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Surface arsenic speciation of a drinking-water treatment residual using X-ray absorption spectroscopy

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Abstract

Drinking-water treatment residuals (WTRs) present a low-cost geosorbent for As-contaminated waters and soils. Previous work has demonstrated the high affinity of WTRs for As, but data pertaining to the stability of sorbed As is missing. Sorption/desorption and X-ray absorption spectroscopy (XAS), both XANES (X-ray absorption near edge structure) and EXAFS (extended X-ray absorption fine structure) studies, were combined to determine the stability of As sorbed by an Fe-based WTR. Arsenic(V) and As(III) sorption kinetics were biphasic in nature, sorbing $>90\%$ of the initial added As ($15{,}000\ \mathrm{mg\,kg^{-1}}$) after 48 h of reaction. Subsequent desorption experiments with a high P load ($7500\ \mathrm{mg\,kg^{-1}}$) showed negligible As desorption for both As species, approximately $<3.5\%$ of sorbed As; the small amount of desorbed As was attributed to the abundance of sorption sites. XANES data showed that sorption kinetics for either As(III) or As(V) initially added to solution had no effect on the sorbed As oxidation state. EXAFS spectroscopy suggested that As added either as As(III) or as As(V) formed inner-sphere mononuclear, bidentate complexes, suggesting the stability of the sorbed As, which was further corroborated by the minimum As desorption from the Fe-WTR.

Keywords: Residuals; Drinking water; Stability; Arsenic (As); XANES; EXAFS; Remediation

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1. Introduction

Enhanced coagulation, activated alumina, granular ferric hydroxide, granular titanium dioxide adsorption, and membrane technologies are typically used to treat As-contaminated soils and waters. However, the use of the aforementioned technologies is usually associated with a significant economic cost [1]. Budget restrictions of small communities and households call for development of low-cost, but equally effective As geosorbents. The utilization of the waste by-product generated from the drinking-water treatment process, i.e., the drinking-water treatment residuals (WTRs), has been suggested as a cost-effective technology for prospective contaminants. Several authors have demonstrated that WTRs can serve as low-cost soil amendments to reduce environmental impacts of various oxyanions, notably phosphorus (P) [2–6]. The WTRs are primarily amorphous masses of iron (Fe), aluminum (Al) hydroxides, or $CaCO_3$ that also contain sediment and humic substances removed from the raw water, as well as coagulating agents added to raw water, such as activated carbon and polymers [2]. Depending on the metal salt used, the resulting WTRs are referred to as Al-WTRs (use of Al salt), Fe-WTRs (Fe salt), or Ca-WTRs ($CaCO_3$).

Earlier batch experiments in our laboratory have demonstrated the huge affinity of WTRs in removing As from aqueous solutions, reaching As sorption capacities of at least $15{,}000\ \mathrm{mg\,kg^{-1}}$ [7]. Our intent of using WTRs to remediate contaminated soils is challenged by the lack of data that support the stability of As sorbed by WTRs. In the case of soils, the stability of As sorbed by WTR-amended soils is currently unknown. A combination of macroscopic and microscopic measurements was undertaken in this study to evaluate the relative stability of As sorbed by WTRs. Sorption kinetics

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experiments and subsequent desorption with a high P load, typically encountered in soil/landfill environments, was used along with measurements that aid in the determination of the bonding strength of bound As ions. The surface complexes between As and WTR were determined using X-ray absorption near-edge spectroscopy (XANES) and extended X-ray absorption fine structure (EXAFS) spectroscopy.

EXAFS spectroscopy has been widely used to study the bonding mechanism of As by common As geosorbents, such as Fe oxy(hydr)oxides [8,9]. EXAFS work has shown inner sphere complexation between As and Fe hydroxides [10–12]. Several EXAFS studies [8,10–12] found that bidentate binuclear complexation was the major bonding mechanism for arsenate adsorption on goethite. Amorphous Fe hydroxides may constitute a major fraction of the chemical composition of the Fe-based WTRs, but other constituents such as humic and fulvic acid with other impurities present WTR particles with a complex organomineral assembly. The highly heterogeneous physicochemical nature of Fe-WTRs limits our ability to predict As(III) and As(V) affinity toward WTR surfaces and the binding mechanism.

Thus, the objectives of this study were (i) to evaluate the effect of As oxidation state (III and V) and reaction time (10 min and 48 h) on the Fe-WTR surface and the speciation of the sorbed As using XANES, and (ii) to determine the effect of As oxidation state (III and V) and reaction time (10 min and 48 h) on the local atomic coordination environment of the As after sorption by the Fe-WTR using EXAFS spectroscopy.

