Adsorption of Fluoride from Water Solution on Bone Char

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The effects of solution pH and temperature on the adsorption of fluoride onto bone char made from cattle bones were investigated in this work. It was found that the maximum adsorption took place at pH 3 and the adsorption capacity decreased nearly 20 times augmenting the pH from 3 to 12. This behavior was attributed to the electrostatic interactions between the surface of bone char and the fluoride ions in solution. The adsorption capacity was not influenced by temperature in the range from 15 to 35 °C. A comparison of fluoride adsorption capacities among several adsorbents revealed that the adsorption capacity of the bone char was 2.8 and 36 times greater than those of a commercial activated alumina (F-1) and a commercial activated carbon (F-400). The adsorption capacity is considerably dependent upon the physicochemical properties of the bone char surface and the solution pH.

1. Introduction

The level of fluoride in drinking water is a very important factor in evaluating the quality of water for human consumption. Depending on the level of fluoride, the ingestion of fluoride-containing drinking water can be either beneficial or detrimental to human health. The World Health Organization has recommended a fluoride concentration of 1.5 mg/L in drinking water. The optimum fluoride level in drinking water is dependent on the mean annual temperature and ranges from 0.7 to 1.2 mg/L in USA.[1] The consumption of drinking water with a fluoride concentration below the optimum level does not help preventing dental cavities. On the other hand, long-term ingestion of water with excessive amounts of fluoride can cause dental fluorosis if it is above 2 mg/L and skeletal fluorosis when it is higher than 4 mg/L.[2]

Many methods have been applied to remove excessive fluoride from drinking water. The current treatment methods are chemical precipitation with calcium and aluminum salts,[3] ion exchange using polymeric resins,[4] adsorption on activated alumina,[3] reverse osmosis,[5] and electrodialysis.[6] The adsorption on activated alumina is one of the most promising processes for fluoride removal because activated alumina exhibits high selectivity for fluoride in water solutions.

Various low-cost materials have been tested for removing fluoride from drinking water, but these materials cannot be applied because their fluoride adsorption capacities are not high enough. Among these materials are bentonite, kaolinite and nirmali seeds,[7] China clay,[8] calcite, hydroxyapatite, fluorspar and quartz,[9] kaolinite and montmorillonite,[10] and tree leaves.[11] Mixed rare earth oxide and laterite, naturally occurring materials in southern and eastern India, respectively, are the only natural materials exhibiting exceptionally high fluoride adsorption capacities.[12,13]

Novel adsorbents for fluoride removal from water solutions have been prepared by impregnating alumina,[14] chelating resins,[15] cross-linked gelatin,[16] and silica gel[17] with rare earth elements. Recently, amorphous alumina supported on carbon nanotubes,[18] aligned carbon nanotubes,[19] ion exchange polymeric fiber,[20] and an ion exchanger based on a double hydrous oxide of Al and Fe ($Fe_2O_3Al_2O_3xH_2O$)[21] have been assayed for removing fluoride from drinking water as well as industrial wastewater. All these adsorbents have shown very promising fluoride adsorption capacities, in some cases many times higher than that of activated alumina, but nowadays they are too expensive to be considered for drinking water treatment. Thus, it is important to develop or find cheaper adsorbents for fluoride removal from water solutions that have fluoride adsorption capacities greater than that of activated alumina.

Sorption on bone char, manufactured by the pyrolysis of crushed cattle bone, had been somewhat used to defluoridate drinking water since 1953. However, this process was abandoned due to cost of the adsorbent and regeneration chemicals. Furthermore, bone char has not been applied broadly due to the problems related to the bad taste of the treated water, and the availability, cost, and quality of this adsorbent material.[22] Nowadays, bone char is being reconsidered as a potential adsorbent for defluoridation of drinking water since bone char can be manufactured in a sufficient amount and quality.

Adsorption of fluoride on bone char has been studied in previous works,[23] and it has been found that fluoride can be effectively removed from water solutions by adsorption on bone char. However, the mechanism of fluoride adsorption on bone char has not been completely elucidated, and the effect of pH on the adsorption isotherm has not been explained on the basis of the interactions between fluoride ions in the solution and surface charge of the bone char.

The main aim of this work is to study the capacity of bone char to adsorb fluoride, as well as the effects of solution pH and temperature on the adsorption capacity. The interactions

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between the bone char surface and the fluoride ions in solution are also investigated to better understand the adsorption and desorption of fluoride adsorbed on bone char. The capacity of bone char for adsorbing fluoride is compared to those of traditional adsorbents as well as novel adsorbents.

2. Materials and Methods

2.1. Bone Char. The granular bone char used is commercially known as Fija Fluor and is manufactured from cattle bones by APELSA, Guadalajara, Mexico. The bone char 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.

2.2. Determination of Textural and Physicochemical Properties of Bone Char. The textural properties of the bone char were determined by the N_2-BET method using a surface area and porosimetry analyzer, Micromeritics, model ASAP 2010. The morphology of the bone char was examined by means of a scanning electron microscope, Philips, model XL-30. The microscope was equipped with an energy dispersive Si(Li) detector EDAX DX4 for microanalysis.

