Hydroxyapatite and bone particle-doped ceramic water filters for the removal of fluoride and bacteria

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Abstract: This paper examines the effects of hydroxyapatite (HA) and bone-particle (BP) doping on the removal of fluoride and bacteria by ceramic water filters (CWFs). The CWFs were produced by mixing clay, sieved sawdust, and either HA or BPs in a weight ratio of 30:50:20 and sintered at 850°C or 900°C to produce micro-/nano-porous structures that remove microbial pathogens (by geometric occlusion) and fluoride (by adsorption) from contaminated water. The HA-doped filters exhibited similar flow characteristics to the BP-doped filters. However, BP-doped CWFs were more effective in removing fluoride and microbial pathogens (such as E. coli) from contaminated water than HA-doped filters. The water flow rates and fluoride removal depended on sintering temperature, with CWFs sintered at 850°C enabling faster flow rates of 2.2Lh⁻¹ and higher fluoride removal of 2.74 mol.cm⁻² than the CWFs sintered at 900°C. Fluoride removal by the HA- and BP-doped filters was well characterized by Freundlich isotherms that reveal the occurrence of spontaneous but heterogeneous adsorption. The implications of the results are

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PUBLIC INTEREST STATEMENT

Many developing countries are working towards the goal of safe water for all in 2025, 2030, etc. This confirms that many of their citizenry lack access to safe water. The World Health Organization attested to this by stating that about 2 billion people lack access to safe and potable water. Leaders, policymakers, and researchers worldwide have made notable efforts towards improving the situation through millennium development and sustainable goals. Fluorosis, be it dental, skeletal, or crippling, is disastrous, as are bacteria-related diseases. Hence, there is a need to find a simple, low-cost, and durable means of securing safe drinking water. Ceramic water filter technology offers a solution for removing particles, chemicals, and pathogens from drinking water. This paper studies the ability of bovine bone particles or hydroxyapatite-doped ceramic water filters to remove fluoride and bacteria from water. This will help to provide safe drinking water to many people in resource-poor settings in developing countries.

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discussed for the design of point-of-use CWFs for the removal of fluoride and microbial pathogens.

**Subjects:** Mechanics of Solids; Materials Science; Civil, Environmental and Geotechnical Engineering

**Keywords:** Ceramic water filters; hydroxypatite and bone particle doping; fluoride and microbial removal; contaminated groundwater

1. Introduction

The fluoride content of drinking water is generally good for the human body if its concentration falls within the World Health Organization (WHO) limit of 1.5 mg/L (WHO, 1984; He, 1996). Within this limit, fluoride prevents dental caries or tooth decay. However, fluorosis occurs when the fluoride concentration exceeds this limit. The following three types of fluorosis have been reported: dental fluorosis (fluoride content between 1.5 mg/L–4.0 mg/L) characterized by pitting, mottling and browning of teeth; skeletal fluorosis (fluoride content between 4.0 mg/L–8.0 mg/L) associated with skeletal malfunctioning and the weakening of bones; and crippling fluorosis (beyond 10 mg/L) characterized by the growing together of bone, fusion of bone junctions and consequently, total immobility (Fawell et al., 2006; WHO, 2011; Zereffa & Bekalo, 2017).

When the fluoride concentration is between 0 and 1.5 mg/L in the human body, the F⁻ ions replace the OH⁻ ions in the hydroxypatite to form fluorapatite in the bone (Fawell et al., 2006). The formation of fluorapatite prevents dental caries by resisting acid attack by forming a protective layer on the tooth enamel. However, the excessive intake of fluoride into the body results in the total replacement of phosphates [(PO₄)₃] in the bone by fluorides leading to the formation of calcium decafluoride, a hard, brittle structure unsuitable for skeletal functioning (Fawell et al., 2006; Lai & Tang, 2003; Mohammed & Adel, 2018). Excess fluoride in the body can also lead to the degeneration of muscle and fiber, low hemoglobin levels, red blood cell deformities, excessive thirst, headache, skin rashes, depression, gastrointestinal problems, urinary tract malfunctioning, nausea, abdominal pains, tingling sensations in the fingers and toes, reduced immunity and neurological manifestations (Dang-I & Soboyejo, 2013; Thole et al., 2011).

In many cases, fluoride is present in natural water sources (Yamada et al., 1988), which can be traced to industrial effluents and agricultural wastes such as herbicides, fungicides, and germicides. Furthermore, natural occurrences, such as the weathering of rocks, sedimentation, and volcanic eruption of fumaric gases and thermal waters, can contribute to fluoride formation (Fawell et al., 2006; Symonds et al., 1988). Groundwater can also have very high fluoride content due to the leaching of minerals (Li & Ge, 1991; Li & Liu, 1995; WHO, 1984).

