34th WEDC International Conference, Addis Ababa, Ethiopia, 2009

WATER, SANITATION AND HYGIENE:
SUSTAINABLE DEVELOPMENT AND MULTISECTORAL APPROACHES

The development of bone char-based filters for the removal of fluoride from drinking water

H. Korir, K. Mueller, L. Korir, J. Kubai, E. Wanja, N. Wanjiku, J. Waweru,
M.J. Mattle, L. Osterwalder & C.A. Johnson, Kenya

REFEREED PAPER 189

Millions of people rely on drinking water that contains excess fluoride. Only few fluoride removal techniques have been implemented on a wider scale in low and middle-income countries. One of these methods, bone char filtration, is highly efficient. However, its lifespan is rather limited. This paper presents first laboratory results and field testing of a new fluoride removal technology, based on a combination of bone char and calcium-phosphate pellets. These chemicals are slowly released to the water for fluoride precipitation. Although this method, commonly referred to as contact precipitation is known, the development of such pellets is new. Fixed-bed laboratory experiments show that this mixture of materials can increase filter uptake capacity by a factor of 3 and more. However, to reduce the phosphate concentration in the treated water, the design of full-scale community filters for field testing has to be slightly modified.

Introduction

According to UNESCO estimates, more than 200 million people worldwide rely on drinking water with fluoride concentrations exceeding the international WHO guideline of 1.5 mg/L (UNESCO, internet source). The main source of fluoride are the aquifer rocks; hence its concentrations in water are mainly governed by geogenic processes (Amini et al., 2008).

While industrialised countries commonly use activated alumina or the membrane technology to remove fluoride from drinking water, defluoridation is still uncommon in low and middle-income countries, though there are some excellent initiatives (NEERI-UNICEF, 2008). The WHO (2006) therefore postulates to investigate the use of alternative fluoride-low sources as a first option before considering defluoridation.

A survey of defluoridation treatment in Eastern Africa revealed that bone char (BC) filtration is an efficient and viable method for fluoride removal (Mueller et al., 2006). Increasing the uptake capacity of BC and thus prolonging the lifespan of filters can, however, reduce maintenance requirements and improve sustainability of the treatment, especially for remote areas.

In the 1990s, first research experiments were conducted to extend the lifespan of BC filters by adding calcium and phosphate to the influent water (Larsen et al., 1999). This new method was referred to as co- or contact precipitation (CP). In 1995, this method was field tested in a community pilot plant in Tanzania (Dahi, 1996). Though filter lifespan was increased, high maintenance requirements related to continuous calcium and phosphate supply hindered large-scale implementation.

In 1998, the Catholic Diocese of Nakuru (CDN), Kenya started a defluoridation programme on request of the drilling section for sustainable solutions in mitigating fluorosis. Specific efforts were made in up-scaling the production of BC and improving the filter design and operation for implementation on both household and community level. After CDN had overcome initial problems related to the production of high-quality bone char, the users fully accepted the filter material. A recent study shows that the material is also accepted in the Oromo region of Ethiopia (Esayas et al., 2009).

To overcome above mentioned drawbacks with CP, CDN accepted the challenge of developing pellets containing calcium and phosphate mixed with the bone char filter material. These pellets slowly release the required chemicals into the water for fluoride precipitation without creating additional maintenance requirements for the end users.

Research objective

First column experiments with BC and CP were carried out under controlled laboratory conditions. The aim was to assess and compare the uptake capacity and removal efficiency of these two different methods for both distilled water spiked with fluoride and natural Kenyan groundwater. A continuous and regular monitoring of the treated water of a CP community filter in Kenya enabled a first comparison between laboratory and "real" field conditions.

Material and methods

Filter material

Both bone char and Ca-phosphate pellets are produced in Kenya by CDN.

Dry animal bones are charred in a specially designed furnace (see Figure 1) with limited oxygen supply and charring temperatures between 350 - 400°C. Due to the charring process, the bones are brittle and easy to crush followed by sieving into different fractions. The material is then washed with caustic soda (NaOH) to reduce residual organic material (CDN et al., 2007). According to Bregnhøj (1995), the resulting product can be described as an altered hydroxyapatite ($Ca_5(PO_4)_3OH$).

