Arsenite oxidation by three types of manganese oxides

FENG Xiong-han[1], ZU Yan-qun[1,2], TAN Wen-feng[1], LIU Fan[1,*]

(1. College of Resources and Environment, Huazhong Agricultural University, Wuhan 430070, China. E-mail: liufan@mail.hzau.edu.cn; 2. College of Resources and Environment, Yunnan Agricultural University, Kunming 650201, China)

Abstract: Oxidation of As(III) by three types of manganese oxides and the effects of pH, ion strength and tartaric acid on the oxidation were investigated by means of chemical analysis, equilibrium redox, X-ray diffraction (XRD) and transmission electron microscopy (TEM). Three synthesized Mn oxide minerals, birnessite, cryptomelane, and hausmannite, which widely occur in soil and sediments, could actively oxidize As(III) to As(V). However, their ability in As(III)-oxidation varied greatly depending on their structure, composition and surface properties. Tunnel structured cryptomelane exhibited the highest ability of As (III) oxidation, followed by the layer structured birnessite and the lower oxide hausmannite. The maximum amount of As (V) produced by the oxidation was in the order (mmol/kg) of cryptomelane (824.2) > birnessite (480.4) > hausmannite (117.9). As pH increased from the very low value(pH 2.5), the amount of As(III) oxidized by the tested Mn oxides was firstly decreased, then negatively peaked in pH 3.0—6.5, and eventually increased remarkably. Oxidation of As(III) by the Mn oxides had a buffering effects on the pH variation in the solution. It is proposed that the oxidative reaction processes between As(III) and birnessite(or cryptomelane) are as follows: (1) at lower pH condition: $(MnO_2)_x + H_3AsO_3 + 0.5H^+ \longrightarrow 0.5H_2AsO_4^- + 0.5HAsO_4^{2-} + Mn^{2+} + (MnO_2)_{x-1} + H_2O$; (2) at higher pH condition: $(MnO_2)_x + H_3AsO_3 \Longrightarrow 0.5H_2AsO_4^- + 0.5HAsO_4^{2-} + 1.5H^+ + (MnO_2)_{x-1} \cdot MnO$. With increase of ion strength, the As(III) oxidized by birnessite and cryptomelane decreased and was negatively correlated with ion strength. However, ion strength had little influence on As (III) oxidation by the hausmannite. The presence of tartaric acid promoted oxidation of As(III) by birnessite. As for cryptomelane and hausmannite, the same effect was observed when the concentration of tartaric acid was below 4 mmol/L, otherwise the oxidized As(III) decreased. These findings are of great significance in improving our understanding of As geochemical cycling and controlling As contamination.

Keywords: oxidation of As(III); As(V); Mn oxides; pH; ion strength; tartaric acid

Introduction

Arsenic (As) contamination often occurs in aquatic and terrestrial environments from sources such as use of arsenical pesticides, smelters, coal-fired power plants (Smith *et al.*, 2002; Deschamps *et al.*, 2003) and geochemical reasons, such as dissolution of As-enriched minerals (Thornburg and Sahai, 2004). Arsenic is thought to cause skin lesions and cancers of the brain, liver, kidney and stomach (Smith *et al.*, 2002b). The World Health Organization recommended a new standard for arsenic in drinking water of 10 μg/kg in 1993. This standard was recently adopted by the U.S. Environment Protection Agency and the European Union, replacing the old one of 50 μg/kg.

The main oxidation states of arsenic are As(III) and As (V), with the former being much more toxic, soluble and mobile than the latter(Ferguson and Davis, 1972). Arsenic chemical species are highly dependent on the oxidation of As(III), thus to a large extent, the oxidation of As(III) influences and/or controls the transport, transformation, bio-availability and bio-toxicity of As in the environment(Oscarson *et al.*, 1980, 1981; Deschamps *et al.*, 2003; Ferguson *et al.*, 2005). Manganese(hydro)oxides are widely distributed

