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Research article

Arsenic and fluoride removal from contaminated drinking water with Haix-Fe-Zr and Haix-Zr resin beads

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ABSTRACT

The objective of the study was to carry-out batch tests to examine the effectiveness of Haix-Fe-Zr and Haix-Zr resin beads in the removal of As(III), As(V) and F^- from groundwater with a similar geochemistry to a site where a community-based drinking water plant has been installed in West Bengal, India. The groundwater was spiked separately with ~200 μg/L As(III) and As(V) and 5 mg/L F^-. Haix-Zr resin beads were more effective than Haix-Fe-Zr resin beads in removing As(III) and As(V). Haix-Zr resin beads showed higher removal of As(V) compared to As(III). Haix-Zr resin beads removed As(V) below the WHO (10 μg/L) drinking water standards at 8.79 μg/L after 4 h of shaking, while As(III) was reduced to 7.72 μg/L after 8 h of shaking. Haix-Fe-Zr resin beads were more effective in removing F^- from the spiked groundwater compared to Haix-Zr resin beads. Concentrations of F^- decreased from 6.27 mg/L to 1.26 mg/L, which is below the WHO drinking water standards (1.5 mg/L) for F^-, after 15 min of shaking with Haix-Fe-Zr resin beads. After 20 min of shaking in groundwater treated with Haix-Zr resin beads, F^- concentrations decreased from 6.27 mg/L to 1.43 mg/L. In the removal of As(III), As(V), and F^- from the groundwater, Haix-Fe-Zr and Haix-Zr resin beads fit the parabolic diffusion equation (PDE) suggesting that adsorption of these contaminants was consistent with inter-particle diffusion.

1. Introduction

Arsenic and F^- contamination of water resources are rapidly spreading globally, necessitating an urgent need to provide safe drinking water to these areas. Drinking water harvested from underground sources in many parts of the world, especially in India, contain concentrations of As well above the Bureau of Indian Standards BIS:10500 (BIS, 2012), World Health Organization (WHO, 2011) and US Environmental Protection Agency (EPA) limits of 10 μg/L (EPA, 2001). The As contamination of drinking water in the Ganga–Meghna–Brahmaputra (GMB) plain with an area of 569,749 km^2 and a population of >500 million covering a large area of Bangladesh and India, is considered one of the worse catastrophes in recent times (Ravenscroft et al., 2005; Bhattacharya et al., 2007; Bundschuh et al., 2012). This crisis affects millions of people and has spread to Northeast Asia, affecting Vietnam, Cambodia, Laos, Myanmar, and other nearby countries (Berg et al., 2007; Stanger et al., 2005; Bearak, 1998). Initial stages of health effects, referred collectively as arsenicosis, usually manifests after about 10 years of chronic exposure of >50 mg/L of As. Common arsenicosis manifests as skin lesions, particularly in the palm of the hands and bottom of the feet, which over time become cancerous and eventually lead to gangrene. Lung, bladder, and kidney cancer are associated with later stages of arsenicosis (Bagla and Kaiser, 1996). To add to this crisis, growing agricultural demand and increased populations have resulted in excessive groundwater withdrawals, which have increased the dissolution of As due to weathering of minerals in the aquifers (Bagla and Kaiser, 1996).

Fluoride contamination is commonly high in soil and rock materials in arid regions. The North-western states and the Deccan Plateau region of India are especially affected. Elevated concentrations of F^- can occur in drinking water from a range of groundwater sources. It is well known that a very small amount of

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F^- is good for the teeth and bones. However, prolonged consumption of F^- contaminated groundwater >1.5 mg/L/day can lead to fluorosis (mainly skeletal and dental), especially if the person is malnourished (Krishnamachari, 1976). Fluorosis is a growing world-wide problem estimated to affect 200 million people from 25 nations (Raj and Umayorubhagan, 2013). Additionally, there is evidence that the rapid spread of elevated concentrations of F^- in drinking water collected from shallow wells is linked to soil degradation (Jaglan and Qureshi, 1996; Jacks et al., 2005).

Most of the populations suffering the effects of either As or F^- contaminated groundwater are in impoverished rural communities in arid environments where temperatures are elevated resulting in the need to consume more water. Drinking of groundwater is preferred to surface water in these areas because it is more hygienic, tastes better and easily available. Therefore, it is crucial to set-up As and F^- removal systems for drinking water on an emergency basis. Several As and F^- removal technologies for safe drinking water have been developed over the last three decades and have gained wide-scale field applications, such as the Subterranean Arsenic Removal (SAR) technology which uses oxidation accelerated by autocatalytic effects of the oxidation products and chemo-autotrophic microorganisms (Sen Gupta et al., 2009).

