



## Enhanced removal of arsenite from water by a mesoporous hybrid material – Thiol-functionalized silica coated activated alumina

Jumin Hao, Mei-Juan Han, Chao Wang, Xiaoguang Meng\*

Center for Environmental Systems, Stevens Institute of Technology, Hoboken, NJ 07030, United States

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### ABSTRACT

A novel mesoporous hybrid adsorbent prepared by coating an activated alumina (AA) with a mercapto-propyl-functionalized silica was tested for removal of arsenite [As(III)]. Batch experimental results indicated that the thiol-functionalized AA (AA-SH) had an improved adsorption capacity and an enhanced adsorption rate for As(III) compared with AA. In the pH range from 4 to 11, AA-SH exhibited much higher removal efficiency than AA, and the maximum percent removal appeared at pH 7.0 and 8.5 for AA-SH and AA, respectively. The advantages of the hybrid material were further demonstrated by column filtrations using As(III)-spiked aged tap water and groundwater. Approximately 3200 and 350 bed volumes of spiked tap water containing 300 µg/L of As(III) were filtered by AA-SH and AA at pH 7, respectively, before the effluent arsenic concentration increased to the USEPA MCL of 10 µg/L. In a field column test with actual raw groundwater containing ~70 µg/L of total arsenic (~80% as As(III)) and having a pH value of ~7.3, the breakthrough bed volumes were found to be ~3100 and ~800 for the AA-SH and AA, respectively. Batch and column studies also indicated that the AA-SH performed better than or similar to some common adsorbents such as granular ferric oxide (GFO) and granular TiO<sub>2</sub>.

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### 1. Introduction

Arsenic is a common contaminant in drinking water supplies, and long-term exposure to arsenic can cause various cancers and other serious disease [1]. The concentration of arsenic in the environment may be elevated due to certain anthropogenic activities and natural processes [1,2]. Arsenic in drinking water may have affected more than 100 million people worldwide. Many countries including the US have promulgated a more stringent drinking water standard for arsenic with the maximum contaminant level (MCL) of 0.01 mg/L (ppm) [1]. The new arsenic MCL of 0.01 mg/L may affect about 3000 community water systems (CWSs) serving up to 11 million people in the US [3].

In natural waters, arsenic exists primarily as inorganic forms in two predominant oxidation states: pentavalent arsenic As(V) predominating in oxygenated waters and trivalent arsenic As(III) prevailing in more reductive environments [2,4]. In groundwater, which is a major source of drinking water throughout the world, As(III) accounts for up to 67–99% of total arsenic in some areas [5,6]. Compared with As(V), As(III) is more toxic to humans and has higher mobility in the environment [7,8]. Moreover, the removal of As(III) is more difficult than As(V), and therefore, to enhance total arsenic removal, a pre-oxidation of As(III) to As(V) is usually required [9]. However, there are many disadvantages asso-

ciated with pre-oxidation processes including increased chemical cost, prolonged treatment time, extended operational complexity, and especially, the overall viability of the fixed-bed process is diminished to a great extent [10]. Therefore, it is urgent to develop simple and cost-effective As(III) remediation technologies without use of pre-oxidation processes.

Some of the most promising technologies for arsenic removal from groundwater supplies are adsorption processes using metal (hydr)oxide media/minerals such as aluminum (hydr)oxide [11–13], ferric (hydr)oxide [14–18], titanium oxide [19–21] and zirconium oxide [22]. Activated alumina (AA), as a low-cost adsorbent possessing a high surface area and a distribution of both macro- and micropores, has been used as the arsenic adsorbent extensively and classified among the best available technologies (BAT) for arsenic removal from water [1,12]. However, the conventional commercially available AA has ill-defined pore structures, low adsorption capacities and exhibits slow kinetics [23]. Furthermore, the uptake of As(III) by AA is much less than that of As(V) [24]. For these reasons, modifications of AA with iron oxide [25–27], iron hydroxide [28], manganese [29], alum [30] and biopolymer chitosan [31] have been conducted to obtain hybrid adsorbents with enhanced adsorption performance for arsenic.

