Chemically activated cow bone for increased fluoride removal from drinking water

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ABSTRACT

Thermally activated cow bone is widely utilized for treating fluoride impacted drinking water to meet the World Health Organization guideline value of 1.5 mg/L. However, the fluoride removal capacity of bone char is low, leaving room for further improvement. This study, therefore, strives to improve the fluoride adsorption capacity of cow bone by using chemical activation in place of thermal activation. Chemically activated cow bones (CABs) had, on average, a four-fold higher fluoride adsorption capacity than bone char. Characterization of the most effective CAB were made to explore potential reasons for the increased fluoride adsorption capacity. The X-ray diffraction pattern of the CAB showed formation of bassanite and monetite minerals which may be responsible for the higher fluoride adsorption capacity. Chemical activation is also a lower-cost production process than the thermal activation of cow bone. Further, a higher mass of media was recovered per unit mass of starting material during chemical activation. Therefore, this research shows that increased fluoride removal capacity can be achieved with chemical activation of cow bone while reducing activation costs and greatly increasing product yield per unit mass of starting material, all of which support further evaluation and field testing of this material.

Key words | bassanite, chemical activation, cow bone, fluoride removal, low-cost adsorbent, monetite

INTRODUCTION

Consuming drinking water with excess fluoride concentrations remains a major health hazard and environmental problem in the 21st century. Globally, more than 200 million people consume water above the World Health Organization’s guideline threshold of 1.5 mg/L (Amini et al. 2008). Fluoride concentrations above the 1.5 mg/L threshold are harmful to human health (WHO 1984) and can cause dental and skeletal fluorosis (Dissanayaka 1991; Fawell & Balley 2006). Although not life-threatening illnesses, dental and skeletal fluorosis often produces many adverse effects, including added health costs, loss of labor, and significant psychological stress for affected populations (Apambire et al. 1997). Therefore, it is critical to treat excessive fluoride-rich groundwater or provide alternative water sources to at-risk communities. Various treatment methods such as adsorption, membrane processes, and electrolytic defluoridation have been investigated for removal of excess fluoride from drinking water (Mohapatra et al. 2004; Fawell & Bailey 2006; Ayoob et al. 2008). Of all these treatment methods, adsorption is often the preferred option for fluoride removal due to its high efficiency and its low cost of operation and maintenance (Jagtap et al. 2012).

Thermal activation of bone, a process of heating cow bones in a furnace to high temperature under restricted access of atmospheric oxygen, increases fluoride adsorption capacity by decreasing the organic matter content of the bone (Bhargava & Killedar 1991). Thermally activated cow bone, commonly known as bone char, is among the...
adsorbents used to remove excess fluoride (Fawell & Balley 2006; Medellin-Castillo et al. 2007; Ayoob et al. 2008) owing to its large surface area and the high fluoride affinity of hydroxyapatite, the main constituent of cow bone. It is also widely available at low cost in developing countries, e.g., in the Rift Valley area in Ethiopia (Mutheki et al. 2011), and Nakuru area in Kenya (Jacobsen & Muller 2007). Initially, bone char was imported from Kenya to assess technical performance and user acceptance (Johnson et al. 2011) and subsequently a production facility was established in Ethiopia by Oromo Self Help Organization in 2011 (Osterwalder et al. 2014).

To our knowledge, chemical activation of cow bone has not been evaluated as an alternative to thermal activation for fluoride removal. Results in the literature indicate that thermally activated bone can achieve an average fluoride adsorption capacity ($Q_{1.5}$) of 1.5 mg/g at an equilibrium dissolved fluoride concentration of 1.5 mg/L (Abe et al. 2004; Brunson & Sabatini 2009). Although, the bone char’s $Q_{1.5}$ is better than that of activated alumina ($Q_{1.5} = 0.5$ mg/g) and wood char ($Q_{1.5} = 0.2$ mg/g) (Brunson & Sabatini 2014), there is still room for further improvement. Moreover, thermal activation is energy intensive, requiring carbonization temperatures above 400 °C (Lussier et al. 1994).

