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Arsenic removal by iron-modified activated carbon

Weifang Chen, Robert Parette, Jiying Zou, Fred S. Cannon, Brian A. Dempsey*

Department of Civil and Environmental Engineering, The Pennsylvania State University, 212 Sackett Building, University Park, PA 16802, USA

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ABSTRACT

Iron-impregnated activated carbons have been found to be very effective in arsenic removal. Oxyanionic arsenic species such as arsenate and arsenite adsorb at the iron oxyhydroxide surface by forming complexes with the surface sites. Our goal has been to load as much iron within the carbon pores as possible while also rendering as much of the iron to be available for sorbing arsenic. Surface oxidation of carbon by HNO_3/H_2SO_4 or by $HNO_3/KMnO_4$ increased the amount of iron that could be loaded to 7.6–8.0%; arsenic stayed below 10 ppb until 12,000 bed volumes during rapid small-scale tests (RSSCTs) using Rutland, MA groundwater (40–60 ppb arsenic, and pH of 7.6–8.0). Boehm titrations showed that surface oxidation greatly increased the concentration of carboxylic and phenolic surface groups. Iron impregnation by precipitation or iron salt evaporation was also evaluated. Iron content was increased to 9–17% with internal iron-loading, and to 33.6% with both internal and external iron loading. These iron-tailored carbons reached 25,000–34,000 bed volumes to 10 ppb arsenic breakthrough during RSSCTs. With the 33.6% iron loading, some iron peeled off.

1. Introduction

With its well-established consequences to human health, the presence of arsenic in water has become an important issue in water and wastewater treatment. Long-term exposure to arsenic can cause cancer of the bladder, lungs, skin, kidney, liver and prostate (NRC, 1999). Sources of arsenic contamination include both natural and anthropogenic (industrial waste, mining, agricultural, etc.) (Berg et al., 2001; Jekel, 1994). New USEPA regulations effective on February 2002 reduced the maximum contaminant level (MCL) to 10 μg/L by the year 2006 (USEPA, 2002). The lowering of this MCL makes it necessary to find novel technologies to meet the regulation. Enhanced coagulation, membrane filtration, ion exchange and adsorption are technologies that have received much attention in recent years. In general, adsorption is considered to be more effective and efficient than membrane filtration. Moreover, adsorption processes need not produce sludge as with coagulation (Schnoor, 1996).

The most widely studied media for adsorption processes include iron hydroxide and oxide (such as amorphous hydrous ferric oxide, ferrihydrite and goethite) (Fendorf et al., 1997; Raven et al., 1998; Driehaus et al., 1998; Appelo et al., 2002), activated alumina (Singh and Pant, 2004; Kuriakose et al., 2004), activated carbon (Huang and Vane, 1989; Vaughan and Reed, 2005; Gu et al., 2005), silica and phyllosilicates (Xu and Axe, 2005), cellulose sponge (Munoz et al., 2002), sand (Lo et al., 1997) and zeolite (Onyango et al., 2003). Studies revealed that iron (III) has a high affinity toward inorganic arsenic species and it is very selective in the sorption process (Deliyanni et al., 2003). Removal has been attributed to ion exchange, specific adsorption to surface hydroxyl groups or coprecipitation. Recent research has focused on creating cheap and stable iron-bearing support

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**Corresponding author.* Tel.: +814 863 8754; fax: +814 863 7304.
E-mail address: fsc1@psu.edu (F.S. Cannon).

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media including sand (Vaishya and Gupta, 2003), activated carbon (Huang and Vane, 1989; Reed et al., 2000; Gu et al., 2005; Vaughan and Reed, 2005), incinerator melted slag (Zhang and Itoh, 2005), cellulose (Guo and Chen, 2005) and macroporous cation exchange beads (DeMarco et al., 2003; Katsoyiannis and Zouboulis, 2002). Gu et al. (2005) surmised that dissolved ferrous iron could diffuse deep into the internal pores of granulated activated carbon. They used an oxidation step (by NaClO) after ferrous diffusion to convert it into ferric. The ferric species would then cross-link with functional groups on the carbon. Deliyanni et al. (2003) indicated the varieties of iron oxides differ in their affinity for arsenic. They reported that akaganeite had higher arsenate adsorption capacity than other Fe mineral phases such as hydrous ferric oxide, am-FeOOH and goethite.

The combination of activated carbon and iron loading would take advantage of the strength of these two materials. The activated carbon serves as an ideal support media for iron preloading. Concertedly, the iron that is preloaded offers high affinity for arsenate and arsenite. Studies have shown that aqueous oxyanions (such as $H_2AsO_4^-$ or $HAsO_4^{2-}$) undergo a ligand exchange reaction with iron speciation on the carbon surface and form an inner-sphere monodentate or bidentate surface complex (Fuller et al., 1993; Grossl et al., 1997). This As adsorption onto Fe is specific. Our hypothesis has been that the amount of arsenic removed is closely related both to the amount of iron loaded, and to the dispersion and surface accessibility of this iron within the activated carbon. The objectives of this research are to enhance iron preloading and increase the availability of the iron for sorbing arsenic.

