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Evidence for the generation of reactive oxygen species from hydroquinone and benzoquinone: Roles in arsenite oxidation

Wenxiu Qin [a, b], Yujun Wang [a, **], Guodong Fang [a], Tongliang Wu [a, b], Cun Liu [a], Dongmei Zhou [a, *]

[a] *Key Laboratory of Soil Environment and Pollution Remediation, Institute of Soil Science, Chinese Academy of Sciences, Nanjing 210008, China*
[b] *University of Chinese Academy of Sciences, Beijing 100049, China*

HIGHLIGHTS

- As(III) was effectively oxidized to As(V) in the presence of HQ or BQ.
- ESR technique was used to identify the ROS for As(III) oxidation.
- Pathways for ROS generated from HQ and BQ solutions were proposed.
- The As(III) oxidation rate constant (k_{obs}) was calculated at different pH.

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ABSTRACT

Natural organic matter (NOM) significantly affects the fate, bioavailability, and toxicity of arsenic in the environment. In the present study, we investigated the oxidation of As(III) in the presence of hydroquinone (HQ) and benzoquinone (BQ), which were selected as model quinone moieties for NOM. It was found that As(III) was oxidized to As(V) in the presence of HQ or BQ at neutral conditions, and the oxidation efficiency of As(III) increased from 33% to 92% in HQ solutions and from 0 to 80% in BQ solutions with pH increasing from 6.5 to 8.5. The oxidation mechanism was further explored with electron spin resonance (ESR) technique. The results showed that semiquinone radicals ($SQ^{\bullet-}$) were generated from the comproportionation reaction between BQ and HQ, which mediated the formation of superoxide anion ($O_2^{\bullet-}$), hydrogen peroxide (H_2O_2) and hydroxyl radical ($^{\bullet}OH$). Both the $SQ^{\bullet-}$, H_2O_2 and $^{\bullet}OH$ contributed to the oxidation of As(III). The increase of pH favored the formation of $SQ^{\bullet-}$, and thus promoted the generation of reactive oxygen species (ROS) as well as As(III) oxidation. Increasing concentrations of HQ and BQ from 0.1 to 1.0 mM enhanced As(III) oxidation from 65% to 94% and from 10% to 53%, respectively. The findings of this study facilitate our understanding of the fate and transformation of As(III) in organic-rich aquatic environments and highlight quinone moieties as the potential oxidants for As(III) in the remediation of arsenic contaminated sites.

1. Introduction

Arsenic is considered as one of the most significant environmental causes of cancer throughout the world, which has contributed to a number of environmental and human health problems (Nordstrom, 2002; Zhao et al., 2010). Nowadays, the environmental fate and behavior of arsenic has caught global attention due to its extensive contamination in ground, air, and drinking waters (Christen, 2001). The behavior of arsenic in the environment and in water treatment processes is strongly dependent on its speciation. Arsenic exists in natural environments primarily as oxyacids arsenite (As(III); $pK_1 = 9.2$; nonionic H_3AsO_3 at neutral pH) and arsenate (As(V); $pK_1 = 2.2$; anions $H_2AsO_4^-$ and $HAsO_4^{2-}$ at neutral pH) (Ilgen et al., 2012). As(III) is more mobile in natural environments and is more difficult to be removed by adsorption or coagulation processes than As(V) (Hug and Leupin, 2003; Ilgen et al., 2012; Yürüm et al., 2014). Additionally, the toxicity of As(III) is much higher than As(V). Therefore, it is advisable to preoxidize As(III) to As(V) in both natural and technical

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[*] Corresponding author.
[**] Corresponding author.
E-mail addresses: yjwang@issas.ac.cn (Y. Wang), dmzhou@issas.ac.cn (D. Zhou).

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systems.

Previous studies demonstrated that the toxicity and mobility of arsenic in the environment were controlled by the adsorption, desorption and redox transformation occurred on the surface of minerals, particularly for iron (hydr)oxides (Bauer and Blodau, 2006; Prucek et al., 2013). For example, enrichment factors of As within Fe crusts revealed concentrations up to 14 and 58 times higher than the background in the sediments of Lake Baikal (Müller et al., 2002). Numerous studies focused on the adsorption of arsenic by different iron compounds (e.g. red muds, zero-valent iron, Fe_3O_4, iron-loaded activated carbons) in water treatment (Castaldi et al., 2010; Lodeiro et al., 2013; Liu et al., 2015). Some complex redox transformation of the adsorbed arsenic on mineral surfaces has also been revealed. Amstaetter et al. (2009) reported the rapid oxidation of As(III) to As(V) in Fe(II)-goethite systems. Manganese oxides minerals were observed to act as potent sorbents and oxidants for the removal of As(III) under natural conditions (Wu et al., 2012, 2015). However, limited attention has been paid to the transformation of arsenic mediated by natural organic matter (NOM).