Acidic and basic sites on bone char were determined by the acid−base titration method proposed by Boehm.[24] The acid sites were neutralized with a 0.1 N NaOH solution and the basic sites with a 0.1 N HCl solution. The acidic and basic sites were determined by adding 50 mL of 0.1 N titrating solution and 1 g of bone char to a 50 mL volumetric flask. The flask was partially immersed in a constant temperature water bath set at 298 K, and it was left there for 5 days. The flask was agitated manually twice a day. Afterward, a sample of 10 mL was taken and titrated with 0.1 N HCl or NaOH solution. The titration was carried out by triplicate using a potentiometer, Orion, model EA940.

The point of zero charge (PZC) and the surface charge for the bone char were determined by the following procedure reported by Babic et al.:[25] 0.1 g of bone char ground in an agate mortar and 20 mL of a 0.01 N KCl−0.004 N KOH solution were added to a glass beaker. The solution was mixed continuously for 48 h. Then, the solution containing the bone char was titrated with a 0.1 N HCl solution using a buret and bubbling N_2 to prevent the CO_2 present in the air from absorbing in the solution and forming CO_3^{-2} and HCO_3^{-1}. The titrating solution was added slowly, 0.1 mL for addition every 10 min, and the volume of the titrating solution added and the solution pH were recorded. This is the titration curve with bone char. On the other hand, the 0.01 N KCl−0.004 N KOH solution was also titrated under the same conditions but without bone char to obtain the titration curve without bone char. The PZC was the pH at which the titration curve with bone char intersected the titration curve without bone char.

2.3. Determination of Fluoride in Water Solutions. The fluoride concentration in an aqueous solution was measured by a potentiometric method using an Orion, model SA720, potentiometer with a fluoride ion selective electrode. This method allowed the determination of fluoride concentrations in the range from 0.1 to 5.0 mg/L. The method required calibration curves prepared with standard solutions of fluoride.

2.4. Determination of Competing Anions in Drinking Water. The concentrations of bicarbonate, carbonate, chloride, nitrate, nitrite, phosphate, and sulfate in drinking water were determined using the methods recommended by APHA.[26]

2.5. Adsorption Equilibrium Data. Adsorption equilibrium data were obtained using an experimental batch adsorber consisting of a 500 mL polyethylene container. The aqueous solution of fluoride and a basket made of Nylon mesh containing the granular bone char were placed together inside the plastic container such that the aqueous solution completely covered the bone char. The adsorber was then capped and was partially submerged in a constant temperature water bath placed over a magnetic stirrer. The adsorber solution was stirred continuously with a Teflon coated stirring bar.

Experimental adsorption equilibrium data were obtained as follows. A 480 mL portion of an aqueous solution of a known initial concentration of fluoride was added to the batch adsorber. A predetermined mass of bone char was added to a Nylon basket and placed inside the adsorber. The bone char doses were 0.5 or 1.0 g, and the initial concentrations of fluoride varied from 1 to 20 mg/L, respectively. The solution remained in contact with the bone char until equilibrium was reached. In a kinetic run it was found that the actual time to reach equilibrium was slightly greater than 1 day so a period from 2 to 3 days was enough to ensure that adsorption equilibrium was attained. The solution pH was measured periodically with a pH-meter and kept constant by adding 0.01, 0.05, and 0.1 N HNO_3 or NaOH solutions as required. The total volume added of the HNO_3 or NaOH solutions was recorded to be considered in the mass balance. The solution was sampled at certain time intervals, and the fluoride concentration of each sample was determined as described previously. Equilibrium was reached when the concentrations of two consecutive samples did not change over time. The mass of fluoride adsorbed at equilibrium was calculated by performing a mass balance of fluoride.

2.6. Desorption Equilibrium Data. The reversibility of fluoride adsorption on bone char was investigated by carrying out desorption experiments which consisted of performing an adsorption experiment as already described. Once equilibrium was reached, the Nylon basket containing the bone char saturated with fluoride was removed from the solution, washed with deionized water to eliminate the fluoride solution caught between the bone char external walls, and then placed inside a batch adsorber containing 480 mL of a desorbing solution without fluoride. The washing step was achieved by submerging the Nylon basket with the bone char into deionized water for 5 s. The saturated bone char and the desorbing solution were left in contact for 3 days until they reached new equilibrium; it was assumed that new equilibrium was reached when the fluoride concentration of two consecutive samples remained constant. The initial pH of the desorbing solution was 7 or 12, and the pH was kept constant during desorption, by adding 0.1 and 0.01 N HNO_3 or NaOH solutions. The mass of fluoride that remained adsorbed on the bone char was estimated by a mass balance.

3. Results and Discussion

3.1. Characterization of Bone Char by Scanning Electron Microscopy. The surface, morphology, and size distribution of the bone char particles were observed by means of a scanning electron microscope (SEM). The morphology of the bone char particles is shown in Figure 1, and it can be observed that the particles presented a fractured and porous surface. The forms and sizes of the particles are very irregular.

