ORIGINAL ARTICLE

TREATMENT DURATION AND ADSORPTION CAPACITY OF CRUSHED BRICKS IN THE REMOVAL OF FLUORIDE FROM DRINKING WATER

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ABSTRACT

BACKGROUND: *Fluorosis, a serious bone disease related to consumption of water with excessive fluoride is a public health problem in the rift valley region of Ethiopia. Defluoridation of drinking water is one of the common fluorosis prevention strategies; however most of the defluoridation methods used in fluorosis prevention programs are inappropriate technologies to be used in poor developing countries. Hence, this study was conducted to determine the treatment duration of a low cost crushed brick fluoride filter media made with sand filter and the fluoride adsorption capacity of the crushed bricks material per unit weight.*

METHODS AND MATERIALS: *Crushed materials made from ordinary bricks were incorporated as part of filtration column in experimental sand filter together with sand, charcoal and gravel in a 200 liter barrel. Fluoridated water samples with known concentration of 8mg/L were poured in to the filter unit in batch system. The filtrate of each batch were collected after two hours of contact time and analyzed for fluoride concentration. To determine the adsorption capacity of bricks, 2 gm of washed dried and crushed bricks material was mixed with 100ml of water sample that had fluoride concentration of 8mg/L and stirred for two hours in polyethylene bottle, centrifuged, and the residual fluoride was analyzed using standard methods. ANOVA, student T-test and correlation coefficient was done to see the significance of the outputs of linear model made for percent fluoride reduction and cumulative volume of water filtered.*

RESULTS: *During the filter run about 300 liters of 8-ppm fluoride water was defluoridated up to the safe fluoride limit. The residual fluoride was observed to increase beyond the permissible upper limit (1.5mg/L) after 300 liters of fluoridated water was filtered. It was also observed that one-gram of crushed brick material can adsorb 0.365 to 0.372 milligram of fluoride from water with fluoride concentration of 8 mg /L.*

CONCLUSION: *this study showed that this experimental filter is effective for a duration of 30-40 days and have a capacity of filtering 300 liters of water with fluoride concentration of 8 mg/l to below 1.5mg/l within 30 minutes. The crushed bricks material has high fluoride adsorption capacity (91.76%) per unit weight. We recommend further large-scale studies to evaluate the utility of the technology in conventional water treatment systems and test the technology in the community to determine the affordability and applicability.*

KEY WORDS: *crushed brick, fluoride filter, and adsorption capacity*

INTRODUCTION

Naturally pure water which free from biological, chemical and/or physical impurities is scares and not available to all. In most cases, the disadvantaged sections of the society consume contaminated water and get ill periodically, often resulting in epidemics. Such waters may be contaminated by natural or anthropogenic sources. One of such contaminant is fluoride, which is a chemical more toxic than lead and less toxic than arsenic (1).

Throughout many parts of the world high concentration of fluoride occurring naturally in ground water has caused wide spread fluorosis. The latest information shows that fluorosis is endemic in at least 25 Countries across the glob. The total number of people affected by this disease is not known but a conservative estimate would number in the tens of millions (2).

Epidemiologically significant fluoride levels in environmental sources are most widespread in Ethiopia's refit valley. Water sources having elevated fluoride concentration is also documented in other parts of the country. Fluorosis caused by drinking water having fluoride concentration above the recommended limit is a major public health problem in the rift valley areas and may also be a health problem in some communities out side the rift valley region (3).

In 1930s, researchers proposed two strategies to prevent fluorosis. These are provision of alternative drinking water source and defluoridation of drinking waters. Since it is not often possible to have alternative drinking water source, which has no elevated fluoride concentration above the recommended value, in regions like the rift valley area, most efforts have been directed at the latter option. On the other hand, a major problem in the delivery of water from low fluoride sources and defluoridated water is the scarcity of piped distribution systems in rural communities and the reliance of households in an individual wells, springs and /or surface sources(3). These situations initiate to develop defluoridation methods that can be applied at individual well and spring sites or household storage tanks and can run without too much technical supervision at household and community level for a period of time.

