Impact of Pretreatment on Defluoridation of Drinking Water by Bone Char Adsorption

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ABSTRACT: *Fluoride concentrations in drinking water in excess of 1.5 mg L-1 are unsafe for human consumption. To reduce excess fluoride intake, developing countries must use low-cost, point-of-use defluoridation techniques. Although previous work has extensively assessed defluoridation using bone char (BC), most of the advanced studies have been based on the use of fluoridated distilled water as a feed solution. In the present study, BC columns were challenged with a range of model solutions, mimicking various pretreatment options. As a result, the relative impact of dissolved organic carbon (DOC) and suspended solids (SS) on the performance of BC filters was assessed. In addition, the performance of a gravity-driven, hollow-fibre ultrafiltration (UF) module was examined with regards to the potential for use as a pretreatment option. SS were observed to severely clog the columns and cause the complete cessation of flow. The subsequent removal of SS by UF improved the general filter performance as well as increasing the BC lifetime by 50 %. The UF module achieved a reduction in DOC of 34 ± 6 %, resulting in an additional 27 % increase in the lifetime of the BC column.*

KEYWORDS: Decentralised treatment, developing countries, low-cost options, ultrafiltration membrane, defluoridation, bone char

1 INTRODUCTION

Excessive fluoride intake is highly toxic to humans (Loganathan et al., 2013) and the World Health Organisation (WHO) has defined a fluoride concentration of 1.5 mgL^{-1} as the maximum concentration in drinking water for human consumption (WHO, 2004). This value is approximate only and adjustment factors exist depending on the climate and consequent water intake of a given country (Maheshwari, 2006).

In regions where drinking water contains excessive levels of fluoride, a range of options are available for reducing fluoride levels. While defluoridation is often implemented in developed countries in centralised, high-tech water treatment plants, low-cost defluoridation techniques can be implemented at a point-of-use domestic level as the most common method for combating dental and skeletal fluorosis (Dahi et al., 2000).

Defluoridation techniques can be categorised into three groups: co-precipitation, adsorption, and contact precipitation processes (Dahi et al., 2000). Several authors have already conducted extensive reviews of defluoridation technology in developing countries (Bhatnagar et al., 2011; Loganathan et al., 2013; Ayoob et al., 2008) and only a brief overview will be provided here.

Of particular interest in this study, defluoridation by adsorption exhibits a number of advantages over well-established co-precipitation techniques such as the Nalgonda process (Loganathan et al., 2013). The salient challenge for adsorption techniques relates to the production and regeneration/replacement of filter material,making selection of the adsorption medium particularly important. A variety of adsorption media have been used for defluoridation over the years, including clay, soil, organic matter such as leaves, activated alumina, activated carbon, and bone char (BC).

BC is produced from the burning and grinding of animal bones and features high fluoride uptake capacity. Able to be produced from locally available materials, BC is recognised as one of the leading contenders for defluoridation in developing countries (Bregnhøj and

