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Hybrid Sorbent-Ultrafiltration Systems for Fluoride Removal from Water

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Sorption, membrane filtration, laterite, bone char, fluoride, ultrafiltration

ABSTRACT

Fluoride contaminated water sources are found in many parts of the world and the consumption of such water is causing dental and skeletal fluorosis in humans, especially in developing countries. Hybrid sorbent-ultrafiltration (UF) systems are proposed for the removal of fluoride from water for the first time in this study. Laterite and bone char were selected as they are low cost, accessible sorbents in developing countries. The performances of the laterite-UF and bone char-UF systems were compared in terms of fluoride removal and membrane permeability under varying fluoride concentration, solution pH and sorbent load. For equilibrium fluoride concentration of 1.5 mg/L, the World Health Organization guideline for safe drinking water, the sorption capacity of bone char (1.1 mg/g) was larger than that of laterite (0.40 mg/g) and this was

attributed to the larger surface area of bone char. For the laterite-UF system, increase in fluoride concentration resulted in a decline in UF permeability whereas for the bone char-UF system there was no influence of fluoride concentration on membrane permeability. The optimal solution pH at which the systems are operated at maximum sorption capacity while avoiding membrane fouling was determined as pH 5-6 for the laterite-UF and pH 7 for the bone char-UF system. For both systems, the permeability declined in a similar manner as the sorbent load increased. Although both systems require further optimization, they showed to be viable defluoridation technologies.

INTRODUCTION

Fluoride concentration in drinking water between 0.5 mg/L and 1.5 mg/L is the critical range essential for healthy bones and teeth (1). Drinking water containing fluoride above 1.5 mg/L (World Health Organization guideline) (2) can cause dental, skeletal or crippling fluorosis in humans, especially in infants, depending on the concentration of exposure (1, 3). Water sources naturally contaminated with fluoride leaching from the earth crust (4) have been located in many parts of the world including developing countries (5). In such countries, the impact of the fluoride problem is larger since the water resources are limited and not easily accessible; hence local and sustainable technologies are urgently needed to reduce the fluoride levels below the guideline and prevent the related detrimental health effects.

Nanofiltration/reverse osmosis, electro/donnan dialysis, coagulation/precipitation and sorption processes are the main technologies which are used for water defluoridation (6, 7). Coagulation/precipitation technique does not adequately remove fluoride from water while NF/RO and electrodialysis require high energy supply (8).

Among the available technologies, sorption seems the most promising process, as it can offer a low cost and accessible solution if a convenient sorbent material is selected. A large number of sorbents have been studied so far for water defluoridation; nevertheless, many of these are expensive, difficult to regenerate, have low fluoride sorption capacity or release toxic metals such as aluminum and iron depending on the chemical characteristics of the sorbent (6). The most commonly used sorbent for defluoridation is activated alumina which is expensive and often inaccessible in developing countries; moreover its performance is affected by the presence of other ions (6, 9). Researchers investigated the use of laterite (10-14) and bone char (15-18) as sorbents for fluoride. Laterite forms out of weathering rocks in tropical climates and covers nearly one third of the Earth's continental land area including developing countries such as Argentina, India and Ghana (19) where fluoride problem exists. Hence, laterite is an accessible and potentially low-cost sorbent for these regions while showing promising results for defluoridation (10, 13, 14). Bone char was considered for fluoride removal in Mexico (16), Kenya (20), Ethiopia (21) and especially Tanzania (17) and can be accessed at relatively low costs depending on the country of production (8).

So far only small scale water treatment applications have taken advantage of such sorbent materials and they are limited to bucket defluoridator and mostly fixed bed reactors (12, 17). Employing smaller size sorbent particles generally increases the fluoride sorption efficiency due to the increased sorbent surface area (10, 17, 18). On the other hand fine powders cannot be applied in fixed bed columns as they cause high pressure drops and undesired fluidization where a physical adsorption becomes negligible (22-24).

Hybrid system bringing sorption and low pressure membrane filtration such as ultrafiltration (UF) together have been proposed and studied for the removal of metals from water (25-28).

Unlike fixed bed column reactors, sorbent-membrane systems enable the use of sorbent particles equal or less than 300 µm as the pressure drop and thus the operation cost is lower than that obtained in fixed bed columns with such small particles (29). UF can ensure an increased efficiency and reduce the cost compared to other membrane systems (30) and therefore shows great potential for application as water treatment technologies in developing countries (31, 32). Additionally with UF, not only the sorbent particles separated from the water efficiently but also water can be disinfected if the right membrane pore size is selected (33); however, the removal of biological contaminants was not investigated in this work.

In this study, two hybrid systems, laterite-UF and bone char-UF, are proposed for the first time to defluoridate water, especially in developing countries. Within this work, a comparison study has been conducted elucidating differences in the fluoride sorption capacity of the two sorbents. Previous studies indicate that the sorption capacity of laterite and bone char can be influenced by various parameters: initial fluoride concentration, sorbent load, sorbent particle size, solution pH, temperature and sorbent characteristics (13, 14, 16, 18). In parallel, all these parameters may also influence the performance of the membrane. Three parameters: initial fluoride concentration, solution pH and sorbent load, are varied here to investigate the performances of the proposed systems in terms of fluoride sorption and membrane permeability.

MATERIALS AND METHODS

Sorbents and Sorbent Characterization

Laterite (LA) was extracted in Bongo, Upper East Region, Ghana (GPS: N10.89522 W0.77871), air-dried and the larger fragments were crushed with a hammer. Bone char (BC) was collected from Ngurdoto Defluoridation Research Station (NDRS), Arusha Region, Tanzania after treatment. Bone char was prepared from cow bones, heat treated in kilns at a ratio of about 8% of charcoal/raw bones, temperature ranging from 400 to 500 °C and controlled air supply by the local researchers in NDRW as described in the study of Mjengera and Mkongo (17). BC was not further treated before sorption and permeability experiments. Sorbent characterization analyses and experiments were conducted in the Laboratories of the University of Edinburgh. An orbital grinder (TEMA, Italy) was used to grind the materials. Grinding time was changed between ten seconds and a minute depending on the size fraction required. Sieves were used to separate the sorbents into <125 μm size fraction which was used for all the sorption experiments. Grinding/sieving was an iterative procedure to get the desired size fractions. Sorbents were not washed prior to any characterization analysis or experimental use.

The zero point charge of laterite and bone char was determined using titration method adapted from Wang and Reardon (34). 0.2 g of sorbent were added into 10 mL ultra-pure water. 150-212 μm and <38 μm size ranges were used for bone char and laterite, respectively. The solution pH was adjusted and the reading was recorded after 15 minutes, while swirling. 0.0025M KCl solution was then obtained by adding 0.5 mL of 0.1 M KCl in each solution and bringing the volume to 20 mL with ultra-pure water. The 0.0025 M solutions were mixed for one hour in a shaker at 25 °C and 200 rpm and the pH ($pH_{0.002M}$) in each bottle was recorded, while swirling. 0.5 mL of 2 M KCl was added into each bottle bringing the KCl molarity up to 0.05 M and the pH ($pH_{0.05M}$) was recorded for the last time while swirling the solution. For each sample, the difference between $pH_{0.05M}$ and $pH_{0.002M}$ was calculated and plotted against $pH_{0.002M}$ to reveal the point where ($pH_{0.05M}$-$pH_{0.002M}$) is equal to zero indicating the point of zero point charge. To validate the titration method, the surface charge analysis of laterite was performed with Zeta Plus (Brookhaven Instruments, New York, USA) by taking the mean of a set of 10 measurements.

Laterite concentration of ~0.2 g/L was prepared in the experimental background electrolyte solution of 1 mM $NaHCO_3$ and 20 mM NaCl. After the pH adjustment the solutions were mixed and left to settle for 10 minutes. The temperature of the samples was allowed to equilibrate in the machine for at least five minutes before the measurements were taken.

X-Ray Diffraction (XRD) was used to characterize the crystalline phase of the sorbents. To carry out the XRD analysis, D8-Advance X-ray Diffractometer (Bruker AXS, Germany), which employs a 2-theta configuration in which the X-rays are generated by a Cu-anode x-ray tube operating at 40 kV and a tube current of 40 mA, was used. The scanning range of the samples was 2θ=2-60° at a scanning rate of 0.01°/sec. EVA analysis package was used to compare the diffractogram results with the 2012 issue of the International Centre for Diffraction Data (ICDD) diffractogram database library. X-Ray Fluorescence (XRF) method was used to determine the major element composition of the sorbents. Before the analysis with a PW2404 automatic XRF spectrometer (Philips, the Netherlands) with a Rh-anode X-ray tube, the samples powder were fused in 40mm diameter discs with a lithium borate flux containing La_2O_3 as a heavy absorber by a method similar to that of Norrish and Hutton (35).

