



Rapid adsorption of arsenic from aqueous solution by ferrihydrite-coated sand and granular ferric hydroxide



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ABSTRACT

The efficiency of As removal by Fe oxyhydroxide-based adsorbents was studied. Water containing micromolar concentrations of As was cleaned using columns containing ferrihydrite-coated grains of sand or the commercial material granular ferric hydroxide, GFH[®]. Adsorption of considerable amounts of arsenate and arsenite were achieved on a sub-minute time scale with both adsorbents. Furthermore, efficient adsorption on GFH[®] can be achieved in seconds of empty bed contact time. Arsenate adsorption was affected by moderate changes in pH, while such an effect was negligible for arsenite. At slightly acidic pH substantially higher amounts of arsenate could be adsorbed. The Fe content of the coated sand was varied and it was found that more As was adsorbed on grains with a higher Fe content, however, the relationship was far from proportional. This is supported by scanning electron microscopy and energy dispersive spectroscopy, which showed that in addition to the occurrence of Fe in compounds coating the flakes, it also occurred adsorbed to the surface. The Fe oxyhydroxide coating was confirmed to be ferrihydrite using EXAFS spectroscopy. Batch experiments with ferrihydrite support the view that almost all can be adsorbed with a sufficient surplus of Fe oxide/hydroxide mineral suspension.

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1. Introduction

Arsenic-enriched drinking water is a global problem and the situation is a particular problem in small scale wells in developing countries, where means for efficient As removal are missing (Smedley and Kinniburgh, 2002). The As in the waters is primarily from geological sources and increased water utilization increases As mobilization in ground water. Arsenic-enriched drinking water is a major health problem, and the limit for As concentration is set as low as $10 \mu\text{g dm}^{-3}$ (WHO, 1993).

Several commercial Fe oxide-based filters have been used in the Bengal and Bangladesh regions which are known for their widespread drinking water As problem. One of the most well-known is the locally produced SONO filter in which household water is filtered through sand, a rusted Fe matrix, brick chips and wood charcoal (Hussam and Munir, 2007). The filter has been shown to be very efficient but works primarily on a household level rather than a community level. To the best of the authors' knowledge, no As decontamination filter is produced or easily available in the target area of Burkina Faso. The commercial material Granular Ferric Hydroxide or GFH[®], produced by GEH Wasserchemie GmbH & Co., is used in municipal drinking water plants for As removal and is said to consist of mesa-porous low crystalline akaganeite (Driehaus et al., 1998). This material is very efficient but has a high

cost per mass unit (Kumar et al., 2008). As arsenic in drinking water is a very local problem, most water plants in the world have no need for a separate As decontamination step.

1.1. Arsenic oxyanion systems

Arsenic occurs in nature in the penta- and trivalent forms, arsenate and arsenite, respectively. Arsenic acid, H_3AsO_4 or $\text{O} = \text{As}(\text{OH})_3$, has similar chemical properties to phosphoric acid, H_3PO_4 or $\text{O} = \text{P}(\text{OH})_3$; the pK_a values are 2.25, 7.05 and 11.58, and 2.15, 7.20 and 12.37, respectively (Greenwood and Earnshaw, 1997; Raposo et al., 2002). The speciation of arsenate in drinking water is dominated by H_2AsO_4^- or HAsO_4^{2-} depending on pH. The structure and H-bonding of the species in the arsenic acid system in water has been studied recently (Mähler et al., 2013). Arsenous acid, $\text{As}(\text{OH})_3$, the dominating As(III) species in natural waters, is considered more toxic as well as more mobile in the environment (Smedley and Kinniburgh, 2002). Arsenous acid results from aqueous dissolution of As(III) oxide, As_2O_3 , or salts containing linear meta-arsenite ions, $[\text{AsO}_2]_n^-$, but the pure acid has not yet been isolated (Greenwood and Earnshaw, 1997). The acidic constants, $\text{pK}_{a1} = 9.25$, $\text{pK}_{a2} = 12.13$ and $\text{pK}_{a3} = 13.4$ (Konopik and Leberl, 1949; Zakaznova-Herzog et al., 2006) show that all protons can be lost in aqueous solution but the high first pK_a value makes only the neutral arsenous acid relevant in the pH range 6.5–8.5, prevailing in drinking water (WHO, 2003a). Dissolved O_2 has ability to oxidize arsenous acid to arsenate but the non-catalyzed process

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is too slow to be used for water cleaning purposes (Bissen and Frimmel, 2003).

