Effect of particle size of drinking-water treatment residuals on the sorption of arsenic in the presence of competing ions

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HIGHLIGHTS

- Al-WTR showed higher As(III) and As(V) sorption capacity than Fe-WTR.
- The effect of particle size on As sorption was more pronounced on Fe-WTR.
- As(III) sorption on both WTRs increased up to neutral pHs and then decreased.
- Competing ligands inhibited As sorption on WTRs following the sequence: OX < CIT < P.
- The higher the As residence time on WTRs the lower the As desorption by ligands.

ARTICLE INFO

ABSTRACT

Arsenite [As(III)] and arsenate [As(V)] sorption by Fe- and Al-based drinking-water treatment residuals (WTR) was studied as a function of particle size at different pHs, and in the presence of competing ligands, namely, phosphate, citrate, and oxalate. Both WTRs showed high affinity for As oxyanions. However, Al-WTR showed higher As(III) and As(V) sorption capacity than Fe-WTR because of their greater surface area. The effect of particle size on As sorption was pronounced on Fe-WTR, where the smaller fraction sorbed more As(III) and As(V) than the larger fractions, whereas relatively minor effects of particle size on As sorption was observed for Al-WTR. Arsenite sorption on both WTRs increased with increasing pH up to circum-neutral pHs and then decreased at higher pHs, whereas As(V) sorption decreased steadily with increasing pH. The capacity of competing ligands to inhibit sorption was greater for As(III) than As(V) on both WTRs (particularly on Al-WTR) following the sequence: oxalate < citrate < phosphate. It was also a function of As ion residence time on the WTR surfaces: the longer the residence time, the less effective were the competing ligands in As desorption.

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1. Introduction

Arsenic (As) is extremely toxic for humans, animals and plants. It is ubiquitous in nature, and in terms of abundance, it ranks 20th in the earth's crust, 14th in seawater and 12th in the human body [1,2]. Presence of As in the environment may be due to natural processes (weathering reactions, biological activities and volcanic emissions), and/or due to anthropogenic activities [1,3–5]. The most common oxidation numbers of As are (+5), (+3) and (−3), in which the element is able to form both inorganic and organic compounds in the environment, and in the human body [6]. However, it exists predominantly as oxyanions in the nature.

Arsenic contamination of surface and ground waters occurs worldwide and has become a socio-political issue in several parts of the world, particularly in Southeast Asia (e.g., Bangladesh). The greatest risk imposed by As on human health is due to contamination of drinking-water above the World Health Organization recommended maximum limit of 1.33×10^{-4} mmol As L^{-1}. Continued ingestion of drinking-water with hazardous levels of As can lead to arsenicosis, and cancers of the bladder, skin, lungs, and kidneys [1]. At present, more than 100 million people are drinking As-contaminated waters in Gangetic India [7,8] and Bangladesh [9]. People from China [10], Vietnam [11], Taiwan [12], Chile [13], Argentina [14], and Mexico [15] are likely at risk as well.

The majority of the As treatment technologies for contaminated water are cost-prohibitive for small communities, or for developing countries, which are likely to face expensive and technically imposing challenges to meet the recommended maximum limit

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of 1.33×10^{-4} mmol As L^{-1} [16,17] in drinking water. At this time, only a few technologies for As removal at the household level, such as Solar Oxidation and Removal of As (SORAS) seem to be economically feasible in these areas [18,19]. Several models show a wide range of costs for the different technologies, which can hinder effective implementation of As removal programs/technologies from contaminated sources [20]. For these reasons, it is extremely important to investigate sustainable As remediation technologies that have the capability to remove As from contaminated waters in an inexpensive and safe way.

The utilization of industrial by-products, such as the drinking-water treatment residuals (WTR), as As sorbents, is gaining popularity due to their environment-friendly and cost-reductive advantages. These by-products can be easily obtained at minimal costs from the drinking-water treatment plants as they are by-products of the water treatment process. Addition of iron (Fe) or aluminum (Al) salts to raw waters removes colloids, colors and sediments; this process generates the WTRs, which contain very high concentrations of Al- or Fe-hydroxides [21,22]. The drinking-water treatment industry in the US generates more than 2 million tons of WTRs every day [23], thus, making them easily available. Previous studies have reported minimal leaching from the WTRs subjected to TCLP procedure, making them safe to use as a sorbent media [21,22,24].

Makris et al. [21] demonstrated high capacity of Al- and Fe-WTRs in removing As from aqueous solutions, with minimal desorption. X-ray absorption spectroscopy studies showed strong inner-sphere complexes between As ions and the WTR surfaces [24,25]. Sorption of As(V) on these WTRs at different solution pHs has been also studied [22]. However, there is a lack of information on the effect of particle size on the sorption of As(III) and As(V) ions by Al- and Fe-WTRs, and in the presence of competing anions, which are commonly present in aquatic environments. Vice versa, studies on the effect of particle size of other sorbents, such as magnetite, on the sorption of As have been carried out [26,27]. The size of the sorbent particles plays an important role in determining the ultimate applicability of Al- and Fe-WTRs as potential filter media. Larger surface area is typically achieved via reduction of the diameter of sorbent particles [28], which could significantly influence the reactivity of the WTR surfaces toward As ions. However, smaller particle size typically translates to lower hydraulic conductivity [29], which poses a practical problem while developing the filter media. Hence, it is important to strike a balance between particle size and As reactivity on the WTR surfaces.

