Effects of carbonate and Fe(II) on As(III) adsorption and oxidation on hydrous manganese oxide

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ABSTRACT: Manganese oxide plays an important role in redox transformation of arsenic in the aquatic environment. High levels of carbonate and Fe(II) were found as major coexistent ions with arsenic, but their influences on oxidation of arsenite (As(III)) to arsenate (As(V)) by manganese oxide were not fully understood. This work researched oxidation of As(III) on hydrous manganese oxide (HMO) and investigated the effects of carbonate and Fe(II).

1 INTRODUCTION

Manganese oxide is an important oxidant for the transformation of arsenic speciation in the aquatic environment (Ying *et al.*, 2012). It was also proposed as an oxidant for the treatment of arsenic contaminated groundwater (Xu *et al.*, 2011). As(III) oxidation by manganese oxide may be influenced by coexistent ions, such as Ca(II) and Zn(II) (Lafferty *et al.*, 2011). In anaerobic groundwater condition, the concentration of Fe(II) was higher than that of heavy metals (Appelo *et al.*, 2002). However, little is known about its influence on As(III) oxidation by manganese oxide. Fe(II) was reactive and readily oxidized to ferric oxide by MnO₂ (Han *et al.*, 2011), hence may compete with As(III) for the oxidant.

2 METHODS/EXPERIMENTAL

2.1 As(III) adsorption and oxidation

As(III) adsorption and oxidation experiments were performed by contacting As(III) solution with HMO suspensions in batch reactors at 20°C, with the background electrolyte of 0.02 mol L⁻¹ NaCl. 0.1 mL of 1 g L⁻¹ As(III) stock solution was added to 50 mL HMO suspension with the pH pre-adjusted to target value and the initial concentration of 2 mg L⁻¹ As(III) was obtained. The pH of the mixture was maintained constant using 0.05 mol L⁻¹ HCl and/or NaOH solutions.

2.2 Determination of arsenic and iron concentrations

The concentrations of As(III) and As(T) were measured using hydride-generation atomic fluorescence

spectrophotometer (AFS-2202E, Haiguang Corp., Beijing) with a detection limit of 0.01 µg L⁻¹ and duplication analysis agreed within 5%. The concentration of Mn(II) was determined using a flame atomic absorption spectrophotometer (AA240, Varian) with a detection limit of 0.05 mg L⁻¹ and duplication analysis agreed within 7%.

3 RESULTS AND DISCUSSION

3.1 Kinetic studies of As(III) adsorption and oxidation on HMO

The effect of carbonate and Fe(II) on As(III) adsorption and oxidation on hydrous manganese oxide was observed in kinetic studies under Mn/As = 8.5 and pH = 7.0 conditions. Adsorption and oxidation of As(III) in HMO system with carbonate and Fe(II) was compared with pure HMO system (see Fig. 1). The concentrations of As(III) and As(V) in aqueous and solid phase in pure HMO system without coexistent carbonate and Fe(II) were showed in Figure 1. The concentration of As(III) in aqueous phase dropped from 2.0 mg L⁻¹ to 1.7 mg L⁻¹ within 1 h and decreased slowly to a stable level (~1.5 mg L⁻¹) after 48 h reaction. The concentration of As(V) in aqueous phase increased to 0.25 mg L⁻¹ after 48 h reaction. In solid phase, few of As(III) could be detected during 48 h reaction time. The concentration of aqueous As(V) increased to 0.2 mg L⁻¹ within 1 h and reached to 0.25 mg L⁻¹ after 48 h reaction time. The As(V) in solid increased to 0.3 mg L⁻¹ after 48 h reaction time. The results indicated that 30% of added As(III) was oxidized to As(V). About 55% of oxidized As(V) was adsorbed and few of As(III) was adsorbed on HMO. This implied that at the neutral pH HMO has strong

Figure 1. Distribution of As(III) and As(V) (triangle and pentagon respectively) in aqueous and solid phase (open and solid respectively) by contacting As(III) with HMO as a function of time at Mn/As = 8.5 and pH 7.0.

oxidation capacity for As(III) and high adsorption capacity for As(V).

Carbonate and Fe(II) showed distinct effect on kinetics of As(III) adsorption and oxidation on HMO. The addition of carbonate only slightly increased As(V) adsorption at the beginning of the reaction. The addition of Fe(II) increased As(III) oxidation significantly and 60% of As(III) was oxidized to As(V). More As(III) and As(V) were adsorbed on HMO in the presence of Fe(II). The maximum value of As(III) concentration in solid phase at the beginning of the reaction indicated that adsorption and oxidation of As(III) on HMO were competitive process, which controlled the concentrations of As(III) and As(V) in aqueous and solid phase. The addition of carbonate and Fe(II) at the same time mainly exhibited the effect of Fe(II) on adsorption and oxidation of As(III) on HMO.