1.2. Ferrihydrite

In comparison to other Fe hydroxides such as goethite (α -FeOOH), akaganeite (β -FeOOH) and lepidocrocite (γ -FeOOH), ferrihydrite has a less well defined structure with the approximate formula $\text{Fe}_5\text{HO}_8 \cdot 4\text{H}_2\text{O}$ (Schwertmann and Cornell, 2000). The two forms, six-line and two-line ferrihydrite can be distinguished by powder X-ray diffraction, with even lower crystallinity for the latter form. With time, crystallinity increases and ferrihydrite is converted into goethite and other stable minerals via dissolution/precipitation processes (Schwertmann and Cornell, 2000). These processes occur on a time-scale of days to years in natural environments. They can be retarded by organic matter, phosphate or silicate species, or accelerated by the presence of organic reducing agents (Schwertmann and Cornell, 2000). Amorphous materials are often more effective adsorbents than their crystalline counterparts, and amorphous Fe hydroxides are no exception (Pierce and Moore, 1982). The high pH_{pzc} , the pH value at which positive and negative charges at the surface balance each other, of ferrihydrite (≈ 8.1) (Dzombak and Morel, 1990; Gustafsson, 2003) make it a promising candidate as an adsorbent. However, the small particle size of the suspensions poses practical difficulties as filter material. In order to use ferrihydrite as adsorbent in a filter it has to be attached to surfaces of larger mechanically stable particles or incorporated in granular materials.

1.3. Column adsorption

Batch experiments with suspensions are simple and quick to perform, and test materials are homogenous. However, one drawback is that it is not easy to estimate whether an ion or molecule is retained with sufficient strength. Neither do batch experiments

constitute a good representation of a decontamination plant, as suspensions cannot be used in practice. Removal of As from water is preferably performed by passing an influent through a column packed with adsorbent. Such a system offers opportunities to study As adsorption under more realistic conditions. It also opens up the possibility of evaluating the efficiency with which the adsorption occurs by studying break-through volumes. Column length is recommended to be about five times the column diameter (Nikolaidis et al., 2003). An up-scaling approach depending on media grain size between small scale differential columns and pilot sized columns has been suggested (Westerhoff et al., 2005). This assumes proportional diffusivity where surface diffusion is the controlling mechanism and that the diffusivity is linearly proportional to the particle radius (Westerhoff et al., 2005). Iron (hydr)oxide-coated sand and GFH[®] have previously been used for As adsorption in column or sand filter experiments (Benjamin et al., 1996; Driehaus et al., 1998; Thirunavukkarasu et al., 2003a,b; Westerhoff et al., 2005; Herbel and Fendorf, 2006; Guo et al., 2007; Tufano and Fendorf, 2008; Kocar et al., 2010).

1.4. Adsorption to iron oxyhydroxides

Adsorption of arsenite and arsenate on mineral surfaces has been studied extensively and a selection of reports concerning mainly Fe oxyhydroxides is presented in Table 1. Most investigations have been performed as batch experiments but some also used columns or sand filters (Benjamin et al., 1996; Joshi and Chaudhuri, 1996; Driehaus et al., 1998; Nikolaidis et al., 2003; Thirunavukkarasu et al., 2003a,b; Vaishya and Gupta, 2003; Jessen et al., 2005; Westerhoff et al., 2005; Herbel and Fendorf, 2006; Guo et al., 2007; Tufano and Fendorf, 2008; Kocar et al., 2010). In addition to inorganic As species, studies on the sorption of organic As species to Fe oxyhydroxides have been reported, indicating that mono- and dimethylated pentavalent As species adsorb to a lesser extent than inorganic arsenate (Bowell, 1994).

Table 1
Investigations of arsenite and arsenate adsorption on Fe oxyhydroxide surfaces. GFH[®] stands for “Granular Ferric Hydroxide” and is a commercially available adsorbent characterized as poorly crystalline akaganeite.