The reported work evaluated As(III) and As(V) sorption by Fe- and Al-WTR samples as a function of particle size (1000–590, 590–250, 250–125 and <125 μm), in the absence or presence of inorganic [phosphate (P)], and organic [citrate (CIT) and oxalate (OX)] anions that may compete with As anions for adsorption sites on the WTR surface.

2. Materials and methods

2.1. WTR collection and generation of the various size fractions

The Al-based WTR sample was obtained from the drinking-water treatment plant in Bradenton, FL, USA, where the addition of alum and very small amounts of a copolymer of sodium acrylate and acrylamide produce these Al-based by-products. The Fe-based WTR sample was obtained from the Hillsboro River drinking-water treatment plant in Tampa, FL, USA, where iron sulphate is used as the coagulant.

Both WTR samples were originally sampled from stockpiles that were formed within one year of production. They were allowed to air-dry, milled in a china mortar and subsequently passed

through four different sieves having 1000, 590, 250 and 125 μm of pore diameters, respectively, in order to obtain four different sub-samples of Al- and Fe-WTR, each characterized by its own particle size: 1000–590, 590–250, 250–125 and <125 μm.

2.2. WTR characterization

The smallest Al- and Fe-WTR fraction (<125 μm) was characterized for several chemical properties (i.e., total C, N, P, Al, Fe and As) and also by X-ray diffraction (XRD), Fourier transform infrared (FT-IR) spectroscopy, and thermo-gravimetric analysis (TGA).

Total C and N were determined by combustion at 1010 °C using a Carlo Erba NA-1500 CNS analyzer. Samples of Al- and Fe-WTRs (0.5 g each) were weighed into PTFE vessels and digested in 15 mL of HNO$_3$ (65%). Solutions were filtered through 0.22-μm membrane filters and diluted to 50 mL. Total P was determined in the filtrates by inductively coupled plasma atomic emission spectroscopy (ICP-AES, Varian, Liberty 150), total Fe and Al were determined by atomic absorption spectrometer (AAS) using a Perkin-Elmer AAnalist 700 and total As was determined by flow-injection hydride generation atomic absorption spectrometer (Perkin-Elmer AAnalist 700 interfaced with the FIAS 100 hydride generator).

X-ray diffraction patterns of randomly oriented samples were obtained using a Rigaku diffractometer (Rigaku Co., Tokyo) equipped with Cu Kα radiation generated at 40 kV and 30 mA and a scan speed of 2° 2θ min^{-1}. The FT-IR spectra were obtained by diffuse reflectance infrared Fourier transform (DRIFT) spectroscopy using a Perkin-Elmer Spectrum One FT-IR Spectrophotometer (Perkin Elmer USA), with a spectral resolution of 1 cm^{-1}. Thermo-gravimetric analysis (TGA) was obtained using a simultaneous thermal analyzer (Perkin Elmer STA 6000) in a nitrogen flow (20 mL min^{-1}) with a heating rate of 10 °C min^{-1}, using air atmosphere, and temperature ranging from 30 to 900 °C.

The surface area of all Al- and Fe-WTRs sub-samples was determined by H$_2$O sorption at 20% relative humidity [30].

2.3. Arsenite and As(V) sorption on Al- and Fe-WTR

Suitable volumes of 25 mmol L^{-1} solutions containing As(III) as NaAsO$_2$ or As(V) as Na$_2$HAsO$_4$ were added to 100 mg of Al- and Fe-WTR samples. Initial As(III) and As(V) concentrations ranged from 0.125 to 6.25 mmol L^{-1} for the Al-WTR samples and from 7.5×10^{-2} to 2.5 mmol L^{-1} for the Fe-WTR samples. The final volume was adjusted to 20 mL with 10 mmol L^{-1} KCl, and the initial WTR/solution ratio was fixed at 5 g L^{-1}. The pH of each suspension was kept constant at 6.0 for 24 h at 20 °C by adding 100 or 10 mmol L^{-1} HCl or NaOH using an automatic titrator (Potentiograph E536 Metrom Herisau) in conjunction with an automatic syringe (burette 655 Dosimat).

The sorption of As(III) and As(V) onto the Al- and Fe-WTR sub-samples as a function of pH (from 3.0 to 9.0) was carried out by adding suitable amounts of As(III) or As(V) (a quantity 30–40% higher than that necessary to reach a maximum sorption of each WTR sub-samples at pH 6.0, as determined by sorption isotherms) to 100 mg of each sub-sample. The final volume was adjusted to 20 mL with 10 mmol L^{-1} KCl, and the initial WTR/solution ratio was fixed at 5 g L^{-1}. The pH of the systems was kept constant for 24 h at 20 °C by adding 100 or 10 mmol L^{-1} HCl or NaOH using the automatic titrator and syringe.

Suspensions were centrifuged at 5000 × g for 20 min and then filtered through 0.22-μm membrane filters. The filtrates were stored at 2 °C until analysis. The experiments were conducted in triplicates.