The specific surface area analysis of the sorbents was performed using Multi point BET analysis with an Autosorb-iQ (Quantachrome (USA) using nitrogen at a relative pressure (P/Po) range of 0.05-0.30. For the BET method (32), the average of the measurements of three different samples was used and the largest difference between a single measurement and the average was used as the variability. For XRD, XRF and BET analysis, <125 µm sorbent particle size was used.

Membranes

100 kDa flat sheet PLHTK UF membranes (Millipore, USA) were used in the experiments. The membranes were made of regenerated cellulose active layer and polypropylene support layer. Prior to use, the membrane coupons were soaked in 0.1 M sodium hydroxide (NaOH) (Fisher, UK) solution for 30 minutes to remove the glycerine preservative present on the surface. Afterwards they were surface rinsed with tap water followed by 2.5 L of ultra-pure water. Prior to the filtration experiments, the membranes were compacted for 30 minutes and pure water flux was determined in the following hour.

Solution Chemistry and Analytical Methods

Chemicals used were of analytical grade and the solutions were prepared with ultra-pure water (conductivity: 18.2 mS/cm) obtained by PuraLab Ultra (Elga LabWater, UK). 1000 mg/L of fluoride stock solution was prepared fresh every week using sodium fluoride (Sigma Aldrich, UK) and the experimental solutions were diluted from this stock solution. The solution pH for characterization analysis and experiments was adjusted with 0.1 M of HCl or NaOH (Fisher Scientific, UK).

Fluoride concentration in the samples was determined using an ion selective electrode (ISE) for fluoride in conjunction with an Ag/AgCl/KClsat saturated electrolyte reference electrode connected to an ion meter 826 (Ion Meter, Metrohm, UK). For each new stock solution fresh standard fluoride solutions of 0.1, 0.3, 1, 3, 10, 30 and 100 mg/L were prepared and used for the calibration of ISE. All the calibration curves used had a linear regression value between 0.999 and 1.000. Electrodes were immersed in a well mixed 2.5 mL of sample and 2.5 mL of TISAB (total ionic strength adjustment buffer) solution. TISAB was prepared by adding 57 mL glacial acetic acid (Fisher, UK), 58 g NaCl (Fisher, UK) and 4 g of 1,2-cyclohexanedinitrilo-tetraacetic acid (CDTA) (Anachemia, UK) into approximately 500 mL ultra-pure water. The solution was stirred until a homogenous solution was obtained and the solution temperature cooled down to room temperature. 5 M NaOH (Fisher, UK) was added until pH was adjusted to 5-5.5 and then the solution was completed to 1 L. Solution pH was measured using a pH/Cond 340i meter (WTW, Germany).

Stirred Cells Equipment and Filtration Protocol

The dead end filtration experiments were conducted using stainless steel stirred cells, operated at 0.5 bar and at an average temperature of 21±2 °C controlled by the central cooling/heating system in the laboratory. The cell volume was 990 mL and the membrane surface area exposed to the pressurized solution was 0.0033 m^2. The cells contained magnetic stirrer assembly (Millipore, Watford, UK) and were placed on a magnetic stirrer (Fisher Scientific, Loughborough, UK). Permeate of each cell was collected in a beaker placed on an electronic balance (Fisher Scientific, Loughborough, UK) and the weight and hence the volume of the permeate was monitored continuously. The cells contained a pressure transducer (PX209-300G5V) and a thermocouple (TJ2-CPSS-M6OU-200-SB) which were connected to a data acquisition system (OMB-DAQ-56), all purchased from Omega Engineering (Irlam, UK). The data from the acquisition system and the balances were transferred to the computer and processed using the program Labview 8.0 (National Instruments, Newbury, UK).

Initially, sorbent materials were stirred on a magnetic stirrer at 300 rpm in 200 mL fluoride solution prepared in a beaker with a background electrolyte of 1 mM $NaHCO_3$ and 20 mM NaCl for 3 hours, based on the results of preliminary kinetics experiments (See supporting information), to ensure the sorption equilibrium. The solution pH was adjusted throughout the equilibrium process. Once the equilibrium was reached, the solution was filtered by UF membrane in the stirred cell and the first three 50 mL permeate samples were collected. Afterwards, the stirred cell was opened, a sample of 10 mL was taken from the concentrate left in the cell and filtered with 0.45 µm disposable syringe filters (CA, Sartorius). After the rest of the concentrate was filtered by UF membrane and collected as the last permeate, ultra-pure water was filtered for an hour to determine the flux of the membrane with the sorbent deposit.

Data Analysis

M_{ads}, fluoride mass sorbed (mg) on the sorbent particles was calculated through a simple mass balance:

$$M_{ads} = V_f.C_f - \sum_i^n V_{p_i}.C_{p_i} - V_c.C_c - m_{mem} \qquad 1$$

where V_f, V_{Pi} and V_c are the volume (L) of feed, sample permeate, concentrate, respectively, C_f, C_{Pi} and C_c are the fluoride concentration (mg/L) of feed, sample permeate and concentrate, respectively, m_{mem} is the fluoride mass sorbed on the membrane, $_i$ is the identity number of permeate samples and n is the total number of the permeate samples.

m_{mem} was confirmed to be negligible with blank experiments, where no sorbent was added to the system; therefore m_{mem} was neglected. The relative permeability (L_v/L_{v0}) was determined for each filtration experiment, where L_v is the permeability (L/m^2.h.bar) calculated using the final pure water flux data of the membrane with sorbent deposit and L_{v0} is the permeability (L/m^2.h.bar) calculated using the initial pure water flux data of the membrane prior to the experiment.

In each data series for sorption and permeability, a single experimental data point was repeated at least three times and the variability was estimated for that specific point by taking the largest difference among individual experimental data and the mean value. Estimated variability based on repeated experiments was used as an absolute variability for the rest of the data points in the specific series.

RESULTS AND DISCUSSIONS

Membrane and Sorbent Characteristics

The average pure water membrane permeability was measured as 366±65 L/m^2.h.bar and the clean membrane resistance was calculated as $1.06x10^{12}$ L/m at the average operation temperature of 21 °C. The membrane pore size of 100 kDa membrane was estimated as 18.2 nm adapting the method of Worch (36) and as 21.9 nm based on the empirical formula given by Crittenden et al. (37) relating the pore size to the molecular weight cut off (MWCO) of the membrane.

Chemical characteristics of laterite and bone char are reported in Table 1. Major chemical components of laterite are consistent with other studies (10, 11, 14, 38, 39). The absolute value of surface charge for laterite decreased until the zero-point charge (pH_{zpc}) and after that it increased until pH above 8 where it became relatively stable, as displayed in Figure 1. The pH_{zpc} of laterite was found to be between pH 5 and 6. In literature, pH_{zpc} for laterite varies from 3.39 up to 8.72 (10, 13, 14, 38-40); such different values can be due to the variations in geological structure in the locations where the samples were extracted and the differences in preparation method.

For bone char, previous studies have reported calcite and carbon content besides the large percentage of hydroxyapatite (41, 42); however, calcite and carbon were not detected in the sample used in this study. The treatment technique, especially the charring process, plays a significant role in the final chemical composition of the samples and in the carbon content (43, 44) explaining the differences among the bone char characteristics reported in published data. The bone char surface showed no charge within the error in acidic and neutral pH range until becoming negative after pH_{zpc} (Figure 1). The pH_{zpc} of bone char was determined to be within the pH range of 8 to 9 which agrees with the study of Medellin-Castillo et al. (45) where the pH_{zpc} was reported as 8.4. Bone char had a BET surface area of 53±3 m^2/g which was more than triple the surface area of laterite (15±2 m^2/g).

The Influence of Solution pH

Figure 2A shows that fluoride sorption on both laterite and bone char was strongly influenced by the solution pH; as the pH increased above the pH_{zpc} of the laterite and bone char, the sorption capacity declined sharply. As shown in Figure 1, the sorbents became negatively charged at solution $pH>pH_{zpc}$ of the sorbent; therefore, the observed decline in the sorption capacity is attributed to the electrostatic repulsion between the negatively charged sorbents and the negatively charged fluoride ions.