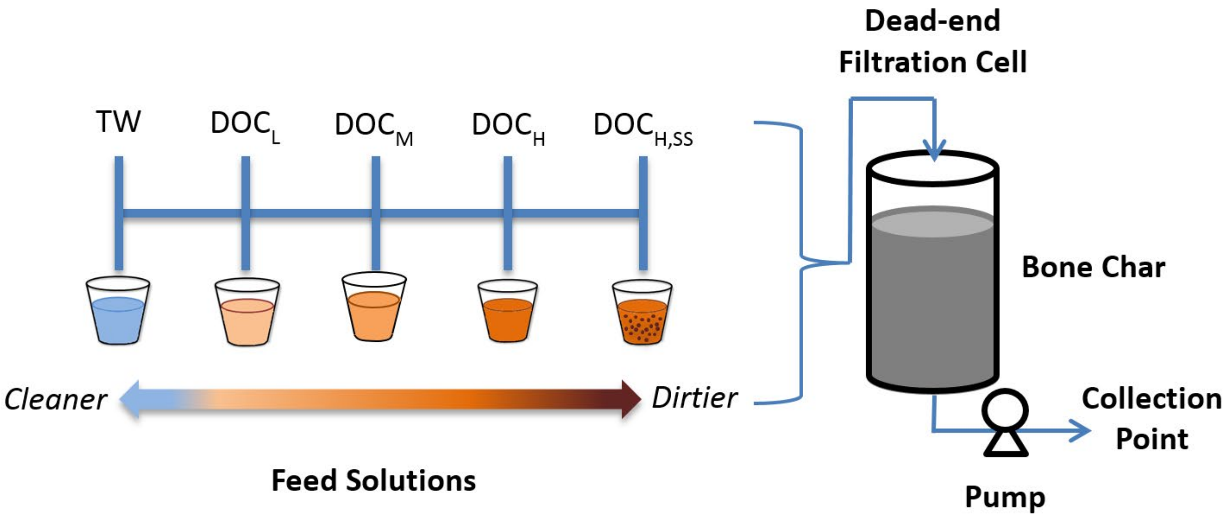

Figure 1: Summary of bone char column tests. Definition of the feed solution acronyms can be seen listed in Table 1.

Dahi, 1995). As a granular adsorption medium, BC also provides flexibility in terms of configuration, an important characteristic for implementation as a point-of-use method (Dahi et al., 2000), although its quality is highly dependent on the production method used (Albertus et al., 2000). The Water Quality Department of the Catholic Diocese of Nakuru (CDN), in Kenya, has been working comprehensively on BC production (Jacobsen and Muller, 2007). The CDN's BC filters are now extensively used in many areas in Kenya, ranging from household to community level configurations.

Mechanisms for the fluoride uptake into the BC include direct adsorption onto empty sites on the BC surface followed by ion exchange with hydroxyl groups (Albertus et al., 2000). Previous work has extensively studied the impact of operating conditions (e.g. pH (Watanesk and Watanesk, 2000a), residence time (Albertus et al., 2000)) on the performance of BC. While most laboratory studies have been based on fluoridated distilled water, a small number of papers have reported the impact of the feed water matrix on filter performance. The impact of ions such as Na^+, K^+, Cl^- and I^- has been studied (Watanesk and Watanesk, 2000b), as well as the performance of BC during parallel treatment of (1) fluoridated distilled water and (2) fluoride-rich ground water (Korir et al., 2009). It was demonstrated that ground water contained buffering ions such as bicarbonate that help maintain a lower pH across the BC columns. This lower pH resulted in a dramatic improvement in fluoride uptake. It was also emphasised that further investigation into the impact of the feed water matrix should be pursued. Another feed matrix study concluded that natural organic matter (NOM) exhibited no competition with fluoride during batch adsorption onto BC (Brunson and Sabatini, 2014). However, it was conceded that batch tests could not accurately represent the kinetic effects of the continuous flow column configurations used in reality. It is indeed expected that the BC column would saturate more quickly when treating water containing large concentrations of compounds competing with fluoride for adsorption sites. The presence of SS in the feed water could also lead to clogging of the filter, a risk which in practice is occasionally mitigated via sand filter pretreatment (Küng et al., 2011).

The aim of this study is therefore to investigate the lifetime of BC columns when challenged with feed solutions that simulate a range of water qualities and pretreatment options. The outcomes of this work will help to assess the need to implement low-cost pretreatment options to improve the lifetime of BC filters. In particular, the study will assess the potential of a gravity-driven, hollow-fibre ultrafiltration module (UF) module as a pretreatment step for BC.

2 METHODS AND MATERIALS

2.1 Summary

Bone char columns were challenged with five different fluoridated feed solutions, each mimicking varying intensities of pretreatment of a model source water recipe (Figure 1). The impact of dissolved organic carbon (DOC) and suspended solids (SS) was assessed by determining the lifetime of the bone char column for each solution i.e. the number of bed volumes (BVs) treated until the effluent fluoride concentration exceeded 1.5 mg L^{-1}. A low-cost, gravity-driven UF membrane was used to prepare one of the feed solutions, enabling the assessment of the impact of this pretreatment on the performance of the bone char column.

