Optimization of regenerated bone char for fluoride removal in drinking water: a case study in Tanzania

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ABSTRACT

This paper presents findings of a study on optimization and application of the regenerated bone char media for the defluoridation of drinking water in Tanzania where more than 30% of all water sources have fluoride concentrations above the 1.50 mg/l which is recommended by the World Heath Organization (WHO). In this study, regeneration temperature, regeneration duration, contact time, regenerated bone char dosage and particle size were investigated. Results indicate that the highest fluoride removal and adsorption capacity were 70.64% and 0.75 mg-F/g-bc, respectively, for a sample with bone char material that was regenerated at 500°C. In this study the optimum burning duration was found to be 120 min, which resulted in residual fluoride that varied from a maximum value of 17.43 mg/l for a 2 min contact time to a minimum value of 8.53 mg/l for a contact time of 180 min. This study further indicated that the smallest size of regenerated bone char media (0.5–1.0 mm diameter) had the highest defluoridation capacity, with residual fluoride which varied from 17.82 mg/l at 2 min contact time to 11.26 mg/l at 120 min contact time. In terms of dosage of the regenerated bone char media it was established that the optimum dosage was 25 g of bone char media with a grain size of 0.50–1.0 mm. This had a fluoride removal capacity of 0.55 mg-F/g-BC. Column filter experiments indicated that regenerated bone media is capable of removing fluoride from dinking water to meet both WHO and Tanzania recommended values.

Key words | bone char, defluoridation, fluoride removal, regeneration

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INTRODUCTION

Fluoride is an ion of the chemical element fluorine, which belongs to the halogen group. It is the most electronegative of all the elements and it is never found in elemental gaseous form except in industrial processes (Handa 1975). Fluoride ingestion by human beings at the optimum value of between 1.0–1.5 mg/l is beneficial to health (WHO 1984). Ingestion of high concentrations of fluoride, however, results in a disease called fluorosis, which is currently a serious public health problem in some parts of Tanzania (Ministry of Water, Energy and Minerals 1979). The seriousness and symptoms of fluorosis vary according to the contamination level of fluoride in the consumer. Fluoride taken at concentration levels less than 0.5 mg/l may result in lack of protection against dental caries, especially for children, while ingestion of between 1.5–3.0 mg/l causes dental fluorosis, which is characterized by mottling and modification of the dental enamel to produce yellow and brown stains. Some studies (Mcharo 1986; WHO 1984) have also reported that long term exposure to levels of between 3–6 mg/l of fluoride concentrations can result in skeletal fluorosis, which is characterized by severe pain and stiffness of the backbone as well as pain in the joints. Fluoride levels beyond 10 mg/l result in crippling fluorosis, which is characterized by bending of the bones and difficulties in walking.

Fluoride ingestion is linked with public health because it is a constituent in the bones and teeth and that, during the years of growth, fluoride is incorporated into these

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tissues in a concentration dependent on the amount ingested with food or drinking water. The structural inorganic part of bones and teeth consist mainly of apatite, a mixture of more hydroxyapatite (HAP), ($Ca_{10}(PO_4)_6(OH)_2$) and less fluorapatite (FAP), ($Ca_{10}(PO_4)_6F_2$). In this structure F^- and OH^- are interchangeable. The parts of the apatite molecules which are FAP determine the properties of this hard tissue. At very low FAP ratios, teeth are easily soluble under acidic conditions, meaning a higher risk of dental carries. At higher FAP ratios, the solubility is reduced. However, too high a ratio causes dental fluorosis.

The World Heath Organization (WHO) recommends a fluoride concentration of 1.5 mg/l in drinking water sources (WHO, 1984). However, some countries, for example Tanzania, allows consumption of drinking water with concentration of up to 8 mg/l of fluoride in areas with no alternative water sources. This is because methods of removing excess fluoride in water (defluoridation) have not yet been well established and a number of water supply sources are contaminated with high fluoride concentrations. As such, if the guidelines set by the WHO were adopted, Tanzania would have about 30% of its water sources deemed as unsuitable for domestic consumption (Bardecki 1974; Ministry of Water, Energy and Minerals 1979; Gumbo 1987).