The elemental chemical composition of the bone char surface was determined by means of the X-ray microanalysis probe (EDS) coupled to the microscope, and the spectrum is presented in Figure 2. The elemental chemical analysis revealed that the bone char was composed of P, Ca, C, O, Si, Al, Na, and Mg. This is due to the main components of bone char being the hydroxyapatite ($Ca_{10}(PO_4)_6(OH)_2$), carbon, and calcite ($CaCO_3$), and their weight percentages may be up to 76%, 11%, and 9%, respectively.[27]

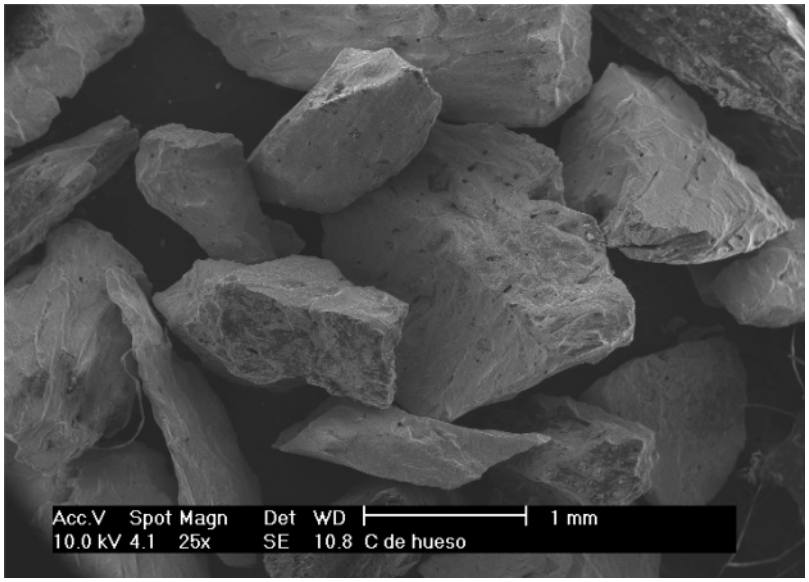

Figure 1. Scanning micrograph of the bone char Fija Fluor particles.

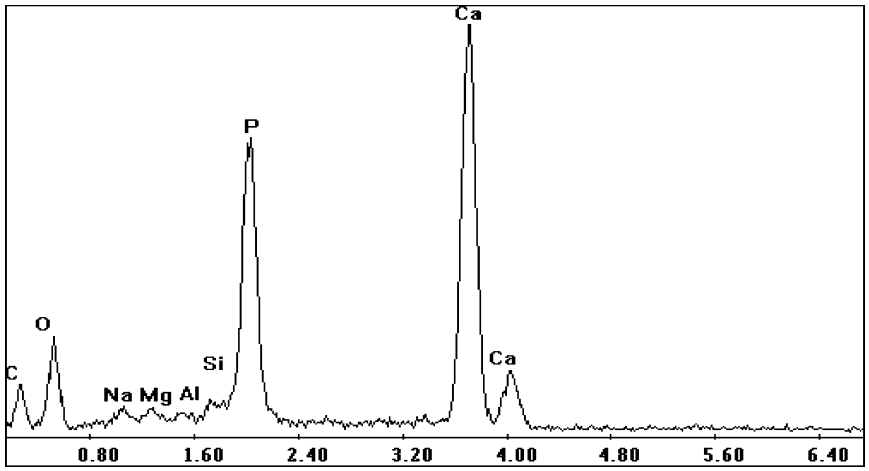

Figure 2. Energy dispersive spectrum of the bone char Fija Fluor.

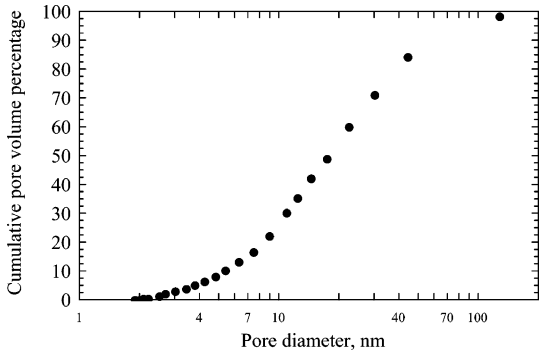

Figure 3. Pore volume distribution of the bone char Fija Fluor.

3.2. Textural Properties of Bone Char. The specific surface area, pore volume, and average pore diameter of the bone char Fija Fluor were determined to be 104 m^2/g, 0.30 cm^3/g, and 11.1 nm, respectively. The textural properties of bone char have been reported in various works,[28−30] and the values are very similar to those presented in this work.

The pore size distribution of bone char Fija Fluor is displayed in Figure 3, and it can be observed that the mesopores (2 nm < pore diameter <50 nm) represented approximately 89% of the total pore volume of the bone char whereas the macropores represent only 11%. This indicated that the porous structure of the bone char was mainly composed of mesopores agreeing with the results reported by other authors.[30]

3.3. Surface Properties of Bone Char. The concentrations of the acidic and basic sites for the bone char Fija Fluor were 0.29 and 0.62 meq/g, respectively. The concentration of acidic sites was below the value reported for a bone char,[23] and that of basic sites was very closed to the value reported for a bone char.[23] The basic and acid sites are formed by the protonation and deprotonation of the hydroxyapatite surface hydroxyl groups.[31] These reactions are illustrated as follows

$$\equiv Ca-OH + H^+ \rightarrow \equiv Ca-OH_2^+ \quad (1)$$

$$\equiv P-OH \rightarrow \equiv PO^- + H^+ \quad (2)$$

where $\equiv$ represents the hydroxyapatite surface. Furthermore, some of the oxygenated groups attached to the carbon may also be deprotonated and protonated to form acidic and basic sites.

