Fluoride Removal Capacity of Regenerated Bone Char in Treatment of Drinking Water

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ABSTRACT

Fluoride plays significant biological roles in human body. However, intake of more than 1.5 ppm fluoride causes serious health concern particularly fluorosis. Drinking water with high levels of fluoride is the major cause of fluorosis. This condition is untreatable and prevention is the best mitigation method. With most of the water treatment methods being costly and out of reach of most poor populations, a conventional fluoride removal method from water that is applicable to smallholders is of much necessity. Bone char regenerated with 2% NaOH was investigated for the feasibility to be used as a cost effective to reduce fluoride concentration in drinking water to acceptable limits. Samples of 40 gms bone char each were packed in columns and 50 ml of 5.96 ppm borehole water were added, after 20 minutes of contact time fluoride analysed using fluoride meter. Fluoride of unknown samples was analysed using fluoride meter. Regenerated bone char was able to treat about 6.85 litres of water before breakthrough of 1.5 ppm as compared to fresh bone char that treated 7.56 litres. This translates to removal capacities of 0.880 and 0.988 mg/g for regenerated and fresh bone char respectively. In conclusion, the results suggest that regenerated bone char is a viable option for reducing excess fluoride in drinking water.

Keywords: Regenerated bone char, fresh bone char, fluorosis, removal capacity

INTRODUCTION

Fluoride has certain physiological properties of great importance in human health. At low concentrations fluoride stabilizes the skeletal system by increasing the size of apatite crystals and reducing their solubility (Moges *et al*., 1996; Notcutt and Davis, 1999; Li *et al*., 2001, CCEFW, 2010). However in excessive exposure mainly in drinking water or in combination from other sources such as brick tea, vegetable juices, high fluoride toothpastes, and agricultural activities can result in a number of adverse effects. These range from mild dental fluorosis to crippling skeletal fluorosis as the level and period of exposure increases (Fawell*et al.,* 2006; Shepherd *et al*., 2012). The maximum permissible level for fluoride in drinking water established by World Health Organisation is 1.5 ppm (WHO, 2004).

To date, several studies on removal of fluoride from drinking water have been carried out over the years using a wide variety of materials giving various efficiencies. The use of polyaluminium salts, magnesite, bone char, activated carbon, magnesium compounds, serpentine, clays, Nalgonda technique and ion exchange have also been applied (Mavura and Tiffany, 2002; Mjengera and Mkongo, 2003; Feenstra*et al.,* 2007; Zevenbergen*et al.,* 1997; Dahi, 2000Bulusu*et al.,* 1979; Bregnhøj *et al.,* 1990). Other methods include;electro dialysis, distillation, reverse osmosis, crystalactor, and memstill technology. Some of these methods demand high cost and skilled man power further becoming prohibitive in developing countries (Fawell*et al.,* 2006; Feenstra*et al.,* 2007; Bhatnagar *et al*., 2011). There is thus, a dire need to develop some economical technology applicable at domestic levels to reduce the fluoride concentration from very high concentrations to acceptable concentrations in drinking water. Bone char defluoridation is simple to perform, usually inexpensive, and applicable for decentralized water treatment (Zhu *et al.,* 2011).

This study was to determine the capacity of 2% NaOH regenerated bone char. The effects of several reaction variables such as the initial fluoride ion concentration and volume of water were evaluated. The capacity of regenerated bone char was determined by batch experiments.

METHODOLOGY

Materials

Fresh brown-grey bone char of 0.63 to 2 mm diameter used for community and household filters commercially available in Catholic Diocese of Nakuru Water Quality Programme. Borehole water samples with 5.96 ppm fluoride collected within the Egerton University.

Fluoride stock solution1000 ppm prepared by weighing 2.21 grams NaF and putting it into a 1 litre volumetric flask. Distilled water was added to dissolve and then water was added to mark. Two-hundred, 100 and 10 ppm were prepared by serial dilution of 1000 ppm of stock solution.

Two percent NaOH solution was prepared by dissolving 20 g of NaOH pellets in 1000 mL distilled water.

Equipment

Fluoride analysis was done using standard method (ALPHA, 1995). The concentration of fluoride ions in the solutions was determined using a selective electrode fluoride ion selective electrode Metrohm 6.0502.150 and reference electrode (Ag/AgCl) Metrohm 6.0733.100.

