A new synthesis route for bone chars using CO2 atmosphere and their application as fluoride adsorbents

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A B S T R A C T

This study describes a new synthesis route for bone chars using a CO₂ atmosphere and their behavior as adsorbent for fluoride removal from water. Specifically, we have performed a detailed analysis of the adsorption properties of bone char samples obtained at different carbonization conditions and a comparative study with samples of bone char obtained via pyrolysis under nitrogen. Experimental results show that the nature of the gas atmosphere (CO₂ versus N₂) and the carbonization temperature play a major role to achieve an effective bone char for water defluoridation. In particular, the best adsorption properties of bone char for fluoride removal are obtained with those samples synthesized at 700 °C. Carbonization temperatures above 700 °C under CO₂ atmosphere cause the dehydroxylation of the hydroxyapatite in the bone char, thus reducing its fluoride adsorption capacity. The maximum fluoride adsorption capacity for the bone char obtained in this study under CO₂ atmosphere (i.e., 5.92 mg/g) is higher than those reported for commercial bone chars.

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1. Introduction

Nowadays, the research and development of low cost materials for the mitigation of environmental pollution have gained interest. Recently, the attention has been paid to the application of materials such as agricultural and industrial wastes, since the cost of these materials is lower than the cost of commercial adsorbents, such as ion-exchange resins or activated carbon [1]. Extensive research has been carried out during the last decade to find low-cost materials and high capacity adsorbents for the removal of water pollutants. In this context, a wide variety of adsorbents has been developed and tested and they include natural and synthetic polymers, zeolites, clays, activated aluminas, ashes, biomasses, industrial and agro-industrial wastes and several activated carbons, among others [2–11]. Other material with potential for adsorption is the bone char [1]. This material has acquired relevance in the treatment of wastewater due to its versatility and economic advantages over other adsorbents. The bone char is a relatively inexpensive adsorbent since it can be obtained as waste from the food industry. Globally, more than 60 million ton of beef are produced annually and 58 million of them are consumed [12]. In particular, Mexico contributes 3 million to this total, being one of the 7 countries with greater production and consumption of cattle [12]. Animal bones are composed about 70% of inorganic matter, mainly hydroxyapatite. The chemical composition of hydroxyapatite is Ca₁₀[PO₄₆(OH)₂. The remaining part of bones is composed of organic matter, mainly fibrous protein such as collagen and osteocalcin. Also, the bone char is an adsorbent, which is mainly composed of calcium phosphate as hydroxyapatite (70–76%), carbon (9–11%) and calcite (7–9%) [13–15]. It is important to highlight that the organic fraction of bone char is primarily linked to the property of adsorbing nonpolar organic species, while the inorganic component provides the ability to adsorb ions [16–18]. Bone char has been applied as a versatile adsorbent for a wide variety of pollutants, including dyes, heavy metals, arsenate and fluoride [19,20]. Therefore, the production of bone char from animal bones sub-products serves a double purpose. First, it converts unwanted surplus meat industry waste, of which billions of kilograms are produced annually, to useful value-added adsorbents. Second, the bone chars are increasingly used in the removal of water pollutant. However, the removal efficiency and the quality of treated water depend largely on the carbonization conditions of bone char. Under this context, this paper reports the evaluation of the synthesis of bone chars under partially oxidative conditions using a CO₂ atmosphere compared to the traditional pyrolysis process. This study aims to
evaluate the nature of the gas atmosphere in the synthesis process of the bone char and its adsorption behavior in the removal of fluoride from water.

2. Experimental

2.1. Synthesis of bone chars via CO2

Cow femur bone was used as precursor for the synthesis of bone chars. The preparation and conditioning of the raw material was performed according to the methodology proposed in the literature by Rojas-Mayorga et al. [20]. Bone char synthesis was performed by a carbonization process using a partially oxidative atmosphere of CO2 (400 mL/min) in a tubular furnace Carbolite Eurotherm CTF 12165/550 with a quartz sample holder. Samples of bone char were synthesized at specific conditions of heating rate, carbonization temperature and duration of thermal treatment, which were defined using a full factorial design N² (see Table 1). All synthesized bone char samples were washed with deionized water until constant pH and dried overnight before their use in fluoride adsorption experiments.

