium.

3. Results and Discussion

3.1. Characterization by Scanning Electron Microscopy (SEM)

The surface and morphology of the BC and HAP particles can be observed in the SEM images shown in Figures 1 and 2, respectively. As seen in Figure 1, the shape of the BC particles is very irregular, and the particle size distribution is not uniform. Moreover, the surface is heterogeneous due to the conglomerates and intercrystalline spaces formed by the HAP and calcite crystals.
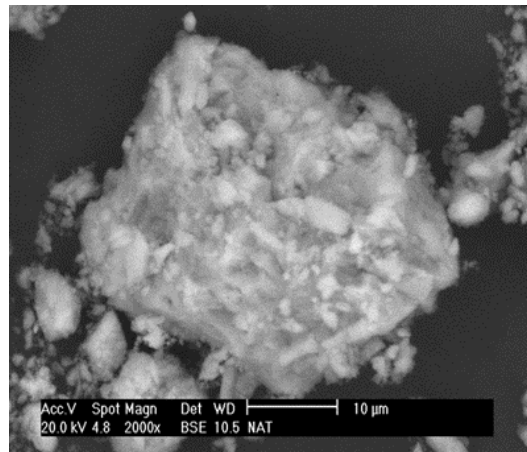

Figure 1. SEM image of BC, magnification=2000×.

The laminar morphology observed in Figure 2 is typical of HAP particles. The size of the HAP particles varies considerably, and the shape of particles is a well-defined layered structure.
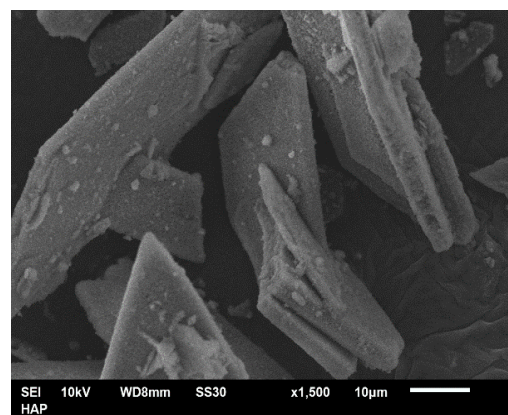

Figure 2. SEM image of HAP, magnification = 1500×.

3.2. Textural Properties

The surface area, mean pore diameter and pore volume of BC and HAP are listed in Table 2. Several authors have reported that the surface area and pore volume of BC ranged from 69 to 117 m^2/g and from 0.225 and 0.64 cm^3/g, respectively (Medellin-Castillo *et al*., 2014; Wilson *et al*., 2003). The values of the surface area and pore volume of BC found in this work are within these ranges. According to the IUPAC classification of pores, both materials can be considered mesoporous since their mean pore diameters (Table 1) are within the range of 2-50 nm.

Table 1. Textural properties of BC and HAP.

Adsorbent	Surface Area (m^2/g)	Pore Volume (cm^3/g)	Average Pore Diameter (nm)
BC	75	0.23	12.3
HAP	18	0.12	26.7

3.3 XRD analysis of BC and HAP

The XRD pattern of BC is depicted in Figure 3. The crystalline species were identified comparing the characteristic peaks shown in the XRD pattern with the database of the diffractometer (Journal of Crystallographic Powder Diffraction Spectra). The characteristic peaks corroborated the presence of HAP and Calcite. The distinctive peaks of HAP occur at the 2Θ values of 25.9°, 31.7°, 46.7° and 49.5° (Medellin-Castillo *et al.*, 2014). Comparing the XRD pattern of BC to that of HAP, it can be noticed that BC is mainly composed of HAP, but the relative intensities of the characteristic peaks for BC are slightly different from those of the HAP due to HAP content in BC and the presence of Calcite and carbon in BC.
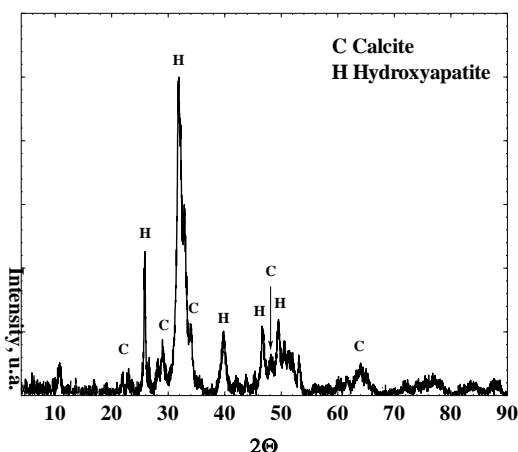