Some studies to investigate fluoride removal methods and removal mechanisms have been carried out in Tanzania (Singano 1991; Mcharo 1986; Mjengera 2001). Singano (1991) indicated that, by using calcinated magnesite or magnesia (MgO) as filter media and polyaluminium chloride (which is a polynuclear complex of polymerized aluminum ions and chloride anions with a general formula of $Al_n(OH)_mCl_{3n-mn}$) as a coagulant in defluoridation, fluoride can be reduced from 22.0 mg/l to 3.0 mg/l.

Bones and enamel are essentially HAP and, in the presence of fluorides, the hydroxides are replaced by fluoride, forming a more insoluble FAP. This compound can be returned to a form suitable for repetitive fluoride adsorption with a caustic solution. This results in the formation of hydroxapatite, with fluoride removed as sodium fluoride. Based on these facts Mjengera (2001) optimized a bone char column media for defluoridation of drinking water at the household level. Bone char reacts with fluoride by ion exchange adsorption between fluoride in the solution and carbonate of the apatite comprising bone char. This reaction can be represented by the following equation:

$$Ca_{10}(PO_4)_6(OH)_2 + 2F^- \Leftrightarrow Ca_{10}(PO_4)_6F_2 + 2OH^-. \quad (1)$$

Another study (Mjengera 1988) indicated that, as the bone char media is continuously used, it gets exhausted. The exhausted media can either be replaced by virgin material or regenerated before it can be re-used. Studies on the use of a 1% solution of sodium hydroxide for bone char regeneration have been reported (Mcharo 1986; Christoffersen *et al.* 1990). Bone char regeneration by heating is a new approach in defluoridation technology, which seems to be potentially beneficial, especially for defluoridation of drinking water at the household level.

The aim of this is paper is to present the findings of a study in which fluoride-saturated bone char material was reactivated by heat and its defluoridation capacity investigated with a view to trying to find a solution to the problem of excessive ingestion of fluoride, especially in rural areas where the use of bone char materials can be economical and easy to handle. The study was prompted by the fact that, although various studies on the use of bone char as defluoridation media have been carried out, heat regeneration of the exhausted media to restore the defluoridation capacity has not been fully studied.

MATERIALS AND METHODS

Media preparation and bone char regeneration

Charring of the bone char

The collected cattle bones were heated in a local kiln using wood charcoal. Heat treatment removes the organic matter, which adds taste and colour to water. As such, the organic phase does not participate in adsorbing the fluoride. Heating thus makes the bone char hygienically acceptable for defluoridation. In this study heating of the bones in the local kiln was controlled and kept to between 400–600°C because, according to Posner (1987), temperatures higher than 600°C may damage the apatite structure, resulting in poor fluoride removal, while temperatures below 400°C may result in a bad taste and odour for the treated water.

Crushing of the charred bones

After charring, the bone char materials were manually crushed using a laboratory crusher. Alternating between sieving and crushing of the same batch was used in order to minimize waste, as recommended by Hauge *et al.* (1994). This method is labour-intensive, but it can be the most appropriate when the priority is to use the greater part of the cattle bone char materials for defluoridation.

Sieving

The bone char was sieved several times to obtain different fractions with only a little range in size. The reason for this is that a mixture with a large range in sizes is less porous in a filter and therefore influences the efficiency of the filter because of clogging and high non-uniform filter resistance. A uniform fraction of bone char in a specific size acts in a uniform way in the filter giving filter resistance and having fewer tendencies to clog.

Saturation of bone char with fluoride

In this process, saturation was prepared by adding sodium fluoride (NaF) to the prepared bone char media in order to obtain fluoride-exhausted bone char material. Natural water from the local source of drinking water in the case study area (Northern Tanzania), which contained a fluoride concentration of 21.26 mg/l, was passed through the media in a filter column. Complete saturation was attained when the concentration in the effluent increased to the same value as in the influent.

Regeneration

The exhausted bone char media with particle sizes between 0.5–3.0 mm in diameter were reactivated by heat at different temperatures using an electric furnace. The mechanism that takes place is as shown in the following equation:

$$Ca_{10}(PO_4)_6F_2 + 2OH^- \xrightarrow{Heat} Ca_{10}(PO_4)_6 + 2HF\uparrow + O_2\uparrow . \quad (2)$$

Eight samples (S1–S8) of 200 g each were reactivated at different temperatures (100–800°C for a period of 2 h, as shown in Table 1. Again the exhausted media were regenerated at the obtained optimum temperature but at durations of 30, 60, 90, 120 and 150 min with the aim of finding out the optimum regeneration time at the optimum temperature. The obtained optimum time and regeneration temperature was used to study the defluoridation capacity of the regenerated media in the column filter experiment.