Based on a literature review, chemical activation of carbonaceous materials produces activated carbon with higher specific surface areas (SSAs) than thermal activation. For example, very large Brunauer–Emmett–Teller (BET) SSAs have been reported for chemically activated carbon materials: 2,395 m²/g using potassium hydroxide for corn cob (Tseng & Tseng 2005) and 2,400 m²/g for coconut shell (Hu et al. 2001). On the other hand, an SSA value of 1,400 m²/g for eucalyptus (Ngernyen et al. 2006) has been reported via thermal activation. This shows that higher SSAs can be achieved via chemical activation as compared to thermal activation. These high SSAs obtained during chemical activation of a range of different carbonaceous materials motivated us to evaluate chemical activation of bone to see if it would increase fluoride adsorption capacity of the CAB media. Another advantage to chemical over thermal activation is the small adsorbent mass losses upon activation (Srinivasakannan & Balasubramanian 2007; Zhang et al. 2010).

Additionally, surface amendment, a process of dispersing aluminum salts into the matrix of the biomaterials (Tchomgui-Kamga et al. 2010), has been applied on thermally activated wood char (Brunson & Sabatini 2014). Dispersing these metals in a protective matrix can provide high fluoride adsorption capacity. Therefore, surface amendment using aluminum salts was evaluated for its impact on the fluoride adsorption capacity of bone char.

The overall goal of this work was to produce a more efficient (fluoride uptake) and effective (mass recovery) cow bone-based fluoride adsorbent. The research questions evaluated in this work were: (1) does the chemical activation process, which has proven to be effective in increasing the SSA of activated carbon and thereby increase its adsorption capacity, result in similar increase in fluoride uptake in cow-bone based adsorbents? and (2) does the chemical activation of cow bone lead to improved mass recovery of the starting materials as compared to thermal activation? To our knowledge, this research is the first to evaluate chemical activation of bone as an alternative to thermal activation for fluoride removal. The specific objectives of this study were: (1) to investigate the fluoride adsorption capacity of CAB; (2) to compare the fluoride adsorption capacity of chemically activated and thermally activated cow bone; (3) to investigate the effect of surface amendment (dispersion of aluminum salts onto the matrix of bone char) on its fluoride removal capacity; (4) to investigate mechanisms for improved fluoride sorption by assessing the chemical and structural properties of the CABs which proved most effective for fluoride removal; and (5) to compare the cost of production of CAB and bone char along with the mass of product versus mass of starting material for each.

**MATERIALS AND METHODS**

**Preparation of CAB**

Cow bone was obtained from a ranch in LaRue, Texas, USA, cut into smaller pieces and soaked in 12% NaOCl solution for 24 hours to remove impurities (Brunson & Sabatini 2009). The soaked cow bone was washed with deionized water to further remove organic matter, dried in an oven for 24 hours, and crushed manually using a metal mortar and pestle. The crushed bone was sieved using number
40/80 mesh sizes (180–425 μm). The fine powders were removed by rinsing with deionized water, oven dried again for 24 hours and stored for subsequent chemical activation.

The chemicals used for activation of cow bone were H₂SO₄ (Fisher Scientific, 660 BAUME, Technical grade), H₃PO₄ (Fisher Scientific, 85%, Certified ACS), KOH (EM science, pellets, solid), and ZnCl₂ (Fisher Scientific, Technical grade, powder). The chemicals were chosen based on previous applications of chemical activation on carbonaceous materials which yielded high SSAs (see Introduction section). AlCl₃ and Al₂(SO₄)₃ were chosen for surface amendment of bone char based on their use in amending other biomaterials, such as spruce wood (Tchomgui-Kamga et al. 2010).

