Bone char from an invasive aquatic species "devilfish" as a sustainable adsorbent for
the removal of fluoride in water for human consumption

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ABSTRACT

In this study, bone chars were obtained from an alien aquatic species “devilfish” bones by pyrolysis of 500-800 °C. Bone chars were evaluated as a sustainable adsorbent of fluoride, it was found pyrolysed bone char at 500 °C adsorbed the most amount of fluoride. The effect of pH indicated that the adsorption capacity increased as the pH decreased. Thermodynamic parameters of fluoride adsorption on devilfish bone chars were estimated as $\Delta H^\circ = 7.213 \text{kJ mol}^{-1}$, $\Delta G^\circ = 23.61 \text{kJ mol}^{-1}$ and $\Delta S^\circ = 103.4 \text{J mol}^{-1} \text{K}^{-1}$ indicating that adsorption is endothermic, spontaneous and with great affinity of fluoride on bone char from devilfish. The fluoride desorption study showed that fluoride is desorbed from the material of 0.24 to 20.06 %, so the adsorption is considered to be partly reversible. The regeneration of the bone char at 400, 500 and 600 °C was studied and it was noted that its adsorption capacity decreases slightly so it could be considered appropriate for the use in water treatment technologies. Adsorption of fluorides from drinking well water of a rural community with dental fluorosis problems and high levels of fluoride in water, revealed that by increasing the amount of the bone char of 0.05 to 0.8 g, the disposal of fluoride increases from 69.1 to 98.7 %. Lastly, it was established that the bone char synthesized from devilfish is a low-cost, viable a sustainable material to remove fluorides from water and represents an environmental management strategy of this alien species.

Keywords: fluorides; bone char; devilfish; drinking water; thermodynamic adsorption properties; alien aquatic species
1. Introduction

The presence of invasive aquatic species affects the imbalance of biodiversity and it is a problem detected in ecosystems worldwide, also it has even generated economic collateral consequences (Thomas et al. 2019) and are the most significant contributors to the extinction of native species (Garcia-Gonzales et al. 2017). Both the number and distribution of invasive species are increasing in various regions of the world.

In addition, the growing global commerce in ornamental aquarium fish is one of the most important routes for aquatic bioinvasion with non-native species (Bijukumar et al. 2015). Other pathways of introduction include drainage of water containing organisms from public tanks and aquariums, biocontrol and aquaculture activities (García-Martínez et al. 2014).

In Mexico, a biological invasion problem has developed over the last 20 years, caused by the family Loricariidae, often referred to as pleco, plecos or devilfish (Garcia-Gonzales et al. 2017; Medellin-Castillo et al. 2020). This family is one of the most diverse, with 716 species described. They are endemic freshwater species from South America, Costa Rica and Panama and are native to the Amazon River basin (Garcia-Gonzales et al. 2017; Ríos-Muñoz 2015; Rosnaeni et al. 2017). Because of their detritivorous qualities, some of these species have been commercialized as ornamental fish and algae controllers. This has promoted their introduction into rivers and lakes in warm climate regions, either in a controlled or accidental manner.

Devilfish displace other species, some of which are endemic, in various ways, including incidental ingestion of their eggs and competition for algae and detritus (Medellin-Castillo et al. 2020; Moncayo-Fernández et al. 2017). They also cause deterioration in water quality due to the suspension of sediment caused by their nesting habits, which consist of digging large galleries (Sandoval-Huerta et al. 2012).
Currently, the devilfish is distributed throughout Mexico, including the Mezcala, Balsas, Grijalva and Usumacinta rivers and their slopes, as also the Infiernillo Dam (Medellín-Castillo et al. 2020; Moncayo-Fernández et al. 2017).

Among the uses given to these fish are as food for the general population, or to obtain by-products as fertilizers, fish silage as a feed supplement for livestock, and fishmeal for fish feed. Human consumption as a feed supplement is possible, although further study is required as certain species of devilfish tend to accumulate heavy metals, which has discouraged their consumption (Maldonado et al. 2015).

Fluoride pollution of water is a major issue worldwide (Akafu et al. 2019; Fan et al. 2019; Kumar et al. 2019; Medellín-Castillo et al. 2020). In drinking water, a fluoride concentration between 0.5 to 1.0 mg L$^{-1}$ can be considered beneficial to teeth and bones (Abeykoon et al. 2020; Medellín-Castillo et al. 2020; Quintáns-Fondo et al. 2019). Nevertheless, fluoride water intake above the World Health Organization (WHO) suggested dose (1.50 mg L$^{-1}$) causes significant health effects such as dental fluorosis, skeletal fluorosis and even in severe cases, cancer (Abeykoon et al. 2020; Emmanuel et al. 2018; Jalil et al. 2019; Quintáns-Fondo et al. 2019).