Surface charge on the bone char is due to the interactions between the ions present in the solution and the functional groups on the bone char surface. The surface charge is important to explain the adsorption of ions on bone char and is dependent on the type of ions present in solution, surface properties, and solution pH. The distribution of the surface charge with respect to the solution pH is shown in Figure 4. The surface is positively

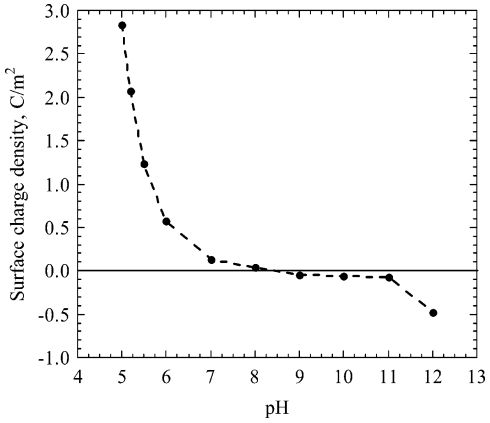

Figure 4. Surface charge distribution of the bone char Fija Fluor.

Table 1. Langmuir and Freundlich Isotherm Constants

		Langmuir			Freundlich		
T (°C)	pH	q_m (mg/g)	K (L/mg)	%D	K (mg$^{1-1/n}$L$^{1/n}$/g)	n	%D
15	7	6.05	0.55	6.04	2.36	2.94	3.7
25	3	11.9	2.58	10.4	6.77	3.29	4.9
	5	7.74	1.55	16.4	3.96	3.28	6.9
	7	5.44	1.22	16.0	2.71	3.52	4.6
	10	2.31	0.52	5.28	0.87	2.95	4.2
	11	4.04	0.05	17.3	0.27	1.45	9.2
	12	1.33	0.15	11.5	0.23	1.92	4.5
35	7	5.07	1.68	12.4	2.67	3.55	3.5

charged when the solution pH is below the point of zero charge (PZC), negatively charged at pH above the PZC, and neutral when the pH is equal to the PZC. As shown in Figure 4, the PZC was approximately 8.4.[32] Besides, the PZC of bone char was basic because the concentration of basic sites was greater than that of acidic sites.

3.4. Adsorption Isotherm of Fluoride. The isotherm models of Langmuir and Freundlich were used to fit the experimental adsorption equilibrium data of fluoride on bone char. These models are represented mathematically as follows:

$$q = \frac{q_m KC}{1 + KC} \tag{1}$$

$$q = kC^{1/n} \tag{2}$$

where C (mg/L) is the concentration of fluoride at equilibrium, K (L/mg), and q_m (mg/g) are the Langmuir constants related to the energy of adsorption and maximum capacity, respectively; k (mg$^{1-1/n}$ L$^{1/n}$ g^{-1}) and $1/n$ are the Freundlich constants related to the adsorption capacity and intensity, respectively; and q (mg/g) is the mass of fluoride adsorbed per mass of adsorbent.

The constants for these isotherms were evaluated by a least-squares method based on an optimization algorithm and are shown in Table 1 along with the average absolute percentage deviation, %D, which is defined as follows:

$$\%D = \sum_{i=1}^{N} \left| \frac{q_{exp} - q_{pred}}{q_{exp}} \right| \times 100\% \tag{3}$$

where N is the number of experimental data points, q_{exp} (mg/g) is the experimental mass of fluoride adsorbed, and q_{pred} (mg/g) is the mass of fluoride adsorbed predicted with the isotherm model.

Both isotherm models were fitted reasonably well to the experimental adsorption equilibrium data since the percentage deviation was less than 17.3% for the Langmuir isotherm and less than 9.2% for the Freundlich isotherm. The isotherm best fitting the experimental data was assumed to be that having the lowest average absolute percent deviation. As shown in Table 1, all the experimental data were better fit to the Freundlich isotherm. Recently, Abe et al.[23] reported that the Freundlich isotherm fitted satisfactorily the equilibrium adsorption data of fluoride on various carbonaceous materials including bone char. Moreover, the Langmuir isotherm was not chosen because the experimental data did not exhibit the asymptotic behavior at higher concentrations that is typical of the Langmuir isotherm.

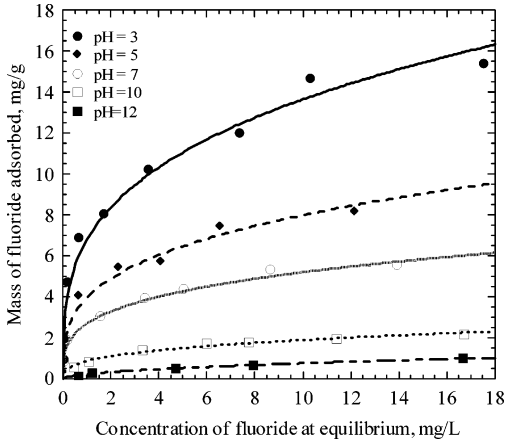

Figure 5. Effect of pH on the adsorption isotherm of fluoride on the bone char Fija Fluor at $T = 25$ °C. The lines represent the Freundlich isotherm.