Regenerated Bone Char

Fresh bone char was soaked with 100ppm fluoride solution in aplastic basin to saturate the bone char for five days and manual stirring done after every 24 hours. After saturation, it was followed by rinsing the bone char with tap water to remove all the free fluoride ions and it was finally dried. The process of regeneration was carried out by exposing the fluoride saturated bone char to 2% NaOH solution in batch through the column. Samples of the water output were taken at different times and analysed for F^- concentration to ensure complete fluoride removal. Bone char was washed with distilled water to reduce pH and to remove all the free fluoride ions. Further, pH was reduced by use of 0.02M HCl enriched water up to pH of 7.84.pH was determined using the pH meter (Orion Combination pH 91-06).Finally excess acid was rinsed using distilled water. Effluent should have a pH of 6.5 to 8.5 according to WHO recommended values. Bone char was then dried for safe storage and use. From this experiment, regenerated bone char was obtained and used to study fluoride removal capacity and efficiency.

Capacity of Regenerated Bone Char

The filter was made by packing a column with 40g of 2% NaOH regenerated bone char.50 ml borehole water containing 5.96 ppm initial fluoride concentration was added in each column and allowed a contact time of 20 minutes as recommended by Catholic Diocese of Nakuru Water Quality. The water coming out of the column was collected and its fluoride concentration tested until the output concentration was above 1.5 ppm. The water output in litres treated before breakpoint of 1.5 ppm was calculated.

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The fluoride removal capacity was calculated using total amount of fluoride in water before treatment minus amount of fluoride in the treated water by dividing it with mass of bone char packed in the column.

The removal efficiency was calculated based on the following equation 3.2:

$$Q_t = [(S_0 - S_t)/S_0]*100 \ldots\ldots\ldots\ldots\ldots 3.2$$

Where Q_t= percentage removal efficiency,S_0 = initial fluoride concentration (mg/l) and S_t =residual fluoride concentration (mg/l).The capacity and efficiency of regenerated bone char was compared to fresh bone char.

RESULTS

Capacity of Regenerated Bone Char

The optimum percentages of fluoride removal were 95.81, 92.45 and 94.63% for the fresh, regenerated and mixture bone char respectively. The results obtained were plotted as output fluoride concentration versus volume of treated water (Figure 1). The graph shows that the concentrations of fluoride removed was high in initial stages, and decreased up with time. This trend may be due to initially all the adsorbent sites being vacant and the solute gradient high for ion exchange but with time the number of sites decreases.

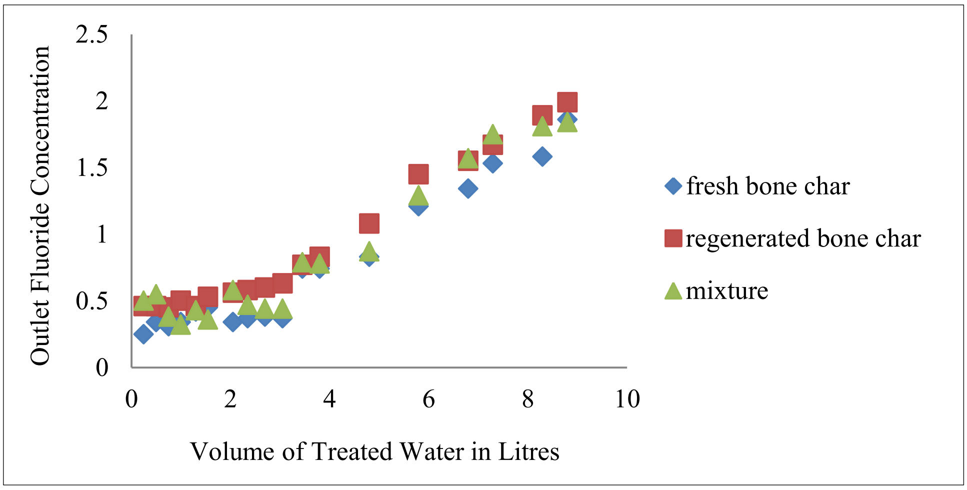

Figure 1. Fluoride concentration released as a function of the amount of treated water. Initial fluoride concentration of water 5.96 ppm.

Equations for the curves in figure 1:

$$y = 0.014x^2 + 0.060x + 0.246 \ldots\ldots\ldots\ldots\ldots (4.1)$$

$$y = 0.013x^2 + 0.075x + 0.377 \ldots\ldots\ldots\ldots\ldots (4.2)$$

$$y = 0.017x^2 + 0.036x + 0.363 \ldots\ldots\ldots\ldots\ldots (4.3)$$

For fresh, regenerated and mixture (1:1) bone char respectively. Where; Y= fluoride output from column in mg/l (ppm) and x= the volume in litres of water treated during the experiment. Integration of the above equations gives the volume of water treated. The amount of water treated before breakpoint of 1.5 ppm was 7.56, 6.85 and 7.18 litres for fresh, regenerated and mixture respectively. Total amount of fluoride in water before treatment was; 45.06, 42.79 and 40.83 ppm and after was; 5.53, 5.54 and 5.64 ppm for fresh, mixture and regenerated bone char respectively.

