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JOURNAL OF ENVIRONMENTAL SCIENCES
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Photooxidation of arsenic(III) to arsenic(V) on the surface of kaolinite clay

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ARTICLE INFO

Article history:
Received 17 December 2014
Revised 14 February 2015
Accepted 12 March 2015
Available online 15 June 2015

Keywords:
Photochemical oxidation
Arsenic speciation
Soil clay minerals
Iron species
Hydroxyl radical

ABSTRACT

As one of the most toxic heavy metals, the oxidation of inorganic arsenic has drawn great attention among environmental scientists. However, little has been reported on the solar photochemical behavior of arsenic species on top-soil. In the present work, the influencing factors (pH, relative humidity (RH), humic acid (HA), trisodium citrate, and additional iron ions) and the contributions of reactive oxygen species (ROS, mainly $HO^{\cdot}$ and $HO_2^{\cdot}/O_2^{\cdot-}$) to photooxidation of As(III) to As(V) on kaolinite surfaces under UV irradiation (λ = 365 nm) were investigated. Results showed that lower pH facilitated photooxidation, and the photooxidation efficiency increased with the increase of RH and trisodium citrate. Promotion or inhibition of As(III) photooxidation by HA was observed at low or high dosages, respectively. Additional iron ions greatly promoted the photooxidation, but excessive amounts of Fe^{2+} competed with As(III) for oxidation by ROS. Experiments on scavengers indicated that the $HO^{\cdot}$ radical was the predominant oxidant in this system. Experiments on actual soil surfaces proved the occurrence of As(III) photooxidation in real topsoil. This work demonstrates that the photooxidation process of As(III) on the soil surface should be taken into account when studying the fate of arsenic in natural soil newly polluted with acidic wastewater containing As(III).

Introduction

Worldwide concerns over inorganic arsenic, a well-known human carcinogen in drinking water, groundwater and soil, have promoted intensive research on its environmental behavior, ecological effects and pollution prevention (Tong et al., 2014; Zan et al., 2014). The toxicity, mobility, and bioavailability of arsenic in the natural soil environment depend strongly on its speciation (Gusiatin, 2014). The predominant inorganic arsenic species on clay surfaces are generally found to be arsenite (As(III)) and arsenate (As(V)). As(III) is more toxic than As(V) in the natural environment. As(V) can be strongly adsorbed onto most soil minerals, including iron and aluminum oxides, especially forming inner-sphere complexes with ferric (hydr)oxides. In contrast, As(III) is poorly associated with minerals, and forms inner- and outer-sphere complexes with ferric (hydro)oxides (Sun and Doner, 1996). Thus, As(III) can be released more readily from the solid phase to the aqueous phase at the mineral–water interface (Manning and Goldberg, 1997). Studies of arsenic speciation and transformation between the two common

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http://dx.doi.org/10.1016/j.jes.2015.03.017

inorganic forms, through both microbiological and chemical processes, are essential in determining the behavior and fate of arsenic in the soil environment (Polizzotto et al., 2013). Furthermore, more attention should be paid to the transformation of As(III) to As(V) in top-soil newly contaminated by acidic mining wastewaters containing As(III).

Significant photooxidation of As(III) was observed in water by ferrous persulfate complexes (Zhou et al., 2013), ferric hydroxy complexes and ferric oxalate complexes (Kocar and Inskeep, 2003). Recent studies from our group indicated that iron from soil minerals (including goethite (Wang et al., 2013a) and montmorillonite (Wang et al., 2013b)) induced the photochemical transformation of As(III) in suspended solutions. Reactive oxygen species (ROS) such as $HO^{\cdot}$ or HO_2/O_2^{-} are responsible for the oxidation. Besides the effect of iron on As(III) oxidation, dissolved organic matter (DOM) has been shown to have the potential to oxidize As(III) in the natural environment under irradiation (Buschmann et al., 2005), and this oxidation was attributed to the production of the excited triplet state of DOM, phenoxyl radical, or both (De Laurentiis et al., 2012).

The importance of the photochemical transformation of pollutants (especially pesticides) on the surface of the soil has been recognized for the last 20 years (Balmer et al., 2000). But for arsenic, no one has considered its changes on the soil surface under sunlight. It is very common that acid mining drainage or some other arsenite-containing wastewaters are poured onto the ground, resulting in soil pollution. In cases when top soil has been newly polluted with arsenite, what will happen with the arsenite on the surface of the soil in a relatively short period (*e.g.* days to weeks), when there are no acclimated microorganisms or the biological transformation is very slow in the soil? Obviously, results from previous published works in suspended solutions cannot answer this question. The photochemical reaction must be investigated on the solid phase of the soil surface, but no such work has been done before.