2.3 Feed Solutions

Five feed solutions of varying contaminant levels were designed to mimic the pretreatment options that were considered for the BC column. Untreated surface water containing high concentrations of SS and DOC was modelled using diatomaceous earth (Sigma-Aldrich) and a mixture of humic acid (Sigma-Aldrich), alginic acid (Sigma-Aldrich), and whey protein isolate (Bulk Powders)

(Table 1). This mixture ($DOC_{H,SS}$) mimicked the theoretical source water prior to any pretreatment. Sand filtration pretreatment (DOC_H) was modelled with a similar recipe, albeit with diatomaceous earth omitted. The omission of SS from this solution modelled the impact of a sand filter removing 100 % of SS while achieving negligible removal of DOC. The impact of UF pretreatment was investigated by passing the $DOC_{H,SS}$ solution through a gravity-driven hollow-fibre UF module (Polyvinylidene fluoride (PVDF), 0.04 μm). The resulting permeate (DOC_M) was used as one of the five feed solutions for the BC columns. This solution modelled the impact of removing 100 % of SS and a fraction of the DOC in the source water. The impact of UF pretreatment on a source water with lower DOC loading than $DOC_{H,SS}$ was also modelled (DOC_L). This solution was included to acknowledge the possibility of lower DOC levels in the original source water as well as to provide a greater range of DOC concentrations with which to challenge the bone char column. Finally, tap water (TW) containing only residual levels of DOC was used to determine the clean water performance of the BC column.

All feed solutions were fluoridated to a concentration of 6.2 ± 0.3 mg L^{-1}. Regular feed samples were collected for each column test for determination of DOC and actual fluoride concentration. Samples submitted for DOC determination were first syringe filtered (0.45 μm). Fluoride concentration was determined by ion chromatography (Dionex).

2.4 Column Operation

Peristaltic pumps were connected to the outlet of each column and used to circulate the feed solution from the feed container through the packed bed. Each column was initially flushed with 2 BVs of tap water at a flow rate of 2 BV h^{-1} to implement the start-up BC cleaning recommended by the CDN (Jacobsen, 2007). The columns were then loaded with the different feed solutions, which were pumped through the bed at a target flow of 2 BV h^{-1}. A constant flow rate was selected for better comparison with previous studies and to control for the impact of residence time on the lifetime of the bone char. Measuring cylinders were used to track the cumulative volume of effluent across the course of the experiment. Effluent samples were collected on a regular basis for determination of pH, DOC and fluoride concentration. The pumps were only operated during the day, with the feed solution allowed to rest in the column each night. Each test was terminated when the effluent fluoride concentration exceeded 1.5 mg L^{-1}.

2.5 UF Pretreatment

The membrane set-up was based on the Skybox™ Water Filtration Unit (Skyjuice Foundation), a low-tech, gravity driven, point-of-use system for developing countries. The filtration (7.5 m^2) was implemented under constant transmembrane pressure (TMP) conditions by maintaining a constant static head of 0.15 m (1.5 kPa) above the module outlet. Prior to loading with $DOC_{H,SS}$, the module underwent a clean water test to determine the flow through membrane in the absence of fouling. During the filtration of $DOC_{H,SS}$, the hydraulic performance was characterised by regularly measuring the flow rate at the outlet. The rejection performance was determined by regular analysis of feed and permeate DOC concentration. The UF module was only operated during the day, with the feed solution allowed to rest in the tub each night.

3 RESULTS AND DISCUSSION

3.1 Impact of Pretreatment on Column Lifetime

Pretreatment options provide a column operator with the means to improve the quality of the original source feed water. Table 1 summarises how different pretreatment scenarios are associated with varying contaminant levels in the column feed. The purpose of the current study was to investigate whether variations in the feed matrix influence the BC performance. This in turn facilitates a discussion into the feasibility of implementing pretreatment methods.

During operation, the column adsorbed fluoride from the feed water and reduced the effluent fluoride concentration below 1.5 mg L^{-1}. In the early stages of each filtration the BC achieved a fluoride removal of above 90 %. As the fluoride began to accumulate in the BC the effluent concentration increased and eventually exceeded 1.5 mg L^{-1}. Figure 2 illustrates a typical breakthrough curve achieved during this study, here obtained with the TW solution. Linear interpolation between the two points either side of the breakthrough point was used to determine the lifetime of the column. In this example, the lifetime was estimated to be 140 BVs. This value is consistent with the clean water lifetime of 100 BVs determined during a

Table 1: Characteristics of the solutions used to model pretreated waters. Humic, alginate and protein values for DOC_M were estimated based on rejection performance of the UF module.