Expensive defluoridation technologies like reverse osmosis and membrane filtration are not applicable to most of the Ethiopian communities due to the demand of high cost and skilled human power. The defluoridation program in Wonji, which uses a resin of activated alumina and bone char for adsorption techniques has faced deficiencies in the operation of the defluoridation process due to lack of spare parts and materials. But in addition to developing large-scale water supply systems for towns and large communities there is a need for evaluations of simple low-cost techniques for use at household level in semiarid rural areas lacking alternative water source and piped distribution systems (4).

Low-cost defluoridation methods have received increasing attention by Ethiopian research institution but are not yet technically feasible or culturally tested and accepted. Particularly the bone meal and bone-char methods reduce fluoride concentration efficiently from 6 mg/L to 0.1 mg/L, but they are not acceptable to the general population due to the unacceptable test of the treated water and to Muslims for religious reasons (3).

Some studies conducted on local clay pots and bricks are showing removal of fluoride at different efficiencies. In a study conducted in Jimma university filtration of fluoride water through local pots have shown about 93.8% fluoride removal efficiency whereas filtration of 8ppm fluoride water through crushed brick fluoride filter made with home made sand filter has shown about 95% fluoride removal with an estimated running cost of 250 Birr (26.75 USD) (5). The running cost is much less than the establishment cost and can be handled by the beneficiaries themselves.

Though this technology is cheap, there are no studies which showed the treatment duration and fluoride adsorption capacity of the crushed brick materials. This study was conduced to determine the treatment duration of a crushed brick fluoride filter media made with sand filter and the fluoride adsorption capacity of the crushed bricks material per unit weight.

METHODS AND MATERIALS

An experimental study was conducted in the Laboratory of School of Environmental Health and Civil Engineering Department, Jimma University; and water samples which had a fluoride concentration of 8mg F^-/L were prepared using tap water and sodium fluoride salt. This concentration is assumed to represent the average ground water fluoride concentration of rift valley region and some other parts of Ethiopia (4).

Each water samples was tested to determine the initial fluoride concentration before filtration. Different volumes of fluoridated water samples were filtered through each of the different arrangements of the filter media.

A 200-litre barrel with a diameter of 74.1cm and a height of 86cm was fitted with a half-inch outlet pipe, under drain valve and out let top. To keep the filter media from drying the outlet tap was fitted in such away that the height of the outlet taps is 3cm above the top layer of the filter sand bed (Fig. 1).

During the study, three different arrangements of filter component were used. In the first case, experimental sand filter was prepared. In this arrangement, the barrel was filled from bottom to top, $1/4^{th}$ of it's volume with gravel under drain bed, $5/8^{th}$ of it's volume with sand bed and the remaining $1/8^{th}$ top left for the raw water.

In the second case, the barrel was filled from bottom to top in the following manner: $1/8^{th}$ of its volume with gravel under drain bed, $1/8^{th}$ of its volume with sand bed $1/8^{th}$ of its volume with charcoal bed with grain size from 0.25 to 0.5mm, $1/4^{th}$ of its volume with crushed brick with a size of 0.25 to 0.5mm and $1/4^{th}$ of it's volume with filter sand bed .The remaining $1/8^{th}$ top was for water sample (Fig.1).

In the third case, the second case was rearranged by removing charcoal bed and substituting by sand. The study was carried out by undertaking four types of experiments.

1. Filtration of Fluoride water through crushed brick in experimental sand filter containing charcoal.

After fully opening the delivery tap of the filter unit, the filter unit was filled to its maximum capacity (60L) water sample with concentration of 8mg F^-/L. Immediately after the water head become above the level of delivery tap the filtrate started to come through the tap. Then at this point, the first sample was collected and the tap was closed to increase the contact time between the fluoridated water and the media.

Afterwards, additional samples were collected at 30, 60 and 120minutes contact times. Then filtrate samples were analyzed for fluoride content to see relationships between contact time and the fluoride removal capacity of the media.

The two hours contact time was used for the rest of experiments as it was found to be the best contact time for maximum fluoride removal capacity of the filter media during the pretest.