Figure 3. XRD pattern of BC.

3.4. Physicochemical Properties of Surface

The concentrations of the acidic and basic sites for the BC were 0.25 and 2.11 meq/g and for the HAP were 1.10 and 0.78 meq/g, respectively. Thus, the surface of BC was basic, whereas the surface of HAP was slightly acidic.

The surface charge of an adsorbent is due to the interactions between the ions present in the solution and the functional groups on the surface. The surface charge is important to explain the adsorption of ions on BC and HAP and is dependent on the type of ions present in solution, surface properties, and solution pH. The surface is positively charged when the solution pH is below the point of zero charge (pH_{PZC}), negatively charged at pH above the pH_{PZC}, and neutral when the pH is equal to the pH_{PZC}. The pH_{PZC} of BC was 8.9, while that of HAP is 7.5.

3.5 Effect of the HAP content on the Adsorption Capacity of BC towards As(V)

The adsorption isotherms of As(V) from aqueous solutions on BC and HAP were determined at T = 25 ºC and pH = 7, and the adsorption equilibrium data and the adsorption isotherms on BC and HAP are graphed in Figure 4. In this work, the adsorption isotherms of As(V) on BC and HAP were interpreted using the Freundlich, Langmuir and
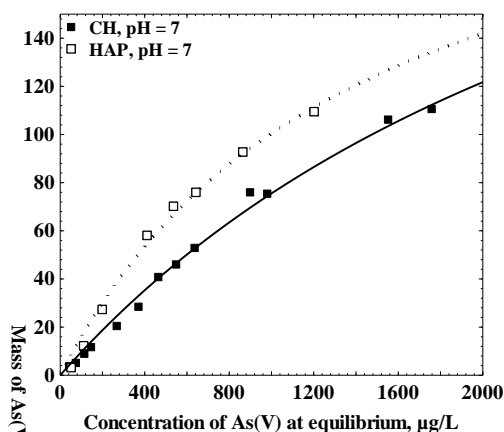
Radke-Prausnitz (R-P) isotherms, and the R-P isotherm best fitted the As(V) adsorption equilibrium data on both adsorbents.

Figure 4. Adsorption isotherms of As(V) on BC and HAP at T = 25 ºC. The lines represent the R-P isotherm.

The capacity of HAP for adsorbing As(V) was greater than that of BC. The adsorption capacities were compared calculating the uptake of As(V) adsorbed on each adsorbent at an equilibrium concentration of As(V) of 300 µg/L and this uptake was denoted as Q_{300}. The values of Q_{300} for BC and HAP were 27.3 and 42.5 µg/g, respectively. The ratio of Q_{300} for BC to that for HAP is 0.64, which is very close to the weight fraction of HAP in BC ranging from 0.70 to 0.75. Thus, the capacity of BC for adsorbing As(V) was highly dependent on the HAP content in BC. This result is in agreement with the results reported by Medellin-Castillo *et al*. (2014) for the adsorption of fluoride on BC.

3.6. Effect of Solution pH on the Adsorption Capacity of BC and HAP

The effect of the solution pH on the adsorption capacity of BC and HAP towards As(V) was investigated by determining the adsorption isotherms of As(V) on both adsorbents at T = 25 °C and pH of 5, 7 and 9. This effect is illustrated in Figure 5 for the adsorption on BC, and it can be noticed that the adsorption capacity was considerably decreased when the pH was raised from 5 to 9. The values of Q_{300} for BC were 40.6, 27.3 and 16.8 µg/g at pH of 5, 7 and 9, respectively, revealing that the adsorption capacity of BC was reduced 2.4 times. A similar trend was observed for the adsorption capacity of HAP, and its adsorption capacity was decreased 2.1 times.