in soils and sediments. Among different components, such as clay phyllosilicates, Mn oxides, Fe oxides and Al oxides, only Mn oxides have been identified as the primary electron acceptors in oxidation of As(III) in the environment (Oscarson *et al.*, 1980, 1981; Deschamps *et al.*, 2003). Many studies have investigated the kinetics of As (III) oxidation by Mn oxides (Oscarson *et al.*, 1980, 1981, 1983a, b; Driehaus *et al.*, 1995; Nesbitt *et al.*, 1998; Tournassat *et al.*, 2002; Deschamps *et al.*, 2003; Powder *et al.*, 2005). Whereas few investigations were reported to compare the oxidation of As (III) by different Mn oxides (Oscarson *et al.*, 1983a; Driehaus *et al.*, 1995). Various manganese oxides exhibit great changes in chemical properties and oxidation ability due to variation of their structures and compositions (Mckenzie, 1989; Post, 1992). Effects of solution conditions, such as pH, ion strength, and co-existing ligand (e.g., organic acids) on extent of As (III) oxidation by different Mn oxides are even less reported(Chen and Fang, 2000).

According to the crystal structures, Mn oxides can be classified into three types: layer structures, tunnel structures and lower oxides (Post, 1992). Birnessite, layer structured, is one of the most common Mn minerals in soils, sediments and ocean

manganese nodules(McKenzie, 1989). Cryptomelane, tunnel structured, also commonly occurs in soils by the transformation of birnessite containing appropriate content of K (McKenzie, 1989; Post, 1992). Hausmannite, low oxide structured, contains divalent and trivalent Mn(formulated as $Mn^{2+}(Mn^{3+})_2O_4$) and is one of two important Mn lower oxides in soils (McKenzie, 1989; Post, 1992).

In this work, three synthesized Mn oxides, commonly distributed in soils and sediments, were taken as the materials. Oxidation of As(III) by each of the Mn oxide in a controlled system and the effects of Mn oxides properties and solution conditions on the oxidation of As(III) were investigated through batch experiments. This study provides further understanding of As(III) oxidation on surfaces of different types of Mn oxides under environmentally applicable conditions where pH, ion strength and concentration of co-existing ligand are varied.

1 Materials and methods

1.1 Syntheses and characterization of Mn oxides

Birnessite was synthesized through reduction of $KMnO_4$ by hydrochloric acid (Mckenzie, 1971). Cryptomelane was synthesized through reaction between $KMnO_4$ and $MnSO_4$ in an acetic acid solution medium (Mckenzie, 1971). Hausmannite was synthesized by oxidation of $Mn(OH)_2$ in a weak alkali medium (Feng, 2003). The synthesized minerals were purified by electrical dialysis at a voltage of 150—220 V until the conductivity of supernatant was below 2.0 $\mu S/cm$ and then freeze-dried.

X-ray diffraction(XRD) analyses were performed on a diffractometer equipped with a monochromated Fe $K\alpha$ radiation. The monochromated radiation had a tube voltage of 40 kV, a tube current of 20 mA and the count time was 0.5 s per 0.02°. Transmission electron microscopy (TEM) analyses were carried out in Philips-CM12. Samples were analyzed for elemental composition using Varian Vizta-MPX ICP-OES. The general molecular formulas of the Mn oxides were determined according to the method described by Kijima *et al.*(2001).

1.2 Chemicals

Distilled deionized water (DDW, 18 $M\Omega$, from Labconco Water Pro Ps) after boiling for 1 h to remove the dissolved air was used throughout the experiment. All chemicals ($NaAsO_2$, NaCl, NaF, HCl and NaOH) were of reagent grade. All glassware and polyethylene centrifuge tubes were rinsed with 0.01 mol/L HNO_3 and DDW before use.

1.3 Oxidation of As(III)

The oxidation experiments were carried out in 25 ml polyethylene centrifuge tubes by shaking at 25 ± 1°C for 48 h to determine oxidation of As (III) by different Mn oxides. Reactions were initiated by

mixing 0.1 g of Mn oxides with 10 ml of freshly prepared $NaAsO_2$ solutions with a series concentrations of 1,2,4,6,8,12 and 16 mmol/L. The ion strength of the solutions had been adjusted to be 0.1 mol/L by KCl and the pH was maintained at 5.5 by adjusting with 0.1 mmol/L NaOH or HCl. After reaction, the tubes were centrifuged at 1.25 ×10⁴ r/min for 10 min. The supernatants were collected for As (V) and Mn^{2+} determination. 10 ml of 0.01 mol/L NaF was added to the residues to desorb As (V) adsorbed on the surfaces of minerals, shaken at 25 ± 1°C for 1 h, and then centrifuged at 1.25 ×10⁴ r/min for 10 min. The supernatants were also collected for As (V) and Mn determination. Total amount of As(V) from the double treatments was regarded as the amount of As(III) oxidized. Each run was made in triplicate. Manganese was analyzed using Varian Vista-MPX ICP-OES. As(V) was determined using the ammonium molybdenum method described by Oscarson *et al.*(1980).