Experimental set-up

Two experimental set-ups, namely a jar test and a column filter, were used in this study. The jar test experiments were carried out by using a dosage of 20 g of bone char materials in one litre of water with an initial fluoride concentration of 21.26 mg/l for different contact times and with a stirring rate of 52 rpm. Samples were collected at different contact times, filtered and analysed for residual fluoride concentrations. The jar test apparatus that was used was of a Phipps type and Birds stirrer 7790 402.

In the column filter experimental set-up, the defluoridation filter was made from a plastic column 53 cm long and a diameter of 30 cm. The filter column was closed at the bottom and fitted with inlet and outlet devices, which included the gate valve for the inlet and outlet portion and a water meter for determination of the quantity of water passing through the filter media.

Sample preparation and analysis

Determination of fluoride concentration

Two fluoride electrodes were used to analyse fluoride in the treated water. One of the electrodes was a fluoride-sensing radiometer F1 052 while the second was a single-junction reference electrode metrohm Ag/AgCl, with sleeve type diaphragm connected to a metrohm potentiometer (ion analyzer specific pH Ion meter model 691). Reference standards were made from appropriate dilutions of a stock solution of sodium fluoride (NaF) 100 mg/l and Total Ion Strength Adjusting Buffer (TISAB) solution. A water sample of 5 ml was transferred into a 25 ml plastic beaker by means of a measuring pipette. After rinsing the pipette by distilled water, 5 ml of TISAB was measured and transferred into the beaker containing the water sample. The electrodes were immersed into the sample and stirred slowly for 30 s, and then the specific pH Ion meter was switched on in order to read the millivolts when a steady state was reached.

Table 1 | Regeneration of exhausted bone char material

Exhausted bone char 200 g	S1	S2	S3	S4	S5	S6	S7	S8
Temperature (°C)	100	200	300	400	500	600	700	800

The concentration of fluoride in mg/l was calculated by interpolation using a scientific calculator.

Defluoridation capacity of regenerated bone char

The defluoridation capacity of the regenerated bone char was calculated by determining fluoride concentrations before and after the contact time using the following equation:

$$DC_{FC} = \frac{S_0 - S_t}{X_{fc}} \quad (3)$$

where

DC_{FC} = defluoridation capacity of regenerated bone char (mg/g),
S_0 = initial fluoride concentration (mg/l),
S_t = concentration after contact time (mg/l) and
X_{fc} = regenerated bone char media (g/l).

Removal efficiency

The quantities absorbed in a given period of contact time and removal efficiency were calculated based on the following equation:

$$Q_t = \frac{S_0 - S_t}{S_0} \times 100 \quad (4)$$

where

Q_t = percentage removal efficiency,
S_0 = initial fluoride concentration (mg/l) and
S_t = residual fluoride concentration (mg/l).

RESULTS AND DISCUSSION

Colour of regenerated bone char

An analysis to relate the colour of the regenerated media with the regeneration temperature is presented in Table 2. Between 100 and 500°C the colour of the bone char media was mainly black. It was then observed to change from black to light brown at 600°C then to a gray colour at 700°C and finally at 800°C it changed to a white colour. Changing of the colour of the bone char materials presumably reflects the changes in the organic matrix from carbon to carbon dioxide when heated, as observed by Hansen *et al.* (1991). On the basis of the observed colour changes and also on the assumption that at 800°C the hydroxyapatite structure of the bone char would have been damaged, the bone char sample prepared at 800°C was not used in the jar test experiments.

Jar test experiments

Optimum regeneration temperature

Figure 1 present residual fluoride variation with contact time as analysed in samples with the same initial fluoride concentration of 21.26 mg/l and a dosage of 20 g/l of bone char material regenerated at different temperatures.