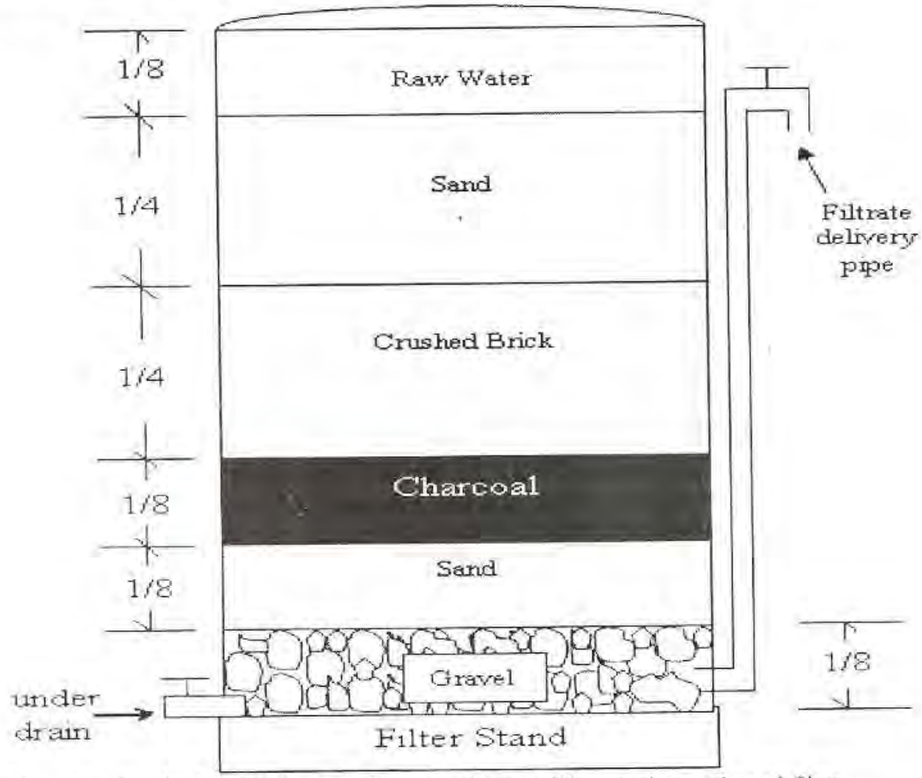

Figure 1. Crushed brick fluoride filter combined with experimental sand filter.

The filtration of fluoride water was performed in batch system filling the filter unit to its maximum capacity (60L). A residual fluoride concentration was measured from sample filtrate of each batch until residual fluoride concentration showed above the safe limit. This was used to determine the duration to which the unit can defluoridate water with 8mg F^-/L to

After 2 hours of detention time, filtrate samples were collected and analyzed for the fluoride content and the results were compared with the measurements of the filtrate found from filter unit made of crushed brick and sand filter.

In filtering fluoridated water through crushed brick in experimental sand filter without charcoal the filter unit was filled to its maximum capacity (60 L) with 8mg F^-/L fluoridated water. After 2 hours detention time, filtrate samples were collected and analyzed for the fluoride content and the results were compared with the results of the filtrate that is found from filter unit made with charcoal.

Adsorption capacities for the sample were determined at 6 pH value by shaking 2 grams of washed and dried (2hrs at 105 °C) crushed brick with 100ml 8mg/L NaF solution for 2 hours in polyethylene bottle at room temperature (25 °C).The mixture were centrifuged and the residual fluoride concentration were determined by using standard methods. Fluoride concentration was measured after 2 and 12 hours. The percent adsorption was calculated using the following formula.

less than 1.5mg F^-/L concentration. In addition, the measurement of the filtrate was resumed even after breakthrough is observed to develop a linear relationship between the % fluoride reduction and the volume of water treated in the apparatus.

In filtering fluoride water through sand filter without crushed bricks, experimental sand filter was prepared in a 200-liter barrel. The filter unit was filled to its maximum capacity (60 L) with 8mg F^-/L fluoridated water.

$$\% \text{ adsorption} = \frac{(C_0 - C_e) \cdot 100}{C_0}$$

Where: C_o is initial Fluoride-Concentration and C_e is Fluoride concentration in the filtrate.

$$\% \text{ adsorption} = \frac{(8 - \text{residual}F^-) \cdot 100}{8}$$

To prevent the adsorption of fluoride ion on to the inner walls of adsorption vessel, blank run was performed.