3.5. Effect of Solution pH on the Adsorption Isotherm. The effect of pH was investigated by determining the adsorption isotherm of F^- on the bone char Fija Fluor at the pH values of 3, 5, 7, 10, 11, and 12, and the results were plotted in Figure 5. No adsorption experiments were carried out at pH greater than 12 since at these conditions fluoride was adsorbed very slightly. In this figure, it can be noticed that the adsorption capacity of bone char was affected significantly by the solution pH. The results also revealed that the maximum adsorption capacity occurred at pH = 3 and that the adsorption capacity diminished drastically while increasing the pH from 3 to 12. The adsorption equilibrium data was not obtained at pH < 3 since it was noticed that the bone char was slightly dissolved at pH < 3.

In the adsorption experiments, the solution pH changed as fluoride adsorption progressed, necessitating addition of 0.1 and 0.01 N HNO_3 or NaOH solutions to keep the pH constant. The solution pH always increased during the adsorption at pH ≤ 7, but always diminished slightly at pH ≥ 8. This observation indicates that the H^+ ions were adsorbed on the bone char at pH ≤ 7 causing an increase in the pH while the H^+ ions were released at pH ≥ 8 causing a decrease in the pH. This behavior is due to the amphoteric character of the bone char since it has both acidic and basic sites.

The effect of pH on the adsorption isotherm was due to electrostatic interactions between the F^- anions in solution and the surface charge of bone char. When the solution pH is below the PZC of 8.4, the F^- anions were attracted to the positively charged surface of the bone char, caused by the protonation of the hydroxyapatite hydroxyl groups, thus favoring F^- accumulation onto the surface. The surface charge of bone char became more positively charged while decreasing the pH below its PZC. Hence, more F^- anions were attracted to the surface causing an increase in the adsorption capacity of the bone char. At pH above the PZC, adsorption of F^- was very slight because the bone char surface was negatively charged, due to deprotonation of the hydroxyapatite hydroxyl groups, causing a mutual repulsion between F^- anions and the bone char surface. If

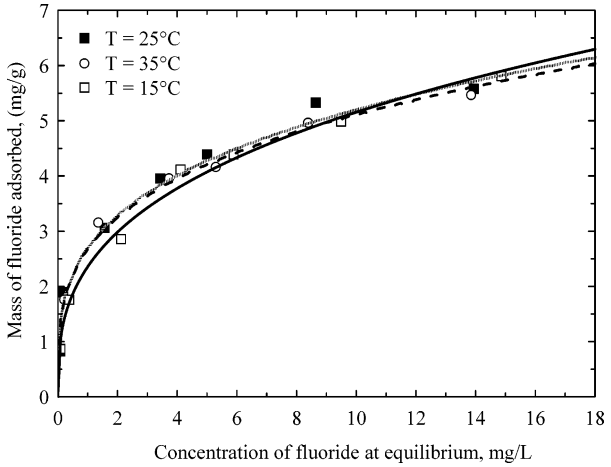

Figure 6. Effect of temperature on the fluoride adsorption isotherm on the bone char Fija Fluor at pH = 6.

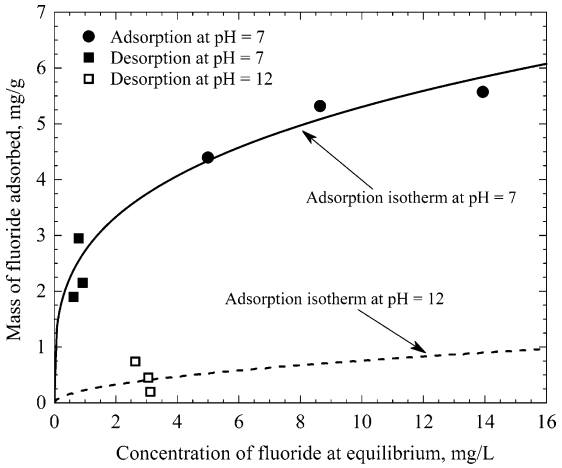

Figure 7. Reversibility of the adsorption isotherm of fluoride on the bone char Fija Fluor at $T = 25$ °C. The lines represent the Freundlich isotherm (Table 1).

adsorption occurred at all, it was not due to an electrostatic attraction but to a chemical interaction with sufficient energy to overcome the surface-fluoride repulsion forces.

3.6. Effect of Temperature on the Adsorption Isotherm. The effect of temperature on the fluoride adsorption isotherm on bone char was studied by determining the isotherms at temperatures of 15, 25, and 35 °C. It was found that adsorption of fluoride was essentially independent of the temperature as seen in Figure 6. This behavior can be explained by assuming that the F^- was exchanged from the solution to the surface of bone char. The enthalpy changes due to ion exchange are usually smaller than 8.36 kJ mol^{-1}.[33] If the heat of adsorption was very small, the adsorption equilibrium would be affected slightly by increasing the temperature.