Various technologies are available for the removal of fluorides, including precipitation, coagulation, reverse osmosis, ion exchange, and adsorption. Of all methods, adsorption is highly effective and economical for the reduction of excess fluoride in water (Abeykoon et al. 2020; Akafu et al. 2019; Alkurdi et al. 2019; Assaoui et al. 2020; Emmanuel et al. 2018; Fan et al. 2019), and it uses a variety of adsorbent materials, including clay, soil, organic matter, alumina, zeolites, nanomaterials, activated carbon and bone char (Alkurdi et al. 2019; Teusner et al. 2016). Bone chars have been widely considered in fluoride removal and have gained considerable attention due to their cheapness, high availability, easy preparation and high adsorption capacity (Alkurdi et al. 2019; Medellín-Castillo et al. 2020).
In this study, we seek to obtain a management alternative for the use of an invasive aquatic species that does not yet have any economic value. Therefore, bone chars from devilfish were prepared to study the influence of the temperature of pyrolysis on the fluoride adsorption capacity of bone chars. Also, the influence of pH and temperature on the adsorption capacity was studied and thermodynamic properties of this process were determined. The thermal regeneration of bone char saturated with fluoride at 400, 500 and 600 °C was evaluated for the design of water treatment technologies. Finally, the use of these materials in the drinking well water of a rural community was studied.

2. Material and Methods

2.1 Collection of fish and extraction of bones

The fish used in this study were fished in the municipality of Tenosique in the State of Tabasco in Mexico, located in the Usumacinta River region. This site was selected because the presence of devilfish has been reported to be an environmental problem that has altered fishing in the region as well as affecting native species (Maldonado et al. 2015). Fig. 1 shows the location of the devilfish sampling site. The organic matter contained in the fish was removed was removed from the bones using a solution prepared with a 3:1 ratio of deionized water and hydrogen peroxide. Bones were left to dry at room temperature and were labelled Bone.
2.2 Synthesis

The synthesis of the bone chars by means of a pyrolysis process was conducted in a tube furnace Carbolite, model CTF-1200°C, at temperatures of 400, 500, 600, 700 and 800 °C, with a flow of N\(_2\) of 100 mL min\(^{-1}\), 10 °C min\(^{-1}\) and a pyrolysis time of one hour at the specified synthesis temperature.
The pyrolysed bones at 400, 500, 600, 700 and 800 °C were labelled as C400, C500, C600, C700 and C800, respectively.

The yield of the production of the bone chars, %R, was determined with the next equation:

\[
\% \ R = \frac{\text{Dried weight of the bone chars}}{\text{Dried weight of the bones}} \times 100
\]  

(1)

### 2.3 Textural and physico-chemical properties

The BET method was used to evaluate the textural properties of the materials obtained, as well as its precursor. The acidic and basic sites were obtained by the Boehm method.

The point zero charge pH\(_{\text{PZC}}\) was determined by a method of salt addition (Ahmad et al. 2018; Medellin-Castillo et al. 2020).

The surface and morphology of the particles were observed in a SEM, JEOL JSM-6610, equipped with a microanalysis system EDS (Electron Dispersive Spectroscopy) Oxford, model 7279. The functional groups of the materials were identified using an FTIR spectrophotometer, Thermo Scientific brand, model Nicolet iS10. Infrared spectra were collected over a spectral range of 500 to 4000 cm\(^{-1}\).

Thermogravimetric analysis was completed using an analyzer Perkin Elmer, model Pyris Diamond.

The crystal structure was analyzed using an X-ray diffractometer (XRD), Bruker brand, Da Vinci model, with a radiation CuK\(\alpha\) (\(\lambda=0.15405\) nm).

### 2.4 Adsorption of fluoride

These data were obtained by conducting batch adsorption experiments, in which 0.2 g of the bone char with a 90 mL volume of a fluoride solution of initial concentrations between 2 and 60 mg L\(^{-1}\) was contacted for 7 days. The pH was set daily using 0.01 and 0.1 N solutions of
HNO₃ or NaOH. The amount of fluoride on the bone char was estimated by means of a mass balance according to:

\[ q = \frac{V_0(C_0 - C_f)}{m} \]  

where \( q \) is the mass of fluoride adsorbed in mg g\(^{-1}\); \( V_0 \) is the initial volume in L; \( C_0 \) is the initial concentration of fluoride in the solution in mg L\(^{-1}\); \( C_f \) is the equilibrium fluoride concentration in mg L\(^{-1}\) and \( m \) is the mass of bone char used in each experiment in g.

2.5 Desorption and regeneration

Experimental data on the reversibility of the equilibrium of fluoride on bone char was obtained by first performing adsorption experiments, as described previously, at a solution pH of 5.0 and upon reaching adsorption equilibrium the desorption or reversibility step was performed, at pH of 5.0 or 9.0.

The amount of fluoride remaining in the adsorbent was estimated by applying a mass balance:

\[ q = \frac{V_0 C_0 + q_0 m - V_f C_f}{m} \]  

where \( q_0 \) is the amount of fluoride on the adsorbent at the outset of the desorption, mg g\(^{-1}\).