Grab sampling technique was employed to take samples of filtrates that were coming out through the delivery pipes of the filter tank. Glass bottles were used as a sample container.

Alizarin photometric fluoride determination method was used to determine the fluoride concentration. The data from the experiment were collected on prepared data collection format. To ensure reproducibility of the test triplicate measurement of each sample was performed.

RESULTS

The crushed bricks fluoride removal filter media with experimental sand filter containing charcoal has a very good effect in the fluoride removal from water. In the experiment conducted to see the relationship between the contact time and fluoride removal capacity of the filter unit, maximum defluoridation occurred immediately after the experiment has started and the efficiency of the defluoridation unit was observed to increase with increasing contact time. The flow rate was recorded to be 1.3 – 1.38L/min in different arrangements.

During the filter run the residual fluoride concentration below the safe recommended limit (<1.5 mg/L) was observed until about 300 liters of raw water that had fluoride concentration of 8mg F^-/L was treated. As the defluoridation process proceeded, the residual fluoride was observed to increase with an increase in the amount of raw fluoridated water filtered.

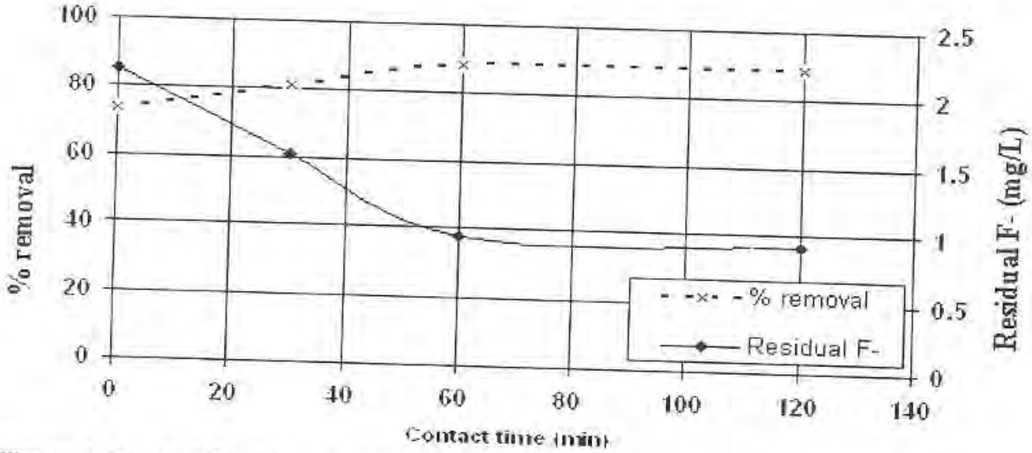

Figure 2. Residual fluoride and percent fluoride removal during the filter run, Jimma University, 2006.

After defluoridation of water with fluoride concentration of F^-/L, a residual fluoride concentration of 0.91mg/L, 1. 50mg/L and 2.00mg/L after filtration of 60, 300 and 360 liters of water, respectively (Table 1). Massive pass through was observed after filtration of 360 liter of fluoridated water sample.

Table 1. Level of residual fluoride during the filter run to defluoridate water sample with fluoride concentration of 8mg/L, Jimma University, 2006

Cumulative volume of filtered water (L)	Residual fluoride (mg/L)	% Removal
60	0.91	88.6
120	0.93	87.7
240	1.04	85.9
300	1.50	81.1
360	2.08	74.9
480	2.72	66.0
600	4.01	49.8
720	4.90	38.7
840	6.32	21.0
960	7.01	12.4
1080	7.76	3.0
1200	8.00	0.1

According to the experiment conducted to see the effect of sand filter and charcoal in the removal of fluoride from water, experimental sand filter have shown the fluoride removal efficiency of 19.9%.