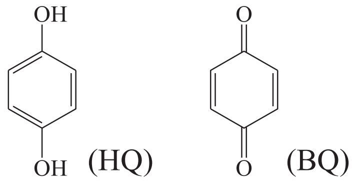
NOM is a ubiquitous component of natural water with concentrations up to 100 mg L^{-1} and plays a critical role in the biogeochemical cycling of trace metals and the mobility of colloidal particles in aquatic environments (Chen et al., 2015; Pradhan et al., 2015). Previous studies showed that NOM dramatically diminished the extent of sorption of both As(III) and As(V) on hematite (Redman et al., 2002). Saada et al. (2003) reported that the coated humic acids on kaolinite facilitated As(V) adsorption at pH 7.0. Besides the complexation speciation of arsenic, NOM also significantly influenced the oxidation of arsenic on the surface of minerals (Redman et al., 2002). It is well known that NOM contains large numbers of carboxyl, methoxyl, enolic-OH, and phenolic-OH groups (Klüpfel et al., 2014), and quinones or quinone-like moieties embedded in NOM molecules are identified as the predominant redox-active center in NOM as confirmed by NMR, fluorescence spectroscopy, and electrochemical methods (MacAlady and Walton-Day, 2011; Jiang et al., 2015). The complex and variability in NOM structure and chemistry make quantitative studies of its redox chemistry particularly difficult, and thus simple quinone couples are commonly used as the redox surrogate of NOM (Orsetti et al., 2013). Simple quinone compounds are not very stable under ambient conditions, and they undergo polymerization reaction in the presence of light or alkaline pH. However, such aromatic condensation reactions generally do not eliminate its reactivity of the quinone group (Sadykh-Zade et al., 1972), and the higher conjugated and substituted environment of the polymers might stabilize the semiquinone radicals which result in higher redox reactivity than the monomers. Similarly, NOM has been found to have similar reaction behavior but more effective than simple quinones in the iron redox reaction (Jiang et al., 2015). It has been reported that semiquinone radicals ($SQ^{\bullet-}$) produced from microbial or chemical reduction of 9,10-anthraquinone-2,6-disulfonic acid (AQDS) could induce As(III) oxidation (Jiang et al., 2009). Dissolved organic matter (DOM) extracted from biochar also enhanced the oxidation of As(III), which was attributed to $SQ^{\bullet-}$ (Dong et al., 2014). However, the generation of reactive oxygen species (ROS) by quinone moieties for As(III) were not reported. In our previous study, $SQ^{\bullet-}$ and ROS were found to be produced by low molecular weight organic phenolic acids, which played important roles in the oxidation of As(III) (Qin et al., 2016). Unfortunately, the mechanisms of ROS formation in the quinone moieties of NOM and the speciation of quinone moieties in the transformation of As(III) in natural environment were not clearly illustrated. Furthermore, our previous studies were conducted at alkaline pH (e.g., 9.0 and 10.0), which were rare in the realistic environment and thus greatly hindered its environmental implication.

Hence, in order to better understand the underlying interaction between As(III) and NOM in the natural environment, hydroquinone (HQ) and benzoquinone (BQ) were selected as the model reduced and oxidized quinone moieties for NOM, which were used to oxidize As(III) in neutral conditions. Electron spin resonance (ESR) technique was used to identify the major free radical species in quinone solution. Furthermore, the corresponding quinone moieties were quantified during the oxidation of As(III). The oxidation pathway of As(III) was proposed on the basis of the ROS identification. In addition, the effects of pH and the concentrations of HQ and BQ on the oxidation of As(III) were assessed. The results of this study would improve our understanding about arsenic transformation in natural environment and give implications on using quinone moieties for the natural attenuation and remediation of arsenic contaminated sites.

2. Materials and methods

2.1. Materials and chemicals

Hydroquinone (HQ, 97%), 1,4-benzoquinone (BQ, 99.5%), NaOH, Na_2HPO_4, NaH_2PO_4 and HCl were purchased from J&K Scientific Ltd, China; $NaAsO_2$ (99%) and 5,5-dimethyl-1-pyrrolidine N-oxide (DMPO, 97%) were obtained from Sigma–Aldrich, Inc. HPLC grade methyl alcohol and ethyl alcohol were supplied from TEDIA Company (USA). Other chemical reagents were of analytical grade or better. Solutions were prepared with deionized water (Milli-Q, Millipore, with resistivity of 18.2 MΩ cm^{-1} at 25 °C). All chemicals were used without any further purification. The stock solutions of HQ and BQ were kept in a refrigerator, protected from light with aluminum foil and used within 7 d. The structures of HQ and BQ were shown as:



2.2. Oxidation experiments

Batch experiments were conducted in conical flasks with stopper at 25 °C, and the total volume of reaction solution was 100 mL, buffered with phosphate solution (PBS) with ionic strength ($[H_2PO_4^-] + [HPO_4^{2-}] = 50$ mM).

Firstly, 5.0 mL of 1.0 mM $NaAsO_2$ stock solution was mixed with 185 mL PBS solution (pH adjusted to 7.5 with NaH_2PO_4 and Na_2HPO_4). Subsequently, 10 mL of 5.0 mM HQ or BQ solution was quickly added to initiate the reaction. The final As(III) concentration was 50 μM, and the HQ or BQ concentration was 0.5 mM. The mixtures were kept horizontally shaking at 200 rpm at 25 °C. Control experiments without HQ or BQ were conducted under the same reaction conditions. All experiments were performed in triplicates. For the analysis of As(III), total arsenic, HQ and BQ, 2.0 mL samples were collected at a given time point (4, 10, 24, 48, 72, 96 h) and quenched by the addition of 0.1 mL 3.0 M HCl solutions, since the oxidation of As(III) would be completely stopped at acidic conditions, and the consumption of hydroquinone compounds was vanished (Strlič et al., 2002).