Experiments were carried out with the same procedure as described above to determine the effects of pH, ion strength and tartaric acid on As (III) oxidation except that different solution conditions were controlled. 16 mmol/L $NaAsO_2$ solutions with ion strength of 0.1 mol/L KCl and with a series of initial pH at 2.0—11.5 were used in pH effect experiments. 16 mmol/L $NaAsO_2$ solutions with a constant pH 5.5 and with a series ion strength of 0, 0.01, 0.1, 0.5, 1.0, and 2.0 mol/L KCl were adopted in ion strength effect experiments. For tartaric acid effect experiments, 16 mmol/L $NaAsO_2$ solutions with different tartaric acid concentrations of 0.5, 1, 2, 4, 6, and 10 mmol/L were used, and pH and ion strength were maintained at 5.5 and 0.1 mol/L KCl, respectively.

2 Results and discussion

2.1 Characterization of Mn oxides

Fig.1 shows powder XRD patterns of the synthesized Mn oxide minerals. The patterns of the birnessite and cryptomelane matched well with the
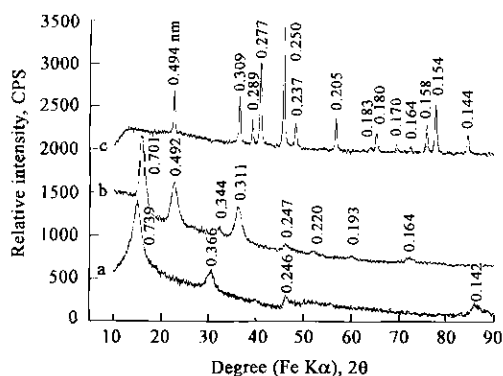

Fig.1   Powder X-ray diffraction patterns of synthesized Mn oxides
a. cryptomelane; b. birnessite; c. hausmannite

JCPDS (Joint Committee for Powder Diffraction Standards) cards 23—1239 and 20—908, respectively. The broad and weak XRD reflections indicated that they were poorly crystallized (Fig.1 a, b), which were consistent to their TEM images. Birnessite consisted of random stacked thin plates, while cryptomelane had a morphology of thin acicular crystals(Feng, 2003).

The prepared hausmannite was well crystallized

as indicated by the narrow and strong peaks in its XRD pattern(Fig.1c) and its micro-morphology(Feng, 2003). These peaks were in good agreement with those of the hausmannite cited in JCPDS 16—364. Hausmannite by had a typical cubic morphology as described by Post (1992). Thus, the synthesized Mn oxides were confirmed to be single crystalline phases. The basic properties of the tested manganese oxides are listed in Table 1.

Table 1   Basic properties of the tested manganese oxides

Sample	Structure	AOS of Mn[1]	Chemical composition[2]	Specific surface area[3], m^2/g	PZC[4]	Crystallinity
Birnesite	Layer	3.96	$K_{0.05}MnO_{2.01}(H_2O)_{0.65}$	48.3	1.75	Weak
Cryptomelane	Tunnel	3.90	$K_{0.24}MnO_{2.07}(H_2O)_{0.48}$	130.1	2.10	Weak
Hausmannite	Lower oxide	2.66	$MnO_{1.33}(H_2O)_{0.14}$	17.0	$>10^5$	High

Notes: 1. Average oxidation state of Mn was determined with the titration method (Kijima *et al.*, 2001); 2. calculated from elemental composition determined by Varian Vista-MPX ICP-OES and AOS of Mn (Feng, 2003); 3. determined by BET measurement with N_2 gas adsorption; 4. point of zero charge was determined by rapid potentiometric titration method (Laverdier and Weaver, 1977); 5. PZC obtained not by rapid potentiometric titration method, but cited from Shaughnessy *et al.* (2003)