Fluorosis associated with high fluoride content in drinking water has been reported to be high in many areas in East Africa (Fawell et al., 2006) and some parts of North Africa, Southern Africa (Fawell et al., 2006), the Middle East, and Germany (Thole et al., 2011). In some regions of Tanzania, fluoride levels as high as 18.6 mg/L have been reported (Fawell et al., 2006). Similar high fluoride content levels have also been reported in India (Prajapati et al., 2017; Thole et al., 2011), Kenya, and Burkina Faso (Fawell et al., 2006). There is, therefore, a need to remove excess fluoride from fluoride-contaminated water with high fluoride contents. This is especially true for deep groundwater sources, where the levels of fluoride contamination may exceed the WHO limits for safe drinking water (Nigay et al., 2018; WHO, 2011). In any case, the de-fluoridation of water can be achieved by: diluting high fluoride water with low fluoride water; introducing chemicals with high Ca or Mg content (Bratovic & Odobasic, Bratovic and Odobasic, 2011; Enyenw & Tesfaye, 2017; Nan, 2012), or doping with materials that adsorb fluoride from contaminated water.

Prior work has shown that fluoride ions can be removed from water by CWFs mainly through adsorption and ion exchange processes (Fan et al., 2003; Kaniewski & Kaniewski, 1985). Different
adsorbents have also been used for fluoride removal. They include: activated alumina, carbon, bone, charcoal, activated sawdust, calcite, serpentine, magnesia, tricalcium phosphate, and activated soil sorbents (Thole et al., 2011). However, in most cases, the removal of fluoride is achieved without removing microbial pathogens that are often present in groundwater sources prior to the point-of-use (Ajibade et al., 2019).

The need to remove excess fluoride and microbial contaminants (from drinking water) stimulated prior work from our research group on the development of hydroxyapatite (HA)-doped ceramic water filters (Yakub & Soboyejo, 2013). This study clearly showed that the doping of CWFs with HA (Clay-HA) could significantly reduce fluoride levels to safe levels for human consumption. It also showed that E. coli removal levels (from the CWFs) were comparable to those reported previously for undoped CWFs (Clay only) that have been used extensively for the purification of water in rural/urban settings (Nigay et al., 2019; Yakub et al., 2012).

However, although the doping of CWFs (with HA) has been shown to be effective in the removal of fluoride, there are concerns about the availability and the cost of hydroxyapatite in rural settings especially in low resource environments. Hence, although the effectiveness of HA in Fluoride and bacteria removal has been demonstrated. There is a need to explore the potential role of locally available animal bone substitutes (which are a rich source of HA in rural/urban communities across the world).

Thus, the current work will compare the effectiveness of frustum shaped CWFs doped with BPs or HA. Such concerns have stimulated the current work on the use of bovine (cow) bone particles because they are composed of 65–70% of hydroxyapatite $\text{Ca}_{10}(\text{PO}_4)_3(\text{OH})_2$ (BPs) as alternatives to HA in the doping of CWFs that can remove fluoride and microbial pathogens from contaminated water. The filters are sintered at two different temperatures (850°C and 900°C) with apatite from two different sources (chemically synthesized hydroxyapatite powder and bovine bone particles). The fluoride and bacterial (E.coli) removal characteristics of the Clay-HA and Clay-BP CWFs are then elucidated along with the flow characteristics of the filters.

The implications of the results are discussed for the transportation of robust CWFs and the purification of groundwater with fluoride and microbial contamination in rural/urban low resource settings. Freundlich isotherms are used to characterize the fluoride adsorption of the filters.

2. Materials and methods

2.1. Materials

Redart clay was procured from The Ceramic Shop, Cedar Heights, Norristown, PA. Sawdust containing 75% oak and 25% Spanish cedar was obtained from J. B. Sawmill, Hopkinton, MA. Hydroxyapatite (Sigma-Aldrich, St. Louis, MO) and bovine (cow) bone grits (Institute of Agriculture and Research Training, Ibadan, Nigeria) were used as sources of apatite. The sawdust and bone grits were sieved with a 500 micron/35 mesh sieve to obtain sawdust and bone particles. The particle size distribution was determined by laser granulometry analysis (Mastersizer 3000, Malvern Instruments, Malvern, UK).

2.2. Processing of ceramic water filters

Three types of CWFs were produced. The first consisted of a mixture of clay, sawdust, and HA in a weighted ratio of 30:50:20, while the second consisted of a mixture of clay, sawdust, and bovine bone particles (BPs) in a weighted ratio of 30:50:20 while the third was a mixture of clay and sawdust in a ratio of 50:50 by weight. The mixtures of clay, sawdust, and HA or BPs were then poured into an industrial mixer (Avanto-Mix 20, The Hobart Manufacturing Company, Troy, OH) before blending for 5 minutes with the intermittent addition of deionized water to the mixture. Blending and wetting were continued until the mixtures rolled up into single big lumps. A total of 1.8 to 2.0 L of water was used up in the blending process (Annan et al., 2016; Iyasara et al., 2016; Mbey et al., 2019; PFP, 2008).
The single lumps were inserted between male and female frustum-shaped molds in a 50-ton hydraulic press (TM Torin Big Red Jacks, Inc, Ontario, Canada). Plastic bags coated with non-stick cooking spray were wrapped around the male and female molds prior to manual pressing with the hydraulic press at a pressure of 140 kPa (20 psi) to press out the filters. After pressing, the filters were labeled for identification and air-dried for 6 days in the laboratory at room temperature (25°C) and relative humidity of 40%. The air-dried CWFs were then fired in a kiln (Dragon Kiln with Sentry 2.0 microprocessor, Paragon Kilns, Mesquite, TX). Pre-heating was carried out between 450–550°C for three hours (heating at a rate of 50°C/h) to burn off the combustible (sawdust). This was followed by heating the CWFs (at 100°C/h) to the sintering temperatures of 850°C or 900°C to avoid thermal cracking of the CWFs produced. The furnaces were held at these temperatures for 5 hours prior to furnace cooling to room temperature (25°C) in air. The adsorption isotherm was determined by using Freundlich isotherm because it is empirical.