Surprisingly, a decrease in fluoride mass sorbed onto laterite (from 0.62 mg/g to 0.52 mg/g) was observed when the solution pH was decreased from 5 to 3. In contrast, the positive charge of laterite increased in parallel to the decrease in solution pH (Figure 1) giving the expectation that fluoride mass sorbed would increase due to the stronger electrostatic attraction to the fluoride ions. pH-dependent fluoride speciation, calculated after Calace et al. (46) (Figure 2A), indicates that 50% of the fluoride ions are present in hydrofluoric acid (HF) form at pH 3.16 (pK_a of HF). Protonated fluoride ions in HF form at solution $pH<pK_a$ were likely to be unavailable for

sorption explaining the lower sorption capacity obtained at pH 3 compared to pH 5. Sujana et al. (13) also reported lower fluoride sorption on lateric ores at acidic range below pH 5. Similarly, Tor et al. (23) suggested that pH dependent ion speciation of fluoride influenced the fluoride sorption on red mud.

For bone char, the fluoride mass sorbed was the highest and constant at $pH<pH_{zpc}$ when the surface charge was stable and it declined as soon as the surface charge became negative; the results agree well with those of Medellin-Castillo et al. (16).

In order to explain the lower sorption capacity of the sorbents in alkaline solution, the underlying mechanisms of fluoride sorption were considered. Apart from electrostatic interactions, ion exchange between the hydroxyl groups on the sorbent surface and fluoride is regarded as another mechanism contributing to fluoride sorption on both laterite (10, 11, 13, 39) and bone char (47). Oxides have a tendency to form hydroxides once they are in aqueous phase (11) and the ionic radius of OH^- (0.140 nm) is similar to that of F^- (0.136 nm) which favors the exchange between these two ions (48). Silicon, iron and aluminium oxides are the major components of laterite (Table 1) as also reported in the literature (10, 11, 14, 38). Silicon hydroxides are not considered to be as readily available for fluoride sorption as the other metal hydroxides (14) and similarly, quartz (SiO_2), showed the poorest sorption capacity for fluoride among five sorbents (49). Therefore silicon oxide is not expected to play a role in fluoride sorption even if it is a major component of the laterite sample in this study. However, there is no consensus on whether aluminium or iron hydroxides constitute the main component responsible for fluoride sorption (14). It is likely that both aluminium and iron hydroxides are responsible for fluoride sorption as suggested by some authors (10, 14). The possible ion exchange reactions between fluoride ions and the hydroxyl ions of iron and aluminium hydroxides are given in Equation 2 and 3, respectively.

$$Fe(OH)_3 + 3F^- \rightarrow FeF_3 + 3OH^- \qquad 2$$

$$Al(OH)_3 + 3F^- \rightarrow AlF_3 + 3OH^- \qquad 3$$

Hydroxyapatite is the main component of bone char (41, 42) and has a high tendency to exchange its OH^- ions with F^- as shown in Equation 4 (49). In addition to hydroxide, phosphate ions can be exchanged with the fluoride ions and contribute to the sorption (50). Dissolution of ions such as calcium and phosphate from bone char and precipitation with fluoride as fluorapatite ($Ca_5(PO_4)_3F$) or fluorite (CaF_2) was also suggested to contribute to the fluoride uptake by bone char (51, 52).

$$Ca_{10}(PO_4)_6(OH)_2 + nF^- \rightarrow Ca_{10}(PO_4)_6(OH)_{2-n}F_n + nOH^- \qquad 4$$

Considering the ion exchange reactions described in Equation 2, 3 and 4, the higher concentrations of OH^- ions at high pH could cause competition between the hydroxyl and fluoride ions and lead to an additional decline in the fluoride sorption observed in the data. Similarly, Medellin-Castillo et al. (16) reported that hydroxyl ions can displace the sorbed fluoride ions from the bone char until the equilibrium is reached between the two ions. Partey et al. (38) reported a decline in arsenate sorption due to the competition between negatively charged arsenate and hydroxyl ions at high pH. It is reasonable to expect a similar competition between negatively charged fluoride and hydroxyl ions at high pH.

Figure 2B displays the influence of pH on the permeability of the membrane when solutions containing laterite and bone char were filtered. At pH values lower or higher than pH_{zpc}, the permeability is expected to increase as the absolute particle charge increases and larger repulsive forces act on the particles resulting in looser deposit layers similar to what has been observed with proteins (53). For the laterite system, the decline in the permeability (L_v/L_{v0}) from 0.97±0.04 to 0.87±0.04 when pH was increased from 3 to 5 is attributed to the decrease in the absolute surface charge of laterite from 24 mV to 1.2 mV. For the bone char system, a change in the permeability was not observed as expected, due to the stable surface charge of the bone char within the pH range 4-8. However, at alkaline pH values further permeability decline was observed for both systems, more severe for the laterite system than for the bone char. This decline was not expected as the sorbent particles became more negatively charged; around -40 mV for laterite at pH>7 and -20 mV for bone char at pH>8. This unexpected permeability decline can be explained by looking again into the mechanisms involved in the sorption of fluoride on the sorbent materials. As presented in Equations 2 and 3, iron and aluminium fluoride complexes form due to the ion exchange between the metal hydroxides and fluoride. The dissolution of Al and Fe ions (mostly in Fe^{+3} state) from laterite was reported by Maiti et al. (10). It is possible that at high pH, dissolved Fe and Al ions interacted with the excess hydroxyl ions to form $Fe(OH)_3$ and $Al(OH)_3$ complexes. With a lower solubility product constant (Ksp) $Fe(OH)_3$ (K_{sp}:1.6x10^{-39}) is more likely to precipitate compared to $Al(OH)_3$ (Ksp:3x10^{-34}) (54). The membrane fouling by iron hydroxide particles in a cross flow system was reported before by Cohen and Probstein (55). In neutral and alkaline solutions, iron solubility is low and iron is found in hydroxide forms (56) suggesting that the precipitation of ferric hydroxide in the system is possible. In the literature, aggregates of small discrete particles (10 nm in diameter) of ferric hydroxide were found in several tenths of micrometers in diameter (57). These discrete particles, smaller than both of the calculated nominal pore diameter of the UF membranes studied here, could block or constrict the membrane pores or form a deposit layer on the membrane surface in case of particle aggregation. Pore constriction, pore blockage or deposit filtration can cause additional resistance in ultrafiltration system and possibly contributed to the permeate decline observed in alkaline solution.

Similarly, calcium and phosphate ions dissolved from hydroxyapatite (51, 52) can interact with hydroxyl ions in alkaline solutions. An increase in calcium precipitation with increasing pH is known (58); therefore, for the bone char system, the decline in permeability at high pH can be possibly attributed to the formation of calcium precipitates.

The Influence of Initial Fluoride Concentration

The data in Figure 3A show that the sorption capacity of bone char was higher than laterite at the studied equilibrium fluoride concentration range, with a sorption capacity of 3.8 mg/g for bone char and 0.37 mg/g for laterite at 1.5 mg/L equilibrium concentration (WHO guideline). When the fluoride mass sorbed was normalized by the total surface area of the sorbents it was observed that the sorption capacity of the sorbents became very similar to each other (Figure 3B) suggesting that available surface area governs the fluoride sorption.

For an equilibrium concentration range of 1.3-33 mg/L, the highest fluoride sorption capacity of laterite obtained in this study is 0.14±0.05 mg/m^2 which agrees well with most of the reported values in the literature (10, 13). In the study of Vithanage et al. (14), the reported capacity is higher but the aluminium and iron content of the laterite sample was ~70%, much higher than in other studies (41-46%) as well as in this one (50%). Rich content of aluminium and iron can contribute to the enhanced sorption capacity of the particular laterite sample investigated.

In the literature, fluoride sorption studies providing the surface area characterization of the bone char are limited. The capacity obtained in the study of Leyva-Ramos et al. (59) was lower than what was obtained here and the difference could be due to the difference in the treatment conditions of the bone char, which were not provided in the particular study. Other studies reported the fluoride sorption capacity of bone char in mg/g together with the equilibrium fluoride concentrations. In the study of Kawasaki et al. (50), the lower sorption capacity (2.26 mg/g) of the cow bones treated at 800 °C than the one obtained in this study (8.8 mg/g treated at 500 °C) can be attributed to the fact that the charring temperatures above 600 °C results in a poor fluoride removal (15). However, a low sorption capacity (2.3 mg/g) of bone char treated at 450 °C is rather surprising, especially considering that the initial fluoride concentration of that particular study was up to 1300 mg/L (18) where the sorption capacity is expected to be higher based on the sorption isotherm in Figure 3A.

