Science of the Total Environment 488–489 (2014) 580–587

Contents lists available at ScienceDirect

Science of the Total Environment

journal homepage: www.elsevier.com/locate/scitotenv

Practical considerations, column studies and natural organic material competition for fluoride removal with bone char and aluminum amended materials in the Main Ethiopian Rift Valley

Laura R. Brunson *, David A. Sabatini [1]

University of Oklahoma, WaTER Center, School of Civil Engineering and Environmental Science, CEES, 202 W. Boyd St., Room 334, Norman, OK 73019, United States

HIGHLIGHTS

- A Rapid Small Scale Column Test model is validated for fluoride removal by animal bone char.
- Natural organic material competition with fluoride removal is investigated.
- Column studies using synthetic water and groundwater from Ethiopia are conducted.
- Sulfate content and high pH (8.22) reduced the fluoride removal of media.

ARTICLE INFO

Article history:
Received 11 April 2013
Received in revised form 4 December 2013
Accepted 9 December 2013
Available online 3 January 2014

Keywords:
Drinking water
Fluoride
Natural organic material
Rapid Small Scale Column Test
Sulfate competition

ABSTRACT

The fluoride removal capacities of three materials, bone char (BC), aluminum oxide coated bone char (ACBC) and aluminum oxide impregnated wood char (AIWC), along with activated alumina (AA) as a baseline material, were investigated in batch and column studies, including comparison between synthetic and natural groundwater. Results suggest that in all cases the laboratory column results exhibited higher fluoride removal efficiency than the field studies conducted in the Ethiopian Rift Valley. Further studies indicate that the reduced effectiveness in the field was likely due to a combination of the high pH of groundwater (8.2) and the presence of competing ions (sulfate). Batch studies testing potential competition from natural organic material (NOM) showed no statistical evidence of NOM competition with BC and minor evidence of competition with ACBC and AIWC. To provide evidence for using Rapid Scale Small Column Test (RSSCT) principles for BC two different column volume and particle sizes were used. The results indicate that RSSCT scaling equations, developed for activated carbon, are applicable for BC removal of fluoride. These results thus provide valuable insights for translating laboratory results of novel sorbents for mitigating fluoride tainted groundwater in the field.

I. Introduction

Lack of access to an improved source of drinking water is a global health issue affecting 780 million people worldwide (WHO and UNICEF, 2012). Not considered in this statistic are an estimated 200 million people who are exposed to groundwater containing fluoride concentrations above the World Health Organization (WHO) guideline value of 1.5 mg/L (Amini et al., 2008; World Health Organization, 2011). Elevated fluoride concentrations occur in numerous groundwater formations globally, including areas of India, China, and the Rift Valley of Africa which includes the Main Ethiopian Rift Valley (MER) (Amini et al., 2008; Fawell et al., 2006; Fewtrell et al., 2006; Rango et al., 2010, 2012). Human consumption of elevated fluoride concentrations is problematic due to the dental and skeletal fluorosis that often result from high fluoride intake (Li et al., 2001; Meenakshi and Maheshwari, 2006; Sivasamy et al., 2001). Dental fluorosis manifests itself as discoloration and pitting of the teeth, resulting in physical and psychological effects, while skeletal fluorosis can cause pain and restriction of movement, which can impair the livelihood of those dependent on sustenance farming or other manual activities (Fewtrell et al., 2006; Meenakshi and Maheshwari, 2006; Tonguc et al., 2011).

When rainwater harvesting or use of alternative water supplies are not practical, fluoride removal from drinking water is the most viable option for providing safe water. Treatment options that have been investigated include: electrolytic defluoridation (Mameri et al., 2001; Gwala et al., 2011), reverse osmosis and membrane processes (Arora et al., 2004; Meenakshi and Maheshwari, 2006), precipitation (Yadav et al., 2006), and adsorption (Abe et al., 2004; Ayoob et al., 2008; Brunson and Sabatini, 2009; Medellin-Castillo et al., 2007; Mlilo et al.,

---

Abbreviations: AA, activated alumina; WC, wood char; ACWC, aluminum oxide coated wood char; AIWC, aluminum oxide impregnated wood char; BC, bone char; ACBC, aluminum oxide coated bone char; RSSCT, Rapid Small Scale Column Test; NAFA, Nordic Aquatic fulvic acid; PPHA, Pahokee Peat humic acid.