3.7. Desorption of Fluoride Adsorbed on Bone Char. Fluoride was adsorbed on the bone char from an aqueous solution at pH 7 (adsorption step) and was then desorbed by placing the bone char loaded with fluoride in an aqueous solution without fluoride at either pH 7 or 12 (desorption step). Under these conditions, the fluoride was now transferred from the bone char to the solution until new equilibrium was reached.

The results of the adsorption−desorption steps as well as the adsorption isotherms at pH 7 and 12 are shown in Figure 6. The Freundlich isotherms at pH 7 and 12 were plotted using the isotherm constants reported in Table 1. As seen in Figure 7, the desorption equilibrium data at pH 7 was on the adsorption isotherm. This means that the new equilibrium reached in the desorption step was the same as that of the adsorption step. Thus, the adsorption of fluoride on bone char was reversible.

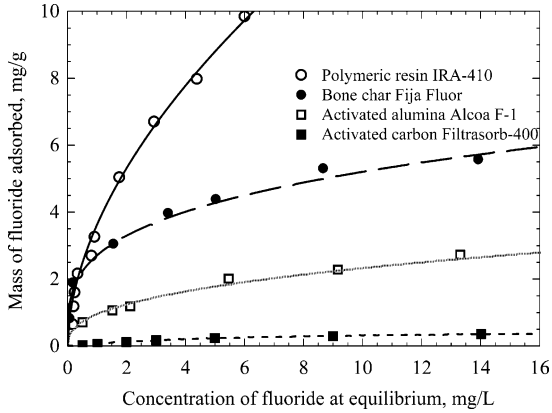

Figure 8. Adsorption isotherms of fluoride on various traditional adsorbents. $T = 25$ °C, and pH = 7. The lines represent the Freundlich isotherm.

The experimental desorption data at pH 12 were approximately on the adsorption isotherm at pH 12 (see Figure 6) indicating that the adsorption of fluoride was also reversible at pH 12. More fluoride was desorbed at pH 12 than at pH 7 because the concentration of OH^- at pH 12 was much higher than the fluoride concentration in solution. Hence, the OH^- ions displaced the fluoride ions adsorbed on the bone char until reaching equilibrium. These results indicate that the regeneration of bone char loaded with fluoride may be carried out at pH greater than 12 to desorb most of fluoride.

3.8. Comparison of Adsorption Capacity. The fluoride adsorption capacity of the bone char Fija Fluor was compared to that of a commercial polymeric resin (IRA-410), a commercial activated alumina (Alcoa F-1), and a commercial granular activated carbon (Filtrasorb F-400).[34] These adsorbents were chosen because activated alumina is the most commonly used adsorbent for removing fluoride from drinking water, polymeric resins are also known as excellent ion exchangers for fluoride, and activated carbon is the most important adsorbent in liquid phase adsorption. The adsorption isotherms at $T = 25$ °C and pH 7 are displayed in Figure 8. The bone char exhibited the second largest adsorption capacity, and the adsorption capacity decreased in the following order: polymeric resin > bone char > activated alumina > activated carbon.

The adsorption capacity of the adsorbents can be compared by calculating the mass of fluoride adsorbed on the different adsorbents at an equilibrium fluoride concentration of 1 mg/L. This concentration was chosen because it is a reasonable concentration of fluoride in drinking for health standards. The mass of fluoride adsorbed on the polymeric resin, bone char, activated alumina, and activated carbon was 3.62, 2.71, 0.96, and 0.075 mg/g, respectively. The adsorption capacity of bone char was 1.3 times smaller than that of the polymeric resin and 2.8 and 36 times greater than that of the activated alumina and activated carbon, respectively. As expected, fluoride was slightly adsorbed on activated carbon since anions do not generally adsorb on activated carbon. It is important to point out that the adsorption capacity of the polymeric resin was more than twice that of the bone char for concentrations of fluoride at equilibrium above 6 mg/L; however, in the removal of fluoride from drinking water the final concentration of fluoride must be near 1 mg/L. In other words, the polymeric resin can be efficiently applied for removing fluoride from water solutions when the final concentration of fluoride at equilibrium would be higher than 6 mg/L.

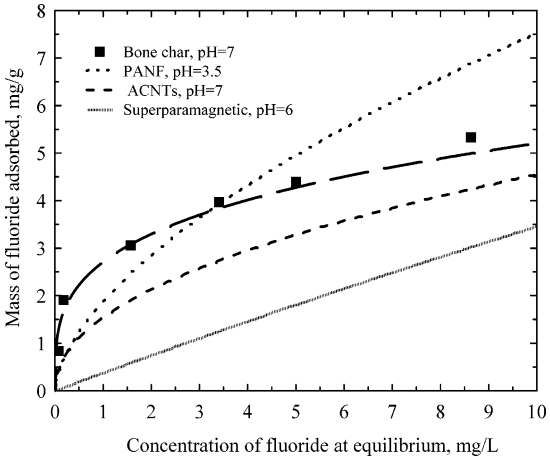

Figure 9. Adsorption isotherms of fluoride on PANF (pH = 3.5), ACNTs (pH = 7), and superparamagnetic bayerite (pH = 6) at T = 25 °C. The lines represent the isotherm models.