Simulated Pretreatment	Description (Abbreviation)		Humics (mg L^{-1})	Alginate (mg L^{-1})	Protein (mg L^{-1})	SS (mg L^{-1})	DOC (mg L^{-1})
Clean Water	Tap Water	(TW)	0	0	0	0	5.7 ± 0.1
UF, Low DOC Load	Low DOC, no SS	(DOCL)	5	0.5	2.5	0	7.7 ± 0.3
UF, High DOC Load	Med DOC, no SS	(DOCM)	30	3	15	0	17.6 ± 1.6
Sand Filtered	High DOC, no SS	(DOCH)	30	6	30	0	27.9 ± 2.4
Unfiltered	High DOC, SS	(DOCH,SS)	30	6	30	300	28.3 ± 3.1

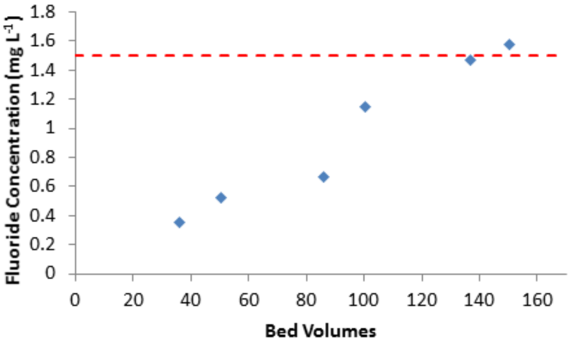

Figure 2: Breakthrough curve for filtration of TW (tap water) solution

similar investigation (Brunson and Sabatini, 2014), with the difference likely the result of the lower feed fluoride concentration used in the current study.

The lifetimes of the adsorption columns for the other model solutions were also determined using breakthrough curves, with the exception of the $DOC_{H,SS}$ test. In this specific experiment, the SS clogged the column outlet and caused the complete cessation of flow before the breakthrough concentration was reached. The lifetime of this column was determined as the number of BVs treated prior to clogging. Column lifetimes are presented in Table 2. These values clearly demonstrate the benefit of removing SS before BC treatment: the DOC_H test had a lifetime 50 % greater than that of the $DOC_{H,SS}$ test. In situations where feed waters are high in SS, this result indicates a clear incentive to implement basic pretreatment methods capable of removing SS, such as sand filter or rapid settling techniques.

Table 2: Column lifetimes for the various feed matrices

Feed Solution	Lifetime (BVs)
$DOC_{H,SS}$	74 (clogged)
DOC_H	110
DOC_M	140
DOC_L	120
TW	140

Table 2 provides an insight into the impact of pretreatment scenarios that result in a lower DOC loading on the BC column. Of the four tests with no SS, the shortest lifetime was observed for the feed solution with the highest DOC concentration, DOC_H. Furthermore, when the DOC was reduced by 34 ± 6% using UF pretreatment (as simulated by DOC_M), the column lifetime increased by 27 %. Although this trend was not borne out by the DOC_L and TW tests, this was likely the result of undesired variations in hydraulic retention time across the different column tests (average flow of 1.80 ± 0.61 BVs h^{-1}). Repetitions of each test would mitigate this issue in future investigations.

The impact of DOC on the column lifetime is likely the result of competition between the DOC and fluoride for adsorption sites on the BC, which would be consistent with findings that BC is an effective adsorbent of DOC (Lambert and Graham, 1995). This is supported by Figure 3, which indicates that the BC removed significant amounts of DOC in every column test. The increase in lifetime that was achieved using UF pretreatment provides a strong incentive for further investigation into how such pretreatment may improve the performance of BC columns in the field. This result contrasts with the negligible DOC/fluoride competition observed in a previous batch adsorption study (Brunson and Sabatini, 2014). This

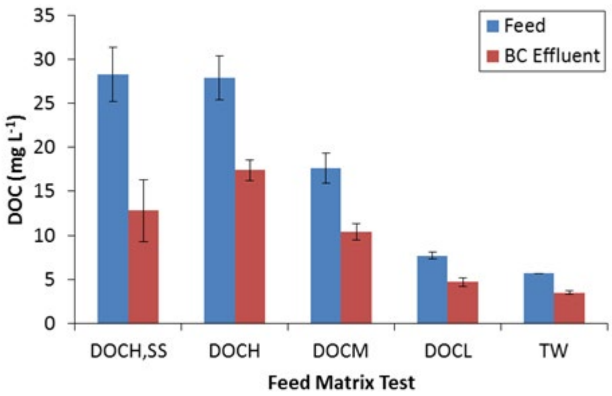

Figure 3: Average DOC concentrations for the feed and effluents of BC adsorption column for each feed matrix

may highlight the significance of column versus batch configurations, although further repetition would be necessary for confirmation.