Table 2 | Effect of regeneration temperature on the colour of bone char material

Sample number	Regeneration temperatures (°C)	Final colour of the regenerated sample
1	100	Black
2	200	Black
3	300	Black
4	400	Black
5	500	Black
6	600	Light brown
7	700	Gray
8	800	White

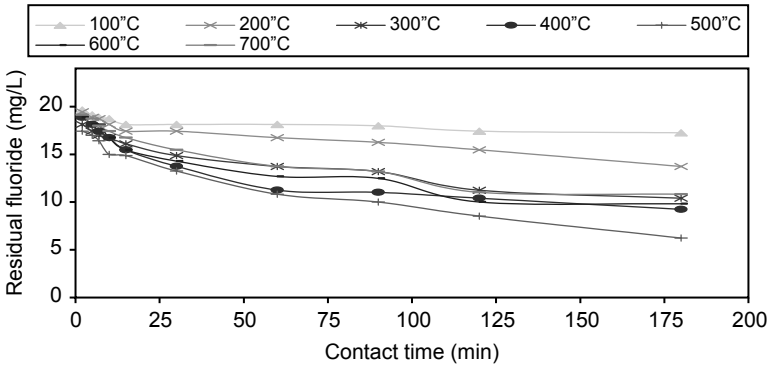

Figure 1 | Variation of residual fluoride (mg/l) with the regeneration temperature of the bone char material.

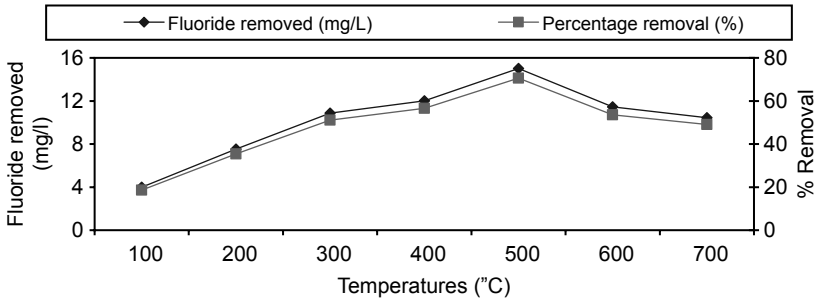

Figure 2 | Variation of fluoride removed (mg/l) and percentage removal capacity with regeneration temperatures (°C).

The diameter of the bone char material ranged between 0.5–3.0 mm.

Figure 2 indicates the variation of fluoride removed (mg/l) and fluoride percentage removal capacity with the temperatures (°C) at which the bone char materials were regenerated. Fluoride removal capacities (mg-F/g-bc) at different regeneration temperatures are presented in Figure 3.

These results indicate that the highest fluoride removal and adsorption capacity were 70.64% and 0.75 mg-F/g-BC, respectively. These were obtained from a sample with bone material that was regenerated at 500°C. The lowest fluoride removal (0.2 mg-F/g-bc or 18.6%) was obtained for a sample with bone char material that was heated at 100 °C.

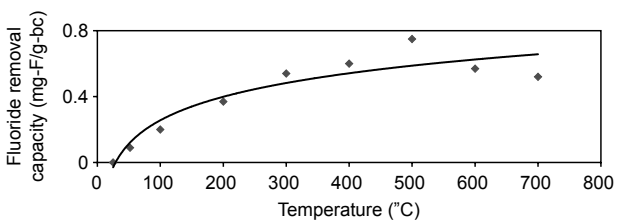

Figure 3 | Fluoride removal capacities of regenerated bone char at different temperatures.

Colour analysis of the regenerated bone char presented in Table 2 suggests that at regeneration temperatures of up to 400°C burning of the bone char might have been incomplete, thus resulting in less fluoride uptake by the bone char material. Removal capacity at temperatures beyond 500°C (600–700°C) was again reduced, which is in agreement with the hypothesis that regeneration of bone char material at high temperatures damages the hydroxyapatite structures (Posner 1987). Experiment on the 800°C regenerated bone char, which had even turned white suggesting perhaps a complete destruction of hydroxyapatite structures, was not performed since the removal capacity trend from the bone char heated at 600°C and 700°C was already observed to be diminishing.