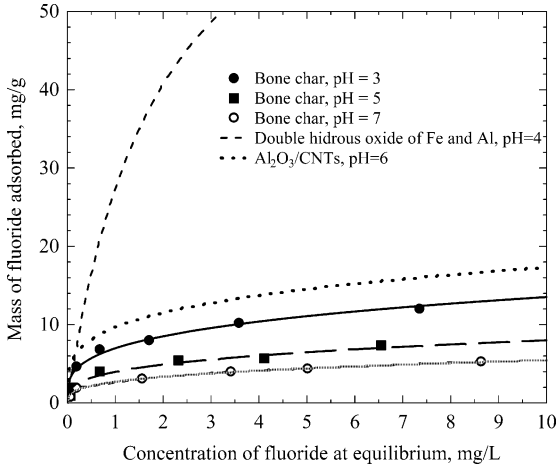

Figure 10. Adsorption isotherms of fluoride on double hydrous oxide of Al and Fe (pH = 4) and Al_2O_3/CNTs (pH = 6) at T = 25 °C. The lines represent the Freundlich isotherm.

Recently, several novel adsorbents have been developed for removing fluoride from water solutions. Some of these novel adsorbents are amorphous Al_2O_3 supported on carbon nanotubes (Al_2O_3/CNTs),[18] ion exchange polyacrylonitrile fiber (PANF),[20] aligned carbon nanotubes (ACNTs),[19] a double hydrous oxide of Al and Fe ($Fe_2O_3Al_2O_3{\cdot}xH_2O$),[21] and superparamagnetic nanoscale bayerite/SiO_2/Fe_2O_3.[35] The adsorption capacity of the bone char Fija Fluor was compared to those of the novel adsorbents. If these adsorbents can be applied for removing fluoride from drinking water, then the comparison of their adsorption capacities should be performed at a pH range 6−7. However, in some cases this was not possible since the adsorption isotherm was not reported at this pH range. Moreover, the comparison has to be done at a concentration of fluoride at equilibrium near to 1 mg/L as explained earlier.

The adsorption isotherms of fluoride on the novel adsorbents which have adsorption capacities smaller than those of bone char are shown in Figure 9. At a concentration of fluoride at equilibrium of 1 mg/L, the mass of fluoride adsorbed on bone char (pH = 7), PANF (pH = 3.5), ACNTs (pH = 6), and superparamagnetic bayerite/SiO_2/Fe_2O_3 (pH = 6) was 2.71, 1.88, 1.54, and 0.38 mg/g, respectively. Thus, the adsorption capacity of bone char was 1.4, 1.8, and 7.1 times greater than that of PANF, ACNTs, and superparamagnetic bayerite/SiO_2/Fe_2O_3.

The adsorption isotherms of fluoride on Al_2O_3/CNTs and double hydrous oxide of Al and Fe are displayed in Figure 10. Both adsorbents exhibited higher fluoride adsorption capacity than the bone char. At a pH = 6 and concentration of fluoride at equilibrium of 1 mg/L, the mass of fluoride adsorbed on Al_2O_3/CNTs and the bone char was 9.68 and 3.33 mg/g, respectively. The last value was estimated by averaging the mass of fluoride adsorbed on the bone char at pH = 5 (3.96 mg/g) and that at pH = 7 (2.71 mg/g). The mass of fluoride adsorbed on the double hydrous oxide of Al and Fe was 27.3 mg/g at pH = 4; however, this pH value is out of the range for treating drinking water. Chubar et al.[20] reported that the adsorption capacity of the double hydrous oxide of Al and Fe was reduced about 2.8 times increasing the pH from 4 to 7. At pH = 7, the mass of fluoride adsorbed on the double hydrous oxide of Al and Fe was estimated to be around 9.75 mg/g. On average, the adsorption capacities of the double hydrous oxide of Al and Fe and Al_2O_3/CNTs were 3.6 and 3.3 times higher than that of the bone char.

3.9. Removal of Fluoride from Drinking Water. The potential application of bone char for removing fluoride from drinking water was tested by determining the adsorption equilibrium isotherm using a sample of actual drinking water from the city of San Luis Potosi, Mexico. The sample was taken from the public water system, and the sampling point was chosen to have high fluoride concentration. All the experimental conditions for the adsorption of fluoride from drinking water are given in Table 2. The fluoride concentration of the drinking water sample was 4.02 mg/L. This concentration was well above 1.5 mg/L which is the guideline value recommended by the World Health Organization.[36]

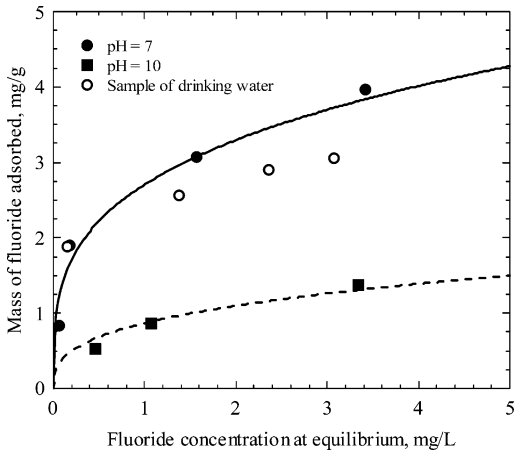

Figure 11. Adsorption isotherm of fluoride from drinking water on bone char. The lines represent the Freundlich isotherm.