Both Langmuir and Freundlich models were used in Figure 3A to describe the fluoride sorption on the sorbents under varying equilibrium concentrations as usually done in the literature (6). The Langmuir isotherm assumes a monolayer sorption whereas the Freundlich isotherm model assumes that the sorption sites are heterogeneous. Both models were fit to the data and can represent the data well in the range of concentration investigated with the coefficients presented in Table 2.

Figure 3C shows the influence of the equilibrium fluoride concentration on the membrane permeability for both laterite and bone char systems. The increase in initial fluoride concentration was parallel to the increase in equilibrium fluoride concentration. For both systems, at initial fluoride concentrations below 20 mg/L, permeability declined 15%. This decline can be attributed to the hydraulic resistance created by the sorbent deposit on membrane surface. For all fluoride concentrations tested above 20 mg/L the permeability decline stayed the same (15%) in the bone char system. However, for the laterite system, an exponential decrease in permeability was observed as the initial fluoride concentration increased above 20 mg/L. As shown in Figure 3A and C, the trend of decrease in permeability followed the trend of the increase in fluoride mass sorbed.

Co-precipitation of fluoride with aluminium hydroxide flocs is a known mechanism for applications with alum (8). Similarly, fluoride co-precipitation with iron complexes is possible. Such precipitation mechanisms need to be investigated further in order to clarify the correlation between the decline in the permeability at higher equilibrium fluoride concentration and the sorption for the laterite system.

3.4 The Influence of Sorbent Concentration

As displayed in Figure 4A, the permeate fluoride concentration decreased as the amount of sorbent added to the system increased and then reached a plateau at certain sorbent load for both systems. More than 20 g/L of laterite was required to bring the fluoride concentration from 10 mg/L to below 1.5 mg/L whereas 2.5 g/L of bone char was sufficient to obtain the same permeate concentration. Once the bone char load reached 5 g/L, the fluoride mass available was completely depleted. For the laterite system, a small decline in permeate fluoride concentration was observed once the sorbent load was increased up to above 30 g/L. These results are in agreement with the studies in the literature (11, 13).

As shown in Figure 4B, the permeability declined as the sorbent load increased for both laterite and bone char systems. The decline in the permeability was attributed to the increased resistance due to the increased sorbent deposit thickness. When 20 g/L of laterite was used in the system, the equilibrium fluoride concentration achieved was 1.6 mg/L and the permeability decline was

16%. On the other hand, 1.2 mg/L fluoride concentration was achieved with only 2.5 g/L bone char and at such low sorbent load the permeability decline was 7%.

CONCLUSIONS

This fundamental investigation on the performance of laterite-UF and bone char-UF systems showed that both systems are promising technologies for defluoridation in developing countries. The selection of the sorbent is highly dependent on the availability and accessibility of the sorbent at the country where the technology is to be applied. For the countries where both of the sorbents are abundant, bone char seems to be a better option for several reasons. As the results indicated, at initial fluoride concentrations above 20 mg/L, the membrane performance of the laterite-UF system is hindered. Additionally, the amount of bone char required to bring the fluoride level to 1.5 mg/L (WHO guideline) is less than that of laterite as bone char has a higher sorption capacity. Another advantage of the bone char-UF system is that it can be operated at neutral pH with an expected relative small decrease in permeability and does not require additional pH adjustment for the treated water whereas laterite-UF system may require additional pH adjustment to ensure neutral pH for the treated water. Nevertheless cost-benefit and social acceptance of the technology need to be analyzed before any application. Bone char requires pre-treatment which determines the final cost of the material whereas no treatment is required for laterite. Lastly, some of the concerns which can influence the social acceptance of the technology and has to be investigated further include the possible leaching of iron and aluminum from the laterite in the treated water to concentrations above the guidelines or odor/color problems due to the organic matter residual of the bone char.

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Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript. ‡These authors contributed equally.

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EPSRC/RSC Analytical Studentship and Leverhulme Royal Society Africa Award.

ABBREVIATIONS

BC, Bone Char;

BET, Brunauer–Emmett–Teller;

CDTA, 1,2-cyclohexanedinitrilo-tetraacetic acid;

DA, Dubinin-Astakhov;

F, Fluoride;

ICDD, International Centre for Diffraction Data;

ISE, Ion Selective Electrode;

LA, Laterite;

MWCO, Molecular Weight Cut-Off;

TISAB, Total Ionic Strength Adjustment Buffer;

UF, Ultrafiltration;

UK, United Kingdom;

USA, United States of America;

WHO, World Health Organization;

XRD, X-Ray Diffraction;

XRF, X-Ray Fluorescence;

pHzpc, zero point charge.

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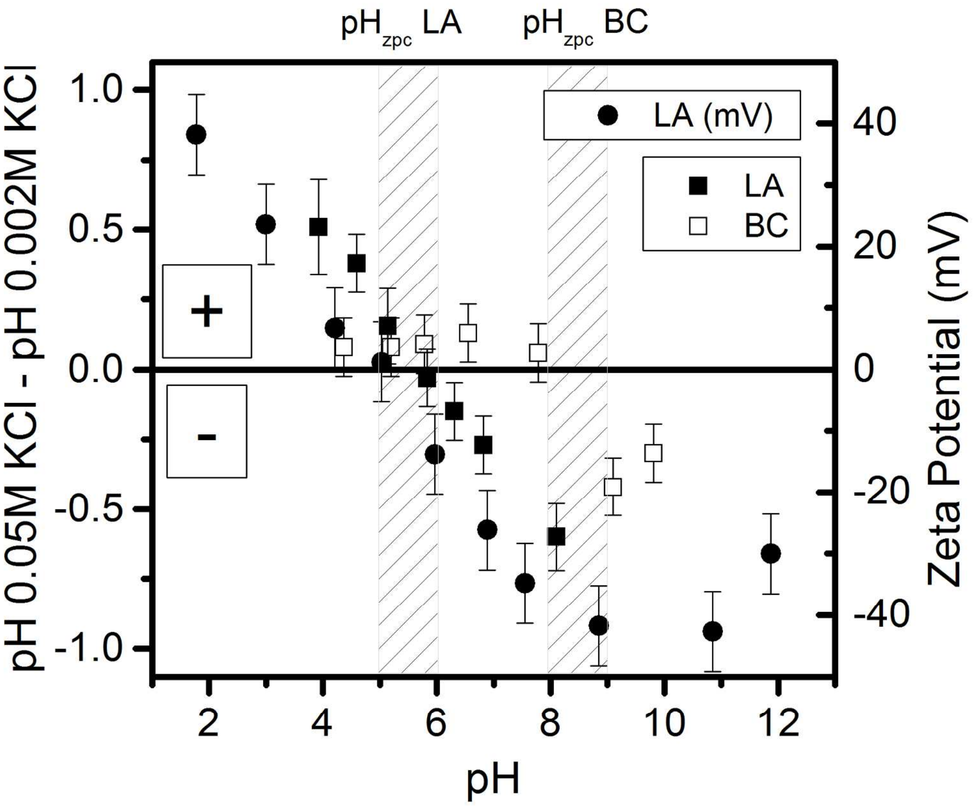

