Enhanced oxidation of arsenite to arsenate using tunable K^+ concentration in the OMS-2 tunnel[☆]

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ABSTRACT

Cryptomelane-type octahedral molecular sieve manganese oxide (OMS-2) possesses high redox potential and has attracted much interest in its application for oxidation arsenite (As(III)) species of arsenic to arsenate (As(V)) to decrease arsenic toxicity and promote total arsenic removal. However, coexisting ions such as As(V) and phosphate are ubiquitous and readily bond to manganese oxide surface, consequently passivating surface active sites of manganese oxide and reducing As(III) oxidation. In this study, we present a novel strategy to significantly promote As(III) oxidation activity of OMS-2 by tuning K^+ concentration in the tunnel. Batch experimental results reveal that increasing K^+ concentration in the tunnel of OMS-2 not only considerably improved As(III) oxidation kinetics rate from 0.027 to 0.102 min^{-1}, but also reduced adverse effect of competitive ion on As(III) oxidation. The origin of K^+ concentration effect on As(III) oxidation was investigated through As(V) and phosphate adsorption kinetics, detection of Mn^{2+} release in solution, surface charge characteristics, and density functional theory (DFT) calculations. Experimental results and theoretical calculations confirm that by increasing K^+ concentration in the OMS-2 tunnel not only does it improve arsenic adsorption on K^+ doped OMS-2, but also accelerates two electrons transfers from As(III) to each bonded Mn atom on OMS-2 surface, thus considerably improving As(III) oxidation kinetics rate, which is responsible for countering the adverse adsorption effects by coexisting ions.

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1. Introduction

Arsenic (As) has received much attention due to its high toxicity and carcinogenicity even at concentrations of up to $10\,\mu g\,L^{-1}$. In arsenic-containing groundwater, As is mainly present in its inorganic state, with arsenate [As(V)] and arsenite [As(III)] being the two predominant species. It has been reported that the emission of wastes As species in many industrial processes such as metallurgic industries, mainly exists as As(III) species, which is very stable in aqueous environments under slightly reducing conditions (Gutiérrez-Ruíz et al., 2005). Since As(III) has greater toxicity, but weak adsorption characteristics compared to As(V) (Ventura-Lima et al., 2011), oxidation of As(III) to As(V) is a desirable process, in order to reduce As toxicity and promote total As removal. However, oxygen-driven oxidation of As(III) is reportedly very slow in groundwater, having reaction kinetic half-times in the range of several months to a year (Gorny et al., 2015). Therefore, additional oxidants are still required for the efficient oxidation of As(III) prior to treatment by coprecipitation and adsorption (Mondal et al., 2013).

Manganese oxides are ubiquitous in terrestrial environments and possess high redox potential (Fischel et al., 2015; Villalobos

et al., 2014), being highly efficient oxidants of As(III), and potentially promoting total As removal (Chakravarty et al., 2002; Chen et al., 2018; Deschamps et al., 2005; Maliyekkal et al., 2009; Neumann et al., 2013; Zhang et al., 2013, 2007). For example, Zhang et al. observed that synthetic Fe-Mn binary oxides had a high removal capacity for As(III), which was attributed to the oxidation ability of manganese oxides for As(III) and adsorption performance of iron oxides for produced As(V) (Zhang et al., 2014, 2007). Deschamps et al. evaluated the removal of As(III) and As(V) from groundwater using a natural Fe and Mn enriched ore (denoted as cFeMn) through batch and column experiments (Deschamps et al., 2005). They revealed that cFeMn (45% Fe_2O_3 and 35% MnO_2) demonstrated efficient removal of 100 $\mu g\,L^{-1}$ As(III) to the drinking water standard when total throughput was lower than 7400 BV (Bed Volume). Although both synthetic Fe-Mn binary oxides and Fe and Mn enriched samples present highly efficient removal for As(III), their As(III) oxidation kinetic rates are very slow, i. e., As(III) can be completely oxidized to As(V) only after 8 h (Zhang et al., 2007) and 50 h (Deschamps et al., 2005), respectively. It is well known that widespread coexisting ions such as phosphate, readily bind to manganese oxide surface active sites, and these may hinder As(III) contact with manganese oxide and subsequently impede their oxidation (Hou et al., 2017a; 2017b; 2016; Lafferty et al., 2010). This result means that As(III) oxidation rate and extent are inevitable to be affected by coexisting ions once manganese oxide has slow As(III) oxidation rate. Therefore, it is of scientific and technological importance to seek a novel approach to improving As(III) oxidation rate on manganese oxide by reducing the adverse effect of coexisting ions. It is commonly accepted that arsenite oxidation on manganese oxide follows typical electron transfer mechanism: As(III) species adsorb onto manganese oxides forming a bidentate complex, subsequently two electrons transfer from As(III) to Mn, thus resulting in the production of As(V) and Mn^{2+} ions (Moore et al., 1990; Nesbitt et al., 1998). According to above mechanism, the key of improving the As(III) oxidation rate is to reveal the impact factors of arsenic adsorption on manganese oxide and the As(III) electrons transfer rate, and explore a practicable strategy to improve arsenic adsorption and accelerates electrons transfer from As(III) to Mn.