3.2 Opportunity to Use Gravity-fed Ultrafiltration

One of the aims of the current study was to assess the performance of a low cost, gravity driven, hollow-fibre UF module. In addition to determining contaminant rejection, this work investigated the suitability of this technique for "low-tech", point-of-use scenarios. This included measures of stabilised flux at high fouling and the efficacy of simple membrane cleaning techniques.

As expected, no SS were detected in the UF permeate. Removal of SS was aided by the configuration of the module, with significant deposition of SS occurring at the bottom of the tub and on the horizontally-placed fibre module. By contrast, the average rejection of DOC was 34 ± 6 % when filtering the $DOC_{H,SS}$ solution. This lower than expected rejection of DOC may be due to the relatively small size of the organic compounds used in the feed mixture. The UF module was nonetheless an effective means of assessing the impact of DOC removal on the performance of the BC column.

Figure 4 shows the flux decline of the UF module during the filtration of the $DOC_{H,SS}$ solution to produce the DOC_M solution. After approximately 20 h of operation, the flux stabilised at around 1 L $m^{-2}h^{-1}$. This low flux value was due to the small hydraulic head imposed on the module, equivalent to a pressure of 1.5 kPa. As a result, the skybox

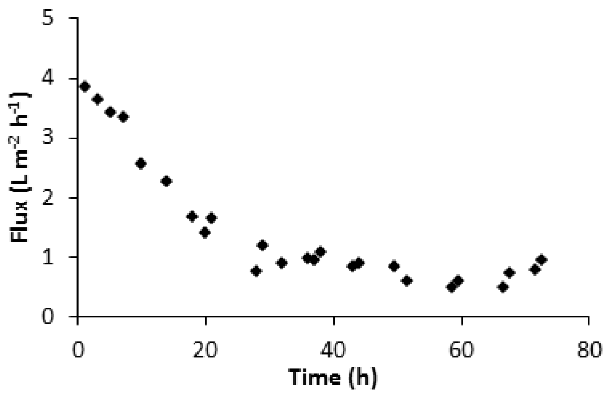

Figure 4: Permeate flow decline during filtration of $DOC_{H,SS}$

Table 3: Flow recovery after membrane cleaning

	Final Flow (L h^{-1})	Recovery (%)
Initial	37.8	-
Shaking/Rinsing	33.0	89
Backwashing	39.3	106

is estimated to produce a relatively stable flow rate of 7.5 L h^{-1} for extended periods of time.

After the filtration, the membrane module underwent two consecutive cleaning methods, which were selected for their potential ease of practical implementation. In the first instance, the module was manually shaken and rinsed with tap water. A clean water test was then performed to determine the extent of flow recovery. Finally, the module was cleaned using a backwashing technique, after which another clean water test was performed (Table 3). The simple shaking/rinsing technique restored the flow by about 90 %. Flow was then fully restored by backwashing (with recovery higher than 100% reflecting experimental errors rather than membrane damage). These results are due to the low flux operation and are promising for the practical implementation of cleaning methods for the gravity-driven UF module.

4 CONCLUSIONS AND RECOMMENDATIONS

This study demonstrated the importance of considering pretreatment as a means of improving the lifetime of BC columns. It was shown that SS significantly retard the performance of BC columns and that the removal of SS resulted in an increase in column lifetime of 50 %. It was also found that low-cost, gravity-driven, PVDF UF membrane technology reduced the level of DOC in the feed matrix by 34 ± 6 %. This reduction resulted in a 27 % increase in BC column lifetime, indicating the possibility of competitive adsorption between DOC and fluoride. Future research should focus on the impact of DOC, especially with a focus on the mechanisms involved. In practical terms, the current work established an incentive for further investigation into the benefit of low-cost UF pretreatment for the lifetime of BC columns in the field. This has important implications for the frequency of filter media regeneration and the consequent time, labour, and cost inputs of bone char defluoridation.

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