Figure 1. Variation of the sorbent surface charge (pH0.05M-pH0.002M) as a function of pH as determined with the titration method for LA and BC and zeta potential of LA in 1 mM NaHCO3 and 20 mM NaCl background electrolyte solution (right axis), LA: Laterite, BC: Bone char.
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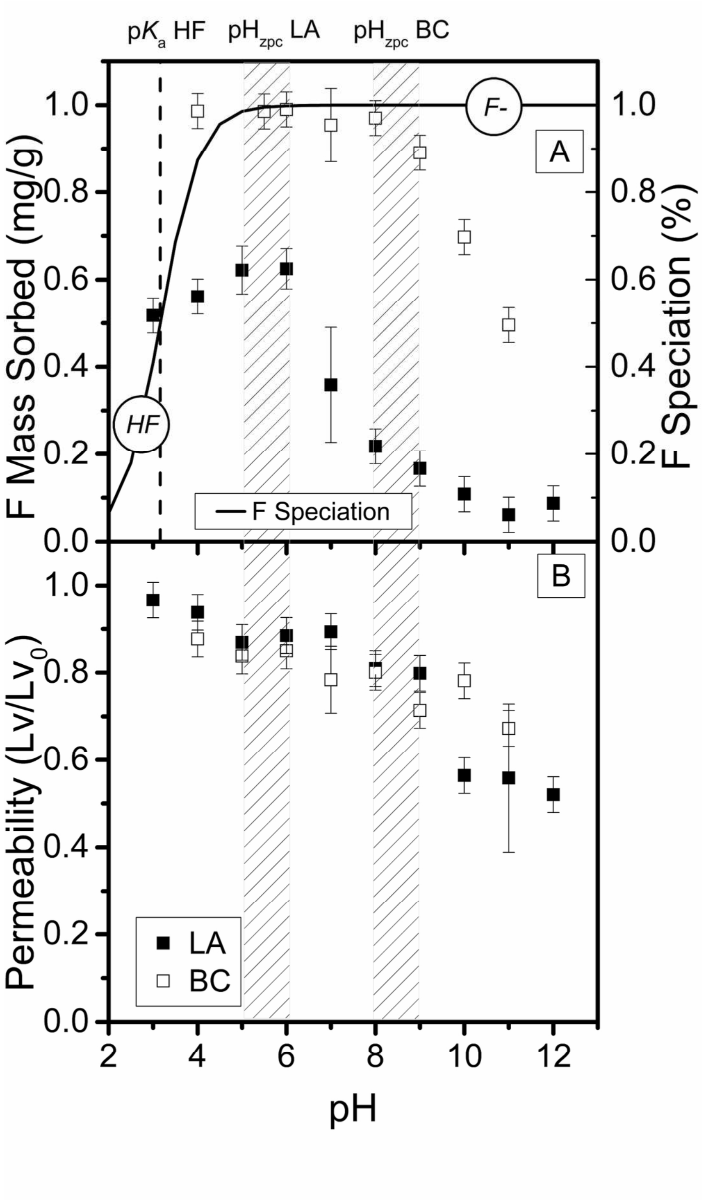

Figure 2. A) Fluoride (F) mass sorbed and speciation and B) permeability with changing pH. Experimental conditions: fluoride concentration 10 mg/L in 1 mM NaHCO3 and 20 mM NaCl background electrolyte solution, sorbent load 10 g/L, sorbent particle size <125 µm, LA: Laterite, BC: Bone char.
60x104mm (600 x 600 DPI)

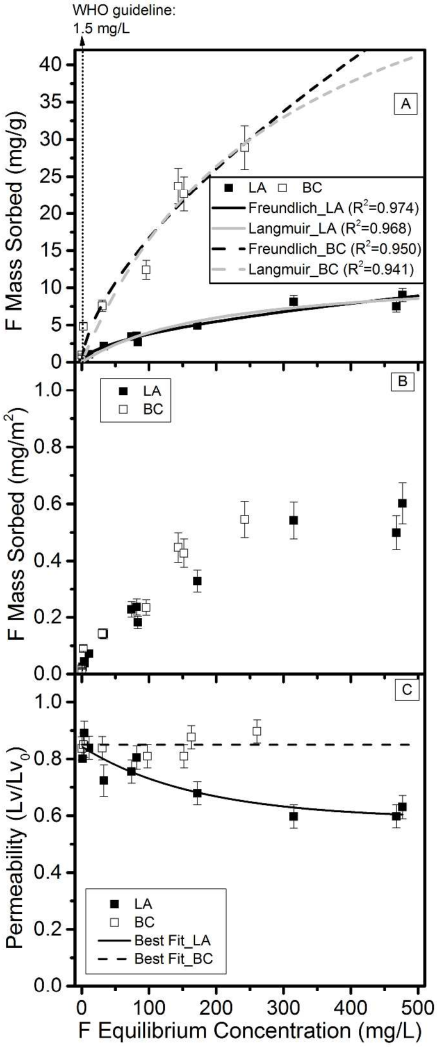

Figure 3. A) Fluoride (F) mass sorbed per sorbent mass (mg/g), B) fluoride mass sorbed per sorbent surface area (mg/m2) and C) permeability with changing equilibrium fluoride concentrations. Experimental conditions: 1 mM NaHCO3 and 20 mM NaCl background electrolyte solution, sorbent load 10 g/L, sorbent particle size <125 μm, pH 5 for laterite (LA) and pH 5.5 for bone char (BC). Regression performed with the linearized form of both Langmuir and Freundlich isotherms.
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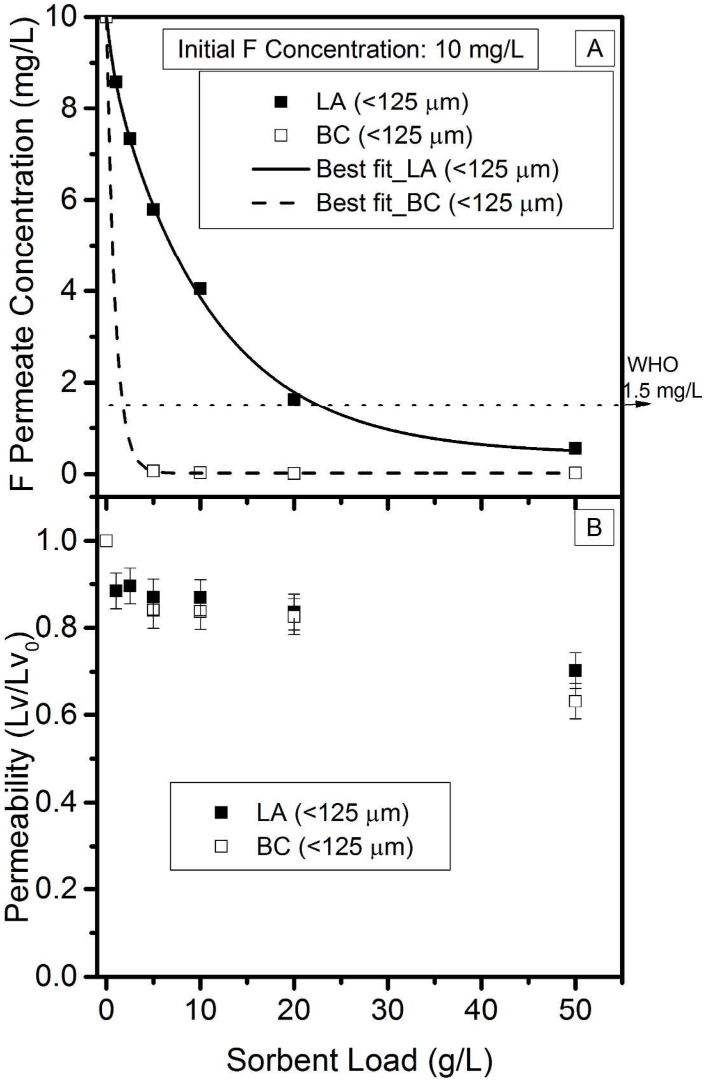

Figure 4. A) Permeate fluoride (F) concentration and B) permeability with changing sorbent load. Experimental conditions: fluoride concentration 10 mg/L in 1 mM NaHCO3 and 20 mM NaCl background electrolyte solution, sorbent particle size <125 µm, pH 5 for laterite (LA) and pH 5.5 for bone char (BC).
177x304mm (300 x 300 DPI)

Table 1. Chemical characteristics of laterite and bone char

	Laterite	Bone Char
Oxide components (weight %) XRF		
SiO_2	39	0
Al_2O_3	12	0
Fe_2O_3	38	0
MgO	0	1
CaO	n.d.	54
Na_2O	n.d.	1
TiO_2	1	0
MnO	1	0
P_2O_5	0	38
Loss on Ignition	9	6
Crystalline components (weight %) XRD		
Hydroxyapatite ($Ca_{10}(PO_4)_6(OH)_2$)	0	100
Quartz (SiO_2)	51	0
Goethite (FeO(OH)	41	0
Hematite (Fe_2O_3)	8	0

n.d., not detectable

Table 2. Sorption isotherm models and coefficients

Model	Linearized Equation	Sorbent	Coefficients		
			a (mg/g)	b	R^2
Langmuir* $Q_e = \frac{abC_e}{1+bC_e}$	$\frac{C_e}{Q_e} = \frac{1}{ab} + \frac{1}{a}C_e$	LA	12.05	0.004912	0.968
		BC	66.07	0.003321	0.941
			$k \left(\frac{mg/g}{mg/L}\right)$	n	R^2
Freundlich* $Q_e = kC_e^{1/n}$	$\log Q_e = \log k + \frac{1}{n}\log C_e$	LA	0.3208	1.87	0.974
		BC	0.8720	1.56	0.950

Q_e, fluoride mass sorbed (mg/g); C_e, equilibrium fluoride concentration (mg/L); a, maximum fluoride sorbed per mass sorbent; b, coefficient describing the affinity of fluoride on sorbent materials; k and n, empirical constants; LA, laterite; BC, bone char; *model was fit to the data in the linearized form with MATLAB (vR2009b, The MathWorks, Natick, MA, USA)

LIST OF FIGURES

Figure 1. Variation of the sorbent surface charge ($pH_{0.05M}$-$pH_{0.002M}$) as a function of pH as determined with the titration method for LA and BC and zeta potential of LA in 1 mM $NaHCO_3$ and 20 mM NaCl background electrolyte solution (right axis), LA: Laterite, BC: Bone char.