Table 1. Efficiency of Regenerated, Fresh and Mixture (1:1) Bone Char

Volume of Treated Water in Litres	*Fresh bone char*		*Regenerated bone char*		*Mixture*	
	Final Fluoride concentration in ppm	*Efficiency in %*	*Final Fluoride concentration in ppm*	*Efficiency in %*	*Final Fluoride concentration in ppm*	*Efficiency in %*
0.25	0.25±0.085	95.81	0.46±0.035	92.37	0.50±0.099	91.61
0.50	0.34±0.000	94.30	0.46±0.007	92.37	0.55±0.035	90.69
0.75	0.31±0.000	94.80	0.45±0.028	92.45	0.38±0.014	93.62
1.00	0.34±0.014	94.30	0.50±0.014	91.61	0.32±0.042	94.63
1.30	0.42±0.035	93.04	0.46±0.064	92.37	0.43±0.007	92.87
1.55	0.45±0.163	92.53	0.53±0.007	91.19	0.36±0.028	93.96
2.05	0.34±0.064	94.38	0.56±0.007	90.69	0.58±0.113	90.27
2.35	0.37±0.042	93.79	0.58±0.000	90.27	0.47±0.057	92.11
2.70	0.38±0.078	93.71	0.60±0.007	90.02	0.44±0.021	92.70
3.05	0.37±0.085	93.79	0.63±0.014	89.43	0.44±0.035	92.70
3.45	0.74±0.021	87.67	0.77±0.021	87.16	0.79±0.212	86.74
3.80	0.74±0.028	87.58	0.83±0.021	86.16	0.78±0.035	87.00
4.80	0.83±0.071	86.07	1.08±0.035	81.96	0.87±0.078	85.49
5.80	1.21±0.021	79.78	1.45±0.092	75.76	1.29±0.042	78.36
6.80	1.34±0.106	77.60	1.55±0.127	73.99	1.57±0.000	73.66
7.30	1.53±0.021	74.41	1.67±0.057	71.98	1.75±0.028	70.64
8.30	1.58±0.163	73.57	1.89±0.035	68.37	1.81±0.071	69.63
8.80	1.86±0.262	68.88	1.99±0.021	66.69	1.84±0.049	69.21

DISCUSSION

The efficiency of regenerated bone char was compared to fresh bone char and results have showed that there was no significant difference at 95% confidence interval. This is in agreement with previous experiments carried out (Kaseva, 2006). That is, the first regenerated bone char was capable of removing fluoride from drinking water to meet the Kenyan and WHO recommended values of 1.5 ppm. It indicated that a large part of the hydroxyapatite structure is not damaged during the regeneration process. Mixing of regenerated and fresh bone char does not add any advantage in improving the efficiency of

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bone char, that is the efficiency of mixture and that of regenerated bone char was not statistically different.

The useful removal capacity of the bone char was defined as the volume of treated water before the breakthrough point at concentration of 1.5 ppm (Bhargava, 1997). The amount of fluoride retained in bone char at C_o of 5.96 mg F/L for regenerated bone char, fresh bone char and mixture of bone char were 35.19 mg F, 39.53 mg F, and 37.25 mgF respectively. This corresponds to removal capacities of about 0.880, 0.988 and 0.932 mg/g respectively which is equivalent to 0.880 0.988 and 0.932 g/kg. This showed that the removal capacity has decreased by 10.93% only. The capacities found in this experiment were smaller but in the same order of magnitude. This suggests that results from different tests of bone char may not be directly comparable due to variations in the design of the experiments. The estimated removal capacities from small-scale experiments can therefore not be used as an exact determination of the capacities. They are however very useful for the purpose of comparing different types of bone chars and can rank them by quality for adsorption (Albertus *et al.*, 2000). This work was to compare the regenerated and fresh bone char with respect to their capacity to remove fluoride.

Some adsorption of fluoride occurs onto the activated carbon, although the primary uptake reaction is believed to be ion exchange between hydroxyapatite and fluoride resulting in formation of fluoroapatite (Bregnhøj and Dahi, 1995; Crittenden *et al.*, 2005).

$$Ca_{10}(PO_4)_6(OH)_2 + 2F^- \longrightarrow Ca_{10}(PO_4)_6F_2 + 2OH^-$$

Bone char is also soluble in acid, due to this; some of its efficiency could have been lost during acid neutralization of sodium hydroxide used for regeneration.

CONCLUSIONS

Based on these results, the regenerated bone char is a potential material that can be used in communities where fluoride concentration in the water system is above the recommended level. Considering that these communities constitute a poor population that constitute a non-lucrative sector for water treatment method development and investment, this study goes a long way in preventing health complications like fluorosis, neurological problems and allergic manifestations.

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