2.2. Fluoride adsorption experiments

For all samples established in the experimental design (Table 1), the product yield and the fluoride adsorption properties of bone char samples were determined. Particularly, the adsorbed amount of fluoride on bone chars was used as the response variable of this experimental design. The amount of fluoride adsorbed on the different samples was calculated using the data obtained from batch adsorptions experiments, which were performed by triplicated and using an initial fluoride concentration of 60 mg/L. The experimental conditions were 30°C, pH 7, equilibrium time of 24 h and an adsorbent dosage of 2 g/L. Fluoride uptake of bone chars (mg/g) were calculated using a mass balance:

\[ q_F = \frac{(|F^-|_0 - |F^-|_f)}{m} V \]

where \(|F^-|_0\) and \(|F^-|_f\) are the initial and final fluoride concentration in the adsorption experiments given in mg/L, \(m\) is the mass in g of bone char and \(V\) is the volume of fluoride solution given in L, respectively. Fluoride concentration in solution was quantified using a selective electrode and TISAB chemical reagent according to the procedure described in the Standard Methods of Examination of Water and Wastewater [21]. Statistica® software was used for data analysis of the results obtained from this experimental design. This statistical analysis was performed to determine the effect of carbonization conditions in the adsorption behavior of bone char for fluoride removal. This analysis was also used to identify those operating parameters of the carbonization process that improve the adsorption behavior of this adsorbent for water defluoridation. Fluoride adsorptions isotherms were obtained at a concentration range of 5–80 mg/L, 30°C, pH 7 and equilibrium time of 24 h. These conditions were used to achieve the saturation of the adsorbent and to determine the maximum adsorption capacity of selected samples of bone chars.

2.3. Characterization of raw bone and bone chars

Several characterization techniques were used for determining the most relevant physicochemical properties of bone char samples obtained in this study. Specifically, the textural parameters of synthesized samples were determined using N2 adsorption-desorption isotherms at -196°C using a home-made fully automated equipment designed and constructed by the Advanced Materials group (LMA), now commercialized as N2 Gsorb-6 (Gas to Materials Technologies; www.g2mtech.com). The functional groups were determined using a Transmission FT-IR spectra (KBr) recorded on a Bruker IFS 66/S spectrophotometer and the sample was analyzed together with spectroscopic grade KBr, where 200 scans and resolutions of 4 cm⁻¹ were used. The crystalline structure of bone char sample was analyzed using an X-ray diffractometer Bruker D8-Advance with mirror Goebel having a tube with copper anode RX and radiation Cu Kα (\(\lambda = 1.5406 \text{ Å}\)). The diffractionograms were obtained on a range of 10 ≤ 2θ ≤ 80. The database available is from ICDD (International Center for Diffraction Data). The average crystal size can be estimated semiquantitatively by the Scherrer equation:

\[ \beta = \frac{(K\lambda)}{(D\cos\theta)} \]

where \(\beta\) is the average crystal size, \(K\) is the crystal form factor (0.9), \(\lambda\) is the wavelength of the X radiation used given in Å, \(D\) is the width at half height of the diffraction peak at 2θ and \(\theta\) is the angle of the

<table>
<thead>
<tr>
<th>Sample name</th>
<th>Carbonization conditions</th>
<th>Bone char performance</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Temperature (°C)</td>
<td>Heating rate (°C/min)</td>
</tr>
<tr>
<td>C-BC1</td>
<td>650</td>
<td>5</td>
</tr>
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<td>5.44 ± 0.06</td>
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<td>C-BC6</td>
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<td>C-BC20</td>
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</tbody>
</table>