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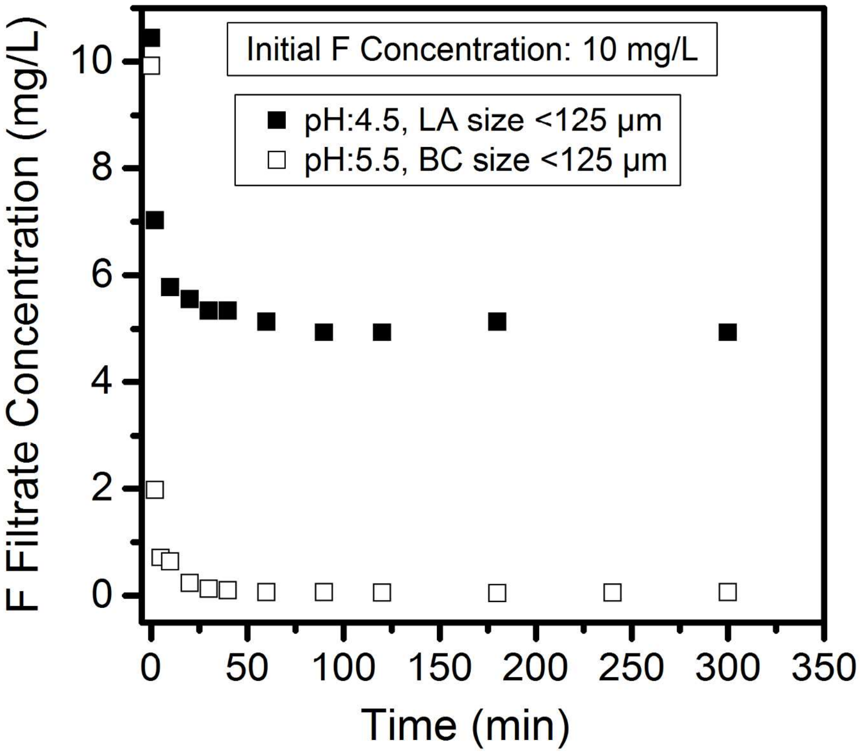

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ANSWERS TO THE REVIEWERS AND EDITOR

Dear Editor and Reviewers,

We would like to thank you for the time spent on the manuscript and for very valuable advices and comments. We will address all the points raised in the following with reference to the new manuscript. For clarity we left the reference to the line number in the original manuscript in the reviewers' comments and added the new line number in our response. Hopefully we managed to clarify the methods used and the conclusion reached.

Reviewer: 1
Comments to the Author
*Introduction is a little centralized on the advantages to use bone char or laterite sorbents from economic point of view. The problems of hybrid sorbent/filtration processes could have been highlighted more***.**

The introduction has been rewritten and expanded to address more specifically the challenges of the hybrid systems.

Method:

- *The authors should correct some typos or missing spaces (specially for units): L113 p.5 (kV); L120 p.6; L142 p.7; L178 p. 8 (Sartorius); same comments for the description of figures.*

Typos and missing spaces have been corrected both in the text and in the figures.

- *Reference of the membrane should be corrected L132 p.6*

L136, p.7 Reference has been changed.

- *Saturated electrolyte should be added to the reference electrode and author should write : "Ag/AgCl/KClsat" L149 p.7*

L152, p.7 – "Saturated electrolyte" was added in front of "reference electrode" on the line. "Ag/AgCl" is replaced by "Ag/AgCl/KClsat"

Results:

- *A further analysis of the deposit structure would have explained or at least given some clue about the difference in permeability at different pH (authors could give the deposit thickness as interesting information) and would have clarified the suspected co-precipitation of fluoride with metal or ion hydroxides. Nevertheless, the precipitation should be lowered at pH 5.*

Our main objective in this paper is to examine the initial feasibility of the proposed novel hybrid sorbent-membrane system. Understanding the mechanism behind the decrease in the permeability with changing parameters is crucial to design the system; detailed analysis of the membrane fouling and the nature and structure of the deposit is also required and we believe that this needs a separate further paper to be properly discussed in full.

Discussion:

- *Some information is given about the use of smaller size fraction of BC sorbent (<63 µm) in materials part and in the figure 4. But it was not presented in the results part nor discussed. The authors should remove results about this smaller fraction or discuss these results.*

Due to limitations in space, we removed the fluoride sorption and permeability data for BC of <63 µm from Figure 4 as suggested, instead of adding the discussion of the lower size range that would have required the addition of further data for laterite as well. We would like to comment here that for sorbent loads above 5 g/L, the particle size had a small influence on the sorption capacity due to the fact that the surface area available is in excess of what needed for the specific fluoride concentration even for the larger particles. This cannot be generalised and has to be properly addressed for other ranges of particle sizes.

Conclusion:

The authors claim that bone char-UF system other advantage is to be operational at neutral pH, but final experiments in figure 4 are operated at pH 5.5. So, they cannot directly conclude that this process will not require pH adjustment. Moreover, working at neutral pH will probably affect the permeability. Authors should at least replace the sentence L398 p.18: "As another advantage, bone char-UF system is operated at neutral pH and does not require additional pH adjustment for the treated water" by "As another advantage, bone char-UF system can be operated at neutral pH with an expected relative small decrease in flux and does not require additional pH adjustment for the treated water"

L395, p.18 – The sentence was replaced with "Another advantage of the bone char-UF system is that it can be operated at neutral pH with an expected relative small decrease in permeability and does not require additional pH adjustment for the treated water whereas laterite-UF system may require additional pH adjustment to ensure neutral pH for the treated water.". As a further comment we would like to point out that our data in Figure 2, fully support the statement that the decrease in flux at neutral pH is small.

Reviewer: 2

Comments to the Author:

This paper is an important contribution however many details and explanations are missing which make some of the interpretation sparse. In some cases the scientific claims appear to not be supported by the data. This is a study worth doing (and eventually publishing) but still needs substantial work before the final version.

We really appreciate the detailed analysis of the paper that the reviewer provided. We addressed most of their comment in the text, but it should be appreciated that due to word constraints on the manuscript, we weren't able to introduce longer explanation. We added some supporting information that hopefully will clarify some data and interpretation.

The major problems were related to the methods, we added information on the preparation and characterisation methods, referencing similar studies were the methods are explained at length.

Here are a number of comments that need to be addressed prior to publication:

- *Line 13 – start with the need! Why is it important?*

L13, p.1 - The sentence "Fluoride contaminated water sources are found in many parts of the world and the consumption of such water is causing dental and skeletal fluorosis in humans, especially in developing countries." was added at the beginning.

- *Line 23 – if the optimal laterite pH is 5 - 6 is this practical? Does pH need adjusting for real waters? Needs addressing*

The requirement of the pH adjustment is the obvious disadvantage of the laterite-UF system compared to BC-UF system; this was highlighted with the following sentence added to the conclusions:

L395, p.18 - "Another advantage of the bone char-UF system is that it can be operated at neutral pH with an expected relative small decrease in permeability and does not require additional pH adjustment for the treated water whereas laterite-UF system may require additional pH adjustment to ensure neutral pH for the treated water.".

- *Line 32 - Is fluoride a natural contaminant? Discuss*

L35, p.2 - The sentence "Water sources with high fluoride concentration have been located in many parts of the world including developing countries" was replaced by "Water sources naturally contaminated with fluoride leaching from the earth crust (4) have been located in many parts of the world including developing countries (5)."