Table 2. Comparison of Fluoride removal efficiency of different resins in different type of filter units to defluoridate water with fluoride concentration of 8mg/L, Jimma University, 2006.

Types of Filter unit	Residual fluoride (mg/L)	% Reduction
Sand Filter without crushed brick and charcoal	6.408	19.9
Crushed brick fluoride filter made with sand filter (with charcoal)	0.911	88.6
Crushed brick fluoride filter made with sand filter but without charcoal	1.074	86.5

In the other experiment conducted to determine the fluoride adsorption capacity of the crushed bricks per unit weight, one gram of crushed bricks material can adsorb 0.365 to 0.372 mg of fluoride.

Table 3. The ability of crushed bricks material to adsorb Fluoride from water sample containing 8mg/L at pH 6, Jimma University, 2006.

	Sample 1	Sample 2	Sample 3	Mean	Min	Max	SD
Residual F^-	0.57	0.67	0.685	0.64	0.57	0.69	0.06
F^- adsorption (mg/L)	0.372	0.366	0.365	0.37	0.37	0.37	0.0038
% F^- adsorption	92.8	91.6	91.4	91.93	91.4	92.8	0.76

When the residual fluoride concentration started to increase beyond the permissible level, the removal efficiency of the bricks in the filter tank failed dramatically(Fig.4).

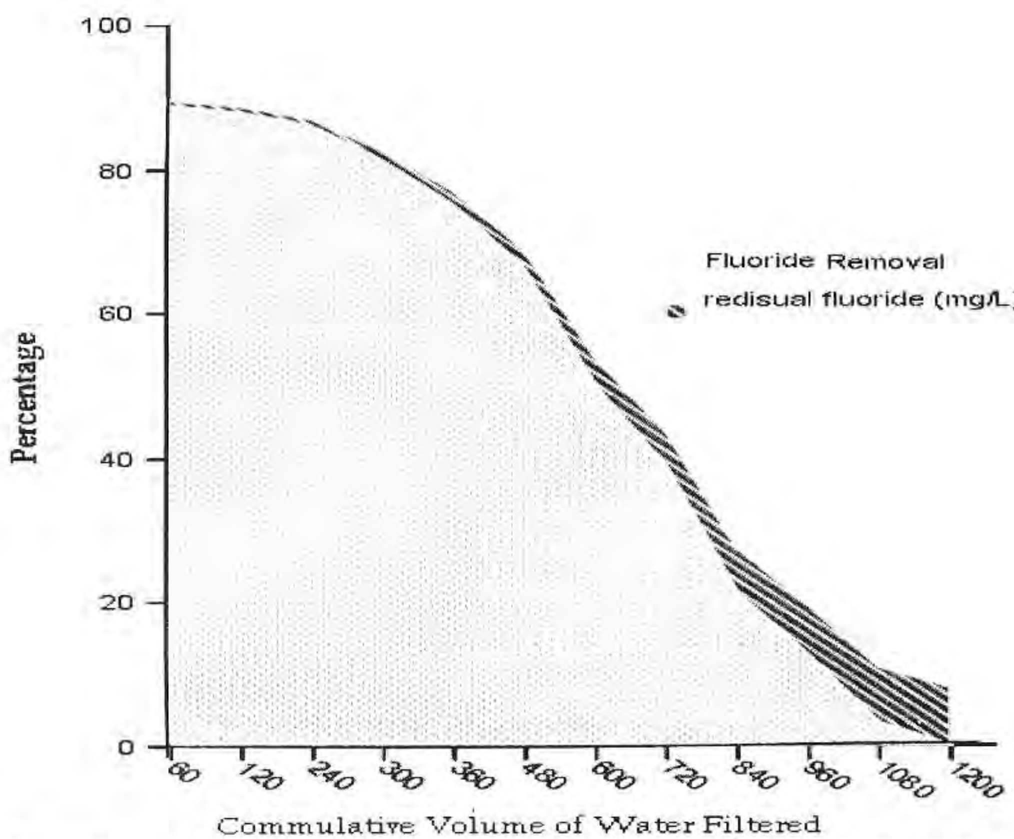

Figure 3. Trend of percentage of fluoride removal and increment of residual fluoride as the volume of fluoridated water filtered increase, Jimma University, 2006.