Table 1: Experimental design used for the synthesis of bone char via CO2. Gas flow: 400 mL/min.
diffraction peak. Finally, X-ray photoelectron spectroscopy (XPS) measurements were used to estimate the fluorine content at the surface of the bone char samples. This analysis was performed with a PerkinElmer XPS spectrometer equipped with a hemispherical analyzer (VG SCIENTA R3000). Spectra were taken using a monochromatized aluminum source Al Kα (E = 1486.6 eV). The binding energy signal was calibrated using the Au 4f7/2 line of a cleaned gold sample at 84.0 eV. Finally, the surface composition was analyzed taking into account the areas and binding energies of F 1s core level.

3. Results and discussion

3.1. Adsorption studies

Table 1 describes the color of the synthesized samples, the product yields and the fluoride adsorption capacities for the bone chars obtained at different carbonization conditions. Experimental results show that, as the carbonization temperature is increased, a transition in the color of the bone char samples synthesized is observed (see Table 1). The color of the raw bone was light yellow, but during the heat treatment at temperatures from 650 to 800 °C, the bone char color changes from black to gray. For temperatures above 900 °C, samples become white thus suggesting complete elimination of the organic matter of the material. According to literature, these color changes are associated with the thermal degradation of the organic matrix (i.e., collagen) of bone char with temperature. On the other hand, darker colors indicate the incomplete removal of organic compounds [22], the color arising from elemental carbon present in the inorganic structure. Based on these observations, our results indicate that it is possible to synthesize bone chars under a CO2 atmosphere in the temperature range 650–700 °C. The yields of bone char range from 66.07% to 76.49% at evaluated experimental conditions, thus suggesting that the tested carbonization conditions do not have a significant impact on the product yield of bone chars. Concerning the adsorption performance, the best fluoride uptake was 5.92 mg/g for the sample synthesized at 700 °C, using a residence time and heating rate of 2 h and 10 °C/min, respectively. It is important to highlight that, when the carbonization temperature is higher than 700 °C, the fluoride adsorption capacity of the bone chars decreases significantly from 5.92 mg/g to 0 mg/g. In fact, the removal performance for bone chars synthesized at 800, 900 and 1000 °C is unsatisfactory for water defluoridation (i.e., adsorption capacity < 0.8 mg/g). This trend in the adsorption performance is in agreement with the study of Kawasaki et al. [18], which indicates that bone chars obtained at higher temperatures may show low fluoride uptakes due to the thermal degradation of surface functional groups that must be involved in the fluoride removal process. The results of fluoride adsorption reported in Table 1 and the statistical analysis (i.e., variance analysis) of the full factorial experimental design indicate that the carbonization temperature has the most significant effect on the fluoride adsorption properties of bone chars. To provide more insight into the role of remaining carbon in the adsorption behavior of bone chars, the fluoride adsorption capacities of bone char samples obtained via a calcination process using air are reported in Table 1. In this case, the fluoride uptake was <0.5 mg/g. At this point it is important to highlight that this low adsorption capacity may be associated to the change in crystallinity of the adsorbent due to the loss of elemental carbon and to the dehydroxylation of hydroxyapatite, both processes being highly sensitive to the atmosphere used in the bone char synthesis.