Regeneration duration and defluoridation capacity

Analysis of residual fluoride in samples of bone char material heated at 500°C but at different intervals of time

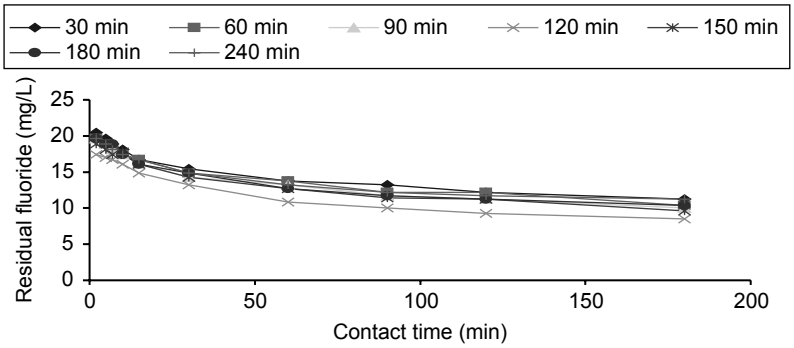

Figure 4 | Effect of regeneration duration on defluoridation.

(30–240 min) was carried out in order to determine the optimum regeneration period. In this experiment bone char material of grain sizes 0.5–3 mm at a dosage of 20 g/l were used. The contact time between bone char materials and fluoridated water was between 2–180 min and the initial fluoride concentration of water was 21.26 mg/l.

Figure 4 indicate that the optimum burning duration of the bone char material that was prepared at 500°C was 120 min. During this period residual fluoride varied from a maximum value of 17.43 mg/l at 2 min contact time to a minimum value of 8.53 mg/l for a contact time of 180 min.

The least fluoride removal was obtained in a sample of bone char media that was regenerated for a period of 30 min. This resulted in a residual fluoride concentration of 20.43 mg/l and 11.26 mg/l at 2 and 180 min contact time, respectively. Figure 5 indicates the fluoride adsorption capacity variation with regeneration temperature. The highest removal capacity (0.64 mg/g) was obtained from bone char material which was regenerated for a duration of 120 min.

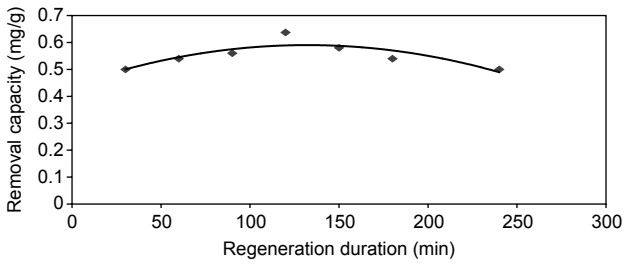

Figure 5 | Adsorption capacity for each regeneration duration.

Grain size and defluoridation capacity

The jar test experiment was carried out for various particle sizes (0.5–1.0, 1.0–1.5, 1.5–2, 2.0–2.5 and 2.5–3 mm) of bone char material regenerated at 500°C for 120 min. Samples were then analysed in order to establish the effect of grain size of the bone char material on fluoride removal capacity. Figure 6 indicates that the sample with bone char material of 2.5–3 mm diameter had the highest residue fluoride. The variation of residual fluoride in this sample was from 21.26 mg/l at 2 min contact time to 15.2 mg/l at 120 min contact time. The residual fluoride was lowest (17.82 mg/l at 2 min contact time and 11.26 mg/l at 120 min contact time) for bone char material with particle sizes 0.5–1.0 mm in diameter, suggesting that the smallest-size regenerated bone char media had the highest defluoridation capacity.

This could be due to the process of uptake of the media with respect to the diameter of the particle size, which favour finer particle (Mjengera, 1988). Hauge *et al.* (1994) have also reported that removal of fluoride by bones is a surface reaction process and that, as the surface area is increased, the effectiveness of the bones in removing fluoride also increases. Too large a surface area, however, has limitations; namely the decrease of the water flow rate through the fine bone char material.

Dosage of regenerated media and defluoridation capacity

Fluoride removal capacity with respect to the dosage of regenerated media was studied by using different dosages (6 g, 15 g and 25 g) of bone char material with particle grain