Additionally, thermal regeneration of bone char synthesized at 500 °C saturated with fluoride was evaluated at temperatures of 400, 500 and 600 °C using the same synthesis conditions as described in section 2.2. The materials were identified as CR400, CR500 and CR600, respectively. These materials were contacted with fluoride solutions to determine their adsorption capacity.

2.6 Fluoride adsorption from drinking well water

The adsorption of fluoride contained in the water of a well in La Laborcilla rural community in the municipality of Villa de Arriaga, San Luis Potosi in Mexico was studied (Fig. 2). The fluoride concentration of the drinking well water from this community had a concentration of
4.7 mg L\(^{-1}\). Experimental data of the adsorption equilibrium were obtained using various masses of bone char that varied from 0.05 to 0.8 g, and a volume of 100 mL of water. The determination of the amount of fluoride adsorbed was described in section 2.4. Also, the % removal of total hardness, chlorides and sulphates from water was evaluated as they can compete in fluoride removal on bone char. The % removal, %Re, was defined according to the following equation

\[
\% \text{ Re} = \frac{C_0 - C_f}{C_0} \times 100
\]

where \(C_0\) is the concentration of the anion in water and \(C_f\) is the concentration to the end of the adsorption experiment.
**Fig. 2.** Laborcilla, Villa de Arriaga: (a) Location; (b) Well; (c) Water dispenser; (d) Dental fluorosis.
3. Results and discussion

3.1 Yield of the synthesis

During the pyrolysis of the devilfish bones samples (Bone), it could be observed that the percentage of yield, %R, obtained decreased when the synthesis temperature was raised from 400 to 800 °C (Table 1). This same behaviour has been observed by other authors (Purevsuren et al. 2017). This reduction can be attributed to the decomposition of some constituents of the bone char with the increases of the synthesis temperature, so that it loses more weight and consequently the %R decreases.

Table 1. Percentage yield, %R, of bone char synthesis

| Sample | Raw material | Synthesis temperature, °C | %R  |
|--------|--------------|---------------------------|-----|
| C400   | Bone         | 400                       | 50.50|
| C500   | Bone         | 500                       | 44.53|
| C600   | Bone         | 600                       | 43.92|
| C700   | Bone         | 700                       | 42.20|
| C800   | Bone         | 800                       | 40.90|

3.2 Textural and physicochemical properties

$N_2$ adsorption isotherms measured at 77 K from the bones and pyrolysed bone chars at different temperatures are shown in Fig. 3.

The $N_2$ adsorption isotherm of sample Bone (Fig. 3a) showed that it is type IIb, which corresponds to non-rigid aggregates, cements, pigments. Furthermore, it presents a hysteresis loop of type H3 which is attributed to a possible interparticle condensation. On the other hand, $N_2$ adsorption isotherms for all bone chars are characteristic of mesoporous solids and correspond to IVa type isotherms. These results are consistent with those reported by other authors for bone chars (Isaacs-Páez et al., 2019).
Fig. 3. Nitrogen adsorption isotherms at 77 K of: (a) Bone; (b) C400; (c) C500; (d) C600; (e) C700; (f) C800

Table 2 shows the textural properties of sample Bone and the synthesized bone chars. These results reveal that the specific area and pore volume of samples increases by increasing the
pyrolysis temperature from 400 to 600 °C and then decreases by increasing the temperature from 600 to 800 °C. Thus, for this study it was observed that pyrolysis at 500 and 600 °C favored the increase in the specific area while there was a decrease at temperatures of 600 to 800 °C which is attributed to the dehydroxylation of hydroxyapatite (Alkurdi et al. 2019).

Table 2. Textural, physical and chemical properties of materials from devilfish

| Sample | Specific surface (m² g⁻¹) | Pore volume (cm³ g⁻¹) | Average pore diameter (nm) | pHₚzc | Basic sites (meq g⁻¹) | Acidic sites (meq g⁻¹) |
|--------|--------------------------|-----------------------|---------------------------|-------|----------------------|------------------------|
| Bone   | 40.35                    | 0.1202                | 9.65                      | 7.01  | 0.35                 | 0.34                   |
| C400   | 102.5                    | 0.24                  | 7.36                      | 6.74  | 0.40                 | 0.62                   |
| C500   | 146.1                    | 0.38                  | 8.52                      | 7.45  | 1.64                 | 0.18                   |
| C600   | 163.0                    | 0.40                  | 8.34                      | 7.75  | 0.40                 | 0.06                   |
| C700   | 132.7                    | 0.37                  | 9.23                      | 8.25  | 1.02                 | 0.06                   |
| C800   | 88.46                    | 0.34                  | 13.1                      | 8.46  | 1.03                 | 0.05                   |

A comparison of the textural properties of sample Bone and its various bone chars shown that the porosity of the bone chars developed significantly during pyrolysis, as a consequence of degradation of organic constituents by heat treatment and exposure of the pores in the hydroxyapatite structure (Medellín-Castillo et al. 2016). As a result, the pyrolysis at 500 °C dramatically improved the porosity and consequently the surface area.