* Corresponding author. Tel.: +1 405 255 9622.
E-mail addresses: lbrunson@ou.edu (L.R. Brunson), sabatini@ou.edu (D.A. Sabatini).

[1] Tel.: +1 405 325 4273.

0048-9697/$ – see front matter © 2013 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.scitotenv.2013.12.048

2010). Many of these options have proven viable for fluoride removal, but also exhibit aspects which make them less than ideal for rural developing areas. For example, electrolytic defluoridation requires an energy source, and reverse osmosis and membrane processes can require large capital costs and produce large volumes of waste solution (Gwala et al., 2011; Jagtap et al., 2012). The Nalgonda technique is a process by which aluminum sulfate and lime are added to water to cause co-precipitation of fluoride and aluminum hydroxides. Nalgonda has been used with some success, including in Ethiopia, but has constraints including the production of large amounts of waste sludge and the daily operational and chemical addition requirements (Fawell et al., 2006; Meenakshi and Maheshwari, 2006; Yadav et al., 2006).

Adsorption is a helpful fluoride removal option because it can be implemented using gravity (no need for a power source), and is helpful in terms of cost and ease of use (Bhatnagar et al., 2011). Researchers have extensively studied activated alumina (AA), a material well known for fluoride adsorption. It has been found that AA works best in the pH range of 5–7.5 and that it has a fluoride removal capacity ranging from 4 to 15 mg of fluoride per gram of AA for laboratory studies and 1 mg/g in a field study; fluoride removal values for AA tend to vary based on water pH, competing ions and the nature of the study (Fawell et al., 2006; Ghorai and Pant, 2005; Hao and Huang, 1986; Tang et al., 2009). A number of activated carbon materials showed minimal fluoride removal capacity despite their high specific surface areas (Abe et al., 2004; Ayoob et al., 2008). Bone char (BC) demonstrated a much higher fluoride removal capacity than activated carbon, which can be attributed to its dual properties of a high specific surface area [111 m^2/g (Brunson and Sabatini, 2009), 100 m^2/g (Cheung et al., 2005) and 104 m^2/g (Medellin-Castillo et al., 2007)] and desirable surface chemistry, a surface that likely exhibits a positive charge at system pH that will attract fluoride ions to the media. Researchers have shown that BC can remove fluoride and arsenic simultaneously with minimal competition, which is helpful in situations where they coexist, as could occur in a variety of MER locations (Rango et al., 2010). Further, BC can be produced using local materials in rural areas of Ethiopia, Kenya and Tanzania (Mjengera and Mkongo, 2002; Abaire et al., 2009; Brunson and Sabatini, 2009). In some cases BC is culturally unacceptable, therefore, alternative materials with similar properties to BC must be evaluated.

When considering the practicalities of removing fluoride from groundwater it is necessary to account for possible competition from competing ions. Often phosphate and sulfate in groundwater are competitors for fluoride removal by adsorptive materials (Jagtap et al., 2012). Natural organic material (NOM) in the groundwater should also be considered as it sometimes competes with other adsorptive processes, particularly adsorption onto activated carbon (Newcombe et al., 1997b), and is found in all groundwater sources (Newcombe et al., 1997a), generally at concentrations of 0.5–10 mg/L (Genz et al., 2008). NOM is composed of humic and fulvic acids and typically has negatively charged surface functional groups (Redman et al., 2002), which suggests it has the potential to compete with fluoride for removal on adsorption media in the same way that negatively charged phosphate and sulfate ions are known to compete. To our knowledge, NOM competition has yet to be studied in relation to fluoride adsorption onto bone or wood chars and competing ion studies have not been conducted on several of the materials studied in this work.