- *Lines 39 – 42 – you describe the main technologies but fail to discuss their effectiveness – bring this together – how does the effectiveness of your system compare to what else is out there?*

The introduction has been rewritten and expanded to address more specifically the effectiveness of the different technologies. Please see Line 43, p.2 onwards.

- *Line 44 What toxic metals are released – seems pretty important in considering the overall feasibility of such a technology*

L49, p.3 - “such as aluminum and iron depending on the chemical characteristics of the sorbent” was added.

- *MAJOR POINT: You sell this as being accessible for remote communities - I agree the laterite and bone char are, but what about the UF system? This needs to be addressed!*

We modified the introduction to address this particular point. See line 70, p.4.

- *Line 61 – explicitly say why the smaller sizes provide higher fluoride sorption*

This is related to the availability of surface area for the physical sorption: L62, p.3 – “due to the increased sorbent surface area” was added to the end of the sentence.

- *Line 75 – 76: You say all of these different things influence performance but you have only chosen to look at three parameters – can you explain why these three were selected (and hence others were neglected)?*

We studied the influence of initial fluoride concentration, sorbent load and solution pH on fluoride sorption within this study. Sorbents were also characterized and the sorption was studied based on the sorbent characteristics as well. The influence of other parameters mentioned (temperature and particle size) was studied as part of the experimental campaign but was deemed outside the scope of this paper. This can be covered in an additional publication.

- *MAJOR POINT: The methods are sparse - much more detail is needed (see next specific points)*
- *MAJOR POINT: Line 85 – how was bone char treated? – this comes up again and again but the reader isn’t provided with the information about what was done with these samples.*

- *Line 86 - What kind of bone char? From animals/humans/etc what type?*

- *MAJOR POINT (LINKED): Line 91 you say “sorbents were not washed or treated” but on line 85 you say bone char was treated – please be very specific here about what was done and why. It sounds contradictory.*

- *Line 220 – again you really need to fully explain your treatment technique*

L89-95, p.4-5 The sentence “Bone char (BC) was collected from Ngurdoto Defluoridation Research Station, Arusha Region, Tanzania, where it was treated and prepared as described in the study of Mjengera and Mkongo (11).” was replaced by “Bone char (BC) was collected from Ngurdoto Defluoridation Research Station (NDRS), Arusha Region, Tanzania after treatment. Bone char was prepared from cow bones, heat treated in kilns at a ratio of about 8% of charcoal/raw bones, temperature ranging from 400 to 500 °C and controlled air supply by the local researchers in NDRW as described in the study of Mjengera and Mkongo (17). BC was not further treated before sorption and permeability experiments. Sorbent characterization analyses and experiments were conducted in the Laboratories of the University of Edinburgh.”

- *MAJOR POINT: Line 89 - Why were all of the sieve fractions selected? Why did you use different ones for the different sorbents? This just looks random and sloppy if it’s not explained well.*

- *Line 95 – why did you used different size ranges for bone char and laterite (linked to above)*

- *Line 129 – again WHY the different fractions and why was this selected (important but linked)*

As mentioned before we will not report on the influence of particle size in this particular paper. For the main body of experiments (sorption and permeability experiments) we used the same particle size fraction. To avoid confusion we modified the text as follow in the methods.

L99, p.5 **-** “which was used for all the sorption experiments.” was added. “Exceptionally, bone char sample was also reduced to 150-212 μm and <63 μm and laterite was reduced to <38 μm” was removed to avoid confusion.

Additionally, fluoride sorption and permeability data of <63 μm were removed from Figure 4 to avoid confusion. We recognise that the influence of particle size cannot be dismissed in few lines but will require to be addressed in a further paper.

Only surface charge analyses, as a part of sorbent characterization, were conducted with bone char with a particle size fraction of 150-212 μm and laterite with a particle size fraction of <38 μm size as specified in the appropriate section. This was due to the limited availability of sorbent sourced from the original location (Tanzania and Ghana).

- *Line 97 – wait 15 minutes then how did you measure pH? In settled samples? Mixed samples? This will affect results.*

L104, p.5 – “, while swirling” was added to the end of the sentence.

- *Lines 99 – 102 – notation is confusing. Where is this used later? What about pH_0.001M?*

L 104-111, p.5 Clarifications were added to the methodology of the titration method. The data obtained from the titration method were plotted in Figure 1 presenting variation of the surface charge of the sorbents as a function of solution pH. Based on the titration method 0.001M KCl solution was not necessary for the analysis so no data were obtained for pH_0.001M.

- *Lines 108: "temperature was equilibrated" – but to what value and what was the variance? I'd expect temperature to make a big difference on sorption – this needs to be addressed*

The temperature of the sample was equilibrated in the Zeta Plus instrument to measure the zeta potential of the sorbents within the scope of sorbent characterisation analyses not for the sorption experiments. This temperature equilibration was required to ensure a reliable zeta potential analysis of the sorbent samples based on the instructions given by the instrument supplier. The sorption experiment were all conducted at 21 ºC (see line 167, p.8).

- *Methods general: where was the analysis done?*

L94, p.5 - "Sorbent characterization analyses and experiments were conducted in the Laboratories of the University of Edinburgh." was added.

- *Line 120 – were XRF samples pelleted? There is lots of important methods information missing.*

L126, p.6 – The sentence has been modified to "the samples powder were fused in 40mm diameter discs with a lithium borate flux containing La_2O_3".

- *Line 136 – surface rinsed or filtration rinsed?*

L140, p.7 – "surface" was added to the sentence

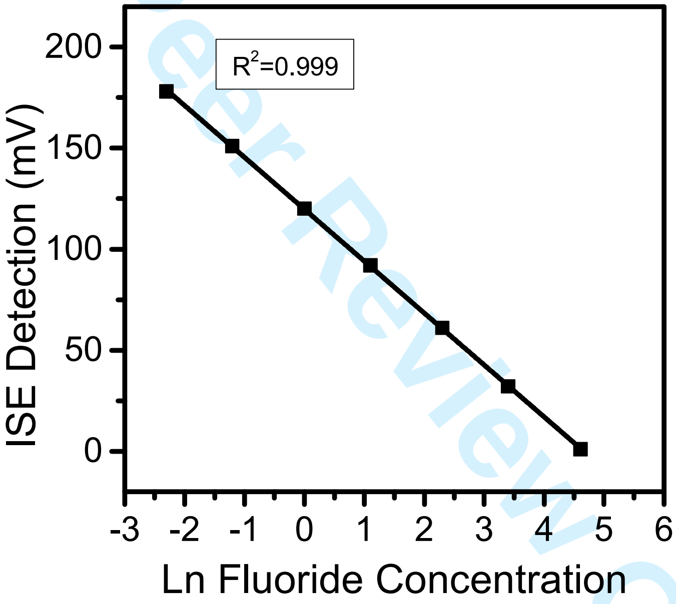
- *Line 144 – how frequently were standards and stocks made? What concentrations? What did your calibration look like?*

- *MAJOR POINT: Line 156: Error analysis of fluoride ISE measurements is needed – it would help here to show calibration data*

L147, p.7– “Stock solution was prepared fresh every week”

L153-156, p.7 - For each new stock solution fresh standard fluoride solutions of 0.1, 0.3, 1, 3, 10, 30 and 100 mg/L were prepared and used for the calibration of ISE. All the calibration curves used had a linear regression value between 0.999 and 1.000.” was added.

For reference an example calibration curve is presented below. We feel this figure will not add to the paper.



Calibration curve for ion selective electrode (ISE)

- *Line 161 how is temp regulated? How much did it change?*

L167, p.8 “controlled by the central cooling/heating system in the laboratory.” was added.

L167, p.8 – “21°C” was replaced by “21±2 °C”

- *Lines 166 please provide details of sensors used*

L173, p.8, "The cells contained a pressure transducer (PX209-300G5V) and a thermocouple (TJ2-CPSS-M6OU-200-SB) which were connected to a data acquisition system (OMB-DAQ-56), all purchased from Omega Engineering (Irlam, UK)."

- *MAJOR POINT: Line 172 How did you ensure sorption equilibrium? Was this tested? It would be good to see a figure here to justify why 3 hours was selected*

Line 180, p.8, "based on the results of preliminary kinetics experiments (See supporting information), to ensure the sorption equilibrium." was added.

An example of kinetic data for both sorbents has been added as a supporting information.

- *Line 177 – don't understand fourth permeate, you say just before that three permeates were collected*

Line 182-187, p.9_ We modified the explanation to make it clearer.