On the other hand, it is well established that As(III) strongly binds to the mercaptan (thiol) groups existing in biomolecules such as amino acids, peptides and proteins including some dehydrogenase enzymes, causing irreversible metabolic impairments and, in some cases, cellular mutagenesis, which explains the higher

\* Corresponding author. Tel.: +1 201 216 8014; fax: +1 201 216 8303.

E-mail address: [xmeng@stevens.edu](mailto:xmeng@stevens.edu) (X. Meng).

toxicity of this species [8,32,33]. Based on the above understanding, some thiol-based media including polymer resins [34–36], silica gels [37,38] and biomass [39] have been developed for As(III) removal, and some of them exhibited the selective removal of As(III) and had high adsorption capacities. Recently, we developed a simple, cost-effective and environmentally benign approach to prepare novel mesoporous hybrid adsorbents by modifying AA directly with a mercaptopropyl-functionalized silica. The hybrid adsorbents i.e. thiol-modified AA (AA-SH) have been proven to be more effective for As(III) removal than unmodified AA [40]. The hybrid adsorbents take advantage of the strengths of AA and mercaptopropyl silica. The AA serves as a good support medium for the preloading of active thiol groups. Concertedly, the thiol groups that are preloaded offer a high affinity for As(III).

In this paper, the novel hybrid adsorbent was evaluated for As(III) removal from water by batch experiments and field filtration tests. Investigations of the As(III) adsorption isotherm, kinetics and pH effect were conducted. Various equilibrium isotherm models and kinetics models were used to fit the experimental data. The performance of the new adsorbent was evaluated by comparing As(III) removal efficiencies and breakthrough behaviors for the hybrid adsorbent and other common adsorbents, such as AA, GFO and TiO<sub>2</sub>.

## 2. Materials and methods

### 2.1. Materials and chemicals

Sodium arsenite (NaAsO<sub>2</sub>, Certified) and (3-mercaptopropyl)triethoxysilane (MPTS, 80%, technical) were purchased from Fisher Scientific (Fair Lawn, NJ, USA) and Aldrich (Milwaukee, WI, USA), respectively. All other chemicals used in the experiments were analytical grade and purchased from Aldrich or Fisher Scientific and used as received. The activated alumina (AA-400G-48 MESH) was obtained from Alcan Specialty Aluminas (Brockville, ON, Canada), and sieved with a 70 mesh sieve to removal fine particles. The sieved AA was measured to have a BET specific surface area of 237 m<sup>2</sup>/g and an average pore diameter of 5.24 nm. The thiol-functionalized mesoporous hybrid adsorbent AA-SH with the surface area of 202 m<sup>2</sup>/g and the average pore diameter of 4.78 nm was prepared by blending the sieved AA with pre-synthesized thiol-functionalized silica sol. Briefly, 10 µL of 1 M HCl solution was added into a solution prepared with 3.3 mL of MPTS and 25 mL of 95% ethanol. The mixture was purged with nitrogen gas for 30 min followed by shaking for 24 h at 75 °C. After the mixture was cooled to room temperature, 30 g of AA was added and mixed completely. The product was air-dried under a hood overnight and then dried at 75 °C for 48 h under vacuum. Thus, the mercaptopropyl-functionalized silica from the MPTS hydrolysis-condensation reaction was coated onto the AA to form the AA-SH adsorbent. This is a sol-gel-like process and physical coating took place. The GFO (30–60 mesh, Apyron Technologies, Georgia), and TiO<sub>2</sub> (40–80 mesh, Graver Technologies, Inc., Glasgow, DE) were used as received. The 1000 mg/L As(III) stock solution was prepared every week by dissolving NaAsO<sub>2</sub> in Milli-Q ultrapure water and kept below 4 °C. The As(III) working solutions used in batch and column experiments were freshly prepared by diluting the stock solution with aged tap water that had been purged with nitrogen gas for at least 30 min prior to use. The chemical compositions of the aged tap water are summarized in Table 1. Oxygen-free nitrogen gas (purity 99.999%, AGL Welding Supply Co., Clifton, NJ, USA) was used in the laboratory experiments.