**Chemical activation of cow bone**

The crushed, rinsed, and oven-dried cow bones were chemically activated using H₃PO₄, H₂SO₄, ZnCl₂, and KOH solutions, each at 20, 30, and 50 wt %. The CABs are represented as HSCB, HPCB, ZnCB, and KCB for H₂SO₄, H₃PO₄, ZnCl₂, and KOH activated cow bones, respectively. The experimental flow chart and procedures for chemical activation are shown in Figure S1. The preliminary screening tests conducted to identify parameters to be used in chemical activation indicated that a heating temperature of 50 °C, a heating duration of 3 hours, and a 1:1 media to activating agent ratio produced both a good quality and quantity of CAB. Activation parameters exceeding these values, i.e., heating temperatures higher than 50 °C, heating durations longer than 3 hours, and media to activating agent ratio higher than 1:1 dissolved the cow bones. The impact of activating agent concentration on mass recovery during activation was also evaluated. High mass recovery, i.e., mass of media recovered per unit mass of starting material during chemical activation of bone was achieved for 20–30% HSCB and HPCB, and for 30–50% KCB activations.

After chemical activation, one sample from each kind of CAB was selected for further thermal treatment to study its effect on fluoride adsorption capacity. The effect of combined chemical and thermal activation of cow bone was investigated by heating the HSCB, KCB, and ZnCB activated cow bones at 540 °C for 3 hours (referred to, for example, as HSCB-540). The CAB samples with the best adsorption capacity (HSCB and KCB), and the lowest adsorption capacity (ZnCB) were selected for characterization (i.e., to measure values of SSA and points of zero charge (PZC)); to identify morphology using scanning electron microscopy (SEM); to determine average elemental composition using energy dispersive X-ray spectroscopy (EDS); and to analyze structure using X-ray diffraction (XRD).

**Surface amendment of bone char with aluminum salts**

Bone char was amended using 1,000 and 2,000 ppm AlCl₃ and 500, 1,000, and 2,000 ppm Al₂(SO₄)₃ solutions in order to promote formation of an adsorbent aluminum (hydr)oxide phase.

The amendment concentrations were created by adding the necessary quantities of AlCl₃ and Al₂(SO₄)₃ to screw cap glass bottles and filling them with 200 mL Nano pure water (18.1 MΩ-cm) and adjusting the pH to 3.5 using 50 mM 2-([N-morpholino] ethanesulfonic acid (MES) and MES salt. Next, 12 g of bone char was added to the 200 mL glass bottles and the mixture was put on a shaker at 200 revolutions per minute (rpm) for 5 days. The solution was then filtered, washed with deionized water, and oven dried overnight at 85 °C. The aluminum salts used for the amendment of bone char are soluble due to the low pH (i.e., pH 3.5) used in the amendment process.

**Batch experiments**

CAB (0.5 g) was added to 50 mL polyethylene bottles containing initial fluoride concentrations ranging from 0 to 150 mg/L. The reactors were agitated on a shaker (Ping-Pong TM # 51504-00) at 200 rpm for 24 hours (Brunson & Sabatini 2009). The pH of the adsorption experiment was fixed at 7.0 and confirmed by measurement, which is the pH of common natural water, by addition of 50 mM 2-[4-(2-hydroxyethyl) piperazin-1-yl] ethanesulfonic acid (HEPES) acid and salt. HEPES was utilized because it does not interfere with fluoride adsorption (Du et al. 2016). Furthermore, HEPES does not tend to complex with cations like Ca²⁺ (Good et al. 1966). After equilibration, each sample was filtered and the fluoride
concentration was determined by ion selective electrode. Prior to analysis, both standards and samples were diluted with total ionic strength adjustment buffer on a 1:1 basis to reduce hydroxide interferences and the formation of HF, and maintain a constant pH and ionic strength during analysis (Larsen & Widdowson 1971). Calibration of the fluoride electrode and measurements of the fluoride concentrations were performed in triplicate. Experimental errors associated with the measurement of $Q_e$ values were calculated using error propagation methods.

**Adsorbent characterization**

**Measurement of SSA and PZC**

SSA of the adsorbents was determined using the BET method. Additionally, the ethylene glycol monoethyl ether (EGME) method (Heilman et al. 1985) was employed for determining the SSAs of the CABs. The difference in the weight of samples before and after EGME coverage was used to calculate surface area. EGME analysis gives a more complete assessment of adsorbent surface area, because the BET method may measure only the external surface area of certain minerals (Yuksel & Kaya 2006), and because the aqueous medium in the EGME method may preserve pores that could collapse under the vacuum conditions applied during the BET method. The PZC of the CAB was determined using methods reported by Milonjic et al. (1985), Noh & Schwarz (1989), and Brunson & Sabatini (2009) (see Supplementary information, Measurement of PZC, available in the online version of this paper).