The values of pore volume and diameter for each of the bone chars are within the range reported by other authors for bone chars (Alkurdi et al. 2019; Murillo et al. 2012; Nigri et al. 2019). According to the IUPAC classification, the materials obtained in this work are mesoporous materials since the average pore diameter varied in the interval from 7.36 to 13.1 nm.

The concentration of active sites of bone chars is shown in Table 2 and it is observed that the concentration of acidic sites of C400 is higher than that of the basic sites, and they decrease as
the temperature of pyrolysis rises, increasing the concentration of basic sites. This is due to the
decomposition of certain bone components, such as organic matter and carbonates (Rogers and
Daniels 2002) which promotes the formation of basic sites.

The concentrations of acidic and basic sites obtained in this work are in accordance with the
values reported in other studies (Murillo et al. 2012). Although the bones used by these authors
for synthesis were pork and chicken, the values coincide since the bones are mainly composed
of hydroxyapatite, 70 %, in addition, 25 % organic matter and 5 % water (Kini and Nandeesh
2012; Terasaka et al. 2014).

3.3 Effect of the pyrolysis temperature of bone char on the adsorption capacity

The fluoride adsorption capacities at pH 7.0, T = 25 °C, C₀ = 10 mg L⁻¹ and 1 g of each bone
char were compared, and the results are shown in Fig. 4. The fluoride concentration was
established according to the values of the study well water and those reported in other areas by
several authors (Alkurdi et al. 2019; Ledon et al. 2018; Otazo-Sánchez et al. 2020). The results
show that at a concentration of 10 mg L⁻¹ of fluorides in solution, the devilfish bone (Bone) has
a fluoride adsorption capacity of 5.06 mg g⁻¹ and this increases to 6.02 and 7.12 mg g⁻¹ when
the bone is pyrolysed at 400 and 500 °C, respectively, however, it decreases to 5.55 mg g⁻¹
when the pyrolysis temperature is elevated from 500 to 800 °C. C500 was the sample with the
highest fluoride adsorption capacity. This may be since it contains a higher concentration of
base sites (Table 2) than the other bone char ones, so it was decided to perform the following
experiments with this material. The results obtained for this study coincide with those reported
by other authors (Bhatnagar et al. 2011; Kaseva 2006). The pretreatment of bones with
hydrogen peroxide solutions prior to pyrolysis generates an increase in the specific area of the
bone chars of up to 1.5 times with respect to those not treated with these solutions and the
generation of pyrolysis subproducts or volatile matter is practically inexistent. Therefore, it can be considered that the conditions used in this study to carry out bone pyrolysis were adequate.

Fig. 4. Influence of the pyrolysis temperature on the fluoride adsorption capacity of Bone, C400, C500, C600, C700 and C800.

3.4 SEM, IR, TGA and DRX Analysis

Fig. 5 shows the SEM images of the surface of Bone, C500 and CF500 particles, respectively. The images reveal that the Bone particles have irregular and slightly rough surfaces, in addition it is possible to observe an agglomeration of smaller particles on the surface, the C500 particles have a porous and irregular surface, and in addition, small crystalline particles are observed on its surface. Also, SEM images of the fluoride-saturated bone char (CF500) particles are observed. In addition, it does not show the crystalline particles that were observed in C500 due to fluoride adsorption on the surface.
Fig. 5. SEM micrographs of (a) Bone; (b) C500 and (c) CF500.

The infrared spectra of the Bone, C500 and CF500 samples are shown in Fig. 6. In the infrared spectra the functional groups of $\text{PO}_4^{3-}$, $\text{CO}_3^{2-}$, OH and organic compounds of each sample were identified. It can be seen that there is an increase in the intensity of the 556, 600, 961 and 1016 cm$^{-1}$ bands, corresponding to the $\text{PO}_4^{3-}$ groups, when the bone is pyrolysed (C500) and at the same time these bands maintain their intensity when saturated with fluoride (CF500). In addition, the 3566 cm$^{-1}$ band corresponding to the OH$^-$ increases when the Bone sample is pyrolysed, revealing the formation of hydroxyapatite, and this band is attenuated when saturated with fluoride, which may indicate an interaction between the hydroxyl groups of hydroxyapatite and fluoride (Nigri et al. 2019). The mass-loss (TG) and derivative mass-loss (DTG) curves of Bone, C500 and CF500 samples are exhibited in Fig. 7 and it is observed that the highest percentage of weight loss occurs with the B sample at 40 %, this due to the organic matter content which degrades in great proportion when submitted to the pyrolysis process at 500 °C. The DTG curves show that the first weight loss for all three materials occurs below 100 °C and is associated with moisture loss, and from 270 to 640 °C the decomposition of proteins, fats, collagen, and others (Bedin et al. 2017). At 700 °C there is a slight curve which is attributed to the decomposition of carbonates or to the dehydroxylation of hydroxyapatite (600 to 800 °C).
(Figueiredo et al. 1999) and finally there is an equilibrium in the weight loss of the material from 800 to 1000 °C.