Continuous flow column studies are important to assess the ability of a media to remove fluoride in a setting similar to a point of use (POU) or community scale column system. Continuous flow tests capture kinetic affects, such as mass transfer and intraparticle diffusion, in a way not possible in batch tests. Ma et al. (2008) conducted batch and column studies and suggested that BC is more effective than AA at fluoride removal and that reducing the bed depth or increasing the flow rate decreased the bed volumes passed until breakthrough, in their case 1 mg/L fluoride. Minimal work has evaluated the fluoride removal potential of bone and wood chars in continuous flow studies, particularly in a field setting utilizing a natural source water (Ayoob and Gupta, 2007; Kloos and Haimanot, 1999).

Assessing filtration technologies for use in community scale systems can be costly and time consuming. One way to reduce time and cost is through the use of Rapid Small Scale Column Test (RSSCT) principles. RSSCTs are helpful for reducing the amount of water and media required, the time needed to conduct studies, and the cost of such studies while producing results representative of full scale systems (Crittenden et al., 1986; Badruzzaman et al., 2004). RSSCT calculations use dimensionless scaling principles based on mass transfer and hydraulic flow conditions as in Eqs. (1) and (2) where EBCT is empty bed contact time, d is the particle diameter of the sorbent, ν is superficial velocity, and SC and LC stand for small-scale and large-scale, respectively (Badruzzaman et al., 2004; MWH, 2005). This approach was used to calculate particle size, flow rate and bed volumes to be used in two column studies to evaluate the validity of this approach for the use of BC for fluoride removal (MWH, 2005). The use of these equations for the RSSCT approach assumes that BC is relatively homogenous with size and that surface diffusivity is constant across different particle sizes (Westerhoff et al., 2005).

$$\mathrm{EBCT}_{SC}/\mathrm{EBCT}_{LC} = [\mathrm{d}_{SC}/\mathrm{d}_{LC}]^{2} \tag{1}$$

$$\nu_{SC}/\nu_{LC} = \mathrm{d}_{LC}/\mathrm{d}_{SC}. \tag{2}$$

While the RSSCT method, first developed for activated carbon, has been used for arsenic removal in iron oxide based media, to our knowledge this approach has not been evaluated in the literature for BC (Westerhoff et al., 2005).

The purpose of this work is to assess the ability of several materials (wood char, aluminum coated wood char, aluminum impregnated wood char, bone char, and aluminum coated bone char) to remove fluoride in a continuous flow system utilizing groundwater with elevated fluoride concentrations from the MER. Continuous flow tests will also be conducted in a laboratory setting to compare the relative fluoride removal capacities between laboratory and field systems. We hypothesize that, based on the relatively homogenous nature of the BC material, the RSSCT approach will be validated for BC, which would allow for quicker and easier scale up of fluoride removal using BC. This work also aims to assess the practical question of whether or not NOM will negatively affect the fluoride removal capacity of several materials. We hypothesize that NOM will have an effect, although minimal, on fluoride removal due to its negative charge.

2. Methods

2.1. Materials preparation

Eucalyptus wood was obtained from Mezozoic Landscapes, Inc. in Florida while fish bone meal was purchased from Peaceful Valley Farm & Garden Supply in California. Chars were prepared by placing raw material in a glaze-free covered porcelain container and charring in an oven at 500 or 600 °C, bone and wood, respectively, for 4 h. Materials were crushed and sieved to a size of 180–425 μm and rinsed in deionized water to remove fines. Aluminum oxide coating was achieved by first using MES buffer, a biological pH buffer, in deionized water to obtain a solution pH of 3.5. Then aluminum nitrate was added at 175 mg/L along with 25 g of char material, based on the work of Levya-Ramos et al. (1999), to 500 mL flasks. This mixture was shaken for 5 days at which point the char material was filtered, rinsed, dried at 100 °C and stored in sealed plastic bags. Aluminum oxide impregnated wood char (AIWC) was prepared based on the work of Tchomgui-Kamga et al. (2010) where small pieces of raw eucalyptus wood were boiled for 1.5 h in a 1 molar aluminum chloride solution. Media were then left to cool in solution for 2 h, air-dried for 2 h, and oven dried at