**SEM/EDS and XRD analysis**

SEM analysis was performed using a Zeiss NEON instrument operating at an accelerating voltage of 10 kV with an iridium sputter coating. EDS analysis was performed to identify the average elemental composition of the CAB. Powdered XRD was employed for structural characterization of the CAB using a Rigaku Ultima IV diffractometer and fitting with reference mineral patterns using materials data (MDI) JADE 2010 analytical software.

**RESULTS AND DISCUSSION**

**Fluoride adsorption capacity of CAB**

The HSCB and HPCB activated cow bone had much higher fluoride adsorption capacities than the thermally activated cow bone (Figure 1). The HSCB and HPCB equilibrium fluoride adsorption capacities ($Q_{1.5}$ fitted with the Freundlich isotherm) were four times higher than that of bone char (Table 1). Additionally, 30% and 50% KCB had higher adsorption capacities than bone chars (Figure 2) although their $Q_{1.5}$ values were not as high as those of HSCB and HPCB (Table 1). The ZnCB activation, on the other hand, led to a lower fluoride adsorption capacity than bone char (Figure 1 and Table 1). The $Q_{1.5}$ obtained for bone char in this study is similar to values reported in the literature at pH 7 (Abe et al. 2004; Brunson & Sabatini 2009) (Table 1). Thus, these results clearly demonstrate that chemical activation of cow bone can achieve fluoride adsorption capacities of up to four times greater than those obtained via thermal activation.

The effect of combined chemical and thermal activation of cow bone was investigated by heating the HSCB and KCB at 540 °C, ZnCB at 500 °C for 3 hours (referred to, for example, as HSCB-540). While the combined thermal–chemical activation process did significantly increase...
equilibrium fluoride adsorption capacity versus thermal activation alone (Figures 1 and 2), the adsorption parameters were not statistically different (95% CI) than chemically activated bone alone (see Q1.5 values in Table 1). This makes a one-step chemical activation of cow bone generally preferable to a combined thermal and chemical activation, since thermal activation requires higher energy consumption than chemical activation (Lussier et al. 1994).