2.3. Material characterization

The constituents of the CWFs (Redart clay, sawdust, HA or BPs) and the mixed adsorbents of clay-HA and clay-Bone were characterized using an energy dispersive X-ray (EDX) spectroscopy system (Oxford Instruments, Abingdon, UK) in an environmental scanning electron microscope (ESEM) (Quanta 200 Field Emission FE-ESEM, FEI, Hillsboro, OR). The structures of the clay, HA, bone, clay-HA, and clay-bone powders were studied using a powder X-ray diffraction system (D8 Focus X-ray Diffractometer, Bruker, Billerica, MA) under Cu-K radiation (j = 1.5406). Scanning was carried out every 2 seconds at 0.05° increments and an angle of 2 θ degrees.

The microstructure and morphologies of the components were also studied using a field emission scanning electron microscope (Quanta 200 FE- ESEM, FEI, Hillsboro, OR) that was operated under Back-Scattered Imaging (BSI) and Secondary Electron Imaging (SEI). The porosities of the CWFs were determined by means of a vacuum immersion method described in detail in prior work in our research group (Nigay et al., 2019). Porosity calculations were made using equation 1, where \( W_1 = \) initial weight, \( W_2 = \) weight when moved out of distilled water, and \( W_3 = \) weight in distilled water (Fernanda et al., 2000).

\[
P_{\text{open}} = \frac{W_2 - W_1}{W_2 - W_3}
\]

(1)

The permeabilities of the CWFs were estimated from Darcy’s law stated in equation 2, where \( k = \) permeability, \( A = \) surface area, \( L = \) thickness of the material, \( \mu = \) dynamic viscosity of water, \( \Delta p = \rho g h(t) = \) pressure difference between top and bottom of the surface.

\[
Q = \frac{kA\Delta p}{\mu L}
\]

(2)

2.4. Flow rate measurements

The water flow rates (through the filters) were determined for six of the CWFs fired at 850°C and 900°C. A standard reference PFP filter (composed of 60:40 clay: sawdust and colloidal silver overlay) was also tested as a control. Since the flow rate testing methods were similar to those used in earlier studies by our research group (Annan et al., 2014, 2016; Nigay et al., 2018, 2019; Yakub et al., 2012; Yakub & Soboyejo, 2013), they will only be described briefly in this paper. Prior to flow rate testing, the CWFs were filled with 10 L of deionized water. The water was then allowed to flow through the ceramic walls into a collecting bucket that was mounted on a PGL 20001 weighing balance (Adam Equipment, Oxford, CT, USA) that was connected to a computer for data acquisition. In this way, the volume of water discharged was obtained by dividing the mass of the filtered water by the density of water (1 g/cm³). The volumetric flow rates were determined from measurements of the filtered volumes of water over 24-hour durations.
2.5. Fluoride removal

A fluoride stock solution with a concentration of 1000 ppm was prepared by dissolving sodium fluoride (Fisher Scientific, Fair Lawn, NJ) in deionized water. 5 L of the fluoride solution (pre-filtrate) was poured into the HA- or BP-doped CWFs placed in plastic receptacles. After 6 hours of filtration, the discharged water (filtrate) was collected. The fluoride concentrations in the pre-filtrate and filtrate solutions were determined using an Ion Chromatography System (ICS) (Dionex ICS 6000, Thermo Fisher Scientific, Waltham, MA). Solutions with known fluoride concentrations were also prepared by serial dilutions of the stock fluoride solution and run with the ICS to generate the calibration curves used to determine the fluoride concentrations.

2.6. Bacteria removal

The bacteria removal provided by the six CWFs (sintered at 850°C and 900°C) was characterized using Escherichia coli (E. coli) bacteria (C-300 Strain, ATCC, Manassas, VA, USA). The E. coli were cultured in nutrient broth at 37°C for 24 hours in a shaker incubator (Model G25, New Brunswick Scientific, Edison, NJ, USA) that was operated at 100 rpm until the stationary phase was reached. 4 mL of the stationary phase culture was then mixed with 4 L of sterile deionized water to produce pre-filtrate suspension containing approximately $10^6$ to $10^7$ colony forming units (cfu/ml). The 4 L of pre-filtrate was then poured into the CWF prior to the collection of the filtrate into a covered plastic bucket. The pH of the pre-filtrate and filtrate solution was then measured with a pH meter (Platinum Series pH Electrode, Model 51910, Hach, Loveland, CO).