Fig. 6. FT-IR spectra of Bone, C500 and CF500.

Fig. 8 shows the diffractograms of Bone, C500 and CF500, and the peaks identified in all the samples correspond to hydroxyapatite, $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$. The characteristic maximum peaks of hydroxyapatite are found in the values of 25.9°, 31.7°, 46.7° and 49.5° on 2θ and are consistent with those reported by some authors (Bedin et al. 2017; Medellin-Castillo et al. 2020). Similarly, the peaks of hydroxyapatite observed in sample Bone increase when pyrolysed, indicating that the percentage of hydroxyapatite increases, and these peaks present a decrease in the CF500 sample indicating a saturation of fluoride on the hydroxyapatite.
Fig. 7. TGA samples of Bone, C500 and CF500.
Fig. 8. XRD patterns of Bone, C500 and CF500.

3.5 Adsorption isotherms

The experimental data of the fluoride adsorption on bone char from devilfish were matched to the Langmuir, Freundlich and Prausnitz-Radke adsorption isotherm models which are shown in equations 5, 6 and 7, respectively.

\[ q = \frac{q_m K C_e}{1 + K C_e} \]  \hspace{1cm} (5)

\[ q = k C_e^{1/n} \]  \hspace{1cm} (6)

\[ q = \frac{a C_e}{1 + b C_e} \]  \hspace{1cm} (7)
where $q$ (mg g$^{-1}$) is the fluoride adsorption capacity, $C_e$ (mg L$^{-1}$) is the fluoride concentration at equilibrium. The Langmuir constants $K$ (L mg$^{-1}$) and $q_m$ (mg g$^{-1}$) describe adsorption energy and maximum adsorption capacity, respectively; $k$ (mg$^{1-1/n}$L$^{1/n}$g$^{-1}$) and $1/n$ are the Freundlich constants, and the parameters $a$ (L g$^{-1}$), $b$ (L mg$^{-1}$)$^{\beta}$ and $\beta$ are the Prausnitz-Radke constants. The constants of these isotherms were evaluated using a method of least squares based on the Rosenbrock-Newton optimisation algorithm and using a criterion of minimum percentage standard deviation, which is defined as

\[
\%D = \left| \frac{q_{exp} - q_{cal}}{q_{exp}} \right| \times 100
\]

where $q_{exp}$ (mg g$^{-1}$) is the experimental amount of adsorbed fluoride and $q_{cal}$ (mg g$^{-1}$) is the amount of adsorbed fluoride predicted.

The isotherm constant values and their %D for the fluoride adsorption equilibrium on C500 are shown in Table 3. As it can be seen, the experimental data were better interpreted by three-parameter isotherm model, as the %D were less than 8.70, 11.37 and 19.84 % for the Prausnitz-Radke, Langmuir and Freundlich isotherms, respectively.

Table 3. Isotherms parameters for the fluoride adsorption on C500 at T= 25 °C.

| T (°C) | pH  | Langmuir |  | Freundlich |  | Prausnitz-Radke |  |
|-------|-----|----------|---|------------|---|----------------|---|
|       |     | $q_m$ (mg L$^{-1}$) | $K$ (L mg$^{-1}$) | $\%D$ | $k$ (mg$^{1-1/n}$ L$^{1/n}$ mg$^{-1}$) | $1/n$ | $\%D$ | a (L g$^{-1}$) | b (L mg$^{-1}$)$^{\beta}$ | $\beta$ | $\%D$ |
| 15    | 7   | 12.1     | 0.65 | 11.2 | 4.31 | 3.15 | 9.67 | 14.5 | 1.95 | 0.85 | 4.34 |
| 25    | 5   | 22.6     | 1.44 | 8.83 | 9.71 | 2.74 | 19.8 | 33.1 | 1.49 | 0.99 | 8.70 |
|       | 7   | 12.7     | 0.73 | 4.30 | 4.65 | 3.21 | 8.95 | 12.5 | 1.31 | 0.91 | 0.88 |
| 9     |     | 9.99     | 0.16 | 10.7 | 2.08 | 2.44 | 3.36 | 18.1 | 7.74 | 0.62 | 2.69 |
| 35    | 7   | 15.2     | 0.79 | 11.4 | 5.58 | 3.06 | 8.11 | 23.9 | 2.62 | 0.83 | 2.36 |
3.6 Adsorption capacity and its effect by the solution pH

The fluoride adsorption on C500 was studied at 25 °C and at different solution pH (5.0, 7.0 and 9.0) to evaluate its effect on the adsorption capacity, the results are shown in Fig. 9, a higher amount of fluoride adsorbed from the aqueous solutions at pH= 5.0, compared to the higher pH values show that the adsorption capacity of the C500 sample was significantly dependent on the pH. This behavior coincides with that reported by other authors, who also studied the adsorption of fluorides in bone char (Medellín-Castillo et al. 2020; Zúñiga-Muro et al. 2017).