2.2 Oxidation of As(III) by different Mn oxides

Our preliminary kinetic experiments confirmed that As(III) maintained unoxidized for 72 h without Mn oxides as reported by other researchers(Oscarson *et al.*, 1980, 1981). The reactions between As(III) and Mn oxides occurred rapidly within 1 h, and subsequently became slower and approached to an equilibrium after 48 h. Fig.2 shows the curve of As (III) oxidized to As(V) by the three Mn oxides. They followed a similar trend in the course of oxidizing As (III) to As(V), but differed in oxidation capacity. When the concentration of As (III) was below 8 mmol/L, the amount of As (V) produced by the oxidation of Mn oxides increased sharply with increase of the added As(III), then increased slightly when the concentration of As (III) was between 8 and 12 mmol/L. While the concentration of As(III) was above 12 mmol/L, the increase of produced As(V) gradually tended to keep stable and approach a maximum value.
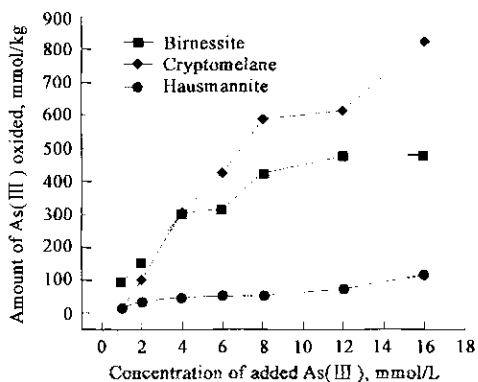
The magnitude order of the maximum amount of As (III) oxidized by the oxidation of Mn oxides was (mmol/kg): cryptomelane(824.2) > birnessite(480.4)> hausmannite(117.9).

The Mn^{2+} released from three Mn oxides increased with the increase of As (III) oxidation, and was different in amount and amplitude (Fig.3). The amount of Mn^{2+} released from the birnessite and the cryptomelane increased slightly with the progress of As(III) oxidation. In contrast, hausmannite released much more Mn^{2+} to the solution than birnessite and cryptomelane. Mn^{2+} released from hausmannite increased quickly at the early stage of As (III) oxidation. When the amount of As (III) oxidation exceeded 80 mmol/kg, Mn^{2+} released in amount was much more than As (III) oxidized. Because hausmannite is one of low oxides (Table 1), it consisted of Mn^{2+} and Mn^{3+}. Besides production of Mn^{2+} from the electron transfer of Mn^{3+} with As(III), part of Mn^{2+} in its crystal lattice directly released to solution due to decomposition of hausmannite during oxidation of As(III) by hausmannite.

The properties of minerals are determined by both their compositions and crystal structures. Birnessite is constructed with stacked layers of Mn-O octahedra that share edges with each other (Post, 1992). The disordered H_2O/K sheets are sandwiched between the Mn octahedral layers of birnessite. They are combined by van der Walls force and hydrogen bonds between hydroxyl in H_2O/K sheet and O atoms on Mn layer. In addition, the highest Mn AOS(Table 1) also imparts birnessite strong oxidation of As(III). Cryptopmelane has a 2×2 tunnel structure consisting of double chains of Mn-O octahedral with K^+ situated in tunnel. Its greater amount of active oxygen in tunnel

Fig.2 Oxidation of As(III) by different Mn oxides, the ionic strength of background electrolyte KCl is 0.1 mol/L and the solution pH is 5.5

structure (Yin *et al*, 1994) and the highest specific surface area (Table 1) may account for its greatest oxidation capacity of As (III) among the tested Mn oxides. The synthesized hausmannite had a much lower Mn AOS than the birnessite and cryptomelane (Table 1). It is the most thermally stable Mn oxide mineral, having a spinel-like structure with Mn^{2+} in the octahedral and Mn^{4+} in tetrahedral sites (Post, 1992). This may result in its the least As(III) oxidation capacity.
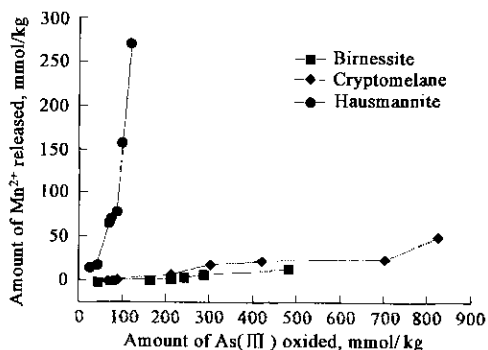