The number of viable cells (concentration of E. coli) in the pre-filtrate ($C_{pf}$) and filtrate ($C_f$) suspensions were determined by serially diluting the suspensions and plating 1 mL aliquots onto E. coli count plates (Petrifilm, 3M, St. Paul, MN). The plates were then incubated at 37°C for 18–24 hours before counting the number of colonies on the Petrifilm. The concentrations of E. coli in the suspensions were then determined as the number of colony forming units per ml (cfu/ml). These were used to calculate the percentage removal and log reduction values (LRVs) (yield filtration efficiency) from equations 3 and 4:

$$% \text{removal} = \frac{C_{pf} - C_f}{C_{pf}} \times 100$$

$$LRV = -\log_{10} \left( \frac{C_f}{C_{pf}} \right)$$

where $C_{pf}$ is the concentration of E. coli in the pre-filtrate suspension (cfu/ml), and $C_f$ is the concentration of E. coli in the filtrate suspension (cfu/ml). The values obtained are presented in Figure 4.

2.7. Mechanical properties

The mechanical properties of the CWFs were characterized via compressive, flexural, and fracture toughness tests. The samples were made from the top sections of each CWF (considering the bottom, middle and top sections). Samples were cut in a vertical direction with a wet tile saw. All the mechanical tests were carried out using an Instron Model 3366 electromechanical testing machine (Instron, Canton, MA, USA), with different fixtures for compression and three-point bending, equipped with a 5kN load cell.

Rectangular specimens with dimensions (length, $L = 17.5$ cm; breadth, $B = 2.5$ cm, and thickness, $H = 1$ cm) were used for the three-point bending tests, which were carried out at a constant displacement rate of 1 mm/min until the onset of fracture (Nigay et al., 2018) with a loading span of 15 cm. The flexural strength, was calculated from equation 5, where $F_{max}$ is the maximum force; $L$ is the loading span; $B$ is the breadth, and $H$ is the sample thickness. This gives:
\[ \sigma = \frac{3F_{\text{max}}L}{2BH^2} \]  

(5)

The compressive strengths of the CWFs were estimated by compressive loading of rectangular specimens with length, H, of 7.0 cm, breadth, B, of 2.5 cm, and thickness, H, of 2.5 cm. The samples were loaded monotonically to failure at a rate of 0.1 N/s. The compressive strengths were calculated from the following expression:

\[ \sigma_c = \frac{P}{BH} \]  

(6)

where P is the failure load, B is the specimen breadth, and H is the specimen thickness.

The fracture toughnesses of the CWFs were determined using Single Edge Notched Bend (SENB) specimens with dimensions of 17.5 × 2.5 × 1 cm³, notch depths of 2 mm, and length to width ratios of 0.40–0.45. These were tested under three-point bending at a loading span of 15 cm. The specimens were loaded at a displacement rate of 0.1 mm/min until a pop-in was observed at the notch. The fracture toughness \( K_{fc} \) was then estimated from the following expression:

\[ K_{fc} = f\left(\frac{a}{W}\right) \cdot \sigma_f \cdot \sqrt{a} \]  

(7)

where \( a \) is the crack length, \( f\left(\frac{a}{W}\right) \) is the compliance function of the specimen, and \( \sigma_f \) is the fracture stress.

2.8. Statistical analysis

The results obtained from 15 fluid flow experiments, bacterial and fluoride removal (LRV) experiments, and the mechanical property measurements (on the CWFs) were subjected to statistical analysis. The statistical variations in the measured values were then subjected to the Kolmogorov-Smirnov statistical test to determine whether the measured variations could be characterized by normal distributions, with values of \( p \) that were taken to be significant at a significant level of 0.05.

The CWFs tested gave values between 1.33 and 1.34 for the process capability index. This implies that the process used produces CWFs that meets customers’ specification limits.

2.9. Modeling of adsorption kinetics

The adsorption of fluorides can occur in the following stages: (1) the bulk diffusion of fluoride ions to the surfaces of the adsorbent, and (2) intra-particle or pore diffusion processes. Hence, the following two models were explored in the study (Yakub & Soboyejo, 2013):

\[ \ln(1 - \alpha) = -k_pt \]  

(9)

\[ q_t = k_d t^{0.5} \]  

(10)

where \( \alpha \) is the fractional attainment of equilibrium, \( t \) (min) is the duration of adsorption, and \( q_t \) (mg/g) is the quantity of fluoride adsorption at any given time, \( t \). \( k_p \) (min\(^{-1}\)) is the inter-particle rate constant, while \( k_d \) (mg/g.min\(^{1/2}\)) is the diffusion rate constant.

The adsorption of HA and BPs to the CWFs can be fitted to the Freundlich isotherm (Yakub & Soboyejo, 2013). This gives:
\[ q_e = K_e C_e^{1/n} \]

where \( 1/n \) and \( K_e \) (mg \( ^{1-1/n} \) L \( ^{3/n} \) g \( ^{-1} \) ) (mgL \( ^{-1} \) nL \( ^{1} \) ng \( ^{-1} \) ) are Freundlich constants that depend, respectively, on the adsorption intensity and adsorption capacity, \( q_e \) (mg/g), calculated from:

\[ q_e = 10 \cdot 10^{-1} (C_o - C_e) V \]

\[ m \]

where \( C_o \) and \( C_e \) are initial and equilibrium concentrations of fluoride in mg/L, \( V \) (L) is the volume of fluoride solution, and \( m \) (mg) is the mass of adsorbent. The Freundlich constants were obtained from plots of \( \ln(q_e) \) versus \( \ln(C_e) \).