Table 1 | Freundlich parameters of CAB and thermally activated cow bones

<table>
<thead>
<tr>
<th>Adsorbents</th>
<th>$k_f$ ((mg/g)/(mg/L))$^{1/n}$</th>
<th>$1/n$</th>
<th>$Q_{1.5}$ (mg/g)</th>
<th>pH</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>CAB</td>
<td></td>
<td></td>
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</tr>
<tr>
<td>30% HSCB$^b$</td>
<td>4.6 ± 1.2</td>
<td>0.7 ± 0.0</td>
<td>6.1 ± 1.6</td>
<td>7</td>
<td>This study</td>
</tr>
<tr>
<td>30% HPCB$^c$</td>
<td>4.3 ± 1.0</td>
<td>0.5 ± 0.0</td>
<td>5.4 ± 1.3</td>
<td>7</td>
<td>This study</td>
</tr>
<tr>
<td>50% ZnCB</td>
<td>0.4 ± 0.4</td>
<td>0.5 ± 0.4</td>
<td>0.5 ± 0.2</td>
<td>7</td>
<td>This study</td>
</tr>
<tr>
<td>30% KCB$^d$</td>
<td>2.8 ± 0.8</td>
<td>0.4 ± 0.1</td>
<td>3.3 ± 1.4</td>
<td>7</td>
<td>This study</td>
</tr>
<tr>
<td>50% KCB</td>
<td>3.2 ± 0.9</td>
<td>0.4 ± 0.1</td>
<td>3.8 ± 0.3</td>
<td>6.9</td>
<td>This study</td>
</tr>
<tr>
<td>Thermally activated cow bone</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Bone char</td>
<td>1.3 ± 0.4</td>
<td>0.3 ± 0.1</td>
<td>1.4 ± 0.5</td>
<td>7</td>
<td>This study</td>
</tr>
<tr>
<td>Bone char</td>
<td>1.1</td>
<td>0.4</td>
<td>1.2</td>
<td>7</td>
<td>Abe et al. (2004)</td>
</tr>
<tr>
<td>Bone char</td>
<td>0.8 ± 0.0</td>
<td>0.4 ± 0.0</td>
<td>0.9 ± 0.0</td>
<td>7.3</td>
<td>Brunson &amp; Sabatini (2009)</td>
</tr>
<tr>
<td>Bone char</td>
<td>1.8 ± 0.2</td>
<td>0.38</td>
<td>2.10</td>
<td>NR</td>
<td>Brunson &amp; Sabatini (2014)</td>
</tr>
<tr>
<td>Chemical activation followed by thermal activation</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>30% HSCB-540$^e$</td>
<td>4.6 ± 0.8</td>
<td>0.7 ± 0.0</td>
<td>6.3 ± 1.1</td>
<td>7</td>
<td>This study</td>
</tr>
<tr>
<td>30% KBC-540</td>
<td>2.8 ± 0.6</td>
<td>0.4 ± 0.1</td>
<td>3.2 ± 0.8</td>
<td>7</td>
<td>This study</td>
</tr>
<tr>
<td>50% KBC-540</td>
<td>3.1 ± 0.7</td>
<td>0.4 ± 0.1</td>
<td>3.6 ± 0.9</td>
<td>7</td>
<td>This study</td>
</tr>
<tr>
<td>50% ZnCB-500$^f$</td>
<td>1.9 ± 0.5</td>
<td>0.3 ± 0.1</td>
<td>2.2 ± 0.7</td>
<td>6.5</td>
<td>This study</td>
</tr>
<tr>
<td>Amended bone char</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1,000 ppm AlCl$_3$–BC$^g$</td>
<td>0.9 ± 0.3</td>
<td>0.6 ± 0.3</td>
<td>1.2 ± 0.7</td>
<td>6.9</td>
<td>This study</td>
</tr>
<tr>
<td>2,000 ppm AlCl$_3$–BC$^g$</td>
<td>0.9 ± 0.4</td>
<td>0.6 ± 0.4</td>
<td>1.2 ± 0.9</td>
<td>6.9</td>
<td>This study</td>
</tr>
<tr>
<td>500 ppm Al$_2$(SO$_4$)$_3$–BC$^g$</td>
<td>1.3 ± 0.4</td>
<td>0.5 ± 0.3</td>
<td>1.6 ± 1.1</td>
<td>6.5</td>
<td>This study</td>
</tr>
<tr>
<td>1,000 ppm Al$_2$(SO$_4$)$_3$–BC$^g$</td>
<td>0.9 ± 0.3</td>
<td>0.6 ± 0.3</td>
<td>1.2 ± 0.7</td>
<td>6.5</td>
<td>This study</td>
</tr>
<tr>
<td>2,000 ppm Al$_2$(SO$_4$)$_3$–BC$^g$</td>
<td>0.9 ± 0.4</td>
<td>0.6 ± 0.3</td>
<td>1.2 ± 0.7</td>
<td>6.5</td>
<td>This study</td>
</tr>
<tr>
<td>Aluminum Impregnated BC</td>
<td>1.4 ± 0.1</td>
<td>0.42</td>
<td>1.66</td>
<td>NR$^h$</td>
<td>Brunson &amp; Sabatini (2014)</td>
</tr>
</tbody>
</table>

The isotherm parameters ($k_f$ and $n$) were obtained from Freundlich isotherm fitting using SigmaPlot 12.0 and the uncertainties in Q and $1/n$ are calculated using error propagation method.

$^a$ Q1.5 is Q at $C_{eq}$ = 1.5 mg/L.

$^b$ Sulfuric acid activated cow bone.

$^c$ Phosphoric acid activated cow bone.

$^d$ Potassium hydroxide activated cow bone.

$^e$ Sulfuric acid activated bone char at 540 °C.

$^f$ Zinc chloride activated bone char at 540 °C.