			Arsenite	Arsenate
Fe ^(III)	Goethite	α -FeOOH	1, 2, 3, 4, 5, 6, 7	3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14, 15, 16, 17
Fe ^(III)	Akaganeite	β -FeOOH (+ Cl ⁻ + H ₂ O) (Schwertmann and Cornell, 2000)		11
	GFH [®]	$\approx \beta$ -FeOOH (+ Cl ⁻ + H ₂ O) (Driehaus et al., 1998)	18, 19	18, 19, 20, 21, 22, 23
Fe ^(III)	Lepidocrocite	γ -FeOOH	3, 5, 24	3, 5, 11, 12, 24
Fe ^(III)	Ferrihydrite	$\approx \text{Fe}_5\text{HO}_8 \cdot 4\text{H}_2\text{O}$	25, 26, 27, 28, 29, 30, 31, 32, 33, 34	27, 35, 36, 37, 11, 12, 15, 32, 33, 34, 38, 39, 40
Fe ^(III)	Undefined Fe ^{III} hydroxides	$\approx \text{Fe}_x\text{O}_y\text{H}_{(2y-3x)}$	31, 41, 42, 43, 44	31, 41, 42, 44, 45, 46
Fe ^(III)	Schwertmannite	$\text{Fe}_8\text{O}_8(\text{OH})_x(\text{SO}_4)_y$	47, 48	48
Fe ^(III)	Hematite	α -Fe ₂ O ₃	5, 49	5, 14, 38, 49, 50, 51
Fe ^(III)	Maghemite	γ -Fe ₂ O ₃	24	24
Fe ^(II, III)	Magnetite	Fe ₃ O ₄	24, 29, 52	24, 52
Fe ^(II)	Siderite	FeCO ₃	49	49
Fe ⁽⁰⁾	Elemental iron	Fe	53, 54, 55, 56	54, 55, 56, 57
	Misc. Fe		3, 58, 59, 60, 61, 62, 63, 64	3, 15, 58, 59, 60, 61, 62, 63, 64

References: 1: Sun and Doner (1998); 2: Manning et al. (1998); 3: Farquhar et al. (2002); 4: Sun and Doner (1996); 5: Bowell (1994); 6: Stachowicz et al. (2007); 7: Grafe et al. (2001); 8: Loring et al. (2009); 9: O'Reilly et al. (2001); 10: Fendorf et al. (1997); 11: Waychunas et al. (1993); 12: Pedersen et al. (2006); 13: Zhang et al. (2007); 14: Mamindy-Pajany et al. (2009); 15: Fukushi and Sverjensky (2007); 16: Hongshao and Stanforth (2001); 17: Manning and Goldberg (1996); 18: Thirunavukkarasu et al. (2003b); 19: Banerjee et al. (2008); 20: Saha et al. (2005); 21: Guan et al. (2008); 22: Driehaus et al. (1998); 23: Westerhoff et al. (2005); 24: Manning et al. (2002); 25: Jessen et al. (2005); 26: Tufano and Fendorf (2008); 27: Herbel and Fendorf (2006); 28: Bhandari et al. (2011); 29: Ona-Nguema et al. (2010); 30: Voegelin and Hug (2003); 31: Thirunavukkarasu et al. (2001); 32: Raven et al. (1998); 33: Appelo et al. (2002); 34: Jain et al. (1999); 35: Kocar et al. (2010); 36: Carabante et al. (2009); 37: Carabante et al. (2010); 38: Manceau (1995); 39: Waychunas et al. (1996); 40: Fuller et al. (1993); 41: Pierce and Moore (1982); 42: Thirunavukkarasu et al. (2003a); 43: Benjamin et al. (1996); 44: Goldberg and Johnston (2001); 45: Sherman and Randall (2003); 46: Garcia-Sanchez et al. (2002); 47: Liao et al. (2011); 48: Burton et al. (2009); 49: Guo et al. (2007); 50: Waychunas et al. (2005); 51: Arai et al. (2004); 52: Su and Puls (2008); 53: Nikolaidis et al. (2003); 54: Su (2007); 55: Lackovic et al. (2000); 56: Su and Puls (2001); 57: Farrell et al. (2001); 58: Vaishya and Gupta (2003); 59: Chakraborty et al. (2011); 60: Partey et al. (2009); 61: Hsu et al. (2008); 62: Partey et al. (2008); 63: Zeng (2004); 64: Joshi and Chaudhuri (1996).

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