![Fluoride Adsorption Capacity vs Concentration of Fluoride at Equilibrium](image)

**Fig. 9.** Effect of solution pH on the fluoride adsorption capacity on C500 at T= 25°C.

Electrostatic interactions may explain the effect of solution pH. Considering that the pH_{PZC} of C500 is 6.93 (Table 2), this implies that the surface of the bone char is positively charged at solution pH below the pH_{PZC}. Under these conditions, the electrostatic interaction between the fluoride ions in solution and the positive surface of the C500 is the main mechanism of fluorine adsorption. Therefore, at solution pH below their respective pH_{PZC}, electrostatic attraction
favors fluoride adsorption. The positive charge of the surface increases by lowering the pH below the pH\textsubscript{PZC} (Nigri et al. 2019).

In addition, as shown in XRD analysis, the main constituent of bone char is hydroxyapatite, so the groups on the surface of solid that affect its surface charge are phosphates, \(\equiv\text{P-OH}\), and hydroxyl, \(\equiv\text{Ca-OH}\), this groups can interact with the solvent and the ions in aqueous solution (Nigri et al. 2019).

3.7 Effect of solution temperature and thermodynamic properties

Fig. 10 presents the effect of temperature on the fluoride adsorption capacity of the C500 sample at 15, 25 and 35 °C at pH 7. The results obtained show that temperature influences the adsorption capacity, because at a temperature of 35 °C a larger amount of fluoride is adsorbed. Therefore, when the solution temperature is increased, fluoride ions have more energy and therefore more fluoride ions can be adsorbed on the surface of the bone char as they have enough energy (Cooney 1998).

The isosteric heat of adsorption was evaluated in order to determine this thermodynamic parameter that explains the nature of adsorption and relates it to the heat of adsorption. The isosteric heat was evaluated according to the equation:

\[
(\Delta H_{\text{ads}})_q = \frac{R \ln \frac{C_2}{C_1}}{\frac{1}{T_2} - \frac{1}{T_1}}
\]

where \((\Delta H_{\text{ads}})_q\) represents the isosteric heat of adsorption (J mol\(^{-1}\)), \(R\) is the universal constant of the ideal gases (J mol\(^{-1}\) K\(^{-1}\)), \(C_1\) and \(C_2\) (mg L\(^{-1}\)) are the fluoride concentrations at \(T_1\) and \(T_2\), respectively, at the same value of \(q\) and \(T_1\) and \(T_2\) (K) are the temperatures at conditions 1 and 2.
At a mass of fluoride adsorbed on C500 of $q = 7.0 \text{ mg g}^{-1}$ the equilibrium fluoride concentrations were $C_1 = 2.624 \text{ mg L}^{-1}$ and $C_2 = 1.163 \text{ mg L}^{-1}$, at temperatures $T_1 = 288.15 \text{ K}$ and $T_2 = 308.15 \text{ K}$, respectively. The isosteric heat calculated was 30.038 kJ mol$^{-1}$. This indicates that fluoride adsorption on C500 is an endothermic and physical process (<83 kJ mol$^{-1}$).

The Gibbs free energy ($\Delta G^\circ$), enthalpy ($\Delta H^\circ$) and entropy ($\Delta S^\circ$) of the fluoride adsorption process on devilfish bone char was determined through the following equations using the value of the Langmuir constant $K$ at different conditions reported in Table 4:

\[
\Delta G^\circ = -RT \ln K \quad (10)
\]
\[
\ln K = \frac{\Delta G^\circ}{RT} = \frac{\Delta H^\circ}{RT} + \frac{\Delta S^\circ}{R} \quad (11)
\]

The thermodynamic parameters evaluated for the fluoride adsorption process on bone char are shown in Table 4. The estimation of the isosteric heat of adsorption revealed that the fluoride

![Graph](image-url)
adsorption is endothermic. The positive $\Delta H^\circ$ values estimated corroborate the endothermic nature of fluoride adsorption. Positive $\Delta S^\circ$ values show the affinity of fluoride to devilfish bone char.

Table 4. Thermodynamic parameters estimated for adsorption of fluoride on C500 from devilfish.

| Sample | $T$ (°C) | $K$ (L mg$^{-1}$) | $K \times 10^{-3}$ (L mol$^{-1}$) | $\Delta G^\circ$ (kJ mol$^{-1}$) | $\Delta H^\circ$ (kJ mol$^{-1}$) | $\Delta S^\circ$ (J mol$^{-1}$K$^{-1}$) |
|--------|----------|------------------|----------------------------------|---------------------------------|-------------------------------|----------------------------------|
| C500   | 15       | 0.65             | 12.35                            | -22.57                          | 7.213                         | 103.4                            |
|        | 25       | 0.73             | 13.87                            | -23.64                          |                               |                                  |
|        | 35       | 0.79             | 15.01                            | -24.64                          |                               |                                  |

3.8 Reversibility of the fluoride adsorption process and thermal regeneration

The experimental data of the desorption of the adsorbed fluoride on C500 are shown in Fig. 11 and were obtained by first adsorbing the fluoride on C500 at pH 5.0 and $T=25$ °C, and then desorbing the adsorbed fluoride using a non-fluoride solution at pH 5.0 and 9.0 and $T=25$ °C, until a new equilibrium was reached.