Cryptomelane-type manganese oxide (OMS-2) possesses a 2×2 tunnel structure formed by edge- and corner-shared MnO_6 octahedra, which has attracted much interest in its application for As(III) oxidation (Hou et al., 2016; Li et al., 2010; Wang et al., 2012). Since K^+ ion is close to the dimensions of 2×2 tunnels, it has been reportedly used as an ideal template for synthetizing manganese oxide with 2×2 tunnel structures in the laboratory (Liu et al., 2003). Generally, naturally occurring OMS-2 essentially exist as K^+ ions having variable contents due to the difference of mineralization conditions in natural environments. Thus, the varying K^+ concentrations in OMS-2 tunnels inadvertently change their chemical and physical properties, such as magnetic properties and catalytic performance for pollutant purification, which has been observed in previous reports (Hou et al., 2013; Luo et al., 2010). Nevertheless, insufficient work has been reported on K^+ concentration effect, on As(III) oxidation using OMS-2 in terrestrial environments. The mechanism for K^+ ions effect on As(III) oxidation on OMS-2 still remains unanswered. To summarize, understanding the relationship between OMS-2 structure with variable K^+ contents and As(III) oxidation activity, will provide important insights into the transport and fate of toxic As(III) in natural environments.

Consequently, K^+ doped OMS-2 tunnel structures were used to oxidize As(III) to As(V) in this study. For the first time, we observed a significant effect on As(III) oxidation using variable K^+ concentrations with OMS-2. Increasing K^+ concentration in the tunnel promoted As(III) oxidation on OMS-2 whilst reducing the adverse

effect of coexisting ions such as As(V) and phosphate. We also revealed the origin of the effect of K^+ concentration in the tunnel of OMS-2 on As(III) oxidation by combining both experimental and theoretical evidence.

2. Experimental section

2.1. Sample preparation

K^+ doped OMS-2 samples were synthesized using a facile hydrothermal redox reaction among $MnSO_4$, $(NH_4)_2S_2O_8$, and $(NH_4)_2SO_4$ adding different KNO_3 concentrations at 120 °C for 24 h. The detailed preparation procedure is described in previous work (Hou et al., 2013). Potassium nitrate (KNO_3) (0, 0.4044, 1.6176 g respectively) was added to reaction solution systems which corresponded to $KNO_3/MnSO_4$ molar ratios of 0, 0.5, and 2, respectively. The samples were subsequently symbolized as K-OMS-2-A, K-OMS-2-B, K-OMS-2-C, respectively.

2.2. Batch experimental procedures

Batch experiments for As(III) oxidation using K^+ doped OMS-2 samples were performed using a water-bathing rotary oscillator at 160 rpm, at 25 °C. As(III) was prepared from a $NaAsO_2$ stock solution to give a 100 μM working solution. Detailed experimental procedures are described in previous report (Hou et al., 2016). The coexisting ions of As(V), phosphate, and Mn^{2+} that affect As(III) oxidation were evaluated by adding 100 μM of $Na_2HAsO_4 \cdot 7H_2O$, NaH_2PO_4, and $Mn(NO_3)_2$ into 100 μM As(III) solution, respectively. pH effect was investigated using buffer solutions at pH 4.7, 6.0 and 9.16, respectively. An acetate acid/sodium acetate buffer system was utilized to adjust pH to 4.7 and 6.0. A sodium carbonate/sodium bicarbonate buffer system was used to control pH at 9.16. Detailed procedures of the buffer systems are described in previous work (Hou et al., 2016).

2.3. Analysis methods

The concentrations of total As and As(V) in solution were detected using colorimetric spectrophotometry. As(III) concentration in solution was determined by subtracting As(V) concentration from the total As concentration. Detailed analysis procedures are described in previous work (Hou et al., 2016). When phosphate was present in solution, the concentrations of As(III) and total As species were obtained by atomic absorption spectrophotometry (AAS-6880) equipped with hydride generation (LH-2A). Detailed procedures are described in previous work (Hou et al., 2016). Dissolved Mn^{2+} concentrations were determined by AAS-6880. Potassium was determined by inductively coupled plasma/optical emission spectroscopy (ICP-OES, PerkinElmer Optima 4300DV). Redox potential (Eh) was measured using a CHI660B electrochemical workstation at 25 °C. Platinum electrode and reference electrode (saturated calomel electrode) were selected as combination electrodes. Eh values were adjusted by a standard hydrogen electrode (SHE) to obtain true Eh values.

2.4. Isoelectric point test

The isoelectric point (IEP) test of the K^+ doped OMS-2 samples were performed on a zeta potential analyzer (Zetasizer Nano, ZEN3600, Malvern Instruments Ltd., U.K) (Wan et al., 2016; Yan et al., 2014). Typically, each sample (2.5 mg) was added into 500 mL distilled water and sufficiently dispersed through ultrasonication for 0.5 h. A series of 20 mL suspensions (5.0 $mg\,L^{-1}$) were then transferred to centrifuge tubes (50 mL) and 0.1 $mol\,L^{-1}$