From the trend of the residual fluoride level observed during the filter run percent fluoride reduction can be calculated from the formula $y = -0.0895X + 102.68$
Where: Y= % fluoride reduction and
X= the volume of water treated during the filter run.

The value of R^2 which is very close to 1 shows more or less constant rate of decreasing of the percent fluoride reduction during the filter run unit with an increase of the amount of water defluoridated may be attributed to the ongoing saturation of the anion exchange sites.

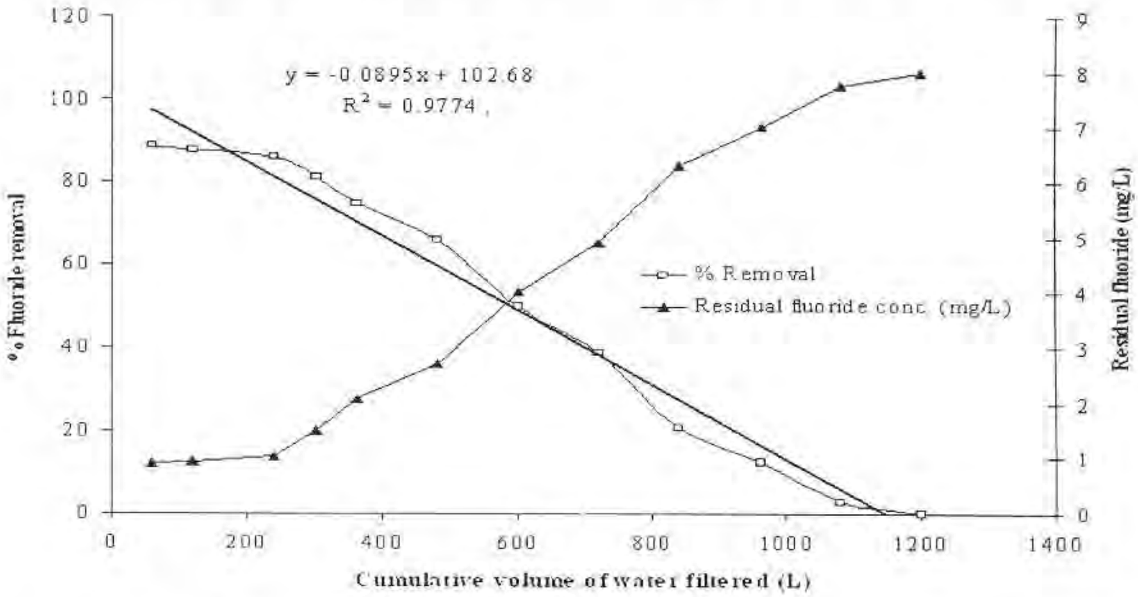

Figure 4. Fluoride removal capacity of the apparatus and residual fluoride during the filter run using water with fluoride concentration of 8mg/L, Jimma University, 2006.

DISCUSSION

In Ethiopia, nowadays different studies are being conducted on clay materials, which are used to remove fluoride at different efficiencies. But, in these studies there was no result showing the duration of fluoride treatment within the recommended limit (5). In addition, the removal capacity per unit weight was not documented. This study showed an increment in the fluoride removal efficiency of the filter media with the detention time. This might be due to an increase in reaction time for the anion- exchange and other chemical reactions under taken in the processes. A study in India showed that red soil and brick have good negative correlation with detention time indicating the fact that the amount of fluoride in treated water decrease with an increase in contact time (6).

Analysis of variance and student T-test showed significant correlation ($p<0.001$) between the calculated and measured values of the percent fluoride removal.

As the filtration proceeded, about 300 liters of 8ppm fluoride water was defluoridated and the concentration observed to increase beyond the permissible upper limit (1.5mg/L). Thus, the 300-liter should be considered as the maximum volume waterto defluoridate to the safe fluoride limit.

Studies recommend that only the water used for drinking and cooking purposes (usually less than 5 liter per person per day) needed to be defluoridated. The entire water demand is often ten times higher and to defluoridate all these would be too expensive as well as producing a large amount of toxic sludge (7).