- *What was the mass of sorbent used?*

The sorbent load for pH (Figure 1) and fluoride concentration experiments (Figure 3) were presented in the figure captions as 10 g/L. We think that the load is a more meaningful way to present these results. The volume of the solution is given in the materials and methods.

- *MAJOR POINT: Line 190 – it is unclear why you neglected mads – where does the fluoride go? Seems an inaccurate assumption to measure mass absorbed in BLANK experiments with NO sorbent added – how can you verify that mads is neglected when there's no sorbent when this is the very thing you are trying got measure?*

m_{ads} represented the fluoride mass sorbed on the membrane. Some membranes have a potential of fluoride sorption as reported in the literature. Therefore blank experiments, with no sorbents added to the system, were conducted to analyse weather any fluoride sorption happens on the membrane. Blank experiments showed that no reduction happens in the initial fluoride concentration indicating that UF membranes used in the study do not have any sorption affinity for fluoride. Hence m_{ads} was neglected in the mass balance equation. M_{ads} (capital M) is the term used to represent the fluoride sorbed in the sorbent (laterite or bone char).

L192, 195, 197, 198, p.9 - To eliminate the confusion between the symbols, m_{ads} was changed to $m_{mem.}$

- *MAJOR POINT: Line 224: this seems a rash conclusion considering that points are all within zero charge (within error) from pH 5 – 8. You carry a lot of weight of your interpretation on the claim that the the pH is between 8 to 9 but that is not justified by your data.*

- *MAJOR LINKED POINT Similarly looking at figure 2, your mass absorbed for BC is constant for much longer than you claimed that your PZC is – compare your results to your zeta potential and reflect your figures (eg the marked zones) and discussion appropriately*

L229, p.11 - the sentence was modified to “The bone char surface showed no charge within the error in acidic and neutral pH range until becoming negative after pH_{zpc} (Figure 1). The pH_{zpc} of bone char was determined to be within the pH range of 8 to 9 which agrees with the study of Medellin-Castillo et al. (45) where the pH_{zpc} was reported as 8.4.”.

Even if between pH 5 and pH 8 the point are within zero charge so a PZC point cannot clearly be identified, after pH8 the charge is clearly negative and we suggest that this influences sorption. For the value of pH at which the surface charge is close to zero, we consistently observed a constant fluoride sorption. We reflected that in the discussion.

L253, p.12 – “For bone char, the fluoride mass sorbed was the highest and constant at $pH<pH_{zpc}$ when the surface charge was stable and it declined as soon as the surface charge became negative; the results agree well with those of Medellin-Castillo et al. (16).“

L296, p.14 – “For the bone char system, a change in the permeability was not observed as expected, due to the stable surface charge of the bone char within the pH range 4-8.”

- *Figures – please make your symbols consistent across all figures*

Figures were checked for consistency with legend modified and units rectified.

- *MAJOR LINKED POINT Lines 238 – 9 you talk about your pH being decreased from 5 to 3 but on your zeta potential you only have ONE point between pH 4.5 – 5 so how can you claim expectations for pH 5 – 4. As such I don’t agree your conclusions are “surprising” they are just incomplete!*

Two analyses were conducted to determine the surface charge of the laterite with respect to solution pH; titration method and zeta potential analysis. Three $pH_{0.05M}$-$pH_{0.002M}$ data points (0.51, 0.38, 0.155) are presented for pH 3.92, 4.59 and 5.14, respectively using the titration method. Four zeta potential data points (mV) (38.18, 23.61, 6.72, 1.22) are presented for pH 1.78, 3.00, 4.21, 5.03, respectively using the zeta potential analysis. Both methods show clearly a decline in the surface charge of laterite when the solution pH is increased from pH 3 to 5.

- *Figure 3 – how do you report a linear regression r^2 for a curve – this is misleading on your plots*

In Table 2 the linearized equations of the isotherms were included. These were used to regress the parameters. Once the isotherm constants were determined, the isotherm curves were drawn for each corresponding equilibrium fluoride concentration. This was added to the note in the table as well.

- *MAJOR POINT Lines 254 – 268 – this would be significantly improved by discussing in terms of the actual compositions of your samples (linking back to Table 1), particularly as SiO2 is the biggest component of your laterite - bring together the discussion from the literature to your actual data*

L262, p.12 - "Silicon, iron and aluminium oxides are the major components of laterite (Table 1) as also reported in the literature (10, 11, 14, 38)." was added.

L266, p.12 - "Therefore silicon oxide is not expected to play a role in fluoride sorption even if it is a major component of the laterite sample in this study." was added.

- *MAJOR POINT Can you look at some sort of solubility/reaction constants for your ion exchange reactions on Eqn 2 and 3 – a feasibility gauge needs to be done*

L306, p.14 - "With a lower solubility product constant (Ksp) $Fe(OH)_3$ (K_{sp}:$1.6x10^{-39}$) is more likely to precipitate compared to $Al(OH)_3$ (Ksp:$3x10^{-34}$)(54)"

- *Line 299 – 314 – if you are attributing a flux decline to iron, then why do you see it in bone char?*

As we explained in Line 318-321, p.14 - the decline in the permeability at high pH can be attributed to the formation of calcium precipitates.

- *MAJOR POINT LIne 299 – 314 – can you measure your other parameters in your permeate samples here, particularly iron? Are these DIW water samples only? (again not sufficiently described in methods) If so, then any Fe HAS to come from your sorbent. Can you analyse what's been released? If iron is a problem – what does this mean for real groundwater and what concentrations have an influence?*

L145, p.7_"prepared with ultra-pure water".

L401, p.18_The sentence was changed as “Lastly, some of the concerns which can influence the social acceptance of the technology and has to be investigated further include the possible leaching of iron and aluminum from the laterite in the treated water to concentrations above the guidelines or odor/color problems due to the organic matter residual of the bone char.”

The concentration of iron and aluminum were measured for some of the permeate samples. Results indicate that aluminum concentrations in the permeate samples were above the WHO guidelines (0.2 mg/L) whereas iron concentration were not above the WHO guidelines (0.3 mg/L). However this does not necessarily mean that iron was not leached from the laterite as iron hydroxide precipitates might have been rejected by the UF membrane and be present in the concentrate. We think that a systematic investigation with respect to both fluoride sorption and membrane fouling is required to properly comment on the leaching metals and their correlated presence in the permeate; this cannot be fully addressed in this paper due to space limitations but can be addresses in a later publication.

- *Lines 341 – 345 – Again this loses meaning with the description of how YOUR samples were treated – more detail are really needed*

L342, p.16 - “treated at 500 °C” was added to the sentence

- *Line 343 – why is low sorption capacity surprising? This all needs to be put into context with your work*

L346, p.16 - “where the sorption capacity is expected to be higher based on the sorption isotherm in Figure 3A.” was added to clarify it further.

- *Lines 351 – 353 – I don’t really believe this as the fits only deviate AFTER your last data point*

L351, p.16 The sentence was modified as “Both models were fit to the data and can represent the data well in the range of concentration investigated with the coefficients presented in Table 2.”

- *Line 361 – not sure if “exponential” is a fair assessment – seems simply to be approaching a plateau which should be discussed*

The data were regressed using an exponential decrease. The slow approach to a plateau correspond to the approach to the saturation capacity for the sorbent according to the isotherms in figure 3A and therefore is related to no more sorption/precipitation of fluoride.

- *Lines 395 – what would you expected?*

We didn't understand what the reviewer meant with this.

- *MAJOR POINT Lines 397 – throughout this is lacking context – what sort of removal is good enough? Suggest overlying drinking water guideline on some of your plots so we know if removal is good enough. You get to your conclusions and claim that is good but it needs to be obvious from your earlier results and discussion*

WHO guideline was added to Figure 3 and 4.

L325, p.15 "with a sorption capacity of 3.8 mg/g for bone char and 0.37 mg/g for laterite at 1.5 mg/L equilibrium concentration (WHO guideline)." was added to the sentence.

- *MAJOR LINKED POINT Lines 401 – 402 your second to last conclusion is that pretreatment makes a big difference but you still haven't discussed in detail what was done here – this is really important and neglecting it makes the paper weak*

To address this point we added the bone char treatment details in the method session (line 89-93, p.4-5).

Editor comment:

Your references are somewhat outdated - very few have been written in the past 3 years. Please carry out a comprehensive literature search to identify and report any pertinent works that have been conducted recently.

The literature review has been updated, adding relevant studies published recently to our reference list.

Thank you very much for your valuable comments.