3. Results and discussion

3.1. Material characterization
SEM + EDX images of the sintered structures of the Clay-HA, Clay-Bone and Clay only CWFs are presented in Figure 1a–1f. EDX determines elements with atomic number of 11 upward. Therefore, it reveals the presence of calcium, phosphorous and oxygen because the three elements have atomic numbers 20, 15 and 16 respectively. This is consistent with the presence of hydroxyapatite in both mixtures. The presence of the carbon peak also confirms the presence of sintered carbon residue from the combustion of sawdust (Annan et al., 2016). The analysis also suggested that the amount of sintered carbon was greater after sintering at 900°C (compared to that obtained after sintering at 850°C). Such sintered carbon can increase the adsorption of chemicals and bacteria during ceramic water filtration (Dang-I & Soboyejo, 2013; Yakub & Soboyejo, 2013).

The XRD patterns obtained for bone particles and the HA are presented in Figure 2. The peaks are in good agreement with those presented by the International Center for Diffraction Data for hydroxyapatite (File Number 73-0293). The XRD results also suggest that the higher sintering temperature of 900°C results in increased crystallinity of the HA. The increased crystallinity will be shown in subsequent sections to affect the adsorption of fluoride. This is consistent with the results of prior work by Fawell et al. (2006) and Li & Ge (1991), who have shown that more crystalline components are associated with reduced levels of adsorption.

3.2. Effects of sintering temperature on adsorption isotherms
A plot of ln(\( q_e \)) against ln(\( C_e \)) is presented in Figure 3 for the filters that were examined in this study. These resulted in Freundlich constants that are summarized in Tables 1a-Table 1c. The correlation coefficient obtained from the Freundlich fit was 0.99871, which implies heterogeneity of the adsorption process. The Freundlich isotherm is chosen because it is empirical, i.e., it gives full account of the adsorption process with high coefficient of determination.

During sintering, the color of the mixtures changed gradually from dark brown to reddish-brown, and finally to a red color. This is consistent with the presence of calcium in the mixtures, which gives the mixtures their brick red color after firing. The temperature effect that results from the Gibbs free energy change (\( \Delta G \)) is given by:

\[ \Delta G = nRT \ln K_{eq} \]

where \( \Delta G \) (Kg/mol) is the change in the Gibbs free energy, \( n \) is the number of moles, \( R \) is the universal gas constant of 8.314 Jmol\(^{-1}\)K\(^{-1}\). \( T \) is the absolute temperature in Kelvin, and \( K_{eq} \) is the thermodynamic distribution coefficient. The degree of spontaneity was higher in CWFs with lower levels of C-HA or C-Bone adsorbents. No obvious trend was observed in the effect of sintering temperature on the Gibbs free energy.
Figure 1. SEM micrographs of: (a) Clay-HA CWF sintered at 850°C; (b) Clay-BP CWF sintered at 850°C, and (c) Clay only CWF sintered at 850°C; (d) EDX spectrum of Clay-HA sintered at 850°C; (e) EDX of Clay-BP spectrum CWF sintered at 850°C; (f) EDX spectrum of Clay only CWF sintered at 850°C.
3.3. Fluoride and bacteria removal efficiency

The fluoride removal was greater in the CWFs with bone particle mixtures than those of Clay-HA and Clay only CWFs. Furthermore, the fluoride removal was higher in the filters that were sintered at 850°C than those that were sintered at 900°C as shown in Figure 4. The higher levels of fluoride removal at 850°C are associated with higher levels of HA crystallinity, which have been correlated with increased adsorption. Furthermore, the bacterial removal was found to be similar in Clay-HA, Clay-Bone and Clay only CWFs. This is consistent with the similar ranges of pore sizes in the CWFs that were sintered at 850 and 900°C.

For E. coli LRV, the mean value for Clay-HA is 4.75 ± 0.17, while for Clay-Bone is 4.78 ± 0.18 and that of Clay only is 4.74 ± 0.17. Hence, the current work suggests that the doping of CWFs with BPs is more effective in the processing of filters with improved fluoride and bacterial removal. Furthermore, the flow characteristics through the doped CWFs are similar to those through undoped CWFs produced by sintering at 850°C. However, higher flow rates of 2.2Lh\(^{-1}\) were obtained from CWFs that were sintered at 900°C.

The adsorption of fluoride also increases as the pH increases (i.e., more OH\(^{-}\) ions) from 1.35 to 2.74 molcm\(^{-2}\). Hence, as F\(^{-}\) ions are adsorbed, there is a greater tendency to form CaF\(_2\) on the surfaces of the CWFs. Such formation and accumulation of CaF\(_2\) can cause skeletal/crippling fluorosis if the particles leach out into the filtered water. Finally, it is important to note that the fluoride removal can be attributed to similar ionic radii of the F\(^{-}\) and OH\(^{-}\) ions, which have respective ionic radii of 1.36 and 1.40 Angstroms. Ion exchange can, therefore, occur relatively easily between the two ions in solution. Furthermore, the central metal ion (Al\(^ {3+}\)) in the Redart clay structure exerts a Coulombic attraction on the F\(^{-}\) ions, which favors fluoride removal.
Figure 3. Freundlich plot of the log of fluoride adsorbed ($q_e$) versus the log of concentration at equilibrium ($C_e$), showing plots for (a) Clay-HA, (b) Clay-Bone and (c) Clay only.