3.2 Equilibrium studies under acidic pH condition

The effect of carbonate and Fe(II) on As(III) adsorption and oxidation on hydrous manganese oxide was observed in equilibrium studies under pH = 3.0 condition. Adsorption and oxidation of As(III) in HMO system with carbonate and Fe(II) was compared with pure HMO system (see Fig. 2). The concentrations of As(III) and As(V) in aqueous and solid phase in pure HMO system without coexistent carbonate and Fe(II) are shown in Figure 2. Under pH = 3.0 condition, both of the As(III) in aqueous and solid phase could be ignored. The concentration of As(V) in aqueous and solid phase increased to 1.4 and 0.6 mg L⁻¹ at Mn/As ratio is 68. This indicated that the influence of pH on As(III) oxidation was great. Under acidic condition As(III) oxidation increased remarkably even at low Mn/As ratio and presented great independence

Figure 2. Distribution of As(III) and As(V) (triangle and pentagon respectively) in aqueous and solid phase (open and solid respectively) by contacting As(III) with HMO as a function of Mn/As ratio at pH 3.0. Solid lines represent model results.

with Mn/As ratio. The reaction was largely driven by the proton concentration (Villalobos *et al.*, 2014). The produced As(V) existed primarily in aqueous phase and presented more in solid phase at higher Mn/As ratios.

3.3 Equilibrium studies under neutral pH condition

The effect of carbonate and Fe(II) on As(III) adsorption and oxidation on hydrous manganese oxide was observed in equilibrium studies under pH = 7.0 condition. Adsorption and oxidation of As(III) in HMO system with carbonate and Fe(II) was compared with pure HMO system (see Fig. 3). The concentrations of As(III) and As(V) in aqueous and solid phase in pure HMO system without coexistent carbonate and Fe(II) are presented in Figure 3. Under pH = 7.0 condition, As(III) concentration in aqueous phase decreased to 0.8 mg L⁻¹ at higher Mn/As ratio. The concentration of As(V) in aqueous and solid phase increased to 0.8 and 0.5 mg L⁻¹ at Mn/As ratio is 68. Under neutral condition As(III) oxidation increased with Mn/As ratio and presented great dependence with Mn/As ratio. Half of produced As(V) existed in aqueous phase at all four Mn/As ratios.

In HMO system with carbonate, fewer of As(V) adsorbed in solid phase than that in pure HMO system at higher Mn/As ratio. This was consistent with the results under acidic pH condition. In HMO system with Fe(II), more As(III) was oxidized to As(V) than that in pure HMO system. Moreover, more As(III) and As(V) was adsorbed in solid phase than that in pure HMO system. This suggested that addition of Fe(II) could increase As(III) oxidation and As(III) and As(V) adsorption significantly. There were two reasons for these results. One reason was that Fe(II) was

Figure 3. Distribution of As(III) and As(V) (triangle and pentagon respectively) in aqueous and solid phase (open and solid respectively) by contacting As(III) with HMO as a function of Mn/As ratio at pH 7.0.

oxidized to Fe(III) oxide at neutral pH and supplied new sites for As(V) adsorption (Ying *et al.*, 2012).

4 CONCLUSIONS

- (1) Addition of Fe(II) decreased oxidation of As(III) on HMO at acidic pH, while increased As(III) oxidation at neutral and basic pH. This indicated that different mechanisms may be involved in the presence of Fe(II). Formation of amorphous ferric arsenate or ferric oxide at different pH is responsible for this.
- (2) Carbonate ions decreased As(V) adsorption at neutral pH under higher Mn/As ratio. Precipitation of MnCO_3 was the major reason because its existence on HMO decreased As(V) adsorption on HMO. Formation of MnCO_3 also immobilized manganese and decreased the concentration of Mn(II) in aqueous phase. This has important

environmental implications in protecting the groundwater from secondary manganese contamination during remediation of arsenic contaminated groundwater using HMO.

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REFERENCES

- Appelo, C.A.J., Van der Weiden, M.J.J., Tournassat, C. & Charlet, L. 2002. Surface complexation of ferrous iron and carbonate on ferrihydrite and the mobilization of arsenic. *Environ. Sci. Technol.* 36(14): 3096–3103.
- Han, X., Li, Y.L. & Gu, J.D. 2011. Oxidation of As(III) by MnO_2 in the absence and presence of Fe(II) under acidic conditions. *Geochim. Cosmochim. Acta* 75(2): 368–379.
- Lafferty, B., Ginder-Vogel, M.A. & Sparks, D.L. 2011. Arsenite oxidation by a poorly-crystalline manganese oxide. 3. arsenic and manganese desorption. *Environ. Sci. Technol.* 45(21): 9218–9223.
- Villalobos, M., Escobar-Quiroza, I. N. & Salazar-Camacho, C. 2014. The influence of particle size and structure on the sorption and oxidation behavior of birnessite: I. Adsorption of As(V) and oxidation of As(III). *Geochim. Cosmochim. Acta* 125: 564–581.
- Xu, W., Wang, H., Liu, R., Zhao, X. & Qu, J. 2011. Arsenic release from arsenic-bearing Fe-Mn binary oxide: Effects of Eh condition. *Chemosphere* 83(7): 1020–1027.
- Ying, S.C., Kocar, B.D. & Fendorf, S. 2012. Oxidation and competitive retention of arsenic between iron- and manganese oxides. *Geochim. Cosmochim. Acta* 96(11): 294–303.