Fig. 1 shows the fluoride adsorption isotherms for the bone char samples obtained via CO2 at different carbonization temperatures (i.e., 650–1000 °C). For the sake of comparison, the bone char sample obtained via pyrolysis under N2 (sample N-BC) is included. The best values of fluoride adsorption capacity are 7.32 and 5.92 mg/g, which correspond to the samples N-BC (using N2) and C-BC7 (using CO2), respectively. Based on the statistical analysis of the experimental design, the best conditions for the synthesis of bone chars via CO2 are: a carbonization temperature of 700 °C, a heating rate of 10 °C/min and a residence time of 2 h. Bone char samples obtained via CO2 showed competitive fluoride adsorption capacities compared with the results of bone char samples via pyrolysis under N2 reported in a previous study by Rojas-Mayorga et al. [20]. It is convenient to highlight that the best fluoride adsorption capacity of bone char prepared in this study using a CO2 atmosphere is higher than those reported in the literature for commercial bone chars [15,16]. Furthermore, this value outperforms the results reported in the literature where the fluoride adsorption capacities ranged from ~1.0 to 3.0 mg/g [17,18]. In summary, the synthesis of bone chars under a CO2 atmosphere gives rise to competitive adsorbents for fluoride removal from water, where the obtained materials show an improved adsorption performance for fluoride than those reported for other commercial bone chars.

3.2. Textural properties

Fig. 2a shows the nitrogen adsorption isotherms for the different bone chars. According to the IUPAC classification, samples N-BC, C-BC3 and C-BC7 exhibit a type IV isotherm, which is characteristic of mesoporous materials with 2–50 nm pore size [23–25]. On the other hand, samples C-BC11, C-BC15 and C-BC19 exhibit a type III isotherm, which corresponds to systems with no porosity and characterized by a weak adsorbate-adsorbent interaction [23–25]. Pore size distributions (PSDs) calculated with the QSDFT model are reported in Fig. 2b. In general, PSDs profiles show broad peaks with pore size >2 nm, which correspond to mesoporous materials. However, N-BC and C-BC7 samples have a better development of mesoporosity with three peaks at 2.2, 3.5 and 4.4 nm, respectively. The textural parameters of selected bone char samples are reported in Table 2. Results show that the temperature and synthesis atmosphere of bone char affect substantially the textural properties of samples obtained. Firstly, the N-BC sample obtained at 700 °C via N2 presents the largest specific surface area

![Fluclde adsorption isotherms at pH 7 and 30 °C on bone chars obtained at different synthesis conditions.](image-url)
SBET with a value of 85 m$^2$/g. Thereafter, samples C-BC3 and C-BC7 (which were obtained at 650 and 700 °C via CO$_2$) showed lower SBET values of 62 and 69 m$^2$/g, respectively. However, the samples C-BC11, C-B15 and C-BC19 show a significant decline in this property with values of SBET < 10 m$^2$/g. According to the literature, when the SBET is increased, the adsorbent-adsorbate contact area increases, thus favoring the adsorption process [24–25]. In this context, the results of fluoride adsorption from water are consistent, since the adsorption capacity of the bone chars is favored with increasing SBET parameter. Moreover, it was found that only the N-BC, C-BC3 and C-BC7 samples have some microporosity in their inorganic structure with micropore volumes ($V_{DR}$) of 0.04, 0.03 and 0.02 cm$^3$/g, respectively. In contrast, samples C-BC11, C-BC15 and C-BC19 have values of $V_{DR}$ close to 0, which indicates the absence of microporosity. This microporosity is located within the bone char and corresponds to pores formed between hydroxyapatite crystals. Although the micropore volume of the samples is small, this parameter may be important to improve the interaction between F$^-$ ions and the active sites of the inorganic bone char structure, thus favoring the removal of this water pollutant. With regard to the volume of mesopores, N-BC and C-BC7 samples showed the same value of 0.20 cm$^3$/g. For all other samples, this value decreases significantly. Interestingly, the volume of mesopores represents approximately 80% of the total pore volume on these adsorbents. It is noteworthy to mention that the C-BC7 bone char obtained via CO$_2$ has the best fluoride adsorption properties, and its textural parameters are similar to the N-BC bone char obtained via N$_2$. Finally, the textural properties of commercial bone char have been reported in previous studies and the values obtained in this study are consistent to the results reported in the literature [15,26].