The effect of pH on the adsorption capacity was attributed to the electrostatic interaction between the anionic species of As(V) and the surface of BC. The predominant species of As(V) were dihydrogen arsenate ($H_2AsO_4^-$), and hydrogen arsenate ($HAsO_4^{2-}$) at pH = 5 and pH = 9, respectively, and both species were almost equally present at pH = 7 (Mendoza-Barron *et al.*, 2011). The surface of BC was positively charged for pH below pH_{PZC} = 8.9 and decreased while increasing the pH from 5 to 9. Thus, the electrostatic attraction between the anions of As(V) and the positively charged surface of BC was disfavored by increasing the pH and resulted in a reduction of the adsorption capacity.
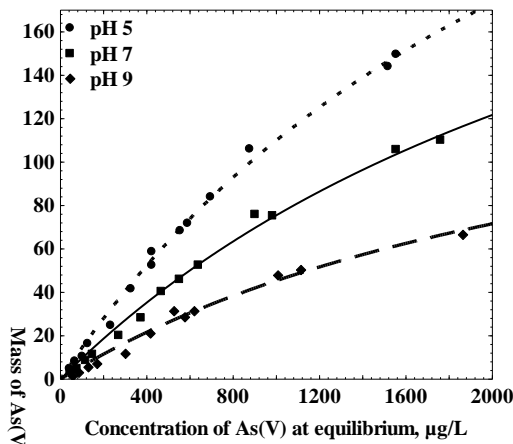

Figure 5. Effect of pH on the adsorption isotherms of As(V) on BC at T = 25 °C. The lines represent the R-P isotherm.

3.7. Effect of Temperature on the Adsorption Capacity of BC and HAP

Normally, the adsorption capacity is dependent on the temperature, and it is important to study the dependence of the adsorption capacity with respect to the temperature. The adsorption equilibrium data and adsorption isotherms of As(V) on BC were obtained at pH = 7 and temperatures of 15, 25 and 35 °C, and are depicted in Figure 6. The values of Q_{300} for BC were 19.3, 26.8 and 65.1 μg/g at the temperatures of 15, 25 and 35 °C, respectively. These results indicate that the adsorption capacity of BC towards As(V) was favored nearly 3.4 times when the temperature was increased from 15 °C to 35 °C. The dependence of the adsorption capacity of HAP presented a very similar trend. Therefore, the adsorption of As(V) on BC and HAP was endothermic.
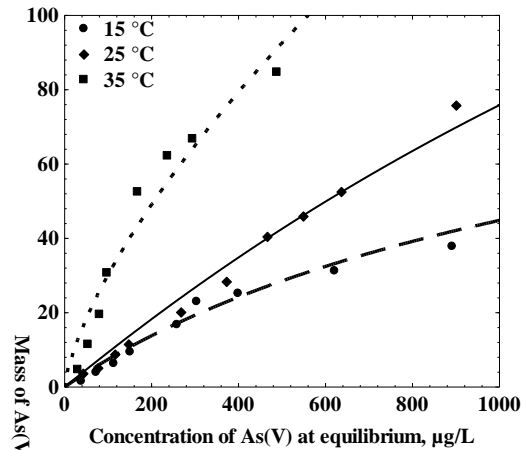
3.8 Adsorption Mechanism of As(V) on BC

The negative charge of the BC surface resulted from the following protonation reactions of the phosphate, ≡P-OH, and hydroxyl, ≡Ca-OH, groups in the HAP contained in BC (Medellin-Castillo *et al.*, 2014):

$$\equiv P\text{-}OH + H^+ \rightarrow \equiv POH_2^+$$

$$\equiv Ca\text{-}OH + H^+ \rightarrow \equiv Ca\text{-}OH_2^+$$
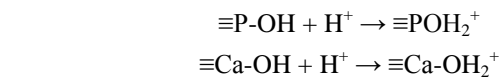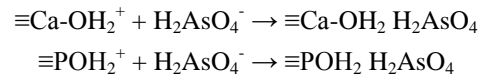
Figure 6. Effect of temperature on the adsorption isotherms of As(V) on BC at pH = 7. The lines represent the R-P isotherm.