In Fig. 11, it can be observed that fluoride is very slightly desorbed from C500 at pH 5.0. The fluoride desorbed from C500 increases as the pH of the solution increases. Therefore, the desorption of fluoride ions at high pH values is related to the repulsive forces between negative charged surface groups due to the deprotonation and the negatively charged fluoride ions in solution as well as the competition between OH$^-$ from the solution and fluoride ions during the adsorption process.
Fig. 11. Fluoride adsorption-desorption equilibrium on C500 at different values of pH and T=25 °C.

This reveals that fluoride is desorbed to a greater extent from C500 at more basic solution pH. That is, the desorption at pH 5.0 shows us that the fluoride that is desorbed goes from 0.24 to 3.06 %, while for desorption at pH 9.0 it goes from 1.03 to 20.06 %, this indicates that the fluoride desorption process in C500 at both pHs is partially reversible, therefore the adsorption is not completely physical, there is also the adsorption by chemisorption or by ion exchange.

The adsorption capacities of the regenerated materials as well as the C500 before regeneration are shown in Figure 12. The results show that the fluoride adsorption capacities are maintained after thermal regeneration as the adsorption capacities vary slightly compared to C500 and show a similar variation to the study of the effect of the pyrolysis temperature of bone char.
Fig. 12. Fluoride adsorption capacities of bone char thermally regenerated.

3.9 Removal of fluoride from drinking well water in a rural community

La Laborcilla rural community has a population of approximately 781 inhabitants whose main economic activities are agriculture, livestock and masonry. This community is supplied with water from a well with an approximate depth of 400 m. Physical-chemical parameters of the drinking water are shown in Table 5. The water is used for human consumption and in all economic activities of the community. In addition, the elementary school Aquiles Serdan is located in this community and it has a registration of 120 students between the ages of 6 and 12 who drink water from water dispenser that are supplied by the well mater. For this reason, it is common to observe the presence of dental fluorosis among the students and inhabitants of this area. Fig. 2 shows some photos of the location of the community, well, water dispensers and dental fluorosis in a child. This type of problem is common in the Altiplano and Central areas of San Luis Potosi, Mexico, as also in other central and northern states of Mexico (Ledon et al. 2018; Otazo-Sánchez et al. 2020). Fluorosis is a serious health problem worldwide and it has
been reported that more than 35 countries have excess fluoride in their drinking water (Alkurdi et al. 2019).

Table 5. Parameters of the drinking water from the rural community La Laborcilla, Villa de Arriaga, Mexico

| Parameter                        | Concentration determined | Permissible limits |
|----------------------------------|--------------------------|--------------------|
|                                  |                          | NOM  | WHO          |
| pH                               | 7.88                     | 6.5-8.5          | NVP          |
| Colour (Co/Pt)                   | 0.00                     | 20.0            | Colourless   |
| Odour                            | Odourless                | Odourless        | Odourless    |
| Turbidity (NTU)                  | 0.50                     | 10.0            | <0.2         |
| Total hardness (mg CaCO₃/L)      | 122                      | 500             | NVP          |
| Ca hardness (mg CaCO₃/L)         | 95.0                     | NVP             | NVP          |
| Mg hardness (mg CaCO₃/L)         | 27.0                     | NVP             | NVP          |
| Chlorides (mg/L)                 | 45.0                     | 250             | NVP          |
| Fluorides (mg/L)                 | 4.50                     | 1.50            | 1.50         |
| Nitrites (mg/L)                  | Absent                   | 1.00            | 3.00         |
| Nitrates (mg/L)                  | 9.30                     | 10.0            | 50.0         |
| Sulfates (mg/L)                  | 45.0                     | 400             | NVP          |
| Mesophilic Aerobic Microorganisms (UFC/mL) | 3904                  | NVP             | NVP          |
| Total coliforms (NMP/100 mL)     | Absent                   | Absent          | Absent       |
| Faecal coliforms (NMP/100 mL)    | Absent                   | Absent          | Absent       |
| Total dissolved solids (mg/L)    | 376                      | 1000            | NVP          |
| Chlorine (mg/L)                  | Absent                   | 0.10—1.50       | 5.00         |

NVP: No value proposed

Fluoride adsorption test were performed by contacting various masses (from 0.05 to 0.8 g) of C500 sample with 100 mL of water of pH= 7.88 and according to the methodology mentioned in section 2.6. Table 5 shows the parameters determined for water, as well as the maximum permissible limit for each parameter measured according to the Official Mexican Standards.
(NOM) and the Guidelines for Drinking-water Quality by World Health Organization (WHO 2017) and it can be noted that the only parameter of the water collected in the community of La Laborcilla that is above the maximum permissible limit set by the Mexican Official Standards and the values suggested by the WHO are fluorides whose concentration is 4.5 mg/L, 3 times higher than the permitted concentration (1.5 mg L\textsuperscript{-1}).