### 3.3. Crystalline structure

Fig. 3 shows the X-ray diffractions for the raw bone (Fig. 3a) and the selected samples of bone chars (Fig. 3b–g). All samples have the same crystallographic planes, the analysis confirming that the diffraction peaks correspond to the crystalline structure of the hydroxyapatite [Ca$_{10}$(PO$_4$)$_6$(OH)$_2$] [27–32]. However, there are different degrees of crystallinity of the samples with respect to the carbonization temperature. Samples C-BC3 and C-BC7 obtained via CO$_2$ at 650 and 700 °C (Fig. 3c and d) have a similar crystalline structure to the N-BC bone char obtained via N$_2$ (Fig. 3b). These samples show broader diffraction peaks mainly due to the small crystal size of the hydroxyapatite as a consequence of the presence of remaining elemental carbon in the inorganic structure. XRD pro-

![Fig. 2. (a) N$_2$ adsorption isotherms at 77 K for bone char samples (filled symbols: adsorption branch; empty symbols: desorption branch) and (b) pore size distribution obtained with the QSDFT model for selected samples.](image)

![Fig. 3. XRD patterns of raw precursor and bone chars obtained at different synthesis conditions. Sample: (a) raw bone, (b) N-BC, (c) C-BC3, (d) C-BC7, (e) C-BC11, (f) C-BC15 and (g) C-BC19.](image)

<table>
<thead>
<tr>
<th>Sample name</th>
<th>Crystal size (nm)</th>
<th>Textural parameters of bone char samples</th>
</tr>
</thead>
<tbody>
<tr>
<td>N-BC$^a$</td>
<td>11.02</td>
<td>85 0.24 0.04 0.20</td>
</tr>
<tr>
<td>C-BC3</td>
<td>11.60</td>
<td>62 0.20 0.02 0.18</td>
</tr>
<tr>
<td>C-BC7</td>
<td>11.62</td>
<td>69 0.23 0.03 0.20</td>
</tr>
<tr>
<td>C-BC11</td>
<td>29.18</td>
<td>9 0.16 0.00 0.16</td>
</tr>
<tr>
<td>C-BC15</td>
<td>38.05</td>
<td>4 0.04 0.00 0.04</td>
</tr>
<tr>
<td>C-BC19</td>
<td>45.37</td>
<td>2 0.02 0.00 0.02</td>
</tr>
</tbody>
</table>

$^a$ Optimum bone char synthesized via pyrolysis (nitrogen flow: 400 ml/min).
files for samples obtained via CO\textsubscript{2} at higher temperature (Fig. 3e–g) show narrower and more intense diffraction peaks, which indicates that the degree of crystallinity of the sample is favored when the carbonization temperature is increased. Based on these results, it can be summarized that changes in the crystallinity of the samples may be associated with the loss of elemental carbon present in the inorganic structure, i.e. elemental carbon (C) may react with CO\textsubscript{2} used as synthesis atmosphere, with the release of CO. Consequently, the structure of bone char is free of C atoms after the thermal treatment, thus favoring the rearrangement of the hydroxyapatite atoms. The molecular arrangement becomes more orderly, crystallinity index is favored, and a more crystalline structure is formed with higher density and lesser gaps between the hydroxyapatite crystals. According to Markovic et al. [33], the width of the diffraction peaks is inversely proportional to the size and perfection of the crystal lattice, so that diffraction profiles will be sharper for crystalline materials constituted by larger crystallites and free of deformations. Herein, it is convenient to highlight that the diffractograms of Fig. 3b–d are very similar among them, which indicates that the synthesis atmosphere does not affect significantly the crystallinity of the bone chars, but only under these experimental conditions. However, the synthesis of bone chars via CO\textsubscript{2} accelerates the crystallinity of the samples as compared with the synthesis of bone char via pyrolysis (under nitrogen atmosphere). This effect can be due to the faster removal of elemental carbon and dehydroxylation of the hydroxyapatite under CO\textsubscript{2}, which may occur already at 700 °C [20,34]. In addition, the average crystal size increases with a further increase in the carbonization temperature up to 1000 °C (see Table 2). This effect must be attributed to the aggregation of the hydroxyapatite crystals at high temperature and in the absence of elemental carbon [32].