### 2.2. Batch experiments

All the batch experiments were conducted in acid-washed PET bottles under nitrogen atmosphere. 1.0 g/L of each adsorbent was

shaken with 100 or 1000 mL of As(III) aqueous solutions with the desired initial concentrations. In order to monitor and ensure that the As(III) was not significantly oxidized during adsorption, speciation analysis was conducted, and the results indicated that only 10–15% of the soluble As(III) was oxidized after three days of mixing.

Adsorption isotherms were obtained by adding different amount of As(III) stock solution to seven suspensions containing 0.10 g AA or AA-SH to obtain a series of 100 mL of mixtures with the desired initial As(III) concentrations (2.00, 5.00, 8.00, 11.0, 14.0, 17.0 and 20.0 mg/L). After the solution pH values were adjusted to 7.0 ± 0.1 by adding 0.1 M HCl and NaOH, the suspension bottles were placed on a rotary mixer and shaken at room temperature. The final pH of the suspension was controlled at 7.0 ± 0.1. After 42 h of mixing, 1.5 mL of sample was taken from each suspension and centrifuged for 10 min to separate the solution from the solid for analysis of residual arsenic concentration. Similar experiments were carried out using an initial As(III) concentration of 5.0 mg/L and varying the solution pH in the range of 4–11 to examine the effect of pH on As(III) adsorption. After 32 h of mixing, the final pH values of the suspensions were measured. For comparison with GFO and TiO<sub>2</sub>, the same experimental conditions were applied to each adsorbent using solutions with an initial As(III) concentration of 5.0 mg/L at neutral pH.

Adsorption kinetics experiments were carried out to determine the adsorption rates and the reaction time to reach adsorption equilibrium. Under nitrogen atmosphere, 5 mL of As(III) stock solution was added to a suspension containing 1.00 g of AA or AA-SH in 995 mL of aged tap water to obtain 1000 mL of suspension with an initial As(III) concentration of 5 mg/L. After the solution pH was adjusted to 7.0 ± 0.1 by adding 0.1 M HCl and NaOH, the suspension bottles were placed in a tumbler and mixed at room temperature. A nitrogen atmosphere and neutral pH were maintained throughout the experiment. At different time intervals (0.08, 0.18, 0.37, 0.67, 1.17, 2.17, 3.5, 5.3, 8, 12, 24, 31, 52, 76, 100 h), 1.5 mL of sample was taken each time and centrifuged for 10 min to separate the solution from the precipitate for analysis of residual arsenic concentration.

### 2.3. Column experiments

In the laboratory column tests, a solution of 300 µg/L of As(III) was prepared by adding the As(III) stock solution into the aged tap water which had been purged with nitrogen gas for about 1 h. After the pH was adjusted to 7.0 ± 0.2 by adding 1 M HCl and NaOH, the solution was pumped downward into two filtration columns (10 mm ID and 100 mm length) packed with 5 mL of AA (4.3 g) and AA-SH (4.8 g), respectively. A constant flow rate of 2.0 mL/min was applied, which corresponded to an empty bed contact time (EBCT) of 2.5 min. Throughout the filtration, nitrogen gas was continuously sparged into the feeding solution to diminish As(III) oxidation. Effluent solution was collected at different time intervals for the analysis of arsenic concentration. A similar experiment was performed using a feeding solution with a pH of 8.5 ± 0.2 to examine the effect of pH on the removal of As(III) in the continuous-flow fixed-bed operational conditions. To compare the new adsorbent with other commonly used adsorbents besides AA, one more test including four columns packed with 5 mL of AA (4.3 g), AA-SH (4.8 g), GFO (2.9 g) and TiO<sub>2</sub> (4.2 g) was carried out. The pH of the feeding solution was kept at 7.0 ± 0.2, and the flow rate of 3 mL/min was applied. Sodium sulfite (Na<sub>2</sub>SO<sub>3</sub>, 75 ppm as sulfide) was added to the feeding solution to minimize the As(III) oxidation.

Field filtration tests were conducted at a well in New Jersey. The chemical compositions of the well water are also summarized in Table 1. The total arsenic content in the well water was about 70 µg/L, with ~80% as As(III). The well water was filtered through

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