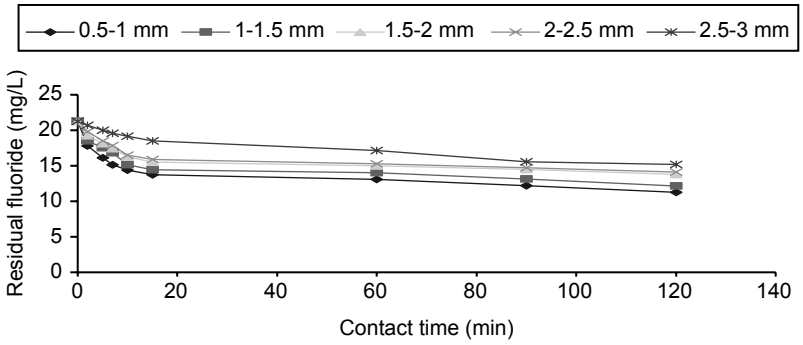

Figure 6 | Effect of regenerated grain size on defluoridation.

sizes of 0.5–1.0 mm and 1.0–2.0 mm diameters for a 1 h contact time. The initial fluoride concentration was 21.26 mg/l and the media had been regenerated at 500°C for 120 min. Figure 7 indicates that fluoride removal capacity is dependent on the dosage of the bone char media and that the higher the dosage the higher the removal efficiency. In this study, the optimum dosage was 25 g bone char media for 1 h contact time with a grain size of 0.5–1 mm. This had a fluoride removal capacity of 0.55 mg-F/g-bc and the residual fluoride was 7.5 mg/l, which is within the acceptable fluoride concentration levels (up to 8 mg/l) in drinking water sources in Tanzania.

Filter column test results

In these tests water containing an initial fluoride concentration of 21.26 mg/l was allowed to flow through a filter column containing fresh bone char media and then through firstly, secondly and thirdly regenerated bone char media. The average flow rate was approximately 0.0021 l/s. Figures 8–11 show the relationship between the volume of treated (deflouridated) water (litres) and the fluoride removed (mg/l) and residual fluoride (mg/l) in the fresh, first, second and third time regenerated bone char media. In the first experiment (with the fresh bone char media), the residual fluoride variation was between 0.12–18.13 mg/l. After the first regeneration the variation of residual fluoride was 0.32–20.96 mg/l, while for the second and third regeneration bone char material the residual fluoride variations were 0.68–19.64 mg/l and 0.13–20.98 mg/l, respectively.

Fluoride removal efficiency for the second and third regenerated bone char material decreased because the media was saturated with fluoride and also a large part of the hydroxyapatite structure was damaged during the regeneration process. Figure 9 indicates that during the first regeneration 160 l of treated water (with residual fluoride of 1.42 mg/l) meets the WHO recommended value for fluoride ingestion, while 350 l meets the allowable Tanzanian

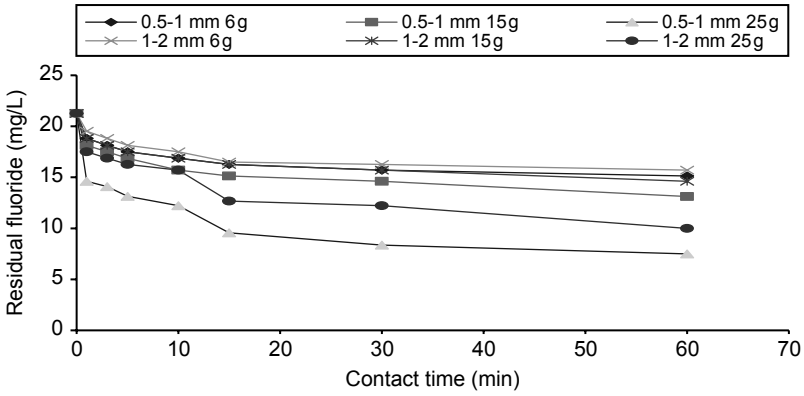

Figure 7 | Effect of the dosage of regenerated bone char media on defluoridation.

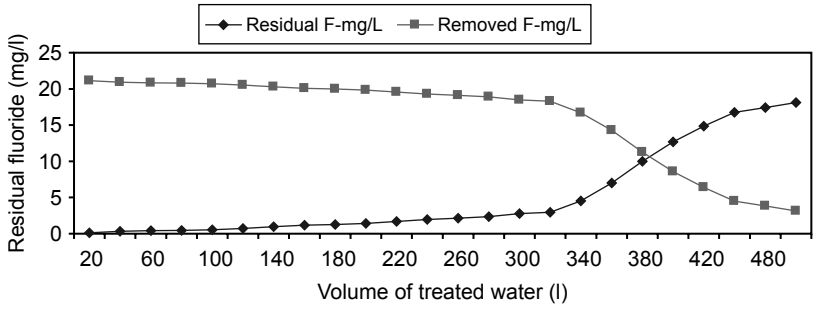

Figure 8 | Column test with fresh bone char material.