Table 1a. Initial and equilibrium concentration and the amount of fluoride adsorbed for Freundlich adsorption for Clay only

| $C_o$ (mg/L) | Adsorption (nm) | $C_e$ (mg/L) | $C_o-C_e$ (mg/L) | $q_e$ (mg/g) |
|--------------|-----------------|--------------|-----------------|--------------|
| 5.0          | -0.089          | 0.039        | 4.961           | 3.895        |
| 10.0         | -0.116          | 0.161        | 9.839           | 7.688        |
| 15.0         | -0.126          | 0.207        | 14.793          | 11.426       |
| 20.0         | -0.146          | 0.278        | 19.722          | 15.542       |
3.4. Statistical distributions results for the ceramic water filters
This will be discussed under the following subheadings:

3.5. Porosity of the ceramic water filters
The statistical distribution of the percentage porosity obtained after firing of Clay-HA, Clay-Bone and Clay only ceramic water filters at temperatures of 850°C and 900°C is presented in Figure 5a. The values range between 34.50 and 48.50% by volume because the pores are homogeneous and well scattered into the clay matrix. This can be related to the sieving of the sawdust giving rise to smaller particle sizes, as shown in Figure 5c. It is observed that the porosity of the filters is well represented by a normal distribution.

3.6. Flow rate performance of the ceramic water filters
The flow rate of the filters was determined to be 1.4–2.2 L.h⁻¹. This is within the range of 1.3–2.0 L.h⁻¹ reported by Yakub & Soboyejo (2013). The statistical variations in the flow rate values (obtained from multiple flow rate measurements) were also normally distributed with a p-value of 0.65 (Figure 5b). This may be traceable to the doping of the filters with HA or BPs, which increases the porosity and consequently the permeability. Conversely, the standard deviation is of significance. The range of the flow rate is from 0.5 to 3.5 Lh⁻¹, as highlighted in Figure 5b. The spread of the distribution could not be linked with the porosity of the CWFs shown in Figure 5a, with a narrow distribution of 39.5 ± 0.27 %. The difference may be due to the moisture of the ceramic water filters. Whenever filters are not thoroughly soaked before water is brought in, some pre-adsorption occur before water starts flowing. This reduces the volume that remains in the filter, consequently lowering the pressure on the base of the filter and reducing the flow rate. However, the normal distribution of the flow rates (Figure 5b) affirms that 10 L of water in the ceramic water filter is discharged in about 5 hours. Hence it could filter at least 40 L of water in a day.

| TABLE 1b. Initial and equilibrium concentration and amount of fluoride adsorbed for Freundlich adsorption for Clay-HA |
|---|---|---|---|---|
| Co (mg/L) | Adsorption (nm) | Ce (mg/L) | Co–Ce (mg/L) | Qe (mg/L) |
| 5.0 | 0.192 | 0.041 | 4.959 | 4.965 |
| 10.0 | 0.221 | 0.178 | 9.822 | 7.534 |
| 15.0 | 0.330 | 0.221 | 14.779 | 11.113 |
| 20.0 | 0.452 | 0.284 | 19.716 | 14.212 |

| TABLE 1c. Initial and equilibrium concentration and amount of fluoride adsorbed for Freundlich adsorption for Clay-Bone CWFs |
|---|---|---|---|---|
| Co (mg/L) | Adsorption (nm) | Ce (mg/L) | Co–Ce (mg/L) | Qe (mg/L) |
| 5.0 | 0.214 | 0.044 | 4.956 | 7.547 |
| 10.0 | 0.342 | 0.183 | 9.817 | 9.134 |
| 15.0 | 0.428 | 0.251 | 14.749 | 16.013 |
| 20.0 | 0.543 | 0.298 | 19.702 | 20.512 |
Figure 4. Plot of LRV values for (a) fluoride removal and (b) E. coli removal of Clay-HA, Clay-Bone and Clay only CWFs at different sintering temperatures: 1 and 2 are for sintering temperature of 900°C; while 3 and 4 are for sintering temperature of 850°C.
Figure 5. Distributions of (a) percentage porosity, (b) flow rates and (c) the particle size distribution for the ceramic water filters.
Figure 5. Continued.

(c) Particle Size Distribution (vol.%) for Clay - HA (nm)

(cii) Particle Size Distribution (vol.%) for Clay - Bone (nm)

(ciii) Particle Size Distribution (vol.%) for Clay Only (nm)
Figure 6. Measurements of LRV obtained for E. coli and fluor-ides from Clay-HA, Clay-bone and Clay only ceramic water filters. (a) Distribution of LRV obtained for E. coli for Clay-HA, Clay-bone and Clay only ceramic water filters. (b) Distribution of LRV obtained for Fluoride for Clay-HA, Clay-bone and Clay only ceramic water filters.
Figure 7. Statistical distributions (probability density functions) of mechanical properties: (a) compressive strengths of the CWFs doped with 20 wt.% of Clay-HA, Clay-bone and Clay only; (b) flexural strengths of CWFs doped with 20 wt.% of Clay-HA, Clay-bone and Clay only, and (c) fracture toughness of the CWFs doped with 20 wt. % of Clay-HA, Clay-bone and Clay only.
Figure 7. Continued.