Calcium-phosphate pellets are formed after mixing calcium hydroxide ($Ca(OH)_2$) and a commercially available phosphate source (Kynofos21, a mixture of $CaHPO_4$ and $Ca(H_2PO_4)_2$) in a concrete mixer. After the addition of water and bone char powder, the pellets are sprinkled with water to enable the formation of a robust calcium carbonate ($CaCO_3$) coating. After washing and sieving, the pellets are ready for use.

Figure 1. Production of BC and calcium-phosphate pellets as carried out by CDN
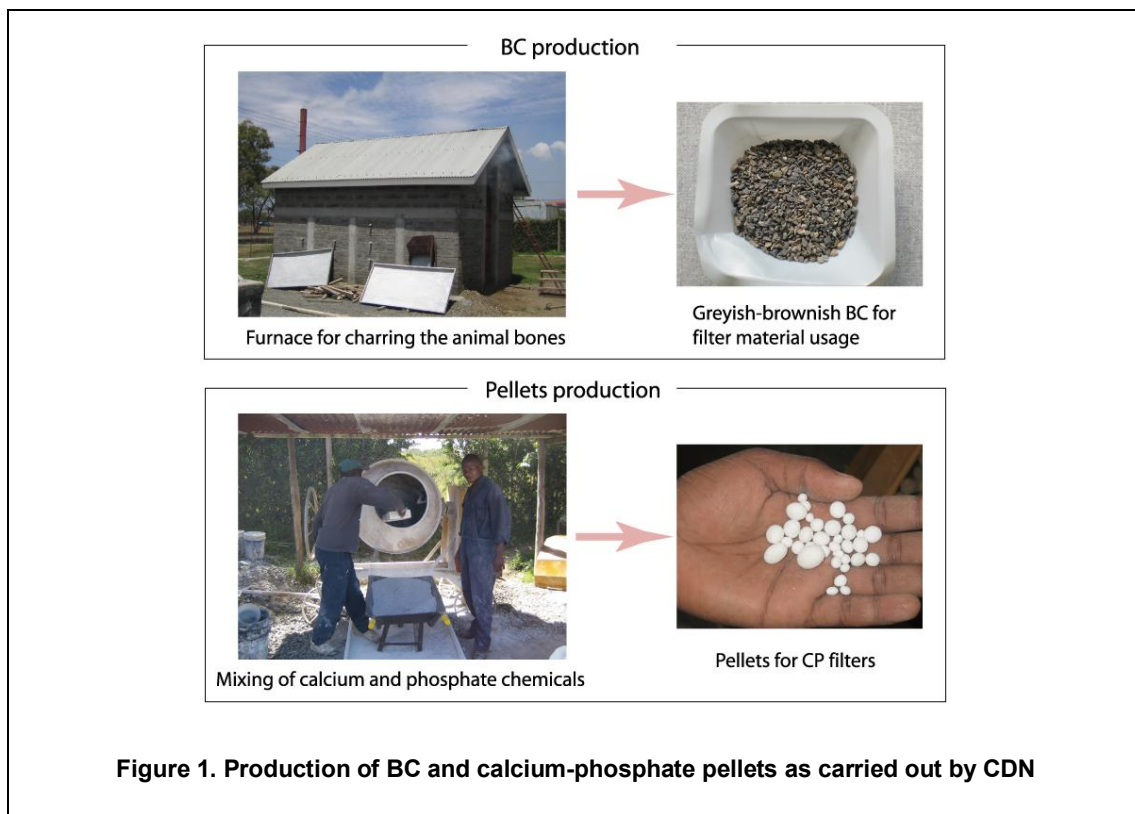
Column experiments

PVC columns were filled with 260 mL of filter material, equivalent to approximately 220 g. For CP, a pellets:BC ratio of 3:1 was used with BC and pellet particle sizes of 1-4 mm and 2-6.3 mm respectively. The columns were run at a constant flow rate of 10 eBV/d (eBV = empty bedvolume, equivalent to 260 mL in our column experiments) and were checked gravimetrically via the outflow. In the laboratory of Eawag, the flow rate was regulated with peristaltic pumps while at CDN, gravity flow with clamps for flow rate regulation was used. For column experiments at Eawag, distilled water spiked with 6 mg F/L was used. CDN's columns were fed with piped water from a Kenyan groundwater source (pH: 8.3 ± 0.1, 6.2 mg/L ± 0.1 F, 2.4 mg/L ± 0.2 Ca, 0.3 mg/L ± 0.1 PO4, 53.7 mg/L CO3-C, 14.8 mg/L SO4, 11.8 mg/L Cl, 129 mg/L Na, 0.1 mg/L Mg, 41.8 mg/L Si, 12.8 mg/L K).