However, many of these technologies also use sorption onto iron, titanium, and zirconium oxides (Suzuki et al., 2000; Dutta et al., 2004; Bang et al., 2005; Aredes et al., 2013). A sorbent medium gaining wide-spread use is anion exchange resin beads, such as Haix-Fe, which use polymeric ligand exchange for selective As removal (Ramana and Sengupta, 1992). Haix-Fe resin beads installed in water treatment plants have had successful field applications in rural villages of India, especially in West Bengal, in treating As contaminated water with large columns connected to tube wells (Sen Gupta et al., 2009). Additionally, a SAR plant has been retrofitted with a Haix column that acts as a polisher for supplying safe drinking water to a growing population (Mukhopadhyay et al., submitted). Groundwater is pumped by electric water pumps or by hand to the top of the column and when the water enters the column it is aerated. Fe^{2+} from the water is oxidized to Fe^{3+} which is then filtered by the adsorbent bed. Hydrated Fe(III) oxide (HFO) nano-particles that form on top of anion exchange Haix-Fe resin beads in the column help remove the As(V) and As(III) from the water before it enters the resin bead section of the column. The resulting arsenic levels will be below the WHO and EPA's safe drinking standards of 10 μg/L (EPA, 2001). Recently, HAIX-Zr resin beads have been developed as an adsorbent that can be used in the community-based water treatment systems/columns that are currently using HAIX-Fe resin beads. HAIX-Zr is designed to treat F containing groundwater, however, its properties also allow it to treat As(V) containing groundwater at a greater capacity compared to F^- (Padungthon et al., 2014, 2015). These beads are durable as no physical or chemical degradation of the Haix-Zr resin beads have been observed after regeneration (Padungthon et al., 2015). By combining these metal oxide nanoparticles with the chemically and mechanically stable polymeric ion exchange resins, a synergistic effect is created from enhancing the ligand sorption affinity of HFO and HZrO which is assisted by the Donnan membrane effect (Smith et al., 2015). Additional batch tests should be carried-out to validate this point.

A community-based water treatment plant installed in a village in West Bengal, India is supplying water to a growing population of people, therefore, a Haix column containing Haix-Fe resin beads has been retrofitted as a polishing unit onto a SAR water treatment plant. The groundwater had elevated As concentration in the range of 150 μg/L, high above the WHO guideline (Mukhopadhyay et al., submitted). This project used groundwater with similar geochemical parameters to groundwater used as drinking water in a this village and nearby areas where F concentrations are also high. This project examines the potential to use the Haix-Zr and Haix-Fe-Zr resin beads at this site and nearby sites. Although the adsorption of HAIX-Zr and HAIX-Fe resin beads have been investigated in other studies (Ramana and Sengupta, 1992; Padungthon et al., 2014, 2015), this is the first time the new hybrid HAIX-Fe-Zr resin beads have been investigated in the removal of As and F. As and F contaminated groundwater is a crisis in Asia, especially in India (Ravenscroft et al., 2005; Bhattacharya et al., 2007; Bundschuh et al., 2012) and is a growing world-wide concern (Berg et al., 2007; Stanger et al., 2005; Bearak, 1998). The HAIX range of resin beads have demonstrated great promise in removing As and F from drinking water, especially in community based programmes, such as Drinkwell, where residents of villages are trained to run the treatment plants and in larger commercial plants in the USA (SenGupta, 2017). Additionally, these beads can be regenerated, therefore, they are a sustainable option for remediating As and F contaminated groundwater. However, more research is need in examining other hybrid HAIX resin beads, such as HAIX-Fe-Zr, in removing As and F. The objectives of this study are to examine the performance of Haix-Fe-Zr and Haix-Zr resin beads in the removal of As and F^- from groundwater with similar characteristics to the contaminated groundwater from West Bengal.

2. Materials and methods

2.1. Resin bead properties

2.1.1. Haix-Fe-Zr resin beads

Haix-Fe-Zr resin beads are small, approximately 0.5 mm to 1.5 mm in diameter (Fig. 1a), with a reddish orange colour from hydrous ferric oxide (HFO) which range in size from 20-100 nm. More detailed analysis by TEM reveals the HFOs as acicular and HZrOs as round platelet nano-particles present on the surface and within nano-porous Haix-Fe-Zr resin beads (Fig. 1b). HZrO and HFO are precipitated on the gel-phase of the macro-porous anion Haix exchange resin when they are synthesized (DeMarco et al., 2003) with quaternary ammonium functional groups (SenGupta and Cumbal, 2007). These nano-sized Fe and Zr oxides are distributed along the surface and internally within the resin beads (Fig. 1b) and are responsible for the efficient removal of As and F^- from contaminated water. Water flows on the surface and within the beads through nano-sized voids where nano-Fe and Zr particles are distributed (Fig. 1b). This means large amounts of As and F^- can be removed from the contaminated water and absorbed on the surface and internal structure of the beads. This adsorption can be explained by the high surface area created by the macro porosity of the beads. Stereomicroscopic observations of polished sections of the Haix-Fe-Zr resin beads show that the reddish HFOs mainly occur concentrically with the roundness of the bead (Fig. 1a). Each bead had individual patterns of HFO precipitation, although some beads had similar patterns.

2.1.2. Haix-Zr resin beads

Haix-Zr resin beads are beige/white coloured small 0.3 mm-1mm macro porous anion exchange resin beads Fig. 1c). TEM micrographs of polished sections of the Haix-Zr resin beads show the rounded/spherical sub-micron sized (ranging in size from 20 nm-100 nm) hydrated Zirconium (Zr^{4+}) oxides (HZrO) particles distributed on their surface and within/through the ion exchange bead (Fig. 1d). These nano-sized HZrO particles are responsible for the efficient removal of As and F^-. This anion exchanger has a positively charged quaternary ammonium functional group, on which anionic ligands such as As(V) and F^- can be absorbed. Water contaminated with F^- and As flows through nano-sized pores