(c) Experimental results and Normal distribution for Clay - HA

(cii) Experimental results and Normal distribution for Clay - Bone

(ciii) Experimental results and Normal distribution for Clay Only
Table 2. Mechanical properties (flexural strengths, fracture toughness, and compressive strengths) of the bone-doped and HA-doped CWFs

| CWF Type       | Sintering Temperature °C | Flexural Strength (MPa) | Fracture Toughness (MPa.m\(^{1/2}\)) | Compressive Strength (MPa) |
|----------------|--------------------------|-------------------------|--------------------------------------|-----------------------------|
| Clay-HA        | 900                      | 3.02 ± 0.02             | 0.20 ± 0.01                          | 0.67 ± 0.02                 |
| Clay-Bone      | 900                      | 3.05 ± 0.03             | 0.21 ± 0.02                          | 0.71 ± 0.03                 |
| Clay only      | 900                      | 3.01 ± 0.02             | 0.19 ± 0.01                          | 0.66 ± 0.02                 |
| Clay-HA        | 850                      | 2.68 ± 0.03             | 0.17 ± 0.02                          | 0.51 ± 0.03                 |
| Clay-Bone      | 850                      | 2.71 ± 0.04             | 0.19 ± 0.03                          | 0.54 ± 0.04                 |
| Clay only      | 850                      | 2.66 ± 0.03             | 0.15 ± 0.02                          | 0.49 ± 0.03                 |

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Continued.
3.7. Filtration performance of the ceramic water filters

The LRV for E. coli for Clay-HA, Clay-bone and Clay only CWFs were 4.71 ± 0.17, 4.73 ± 0.18 and 4.69 ± 0.17 (Figure 6a) with a removal efficiency of 99.997%, which is higher than that obtained from the literature (LRV = 4.00) for a standard filter (Nair & Kani, 2017). This is traceable to the high porosity of the CWFs in which the bacteria are trapped (Akosile & Oguntuase, 2020; Haiyan et al., 2020; Venis & Basu, 2020; Yakub et al., 2012). The result also reveals that the distribution of the LRV for bacterial contaminants’ standard deviation is comparatively narrow, from 4.47 (99.9956%) to 4.89 (99.9966%). This narrow distribution of LRV corresponds to a slim distribution of porosity but at variance with the large distribution of flow rate. This implies that the LRV for the bacterial contaminant is proportional to percentage porosity. In contrast, the flow rate did not exert any meaningful effect on the LRV of bacteria removal. The distribution of E. coli LRV is represented by a normal distribution (Figure 6a). This affirms that the doped filters are effective for removing bacteria contaminants.

Figure 6b present a normal LRV distribution for fluoride removal by the CWFs. It could be noted that the HA-doped CWFs gave fluoride LRV of 2.02 ± 0.15 with an efficiency of 99.992%, BP-doped CWFs gave fluoride LRV of 3.02 ± 0.21 with an efficiency of 99.995% while clay only CWF gave 0.44 ± 0.17 with the least efficiency. This suggests that the HA- and BP-doped CWFs are less effective in fluoride removal than E. coli removal. It also implies that the LRV for fluoride contaminants does not depend on the porosity or flow rate, which has a broad distribution of values. However, Figure 6 shows that the adsorption and removal of fluoride from contaminated water was time-dependent.

Basically, the removal of chemical contaminants from drinking water is controlled by the substitution mechanism (nucleophilic) whose kinetics are faster than the flow rate of CWFs. It can be noted that values for the LRV for chemical contaminants are normally distributed with a p-value of 0.95. Hence the probability of contamination is minimized by a low standard deviation. This enables the doped-CWF to be more capable of removing chemical contaminants regardless of their restricted efficiency.

3.8. Mechanical performance of the ceramic water filters

Figure 7a represents the distribution of the mechanical (compressive) strength obtained after firing the doped CWFs at 900°C. The doped CWF has mechanical strength in the range of 0.49–0.71 MPa. This range is lower than the value available in the literature; 3–4 MPa (Yakub et al., 2012). This can be traced to the high percentage porosity (Figure 6a) with microscopic pores creating defects (Nigay et al., 2018). The HA and BPs that are introduced without chemical interaction into the clay matrix may contribute to the fracture.

However, filtration experiments reveal that the mechanical strength is good enough for application in household water treatment. This is evident when several filling of the CWF is done to its maximum without failure. The values of the mechanical strength range from 0.49 to 0.71 MPa (Figure 7a). This may be due to homogeneous pores and scattering of the additives in the clay matrix arising from sieving of the doping materials and sawdust (Nigay et al., 2018).