Fluoride concentrations were measured potentiometrically with an ion-selective electrode (Eawag: Mettler Toledo DX219, CDN: Methrom 6.0502.150) and an Ag/AgCl-reference electrode (Eawag: Methrom 6.0726.100, CDN: Methrom 6.0733.100). A TISAB buffer was added prior to measurement to attain constant pH and break up fluoride complexes.

pH measurements were carried out with an electrode (Methrom 6.0257.000) while calcium and phosphate concentrations were determined by ICP-OES (SpectroCIros CCD) at Eawag.

Results and discussion

Fluoride removal

Fluoride breakthrough curves for distilled and Kenyan groundwater as a function of water throughput are shown in Figure 2. To allow the comparison with other column experiments of different filter sizes, water throughput is given as empty bedvolumes (eBV), a dimensionless figure for the amount of treated water per volume of filter material.

At the beginning, fluoride removal efficiency is very high, greater than 98% for all column experiments. Fluoride concentrations are reduced from 6 mg/L in distilled water and 6.2 mg/L in the Kenyan groundwater to fluoride levels below 0.1 mg/L. As the filters become saturated the fluoride concentrations in the treated water increases. Breakthrough for the BC filters occur after ~30 eBV and ~100 eBV in the case of Kenyan groundwater. The BC column experiments reach the WHO guideline value (1.5 mg F/L) after 92 eBV and 170 eBV for Kenyan groundwater even though the inlet fluoride concentration is very similar (6 and 6.2 mg/L respectively). The difference in the results is probably related to pH, indicating the pH dependence of the adsorption process. The Kenyan groundwater is buffered by $NaHCO_3$ and the effluent pH value at 1.5 mg F/L is 8.5 whereas the effluent of the distilled water at 1.5 mg F/L is 9.0 (see table 1). At higher pH values, hydroxide ions (OH^-) in solution compete in the sorption process. Possible precipitation processes with naturally occurring calcium and phosphate may also enhance fluoride removal in groundwater.
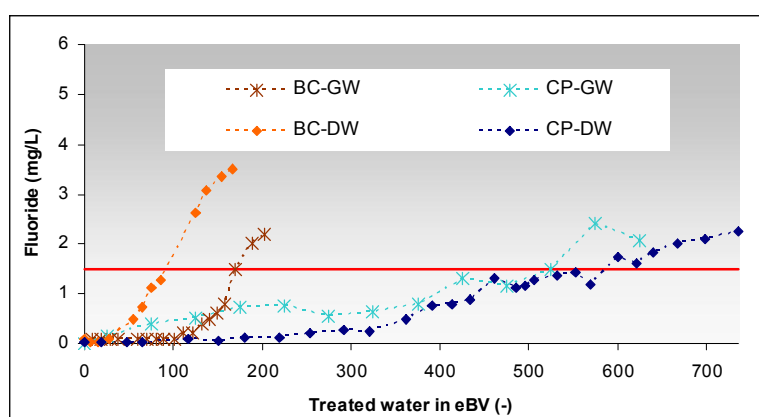
Figure 2. Fluoride breakthrough curves of column experiments carried out with distilled water spiked with 6 mg F/L (BC-DW and CP-DW) and Kenyan groundwater with 6.2 mg F/L (BC-GW and CP-GW). The red line indicates the international WHO guideline for drinking water (1.5 mg F/L).

It is important to understand the influence of groundwater chemistry, though to date the authors are not aware of published research. Apart from a pH dependence it may be postulated that other anions, such as bicarbonate, sulphate or chloride may compete with fluoride for exchange positions. However, such effects must be less important than the factors that enhance fluoride uptake, as the results in Figure 2 show. The release of calcium and phosphate from the pellets obviously has a strong positive influence on fluoride retention.