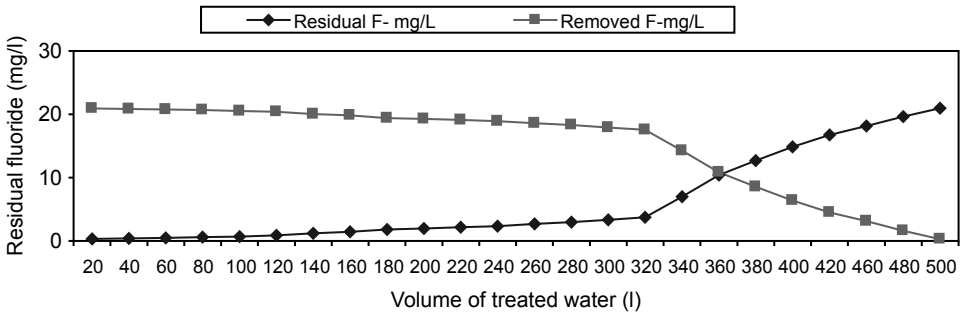

Figure 9 | Column test, first regeneration.

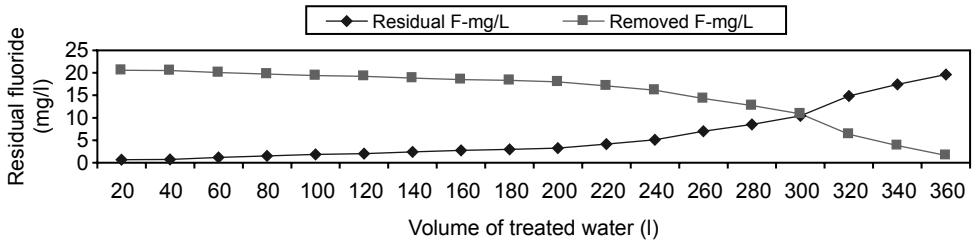

Figure 10 | Column test, second regeneration.

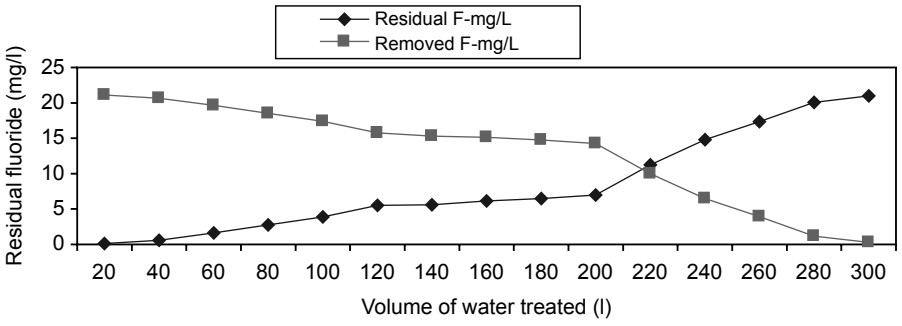

Figure 11 | Column test, third regeneration.

standards (8 mg/l). For the second regeneration (Figure 10), 120 l of treated water meets the WHO recommended standards and 28 l meets the Tanzanian standards. In the third regeneration (Figure 11) 60 l of treated water meet the WHO standards and 200 l meets Tanzanian standards for fluoride ingestion in drinking water.

CONCLUSION

In this study, regenerated bone char was found to be a potential medium for the defluoridation of drinking water. The regenerated bone char media at 500°C for a duration of 2 h was found to be the most practical with a potential for fluoride sorption, while the smallest grain size particles of bone char media (0.5–1.0 mm) yielded the best results in terms of fluoride removal. This suggests that the smaller the grain size of the bone char media the better the fluoride removal capacity because of the large surface area for the adsorption process. A limiting factor for the smaller size, however, can be clogging during the filtration process. Filter column experiments indicated minor differences in terms of fluoride removal capacity between fresh and first regenerated bone char media. As such, water treated by regenerated bone char media gave allowable residual fluoride, which was recommended by both the WHO and Tanzanian temporary standards.

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