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Adsorption mechanism of arsenate by zirconyl-functionalized activated carbon

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Abstract

Arsenate [As(V)] and arsenite [As(III)] sorption at the solid–water interface of activated carbon impregnated with zirconyl nitrate (Zr-AC) was investigated using X-ray absorption spectroscopy (XAS) and surface complexation modeling. The XAS data at the Zr K-edge suggest that the structure of the zirconyl nitrate coating is built from chains of edge-sharing ZrO_8 trigonal dodecahedra bound to each other through two double hydroxyl bridges. The 8-fold coordination of each Zr atom is completed by four O atoms, which share a bit less than the two theoretically possible bidentate nitrate groups. On impregnation, two of the O atoms may lose their nitrate group and be transformed to hydroxyl groups ready for binding to carboxylic or phenolic ligands at the AC surface. As K-edge XANES results showed the presence of only As(V) on adsorption regardless of the initial As oxidation state. Oxidation to As(V) is probably mediated by available carbon species on the AC surface as found by batch titration. Zr K-edge EXAFS data indicate that arsenate tetrahedra form monodentate mononuclear surface complexes with free hydroxyl groups of zirconyl dodecahedra, whereby each bidentate nitrate group is exchanged by up to two arsenate groups. The inner-sphere arsenate binding to the Zr-AC surface sites constrained with the spectroscopic results was used in the formulation of a surface complexation model to successfully describe the adsorption behavior of arsenate in the pH range between 4 and 12. The results suggest therefore that Zr-AC is an effective adsorbent for arsenic removal due to its high surface area and the presence of high affinity surface hydroxyl groups.

Keywords: Arsenate; Adsorption modeling; Activated carbon; Zirconyl; EXAFS

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1. Introduction

The toxic and carcinogenic metalloid arsenic has caused major concerns in groundwater and wastewater quality assessments over the past few decades. Consequently many studies have been undertaken to develop and characterize arsenic cleanup techniques [1]. Among the solutions with the best potential to cover all the different spatial, temporal, and compositional scales at which contamination scenarios may occur are scavenging techniques of aqueous arsenic species by specific sorbents. In order to develop such remediation technologies, the adsorption capacity exhibited by each potential sorbent must be examined in relation to its regeneration behavior and cost. Not only should such techniques effectively remove arsenic from water but also be able to do so under the many different locally prevailing hydrochemical conditions. Other sorbates such as ambient major oxoanions could either become competitive or add to the value of the sorbent if no competitive effects deteriorate coadsorption efficiency. A sorbent which efficiently coadsorbs natural and anthropogenic organic pollutants would be particularly desired in the field of waste remediation technology. Mixtures of complementary sorbents for the removal of organic and inorganic species may prove less favorable with respect to their regeneration and cost [1,2]. Activated carbon (AC) functionalized by water-insoluble metal oxide impreg-

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nations serves as a favorable alternative for this purpose in that it contains an ensemble of independent monoprotic surface groups originating from both its carbon (e.g., surface carboxyls –COOH) and its oxide (surface hydroxyls –OH; Refs. [1,2]). Since a large volume of research exists emphasizing iron oxides as efficient inorganic sorbents, it is not surprising that Fe-treated AC has recently been suggested for adsorption of arsenate and arsenite [3]. Use of rare oxides, e.g., titanium, ruthenium, and zirconium, has become cost beneficial due to the relatively low amount of material necessary for impregnating AC. Unlike with Fe oxides, these oxides are (i) inert to redox variations, (ii) have a much greater sorption capacity, and (iii) the presence of other oxoanions does not interfere significantly with the adsorption of As. Zirconium-loaded activated carbon was first used in analytical procedures as an adsorbent material for preconcentrating inorganic compounds of As(V), Se(IV), Se(VI), and Hg(II) in aqueous solutions [4,5]. Water-soluble zirconyl salts have been suggested in U.S. patents for functionalizing porous polymer resins and AC. Thus prepared Zr-AC sorbents feature fast reaction kinetics, their sorption capacity for As is superior to that of Fe oxides, and its As load can readily be desorbed using alkaline (e.g., NaOH) solutions [6]. However, the mechanism of As adsorption by Zr-AC is not yet known in detail. This knowledge is required in order to predict sorption performance under specific conditions and thus develop an optimized filtering technique.