The CP columns have greater uptake capacities compared to the BC filters. Lifespan of the filters is prolonged by a factor of 6 in the case of synthetic groundwater and a factor of 3 for the Kenyan groundwater. Filter material regeneration or replacement is required after 570 eBV with distilled water and 524 eBV with Kenyan groundwater, corresponding to uptake capacities of 3.7 mg F/g and 3.4 mg F/g of filter material respectively. Uptake capacity of BC at 1.5 mg F/L effluent concentration amounts to 0.6 and 1.2 mg F/g filter material for distilled water and Kenyan groundwater respectively. The CP breakthrough curves are probably very similar because the released phosphate buffers the solutions to a pH value just above 7.

The steep slope of BC breakthrough curves indicate fast removal kinetics. The strong tailing of the adsorption front for CP reveals slow kinetics that makes this treatment strongly dependent on pore water velocity. Subsequent column experiments at different flow rates revealed that the higher the flow rate the lower the uptake capacity (unpublished data). The reasons for this are probably related to the release rate of calcium and phosphate from the pellets, but this remains to be clarified. The co-precipitation process requires dissolved calcium and phosphate that precipitates on the surface of the BC to form fluorapatite ($Ca_5(PO_4)_3F$). The molar ratio of $Ca:PO_4:F$ therefore needs to be close to 5:3:1, which means that the concentration of the former two ions need to be significantly higher than the fluoride content. It should be pointed out, however, that other processes, such as the precipitation of fluorite (CaF_2), may be occurring and that sorption to BC is also likely. To date we do not understand the relative importance of the processes in comparison to surface precipitation.

pH, calcium and phosphate concentrations

Apart from regular fluoride measurements, full-chemical analyzes were carried out to assess leaching from BC filter material and dissolution of calcium-phosphate pellets for the column experiments at Eawag. Table 1 shows the changes in pH, dissolved calcium, phosphate and fluoride concentrations in the effluent for BC and CP columns at different times (given as eBV).

The pH for BC increases from 6.0 in the influent water to 9.0 after filtration of 65 eBV for distilled water. This is not the case for CP as pH is more stable during the whole experiment due to the dissolution of calcium and phosphate from the pellets. As expected, calcium and phosphate dissolution from BC is very small, in general below 1 mg/L except for phosphate during the first flush. For CP, calcium and phosphate concentrations are high at the beginning and decrease subsequently, following a typical washout curve. Both, reduced availability of dissolved calcium and phosphate and limited precipitation sites lead to the observed fluoride increase in the effluent.

Table 1. Comparison of effluent concentrations after filtration with BC and CP for column experiments with distilled water spiked with 6 mg F/L.

	Sampling	pH (-)	Calcium (mg/L)	Phosphate (mg/L)	Fluoride (mg/L)
BC-DW	0.5 eBV	8.5	0.4	5.0	0.1
	65 eBV	9.0	0.1	0.6	0.7
	166 eBV	9.1	0.2	< 0.2	3.5
CP-DW	0.5 eBV	7.6	20.4	86.3	0.02
	65 eBV	7.4	16.0	46.3	0.03
	570 eBV	7.1	4.2	6.8	1.2

Pilot community filter with CP

For the full-scale testing in a community filter, filter design and content was slightly modified compared to the column experiments in the laboratory in order to reduce phosphate concentrations in drinking water (down-flow, 1. layer of filter material with pellets:BC 3:1, 1600L, 2. layer with pellets:BC 2:1, 1050 L, 3. layer only with BC, 650 L). The raw water feeding the community filter derives from the same borehole as the water used for the column experiments at CDN. Continuous and regular monitoring started in September 2007 and is still ongoing.

Up to date 330 eBV of water, equivalent to 990 m^3 have been treated and the effluent concentration of fluoride currently is around 1.2 mg/L. Due to the BC layer at the bottom of the filter initial high phosphate concentrations (>80 mg/L as observed in the laboratory) could be reduced to approximately 40 mg/L. Fluoride uptake capacity at 1.5 mg F/L effluent concentration is expected to be approximately 2.7 mg F/g filter material. This is 20% lower compared to the laboratory findings. However, a direct comparison has to be carried out with caution due to the different filter material content. In the community filter, CP uptake capacity is underestimated due to the BC layer. Estimation of the uptake capacity for the CP layers alone with a given BC uptake capacity of 1.2 mg F/g (from laboratory experiments) amounts to 3.1 mg F / g CP layer, which corresponds nicely to the CP findings from CDN's laboratory (<10% deviation).