According to our study the treatment duration (service life) of the experimental defluoridation unit developed may last for 30 to 40 days when withdrawal of treated water per day is 8 to 10 liter and raw water fluoride concentration is 8 mg/L or more. Similar result was found in Seri Lanka that domestic defluoridation units made of freshly fired brick pieces for 25-40 days to withdraw 8 liters/day form water with fluoride concentration of 5 mg/L (8). This might be attributed to the difference in the size of defluoridation units and the fluoride concentration in the raw water used in each case.

The fluoride removal efficiency of the filter unit was close to zero when the amount of treated water reaches about 1200 liters perhaps this might be due to complete saturation of anion- exchange sites indicating the complete exhaustion of the filter media. Using the same calculation as used for the estimation of the treatment duration, the complete exhaustion time of the filter unit was estimated to be about 120 to 150 days.

The brick used in our study may contain good adsorbent of anions such as: $Al(OH)_3$, FeO.OH and other metal oxides and hydroxides, which are good ion exchangers with fluoride and others. Further more, the heat treatment during the preparation of the bricks may also have contributed to the efficiency of the brick. Other studies have indicated that chemical treatment of the clay substrate with Na_2CO_3 and HCl solutions and heat treatment to 600 °C can improve the adsorption capacities of some clay materials (9, 10); but, the brick used in our study was without special heat and chemical treatment.

This study showed that one gram of crushed bricks material can adsorb 0.365 - 0.372 mg of fluoride and this adsorption capacity may reinforce the assumption that the bricks used may contain potentially good fluoride adsorbent. This finding is similar to the findings reported from South Africa which indicated that clay types containing: Gibbsite ($Al(OH)_3$) can adsorb 0.25 – 0.4 mg of fluoride per gram of clay and Goethite(FeO.OH) can adsorb 0.2 – 0.3 mg of fluoride per gram of clay . The study also ranked the performance of these clay types as high fluoride adsorption capacity (9).

Addition of crushed bricks is an added advantage in the use of experimental sand filter because small portion of fluoride can be defluoridated and help the brick from early saturation. In this study, the experimental sand filter without crushed bricks showed 19.9% fluoride removal, which was almost similar to a small-scale studywhich showed18% fluoride removal when water with 5mg Fluoride/L was passed through sand filter (11). This might be due to presence of crystalline minerals such as Ca^{+2}, Mg^{-2}, Al^{+3}, etc which could adsorb anions such as fluoride. Exchangeable anions such as OH^- are present in many minerals and the proxy of F^- for OH^- would serve as one of the principal contributing factor for defluoridation (6).

Defluoridated filtrates collected from filtration column with and without charcoal showed differences in fluoride removal capacity but their difference was not statistically significant ($p>0.05$). This implies that the presence or absence of charcoal bed in the fluoride removal filtration column has no significant effect in the fluoride removal efficiency of the defluoridation unit. This finding is in agreement with the reports from studies in India (6), which indicated that untreated charcoal have no effect on the reduction of fluoride concentration of water. Though charcoal has no significant impact in defluoridating water, it is highly recommended to add it as a filtration component in a experimental sand filter specifically when crushed brick is used. This is for two reasons: 1) the crushed brick might color the water passing through it and this color can be removed by the charcoal underneath 2) most raw waters often contain organic impurities that can be removed by charcoal (12).

In general, by applying this defluoridation technique to communities where fluoride concentration in the water system is above the recommended level; it is possible to prevent health complications like dental fluorosis, skeletal fluorosis, neurological problems, muscular problems and allergic manifestations (13). However, the affordability and applicability of the water filter in the general community needs to be evaluated.

In conclusion, this study showed that this experimental filter is effective for duration of 30-40 days and have a capacity of filtering 300 liters of water with fluoride concetration of 8 mg/l to below 1.5mg/l within 30 minutes. The crushed bricks material has high fluoride adsorption capacity (91.76%) per unit weight. We recommend further large-scale studies to evaluate the utility of this technology in conventional water treatment systems and test the technology in the community its affordability and applicability.

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