The effectiveness of the sorption processes suggests that As oxoanions may form inner-sphere complexes with Zr-AC surface binding sites. If this is the case, X-ray absorption spectroscopy (XAS) should provide a useful tool for verifying the occurrence of such complexes and characterizing their molecular structure. In adsorption kinetics experiments using different sorbents and different As species, Zr-AC was found to remove aqueous As(V) faster than aqueous As(III), and faster than any other sorbent [6]. The kinetics of As(III) removal indicate that rate-limiting oxidation of As(III) to As(V) catalyzed by surficial carbon compounds may precede the adsorption reaction. This hypothesis is supported by the observation that the concentration of dissolved As(V) increased during the reaction even in an oxygen-free glove box in the presence of AC, but not in the presence of any other inorganic sorbent [6]. A direct speciation of As sorbed on Zr-AC using XAS experiments is thus warranted in order to confirm this hypothesis.

Chemical bonds between Zr and As are known from zirconium arsenates. These materials exhibit highly selective ion-exchange behavior, which is determined by zeolite-like cavities in their layer structures. Only ions that are smaller than the cavities can diffuse into the lattice. A simple coprecipitation method of synthesis is based on mixing As_2O_5 and Zr-dinitrate or Zr-oxychloride in acidified solution, which forms α-zirconium arsenate, $Zr(HAsO_4)_2{\cdot}H_2O$ [7–9]. Its $P2_1/c$ structure consists of layers of ZrO_6 octahedra bridged through hydrogen arsenate moieties that alternate above and below the octahedral layers, with each arsenate tetrahedron bonding to three different ZrO_6 octahedra [7,8]. Another method of synthesis employs hydrothermal treatment of an organic Zr-propoxide solution mixed with As_2O_5 and urea, which forms γ-zirconium arsenate, $Zr(AsO_4)(H_2AsO_4){\cdot}2H_2O$ [10]. Its somewhat more complicated $P2_1$ structure consists of alternating layers of ZrO_6 octahedra and AsO_4 tetrahedra stacked along the 001 direction. Half of the arsenate groups share all four of their oxygen atoms with ZrO_6 octahedra, while the other half are linked axially and possess two exchangeable protons each [10]. Since the formation of such compounds on adsorption of As onto the Zr-AC surface cannot be excluded a priori, both Zr-arsenate modifications were used as reference substances in the present study. If the formation of surface precipitates of these Zr-arsenate compounds plays a role in the adsorption process, similarities in molecular structure between the references and the As-loaded Zr-AC samples should show up in the characteristic features of their respective XAS spectra.

In the present study, the adsorption mechanisms of As(V) and As(III) on Zr-AC were examined using a combination of macroscopic and microscopic techniques including extended X-ray absorption fine structure (EXAFS) spectroscopy and As batch adsorption experiments. The thus elucidated adsorption mechanisms were further used in formulating a surface complexation model to describe As adsorption behavior. The use of these rigorous analytical and modeling approaches enables the accurate determination of the adsorbed arsenic species essential for the prediction of adsorptive properties of these promising new adsorbents.

2. Experimental

2.1. Sample preparation

All stock solutions were prepared using ACS grade chemicals and deionized (DI) water. Granular AC purchased from Chemviron Carbon (Filtrasorb TL 830, bulk volume 1.6 mL g^{-1}) was impregnated with dissolved zirconyl nitrate hydrate solution, $ZrO(NO_3)_2{\cdot}nH_2O$ (purum quality, Fluka 14985-18-3, 25 $g\,L^{-1}$, solution pH 1.3), yielding a Zr concentration of 17 $mg\,g^{-1}$ AC (XRF measurements; Ref. [6]). On thorough washing of the zirconyl-functionalized AC with DI water and gently drying at room temperature, specific surface areas were obtained from nitrogen adsorption isotherms at 77 K using a Micromeritics Gemini 2375 surface area analyzer (Micromeritics, Norcross, GA). The surface areas were determined from adsorption isotherms using the StarDriver v.2.03 software package associated with the surface area analyzer, which by means of the BET equation gave an $S_{BET} = 630\ m^2\,g^{-1}$. Solutions of arsenic were prepared by diluting aqueous standards of As(III) ($NaAsO_2$, 0.05 $mol\,L^{-1}$, Merck) and As(V) (1000 $mg\,L^{-1}$, Merck Titrisol). Three subsamples were then loaded with different As concentrations. For this, a 2.0-g subsample of the Zr-AC was shaken with a solution of either Na-arsenate or Na-arsenite (250 mL carbonate-buffered water solution with an initial As concentration of 200 $mg\,L^{-1}$) for 24 h. The resulting As loadings (dry weight) were 17.1 $mg\,g^{-1}$ (As(V) formulations) and 11.8 $mg\,g^{-1}$ (As(III) formulations) as calculated from the final concentrations in solution (ICP-OES measurements) and confirmed by XRF measurements. Another As(III) sample was processed in an oxygen-free glove box by adding 1.0 g Zr-Ac