2. Materials and methods

2.1. Materials

All chemicals were of reagent grade. Iron chemicals were from Fisher Scientific Company. Arsenic solutions were made from $Na_2HAsO_4 \cdot 9H_2O$ for arsenate and As_2O_3 for arsenite. Both are from Alfa Aesar.

Activated carbons used included UltraCarb from Siemens Water Technologies (formerly US Filter) (bituminous coal carbon), SAI carbon (bituminous) from Superior Adsorbents Inc., SuperDarco carbon (lignite) from NORIT Americas and three wood-based carbons: NORIT C-Gran (from NORIT), Nuchar (from Westvaco) and PICASOL carbon (from PICA). SuperDarco is a mesoporous carbon developed at Penn State (Nowack et al., 2004; Rangel-Mendez and Cannon, 2005) with surface area of 797 m^2/g, a micropore (<20 Å) volume of approximately 0.2 mL/g carbon and a mesopore volume (20–500 Å) of approximately 0.3 mL/g carbon while UltraCarb has a surface area 723 m^2/g, a micropore volume of 0.3 mL/g and a mesopore volume of 0.1 mL/g. The PICA carbon had a surface area of 1462 m^2/g and a micropore volume of 0.4 mL/g.

The groundwater originated from the well of the Cool Sandy Beach Community Water System of Rutland, MA and has been identified as Rutland water herein. The total arsenic in this groundwater was 40–60 ppb with 70–75% As(V) and 25–30% As(III). The total iron of this water was less than 3 ppb, sulfate was 26 mg/L and silica 12.5 mg/L. The Rutland water had a native pH 7.6–8.0 and this pH was not adjusted unless specifically identified herein.

2.2. Methods

2.2.1. Carbon oxidation plus iron loading

Three oxidation protocols were tested:

> *Protocol 1: Oxidation by nitric acid*: 2 g of carbon (US mesh 200 × 400) was mixed with 100 mL of 70% nitric acid for 1 h at room temperature.
>
> *Protocol 2: Oxidation by nitric acid/sulfuric acid mixture*: 2 g of carbon (US mesh 200 × 400) was mixed with 100 mL of acid mixture (50 mL of each concentrated acid) for 1 h at room temperature.
>
> *Protocol 3: Oxidation by nitric acid, acetic anhydride and potassium permanganate*: 3 g of carbon (US mesh 200 × 400) was first mixed with 2.1 g of potassium permanganate and then added to a solution of 15 mL of 70% nitric acid and 20 mL of concentrated acetic anhydride. The whole mixture was then stirred for an hour at room temperature.

Oxidized carbons were thoroughly washed by distilled water to remove residual acid adsorbed before iron loading with 1 L of 10^{-2} M iron solution made from either ferric or ferrous chloride. The pH during iron loading remained between 2.0 and 3.2. The carbon was then filtered, washed and dried at 105 °C for further use.

Boehm titrations (Boehm and Diehl, 1964) were carried out to monitor the acidic surface functional groups of the oxidized carbons. Details of Boehm titrations as adopted for these carbons could be found in Chen et al. (2005).

2.2.2. Iron-impregnation by precipitation

Carbon used for iron impregnation included UltraCarb, SuperDarco and SAI carbon.

Impregnation by precipitation into activated carbon was conducted in a similar manner to that employed by Thirunavukkarasu et al. (2003) for precipitating iron on silica sand. Two grams of carbon was added to 8 mL of 2 M $Fe(NO_3)_3 \cdot 9H_2O$ solution, and 0.1 mL 10 M sodium hydroxide was added to increase the pH to 4–5 and create an iron precipitate. The mixture was heated at 105 °C overnight. Upon cooling, the activated carbon became covered with a thick layer of orange-colored iron oxide. The GAC had to be separated mechanically with a glass rod to separate the grains, and it was then sieved through a US mesh #400 sieve. To remove the external iron fines and carbon fines, the coated activated carbon was then washed thoroughly with deionized-distilled water until the orange-colored precipitates were removed. The sample was designated as *precipitation UltraCarb* or *precipitation SuperDarco*. The *precipitation SAI* was subjected only to sieving without washing and was named *coating SAI* herein.

2.2.3. Iron-impregnation by iron-salt evaporation

This method was adopted from the method proposed by Vaishya and Gupta (2003) for iron-impregnated sand. To achieve an iron oxide impregnation on activated carbon, 2 g