Figure 7c shows the distribution of the fracture toughness obtained after firing the CWF at 900°C. The fracture toughness has a range of 0.15–0.21 MPa.m⁰.⁵. This range is lower than those obtained from literature, which is 0.35–0.37 MPa.m⁰.⁵ (Plappally et al., 2011). This may result from the mechanical strength and fracture toughness that are related to the structure of the CWF. The high percentage porosity of the dopants used (HA and BPs) gave rise to slightly low mechanical properties. Yet, the homogeneous pores and the scattering of the dopants in the clay matrix ensure their reliability.
It is observed that the mechanical properties (compressive, flexural, and fracture toughness) are normally distributed (Figure 7) with p-values approx. 0.96. This implies that the probability of fracture can be predicted, making both the HA and bone-doped CWFs fit for use in household water treatment. Table 2 summarizes the mechanical properties of the HA- and BP-doped CWFs at the 850 and 900°C sintering temperatures.

At sintering temperature of 900°C, the mean value of Flexural strength for the three CWFs is 3.03 ± 0.02, while at sintering temperature of 850°C, the mean value for their flexural strength is 2.68 ± 0.03

Also, for fracture toughness, at sintering temperature of 900°C, the mean values for the three CWFs is 0.20 ± 0.01, while at sintering temperature of 850°C, the mean value for their fracture toughness is 0.17 ± 0.02.

At a sintering temperature of 900°C, the mean value of Compressive strength is 0.68 ± 0.02 while at sintering temperature of 850°C, the mean value for their compressive strength is 0.51 ± 0.03

3.9. Implications
The implications of the current work are significant for the development of CWFs that can remove fluoride and microbial contaminants from contaminated groundwater. Unlike prior work that focused solely on the use of hydroxyapatite doping of clay, the current work compares the effects of HA-doping with the effects of BP-doping with bovine bone particles. BP-doping of the CWFs is found to improve the adsorption of fluoride more than synthetic HA doping. BP doping is also found to increase the removal of E. coli from contaminated water. The lower cost BP-doped filter, which can be produced from locally available bovine bone particles, is shown to be more effective in the removal of microbial pathogens (E. coli) and fluoride from contaminated water. This is particularly important in low resource settings in rural/urban environments in which synthetic HA may not be readily available. In such scenarios, bovine bone particles can be easily processed into clay/bone particle mixtures that can be used for the effective removal of fluoride and bacteria from contaminated groundwater. The resulting CWFs are likely to be affordable to people in low resource settings due to the low cost and availability of bone particles in rural/urban environments.

The results presented in this paper also suggest that the removal of the fluoride by the doped HA or BP particles is pH-dependent, with higher pH values resulting in higher concentrations of adsorbed fluoride that can result ultimately in the formation of calcium fluoride (CaF₂), which can cause bone deformities in humans that are exposed to higher fluoride/fluorite concentrations. There is, therefore, a need to clean such filters more regularly, especially in scenarios in which the pH of the locally available groundwater is high.

Above all, there is a need to ensure that the HA-doped or BP-doped particles are not used for durations that exceed their capacity to adsorb fluoride or occlude bacteria from water. This can be achieved via community management schemes that monitor the effectiveness of the CWFs on a regular basis. Such schemes are needed to avoid the consumption of fluoride-contaminated water in low resource settings in which the local people have limited resources for the replacement of the filters. These are clearly some of the challenges that must be addressed for the safe applications of the BP-doped and/or HA-doped filters in rural/urban communities.

4. Summary and concluding remarks
The study presents the results of an experimental and theoretical study of the combined removal of fluoride and E. coli from contaminated water. CWFs with mixtures of clay, sawdust, and HA or BP are produced by firing at 850 and 900°C. The resulting mixtures are shown to enhance the removal of both fluoride and E. coli from contaminated water. Salient conclusions from this work are summarized below.
(1) Micro- and nano-porous CWFs can be produced by the firing of clay mixtures with HA or bone particles. The doped ceramic water filters have micro- and nano-porous structures with statistical distributions of pores that are well characterized by normal distributions. These also result in ceramic water filter flow rates that are between 1.89 ± 0.36 and 1.76 ± 0.27 Lh⁻¹.

(2) The Clay-HA or Clay-BP CWFs trap bacteria in their micro- and nano-scale pores by geometrical occlusion. This results in 4.91 and 4.89 log reduction in E. coli contents of the filtrates produced, respectively, by BP- or HA-doped CWFs. The resulting filtrates also have sufficiently low E. coli contents for safe drinking water.

(3) The fluorides in the water are removed by the nucleophilic substitution that occurs in the hydroxyapatite network. The bone-doped CWFs exhibit higher LRV values (3.28) than HA-doped CWFs (2.56). Both Clay-HA and Clay-BP CWFs may, therefore, be used to remove fluoride from contaminated groundwater sources that may also contain microbial pathogens.

(4) The statistical analysis of the results obtained from this study suggest that the flow rates through the HA- and BP-doped CWFs are well characterized by normal distributions.

(5) The removal of fluoride from the HA-doped and BP-doped CWFs is well characterized by Freundlich isotherms. Furthermore, the more crystalline HA components obtained after sintering at 900°C are associated with reduced levels of fluoride adsorption in the doped CWFs, compared to those in CWFs produced by sintering at 850°C. The best combination of E. coli removal and fluoride removal was achieved by the sintering of BP-doped clays at 850°C.

Data availability statement
All data from this study are available from the authors upon request.

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