### 3.4. Functional groups

Fig. 4 shows the FT-IR spectra of raw bone, bone char sample obtained via pyrolysis and bone char samples obtained using CO\textsubscript{2} at different carbonization temperatures. In general, all spectra show the 6 characteristic bands of hydroxyapatite centered at 3420, 1620, 1450, 1030, 600 and 565 cm\textsuperscript{-1}. The FT-IR spectrum of raw bone (Fig. 4a) indicates the presence of –OH groups (3000–3600 cm\textsuperscript{-1}), –CH stretching of hydrocarbon (2853–2923 cm\textsuperscript{-1}), C=O, C=C, C=N vibrations of protein and collagen (1465–1744 cm\textsuperscript{-1}), a broad and strong band of phosphate –PO\textsubscript{4}\textsuperscript{3–} (1100–900 cm\textsuperscript{-1}), a carbonate –CO\textsubscript{3}\textsuperscript{2–} peak (720 cm\textsuperscript{-1}), and an additional peak due to calcium Ca\textsuperscript{2+} (550–610 cm\textsuperscript{-1}). After the thermal treatment, the protein and collagen bands, the –OH group (3000–3600 cm\textsuperscript{-1}) and the hydrocarbon –CH stretching vibration (2853–2923 cm\textsuperscript{-1}) lose their intensity due, mainly, to the degradation of the organic matrix as well as the removal of moisture present in the raw material. For bone char N-BC obtained using nitrogen (Fig. 4b) and the samples obtained using CO\textsubscript{2} (Fig. 4c–g), there is a band at 3420 cm\textsuperscript{-1} corresponding to a high energy elongation peak coming from –OH groups on the hydroxyapatite structure [35]. Note that the absorption band of the –OH group loses intensity with an increase in the carbonization temperature, and a drastic change takes place above 700 °C. This effect may be due to dehydroxylation of hydroxyapatite and its structural change [22,36]. It is important to highlight that this change in the surface chemistry of bone chars above 700 °C is associated with the decrease in the fluoride adsorption capacity. FTIR signal at 1620 cm\textsuperscript{-1} is assigned to the vibration of quinone C=O, while the band around 1450 cm\textsuperscript{-1} is assigned to the stretching vibration of the carboxyl group CO\textsubscript{2} [37,38]. Moreover, the characteristic bands of the phosphate group around 600 and 1040 cm\textsuperscript{-1} are observed. These bands are assigned to P–O symmetric stretching mode (570–600 cm\textsuperscript{-1}) and as a major peak is the P–O asymmetric stretching band (1100–960 cm\textsuperscript{-1}) [39,40]. Note that the bands corresponding to the phosphate group are kept regardless of the carbonization temperature. Finally, the absorption band at 565 cm\textsuperscript{-1} corresponds to the calcium present in the inorganic structure; specifically, this band is assigned to the bond between calcium and the phosphate group [40–42].

The bone char sample obtained via CO\textsubscript{2} with the best fluoride adsorption properties was C-BC7. This sample recovered after the fluoride adsorptions experiments was labeled as C-BC7-F and was selected for further characterization.