The electrostatic attraction between $H_2AsO_4^-$ and $HAsO_4^{2-}$ and negative surface of BC was one of the main adsorption mechanism. In the case of $H_2AsO_4^-$, this mechanism can be represented as follows:

$$\equiv Ca\text{-}OH_2^+ + H_2AsO_4^- \rightarrow \equiv Ca\text{-}OH_2\ H_2AsO_4$$

$$\equiv POH_2^+ + H_2AsO_4^- \rightarrow \equiv POH_2\ H_2AsO_4$$

Other mechanisms contributing to the adsorption of As(V) were ion exchange and chemisorption.

3.8. Removal of As(V) from Water for Human Consumption

The BC was tested for removing As(V) from a water sample for human consumption that was collected from a well in the city of San Luis Potosi, Mexico. The concentration of As(V) in the well sample was 24.8 μg/L and was caused by natural pollution. The adsorption isotherm of As(V) on BC was obtained using the well water sample and is graphed in Figure 7. The capacity of BC for adsorbing As(V) from well water was favored by the presence of other compounds in the well water. This effect can be due to an enhancement of the electrostatic attraction between As(V) anions and the surface of BC.
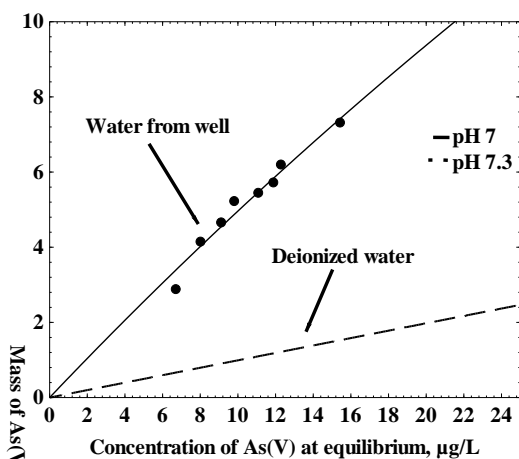
Figure 7. Adsorption isotherms of As(V) on BC from solutions prepared using deionized water and water sample from a well naturally polluted with As(V).

The mass of BC required for treating a volume of 1 L of well water to reduce its concentration to 10 μg/L, was estimated to be 3.4 g. The capacity of BC for adsorbing As(V) was reasonably enough to remove As(V) from well waters having concentrations of As(V) bellow 100 μg/L.

Conclusions

The XRD analysis confirmed that the main component of BC was HAP, and that calcite was also present. The characterization of BC and HAP revealed that both materials are mesoporous, and the surface of BC was basic and that of HAP was slightly basic. The surface of BC was positively charged due to the protonation of the phosphates and hydroxyl groups of the HAP contained in BC.

A comparison of the adsorption capacities of BC and HAP towards As(V) revealed that the capacity of BC for adsorbing As(V) could be attributed to the HAP contained in BC. The predominant adsorption mechanism was electrostatic attraction between the anionic species of As(V) in solution and the positive charge of the BC surface. The adsorption sites for this mechanism were the protonated phosphates and hydroxyl groups of HAP.

The adsorption capacity of BC towards As(V) was considerably reduced by increasing the solution pH. This effect was due to a decrease in the electrostatic attraction caused by a reduction in the positive charge of BC surface. The adsorption of As(V) on BC and HAP was endothermic so that the adsorption capacity of both adsorbents towards As(V) from aqueous solution was promoted by increasing the temperature.

The adsorption on BC can be effectively applied to remove As(V) from well water polluted naturally, and the presence of other compounds in the well water favored the adsorption capacity of BC.

Acknowledgments

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