2. Materials and methods

2.1. WTR collection

The Fe-based WTR was obtained from the drinking-water treatment plant in Tampa, Florida, USA. The Fe-WTR was produced through the addition of $Fe_2(SO_4)_3$, which leads to coagulation and flocculation of organic as well as inorganic contaminants present in the raw water. The Fe-WTR was originally sampled from stockpiles that were formed within 1 year of production. The Fe-WTR subsamples were allowed to air-dry and were subsequently passed through a 2-mm sieve before analyses.

2.2. General physicochemical properties of the Fe-WTR

General chemical characterization of the Fe-WTR has been reported elsewhere [13]. In brief, pH and soluble reactive As concentrations of the WTR were measured in a 0.01 M KCl solution at a 1:10 ($g\,mL^{-1}$) solid:solution ratio after 10 days of reaction. Total C and N were determined by combustion at 1010 °C using a Carlo Erba NA-1500 CNS analyzer. Total recoverable P, As, Fe, and Al were determined by inductively coupled plasma mass spectroscopy (ICP-MS) following digestion according to the EPA Method 3050B [14]. Oxalate-extractable P, As, Fe, and Al were determined by ICP-MS after extraction at a 1:60 solid:solution ratio, following the procedures of McKeague et al. [15]. Method reagent blanks, certified external standard analyses, and new standard curves for each set of samples were used.

2.3. Arsenic(V) and arsenic(III) sorption/desorption

Arsenic sorption isotherms (23 °C) were constructed for the Fe-WTR using batch equilibration experiments. Stock standard solutions of As(V) and As(III) were prepared in 0.01 M KCl from $Na_2HAsO_4\cdot 7H_2O$ (KR Grade, Aldrich, USA) and $NaAsO_2$ (KR Grade, Aldrich, USA), respectively. Phosphate stock solution was prepared from $NaH_2PO_4\cdot H_2O$ (Merck). Plastic reaction vessels were cleaned with 2% HNO_3 and rinsed three times with deionized water before use. All of the sorption experiments were performed using a 0.01 M KCl background electrolyte. The pH of the stock As standard solutions was adjusted to 6, using small quantities of 1 N HCl.

Representative air-dried (<2-mm) samples of the Fe-WTR were reacted with inorganic As in 1:10 ($g\,mL^{-1}$) solutions at As(V) or As(III) loads of 15,000 $mg\,As\,kg^{-1}$ for 48 h to determine As sorption kinetics at 23 ± 2 °C, varying the contact time (0, 1, 2, 4, 8, 16, 32, 48 h). The 1:10 ($g\,mL^{-1}$) solid:solution ratio was selected based on our earlier P sorption experiments with WTRs [13]. In the case of As(III), extra care was taken to remove the air from the test tubes via purging with N_2 gas and butyl rubber capping before initializing the sorption and desorption experiments.

For all experiments, the suspension pH did not fluctuate much during sorption experiments (±0.3 units from initial pH; see Table 1). Suspensions were shaken (120 rpm) during the equilibration period. Following the shaking period, suspensions were centrifuged (3000*g*), filtered (0.45 μm pore size), and analyzed for As and P using an ICP-MS (Elan 9000, Perkin–Elmer).

After sorption, the supernatant was removed and WTR-containing tubes were filled with 750 $mg\,P\,L^{-1}$ phosphate solution (1 g WTR:10 ml P solution ratio) to test the ability of phosphate to produce As desorption from the WTRs. We intentionally chose a relatively high P load that was half of that for As (7500 $mg\,P\,kg^{-1}$) in order to monitor As desorption during a worst-case scenario. Suspensions were reacted for 1, 2, 4, 8, 16, 32, and 48 h. The amount of As desorbed was calculated as the difference between As sorbed and As measured in solution after the desorption step, accounting for entrained soluble As. The amount of residual P in solution after the completion of the desorption stage was also measured using ICP-MS.

2.4. X-ray absorption spectroscopy

2.4.1. XAS data collection

Samples were packed into 1.0-mm Al sample holders with Mylar tape windows. The samples were run on beamline 2–3 at the Stanford Synchrotron Radiation Laboratory facility (SSRL), Stanford University, California, using the As *K*-edge 11.868 keV and an As^0 internal foil for calibration purposes. Sample spectra were recorded using a Ge 13 element fluorescence detector. The beamline operating conditions were