Photochemical experiments on the soil surface might present some challenges not encountered in aqueous systems (Graebing et al., 2003). Aqueous or suspended systems can be well-mixed, and light attenuation in such systems can be precisely measured. But light attenuation by the soil surface and the adsorption process of As(III) and As(V) on soil are more complex than that in aqueous or suspended solutions. Kaolinite is a predominant clay mineral in normal soils, and it can be used as representative clay. Moreover, kaolinite can be used as a simulated soil to study the process of chemical transformation without any interference by biological factors. Balmer et al. (2000) designed a setup for photodegradation of pesticides (p-nitroanisole and trifluralin) on a kaolinite surface. The kaolinite layer was sandwiched between two Pyrex glass plates with controlled thickness (0.01–0.45 mm).

Based upon the above considerations, a kaolinite layer with thickness about 0.2 mm (about the median thickness used by Balmer et al. (2000)) was designed to conduct the photochemical experiments of this work to explore the mechanism of photooxidation of As(III) on the soil surface. The photooxidation of As(III) on the kaolinite surface was investigated using a photochemical chamber with black-light lamps to simulate solar photochemical processes on the soil surface. The results show that photooxidation can be a relevant pathway of the biogeochemical cycle of the species of arsenic, which is important to the understanding and prediction of the speciation and behavior of arsenic in the top soil.

1. Materials and methods

1.1. Materials and chemicals

Kaolinite from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China) was used without purification. Its particle size distribution and X-ray diffraction (XRD) pattern are presented in Appendix A Figs. S1 and S2. The chemical composition of kaolinite was determined by X-ray fluorescence spectroscopy. It mainly consisted of 52% SiO_2, 44% Al_2O_3, 3.0% MnO, 0.89% TiO_2, 0.73% Fe_2O_3, 0.25% K_2O, 0.34% CaO, 0.42% P_2O_5, and 0.22% Na_2O. Dawang soil from contaminated land in Dawang Town (Hubei, China) was used for tests on actual soil. Its X-ray diffraction (XRD) pattern is presented in Appendix A Fig. S3. The chemical composition of Dawang soil was determined by X-ray fluorescence spectroscopy. It mainly consisted of 9.7% Al, 25% Si, 52% O, 4.2% Fe, 2.7% K and 2.0% Ca. According to XRD and XRF, the soil was estimated to be sandy loam soil (nearly 81% quartz and 18% kaolinite). Analytical grade As_2O_3 from Jinchun Reagent Co., Ltd. (Shanghai, China) was used as the As(III) source. Technical grade humic acid (HA, sodium salt) was purchased from Sigma-Aldrich Chemie GmbH Aldrich Chemical Co. Inc. (Steinheim, Germany) and used without purification. Analytical grade trisodium citrate, 1,3,5-trihydroxybenzene, and 1,2-dihydroxybenzene-3,5-disulfonic acid disodium salt (Tiron) were from Sinopharm Chemical Reagent Co. Ltd. (Shanghai, PRC). Analytical grade H_3PO_4 and L-ascorbic acid (VC, $C_6H_8O_6$) were used for the extraction of arsenic from kaolinite. Analytical grade KBH_4, KOH, and HCl were used for As(III)/As(V) speciation analysis. Argon (99.99%) was used as the carrier gas and shielding gas for hydride generation-atomic fluorescence spectrometry (HG-AFS). The pH of kaolinite samples containing As(III) was adjusted with HCl or NaOH. For pH determination, 2 mL water and 2 g dry samples were mixed and stirred without air for 30 min. Ultrapure water for pH determination was boiled for 30 min to remove CO_2, then the pH of the mixture was determined using a pH meter (pH320-S) from Mettler Toledo Co. (Shanghai, PRC) and represented as the pH of the clay sample. All other reagents in the present work were of analytical grade. Purified water with 18 MΩ cm resistivity generated by a water purification system (Liyuan Electric Instrument Co., Beijing, China) was used throughout this work.

1.2. Preparation of clay layers

Glass petri dishes (60 mm in diameter) shown in Appendix A Fig. S4 were used to plate the kaolinite clay layer. As(III) at a specific concentration was sorbed onto the dry clay surface by addition of exact amounts of kaolinite to a defined amount of aqueous As(III) stock solution at specific pH in a sealed tube before application to the plate. The As(III)-clay suspended slurry was mixed for 15 min by ultrasonication in ice water. Clay was applied onto the center of the glass plate using a single aliquot of the slurry (2 mL). In the photochemical chamber, the As(III)-spiked kaolinite layer was air-dried for