Conclusion and outlook

Development and implementation of simple and sustainable defluoridation techniques are urgently needed, especially since groundwater will increasingly serve as a drinking water source. The production of calcium-phosphate pellets, which slowly release these chemicals to the water and hence enable the co-precipitation of fluoride is a new, innovative approach from CDN to prolong filter lifespan and thus increase sustainability of the treatment. The first findings from laboratory and field testing reveal that CP can improve filter performance, however, far more experiments will have to be conducted to scientifically describe this method and hence facilitate future improvements. It appears that the uptake capacity of BC filters depends on water composition, especially pH, calcium and phosphate concentrations, while this is less important for CP columns. Laboratory results from BC experiments in un-buffered solutions therefore need to be interpreted carefully when making estimations or recommendations for the field. Although fluoride uptake capacity for CP is 3 to 6 times higher compared to single BC filtration, its removal kinetics seem to be much slower causing the tailing of the breakthrough curves.

Eawag and CDN are currently conducting comprehensive laboratory analyses to acquire an improved understanding of removal processes and to optimise CP for enhanced filter performance. In parallel, ongoing testing and monitoring of pilot implementations in Kenya and Ethiopia complement the laboratory findings with field data.

CDN-Eawag collaboration on fluoride removal

In 2006, CDN and Eawag initiated a collaboration to i) further develop and optimise low-cost defluoridation methods applicable in low and middle-income countries and ii) facilitate their implementation. The project team is highly interested in an information exchange and/or cooperation with other institutions investigating defluoridation techniques.

Other possible geogenic contaminants in groundwater such as arsenic, selenium or uranium are investigated as part of an integrated project at Eawag entitled Water Resource Quality (WRQ). WRQ focuses on the identification of geogenic contamination in groundwater and the development of water treatment techniques that mitigate the effects of the contamination.

References
Amini M., Mueller K., Abbaspour K. C., Rosenberg T., Afyuni M., Møller K. N., Sarr M., and Johnson C. A. (2008) *Statistical modeling of global geogenic fluoride contamination in groundwaters*. Environmental Science and Technology 42(10), pp. 3662-3668.

Bregnhøj H. (1995*) Processes and kinetics of defluoridation of drinking water using bone char*. PhD, Technical University of Denmark, pp. 112.

CDN, Mueller K. and Jacobsen P. (2007) *CDN's experiences in producing bone char*. Technical report, pp.10. http://www.wrq.eawag.ch

Dahi, E. (1996) *Contact precipitation for defluoridation of water*. In: Proceedings, 22nd WEDC Conference, New Delhi, India, pp. 262-265.

Esayas S., Mattle M.J., Lema F. (2009) *Household Water Treatment: Defluoridation of Drinking Water by Using Bone Char Technology in Ethiopia*. In: Proceedings, 34th WEDC Conference, Addis Ababa, Ethiopia.

Larsen M.J., Pearce E.I.F. (1999) *Partial Defluoridation of Drinking Water Using Fluorapatite Precipitation*. Caries Research 26 (1), pp. 22-28.

Mueller K., Johnson C. A., Meierhofer R., and Wegelin M. (2006) *Fluoride removal in developing countries: State-of-the art of defluoridation techniques in East Africa*. In: Sandec News, No. 7, pp. 12-13.

NEERI- UNICEF (2008) *Integrated Fluorosis Mitigation, Guidance Manual.* http://neeri.res.in/pdf/integrated.pdf

UNESCO Ground water briefing: *Trace elements in groundwater and public health.* http://www.unesco.org/water/third_wwf/groundwater_health.pdf (status 29.2.2008)

WHO (2006) in: Fawell J., Bailey K., Chilton J., Dahi E., Fewtrell L., Magara Y. (Eds.), *Fluoride in Drinking-Water*, IWA publishing, pp. 143.

Contact details

Hillary Korir
Catholic Diocese of Nakuru
P.O. Box 938
20100 Nakuru
Kenya
+254 51 221 62 64/5
cdnwaterquality@yahoo.com

Dr. C. Annette Johnson
Swiss Federal Institute for Aquatic Science and Technology (Eawag)
Ueberlandstrasse 133
8600 Dübendorf
Switzerland
+41 (0)44 823 54 86
annette.johnson@eawag.ch
www.wrq.eawag.ch