Table 2. Experimental Conditions and Results for Fluoride Adsorption from a Sample of Actual Drinking Water

bone char mass (g)	solution volume (L)	ratio m/V (g/L)	fluoride concentration (mg/L)		solution pH		percentage removal
			initial	final	initial	final	
0.250	0.980	0.26	4.02	3.07	8.42	8.41	23.6
0.505	0.980	0.52	4.02	2.36	8.42	8.39	41.2
1.000	0.980	1.02	4.02	1.38	8.42	8.00	65.6
1.046	0.480	2.18	4.02	0.148	8.42	8.04	96.3

The adsorption isotherm of fluoride from actual drinking water is graphed in Figure 11 together with the adsorption isotherms at pH 7 and 10. The adsorption isotherm of fluoride from the actual drinking water was slightly lower than the

adsorption isotherm of fluoride from a water solution at pH 7. This can be explained by recalling that increasing the solution pH caused a decrease in the fluoride adsorption capacity of bone char. The initial pH of the drinking water sample was 8.42, and the final pH ranged between 8.04 and 8.41. The final pH of the actual drinking water always decreased during adsorption as was explained in section 3.5.

The percentage of fluoride removal, % *R*, was estimated using the following equation:

$$\%R = \frac{C_0 - C_f}{C_0} \times 100\% \quad (4)$$

where C_0 (mg/L) is the initial fluoride concentration and C_f (mg/L) is the final fluoride concentration.

The results showed that the percentage removal increased by augmenting the ratio of bone char mass to drinking water volume (*m*/*V*). This result was expected since more fluoride would be adsorbed if more mass of bone char were available per unit volume of drinking water. An *m*/*V* ratio close to 1 would be required to decrease the fluoride concentration from 4.02 to 1.5 mg/L. In other words, 1 g of bone char was needed to treat 1 L of actual drinking water.

Various anions present in the drinking water may compete with the fluoride anion for the adsorption sites on the bone char surface. The presence of these competing anions would affect the fluoride adsorption efficiency of bone char. For a study of the effect of competing anions, the concentrations of several competing ions were also followed during the progress of fluoride adsorption from drinking water. The concentrations of chloride, nitrate, nitrite, and sulfate anions in the actual drinking water were 29.5, 0.12, 0.07, and 43.0 mg/L, respectively. The concentration of phosphate was less than 0.01 mg/L. The chloride, nitrate, nitrite, phosphate, and sulfate anions were not significantly adsorbed onto bone char since their concentrations in the drinking water did not change over time. The hydroxyl anions did not compete with the fluoride since the molar concentration of fluoride was 81 times greater than the molar concentration of hydroxyl. Depending on the *m*/*V* ratio, the concentrations of bicarbonate in the actual drinking water increased from 90 to an average value of 116 mg/L whereas those of carbonate decreased from 0.95 to an average value of 0.46 mg/L. These results revealed that bicarbonate was released from the bone char and that the carbonate was adsorbed on the bone char.

Depending on the *m*/*V* ratio, the mass of fluoride and carbonate adsorbed on bone char ranged from 1.89 to 3.05 mg/g (0.099−0.16 meq/g) and from 0.638 to 1.41 mg/g (0.021−0.047 meq/g), respectively. On the average, the meq of fluoride adsorbed were 4 times higher than the meq of carbonate adsorbed. Thus, the effect of competing ions was not important except for the carbonate anions; however, the fluoride anions adsorbed more selectively than the carbonate anions.

Conclusions

The bone char is a mesoporous adsorbent with a specific surface area of 104 m^2/g and is mainly composed of hydroxyapatite. The concentration of the basic sites is higher than that of acidic sites causing its PZC to be basic.

The adsorption capacity of bone char increased drastically when the solution pH was decreased from 12 to 3; this behavior was due to electrostatic interactions between the F^- anions in water solution and the charge of the bone char surface. The adsorption capacity of bone char was independent of temperature since the adsorption occurs by ion exchange with a low heat of adsorption.

The fluoride adsorption capacity of bone char was compared to those of some traditional adsorbents as well as some novel adsorbents. The fluoride adsorption capacities of the traditional adsorbents decreased in the following order: polymeric resin IRA-410 > bone char Fija Fluor > activated alumina Alcoa F-1 > activated carbon Filtrasorb F-400. The fluoride adsorption capacity of bone char Fija Fluor is about 1.3 times smaller than that of the polymeric resin IRA-410 and 2.8 times higher than that of the activated alumina Alcoa F-1 which is a common adsorbent for removing fluoride from drinking water. The fluoride adsorption capacities of the novel adsorbents diminished in the following order: double hydrous oxide of Al and Fe > Al_2O_3/CNTs > bone char Fija Fluor > PANF > ACNTs > superparamagnetic bayerite/SiO_2/Fe_2O_3.

Defluoridation of drinking water in batch adsorbers showed that fluoride can be effectively removed and that the adsorption capacity was not affected by the presence of other competing anions except for carbonate.

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