$^g$ Aluminum chloride amended bone char at 540 °C.

$^h$ Not reported.

Surface amendment of bone char using AlCl$_3$ and Al$_2$(SO$_4$)$_3$ solutions produced lower Q1.5 values than the fluoride removal capacity achieved through chemical activation of cow bone (Figure S2 and Table 1). This is attributed to the already desirable adsorption properties of the bone char, and the potential for aluminum (hydr)oxide precipitates to block pores and limit access to internal surface area.
Characterization of the CAB

The BET SSAs of chemically and thermally activated cow bones ranged from 9 to 111 m²/g (Table 2). By comparison, the BET SSA of bone char was reported as 104 m²/g (Medellin-Castillo et al. 2013) and 110 m²/g (Brunson & Sabatini 2013). The measured BET SSA of HSCB was a factor of ten lower (9 m²/g) than the SSA measured by the EGME method (134 m²/g), while the BET and EGME SSAs for 50% KCB and 50% ZnCB-500°C differed by a factor of approximately two. The smaller BET SSA for HSCB compared to the EGME BET may be due to the collapse of the mineral structure of the CAB during the vacuum stage of the BET process, suggesting that the EGME may be more representative in this case. Both the BET and EGME SSAs of the CABs showed an increasing trend of HSCB < ZnCB < KCB (Table 2), which does not correspond to the trend in adsorption capacity (Table 1). Generally, there was no clear relationship observed between either BET and EGME SSA and fluoride adsorption capacity of the CABs.

While chemical activation has been found to produce a much higher SSA for carbonaceous materials than thermal activation, this trend was not observed for CAB versus thermally activated bone (bone char). Rather, the BET SSA values were largely the same. And while the EGME surface area of bone char was not measured, the EGME and BET SSAs followed similar trends (Table 2). Thus, SSA cannot account for the four times greater fluoride adsorption capacity of the CAB compared to the bone char. Additional characterization was therefore conducted to look for other possible explanations.

The PZC values for 30% HSCB, 50% KCB, and 50% ZnCB-500 are summarized in Table 2. The PZC value of 50% KCB was 8.4 (Figure S3(a)) which is the same as the PZC value of bone char reported by Medellin-Castillo et al. (2007) and Brunson & Sabatini (2009) (Table 2), yet the adsorption capacity of 50% KCB was significantly higher than that of bone char (Table 1). In addition, the PZC of 30% HSCB (6.6) (Figure S3(b) and Table 2) was the lowest among those measured, and indicates a net negative charge at the pH of the experiments (pH 7), yet this adsorbent had the highest Q₁.₅ of the three adsorbents for which PZC was measured (Table 1). Hence, the PZC also cannot account for four-fold increases in fluoride adsorption capacity of the CAB compared to bone char.

Table 2 | Properties of CAB and amended bone char

<table>
<thead>
<tr>
<th>Description of the adsorbent</th>
<th>SSA (m²/g) (BET method)</th>
<th>SSA (m²/g) (EGME method)</th>
<th>pH₁.₅</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>30% HSCB</td>
<td>9</td>
<td>134</td>
<td>6.6</td>
<td>This study</td>
</tr>
<tr>
<td>50% KCB</td>
<td>111</td>
<td>258</td>
<td>8.4</td>
<td>This study</td>
</tr>
<tr>
<td>50% ZnCB-500 °C</td>
<td>106</td>
<td>245</td>
<td>7.2</td>
<td>This study</td>
</tr>
<tr>
<td>Thermal, bone char</td>
<td>104</td>
<td>NR</td>
<td>8.4</td>
<td>Medellin-Castillo et al. (2007)</td>
</tr>
<tr>
<td>Thermal, bone char</td>
<td>110</td>
<td>NR</td>
<td>8.4</td>
<td>Abe et al. (2004)</td>
</tr>
<tr>
<td>Thermal, bone char</td>
<td>99.1</td>
<td>Not measured</td>
<td>NR</td>
<td>Brunson &amp; Sabatini (2014)</td>
</tr>
<tr>
<td>Aluminum impregnated bone char</td>
<td>91.8</td>
<td>Not measured</td>
<td>NR</td>
<td>Brunson &amp; Sabatini (2014)</td>
</tr>
</tbody>
</table>