Table 6 shows that the % of fluoride removal increases from 69.1 to 98.7 % as the dose of C500 increases from 0.05 to 0.8 g, until almost all the fluoride is removed from the water.

The increase in adsorption with the amount of the adsorbent may be due to a higher specific surface area and concentration of adsorption sites.

Table 6. Removal of fluorides and other anions in drinking water using C500 at T= 25 °C and without pH control.

| Exp | m (g) | Fluoride | Total hardness mg CaCO\textsubscript{3} L\textsuperscript{-1} | Chloride mg L\textsuperscript{-1} | Sulfate mg L\textsuperscript{-1} |
|-----|------|---------|-----------------|----------------|----------------|
|     |      | C\textsubscript{0} (mg L\textsuperscript{-1}) | C\textsubscript{f} (mg L\textsuperscript{-1}) | % Re | q (mg g\textsuperscript{-1}) | C\textsubscript{0} | C\textsubscript{f} | %Re | C\textsubscript{0} | C\textsubscript{f} | %Re |
| 1   | 0.05 | 4.72    | 1.46            | 69.1 | 5.82 | 122 | 117.8 | 3.44 | 45.0 | 45.0 | 0.00 | 45.0 | 45.0 | 0.00 |
| 2   | 0.1  | 4.72    | 0.56            | 88.1 | 3.74 | 122 | 113.8 | 6.72 | 45.0 | 45.0 | 0.00 | 45.0 | 40.5 | 10.0 |
| 3   | 0.2  | 4.72    | 0.16            | 96.6 | 2.06 | 122 | 113.0 | 8.04 | 45.0 | 45.0 | 0.00 | 45.0 | 38.0 | 15.6 |
| 4   | 0.4  | 4.72    | 0.10            | 97.9 | 1.04 | 122 | 111.0 | 9.02 | 45.0 | 45.0 | 0.00 | 45.0 | 35.0 | 22.2 |
| 5   | 0.8  | 4.72    | 0.06            | 98.7 | 0.52 | 122 | 108.8 | 10.8 | 45.0 | 32.5 | 27.8 | 45.0 | 32.5 | 27.8 |

On the other hand, the concentration of total hardness, chlorides and sulfates remain almost constant, so it can be considered that these ions do not compete during the process of adsorption of fluorides on C500.

Also, it was determined that the mass of C500 needed to reduce the concentration of fluoride in water of the community of La Laborcilla, from 4.7 to 1.5 mg L\textsuperscript{-1}, which is the maximum permissible limit of the presence of fluoride in water for human use and consumption indicated by the NOM-127-SSA1-1994, is 0.55 g of C500 for each L of water.
4. Conclusions

The specific area, pore volume and pore diameter of the bone char prepared in this study are within the ranges of values reported in the literature for other bone char from other animals. X-ray diffraction analysis determined that the species or crystalline phase in the bone char is hydroxyapatite [Ca\(_{10}\)(PO\(_4\)\(_6\))(OH)\(_2\)].

The study of the effect of the solution pH in the fluoride adsorption isotherm on C500 sample revealed that the adsorption capacity of this adsorbent to remove fluoride is considerably dependent on the solution pH, as it increases with decreasing pH. The study of the effect of temperature solution revealed that the adsorption on C500 is endothermic.

Fluoride can be desorbed from C500 but the adsorption equilibrium is not completely reversible as the % desorption varied of 0.24 to 20.06 % indicating that fluoride adsorption occurs by physisorption and chemisorption mechanisms. It was determined that fluoride-saturated bone carbonization can be thermally regenerated at 500 °C with a slight decrease in its adsorption capacity. The necessary mass of C500 to reduce the fluoride concentration of 4.7 mg L\(^{-1}\) in the drinking water of the community of La Laborcilla in the state of San Luis Potosí, to a concentration below 1.5 mg L\(^{-1}\) complying with the maximum permissible limit (NOM-127-SSA1-1994), is 0.55 g L\(^{-1}\). The chemical composition of this water as also the characteristics of the well represent typical values for the central and northern zone of Mexico and other countries, whose results may be used for other studies. It was finally concluded that the adsorption of fluoride in aqueous solution on bone char from devilfish can be considered a viable and economic option in the treatment of water for human consumption.

Declarations

Ethics approval and consent to participate

Not applicable

Consent for publication
Not aplicable

**Availability of data and materials**

The datasets used and/or analysed during the current study are available from the corresponding author on reasonable request.

**Competing Interests**

The authors declare that they have no competing interests

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**Authors Contributions**

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