### 3.5. Crystalline structure after fluoride adsorption studies

Fig. 5 shows the X-ray diffractograms for samples C-BC7 and C-BC7-F, before and after fluoride adsorptions experiments, respectively. XRD analysis shows that the crystallinity of the sample increases with the incorporation of F\textsuperscript{–} on the structure. However, the crystallinity is affected by the preferential orientation of the crystallites masking the amorphous phase. In fact, fluorapatite has a lower solubility and higher thermal stability compared to hydroxyapatite, and produces highly crystalline samples [10]. A pure hydroxyapatite has a stoichiometric formula in the form of Ca\textsubscript{10}(PO\textsubscript{4}\textsubscript{3}\textsuperscript{2–}/OH\textsuperscript{–})\textsubscript{2}. In the fluoride removal experiments, some F\textsuperscript{–} ions replace part of the OH\textsuperscript{–} ions and forms Ca\textsubscript{10}(PO\textsubscript{4}\textsubscript{3}\textsuperscript{2–}/F\textsuperscript{–}(OH\textsuperscript{–})\textsubscript{2–}x, that is, the so-called fluoridated hydroxyapatite. In the ideal case, fluorine replaces all –OH group and thus forms fluorapatite Ca\textsubscript{10}(PO\textsubscript{4}\textsubscript{3}\textsuperscript{2–}/F\textsuperscript{–})\textsubscript{2}. In a hydroxyapatite, the F/Ca ratio is equal to 0, since there is no fluorine. In a fluoridated hydroxyapatite, the F/Ca ratio varies from 0 to <0.2. In a pure fluorapatite, the F/Ca ratio is 0.2, which is the stoichiometric limit. In our case, the ratio F/Ca = 0.1082 indicating that the crystalline structure formed is the fluoridated hydroxyapatite. It is important to note that the F/Ca ratio of the C-BC7-F bone char was calculated from the atomic percentage that was obtained through X-ray photoelectron spectroscopy analysis (XPS), (see Table 3).
3.6. Functional groups after fluoride adsorption studies

Additionally, Fig. 6 shows the FT-IR spectra of samples C-BC7 and C-BC7-F. In these spectra we can identify the change in the absorption band corresponding to –OH groups (3000–3600 cm\(^{-1}\)). The band intensity decreases after fluoride adsorption experiments, and this effect can be occurring due to the ionic exchange between F\(^-\) and OH\(^-\) [44].

3.7. XPS analysis

Finally, F1s XPS spectra of the bone char samples before and after adsorption C-BC7 and C-BC7-F, respectively, are reported in Fig. 7. In the bone char C-BC7 before fluoride adsorption experiments the F1s signal does not exist; however, after fluoride adsorption experiments, a new and unique peak is found. This energy band corresponds to F1s with a binding energy at 684.67 eV. According to Hwang et al. [45], this F1s peak corresponds to the fluoride bonded to calcium (CaF\(_2\)), which is formed between the calcium of hydroxyapatite and the fluoride present in solution. Therefore, with this study we confirm that surface reactions exist between fluoride ions and calcium from hydroxyapatite [45–48]. Also, this analysis is in agreement with XRD and FT-IR results.

4. Conclusions

It is possible to obtain bone char with outstanding fluoride adsorption properties using CO\(_2\) as synthesis atmosphere. Carbonization temperature is a critical operating parameter for the synthesis of bone char via CO\(_2\) for fluoride removal from water. Specifically, this temperature has a major effect on the fluoride adsorption properties of bone char due to the change in crystallinity of the sample and to the dehydroxylation process of the hydroxyapatite contained in this adsorbent. Also, the surface area decreased with increments in the carbonization temperature. The
low crystallinity, higher specific surface area and –OH functional groups of bone char improve the fluoride adsorption capacity. The best fluoride uptake of 5.92 mg/g can be obtained if a carbonization temperature of 700 °C is used for bone char synthesis via CO2. The fluoride removal performance of the bone char is better than those reported for several commercial bone chars up to 31%. The bone char C-BC7 obtained via CO2 showed a competitive performance in the fluoride removal from water (i.e., 5.92 mg/g) compared with the optimum bone char obtained via pyrolysis N-BC (i.e., 7.32 mg/g). FT-IR spectroscopy and XPS measurements proved that fluoride removal by this adsorbent occurred via the ionic exchange of surface hydroxyl groups with fluoride. F1s XPS spectra confirmed this theory and the reaction between fluorine and calcium, while the DRX study indicates the fluoridated hydroxyapatite formation.

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