Figure 2 | Fluoride adsorption fitting with Freundlich isotherms for CAB using potassium hydroxide (30% and 50% KCB), and 30% and 50% KCB CAB followed by thermal activation at 540°C, and bone char. The inset panel indicates the fluoride adsorption at lower equilibrium fluoride concentrations. The error bars represent the standard deviations associated with Qₐ and Cₑ calculated from triplicate measurements.
XRD analysis of 30% HSCB that exhibited the highest fluoride adsorption capacity showed the presence of the minerals bassanite (CaSO\textsubscript{4}.0.5 H\textsubscript{2}O) and monetite (CaHPO\textsubscript{4}) (Figure 3(a)) that were not present in bone char (only hydroxyapatite was found in bone char) (Figure 3(b)). This indicates that the phase change to bas-sanite and monetite occurred as a result of the chemical activation. The peaks of the CAB match the XRD pattern applied to bassanite crystals by Abriel & Nesper (1993), and monetite crystals by Frost et al. (2015). The CAB showed a mixture of elongated and rod-like crystals that could be bassanite and monetite, respectively (Figure 3(c)). The EDS elemental analysis of the CAB revealed the presence of higher percentage of calcium, and oxygen peaks (Figure 3(d)) compared to bone char. The CAB has additionally shown sulfur, magnesium, and sodium peaks which were not present in the bone char. Furthermore, it was observed from the EDS analysis that chemical activation fully removed volatile and organic materials (no carbon was detected by the EDS), which are commonly responsible for bad odors in drinking water.

Abe et al. (2004), Masamba et al. (2005), and Ayoob et al. (2008) suggested that the presence of SO\textsubscript{4}\textsuperscript{2-}, Ca\textsuperscript{2+}, and PO\textsubscript{4}\textsuperscript{3-} enhances defluoridation capacity. Therefore, the presence of sulfate in bassanite and phosphate in monetite minerals may be responsible for the high fluoride removal capacity of the CABs versus thermally activated cow bone. The increased fluoride adsorption of the CAB may be due to an ion exchange of PO\textsubscript{4}\textsuperscript{3-}, SO\textsubscript{4}\textsuperscript{2-}, and OH\textsuperscript{-} by fluoride ions from aqueous solution. These concepts should be further explored in future research.

Mass recovery during chemical activation

The chemical activation processes did not result in significant loss of the starting media as compared to losses measured during the thermal activation process (approximately 30% material loss versus approximately 80% loss,
Cost comparison of adsorbent production

The total costs of production of chemically and thermally activated cow bone were found to be $0.30/kg and $0.83/kg, respectively (Table S2). The production of CAB (considering cost of the adsorbents per kg) is about 11 times cheaper than the thermal activation of cow bone (see Calculations in Supplementary information available in the online version of this paper). Thus, chemical activation of cow bone is a very low-cost production process compared to thermal activation of cow bone.

CONCLUSIONS AND RECOMMENDATIONS

Comparison of the fluoride adsorption capacity of CAB showed, on average, about four-fold higher fluoride adsorption capacities than thermally activated cow bone. While chemical activation has been shown to produce a much higher SSA in carbonaceous materials in the formation of activated carbon, it did not likewise produce higher SSA when applied to cow bones. Likewise, the PZC values of CAB were found to be similar to those of bone char. Therefore, SSA and PZC were not able to explain this four-fold increase in fluoride adsorption capacity. Instead, the formation of the minerals bassanite and monetite during chemical activation of cow bone are thought to be responsible for the high fluoride adsorption capacity.

Compared to thermally activated cow bone, CAB achieved a greater mass recovery value than bone char due to fines lost during thermal activation. Chemical activation of cow bone was also found to be a more cost-effective production process than thermal activation. Therefore, CAB has proven to be a highly efficient and effective adsorbent in the laboratory. This shows that it has great potential to mitigate the negative health effects of fluoride impacted drinking water, and will be field tested in future research.

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