Fig.3 Relation between the amount of Mn^{2+} released in solution and As (III) oxidized

The ionic strength of background electrolytes KCl is 0.1 mol/L and the solution pH is 5.5

The redox reaction between Mn oxides and As (III) occurred on the interface of minerals and solution. Adsorption of As(III) and desorption of As (V) on the surface of MnO_2 were two steps for the reaction before and after electrons transfer from As (III) to the MnO_2, respectively(Oscarson *et al.*, 1983a). Adsorption of As(III) on the surface of Mn oxides would enhance the oxidation of As(III), while adsorption of As(V) would block adsorption and subsequent oxidation of As(III). Adsorption of As(III) and As(V) is greatly influenced by the surface charge characteristics of the minerals and the chemical species of As(III) and As(V). Point of zero charge (PZC) is an important parameter to characterize charge properties of the variable-charge surfaces, such as those of Mn oxides. When pH in the system is lower than PZC, the surface possesses net positive charge, otherwise the surface is negatively charged and has more negative charge with the increase of pH. According to the PZC values of the Mn oxides(Table 1), birnessite and cryptomelane possessed much more surface negative charge when pH of the experimental solution was at 5.5, while the surface of the hausmannite was strongly positively charged. Therefore, strong adsorption of Mn^{2+} on the surface of negatively charged birnessite and cryptomelane led to low Mn^{2+} release during the oxidation(Fig.3). The first order acid disassociation constant (pK_{a1}) for H_3AsO_3 is 9.22, the first, second and third disassociation constants for H_3AsO_4 (pK_{a1}, pK_{a2}, pK_{a3}) are 2.20, 6.97 and 11.53. Accordingly the predominant states of As

(III) and As(V) were H_3AsO_3, $H_2AsO_4^-$ and $HAsO_4^{2-}$ at pH 5.5. Hausmannite had a low specific surface area, providing small amount of surface sites per mass for adsorption of H_3AsO_3. This went against to As (III) oxidation. On the other hand, the highly positively charge surface was easily to immobilize the yielded $H_2AsO_4^-$ and/or $HAsO_4^{2-}$, resulting in blockage of reaction sites on the surface of the hausmannite and thus retarding As(III) oxidation. So the differences in surface properties explained why the Mn oxides performed differently on their oxidation of As(III).

2.3 Effects of pH on oxidation of As (III) by different Mn oxides

The curves of As (III) oxidation by three Mn oxides versus pH are similar in shape (Fig.4). When pH was increased from very low value (pH 2.5), the oxidation of As(III) by the Mn oxides was gradually decreased till it reached the minimum in pH range of 3.0—6.5. While pH was continually increased, As(III) oxidation amount by the Mn oxides was remarkably decreased. pHs at which minimum oxidation of As(III) for cryptomelane, birnessite and hausmannite occurred were about 3.4, 6.3 and 4.9, respectively. Such effects could be attributed to two opposing effects: as pH increased, the oxidation ability of Mn oxides restrained, however the reduction ability of As (III) enhanced. In acid medium, standard potentials for the half reactions $(MnO_2+H^+)/Mn^{2+}$ and $(H_3AsO_4+H^+)$ $/H_3AsO_3$ were 1.23 V and 0.56 V; but in alkaline medium, standard potentials for the half reactions $MnO_2/(Mn(OH)_2+OH^-)$ and $AsO_4^{3-}/(AsO_2^-+OH^-)$ were 0.1 V and -0.71 V (He *et al.*, 1998). The lowest potential of the reaction between Mn oxides and As (III) existed at a certain pH value, at which minimum oxidation of As(III) appeared. Compared with the acid medium, the Mn oxides had stronger ability to oxidation of As(III) in alkaline medium.

When pH in the initial solution was at a lower value, H^+ was consumed during the reaction and pH increased after oxidation; on the contrary, when pH was higher in alkali range at the beginning, H^+ was
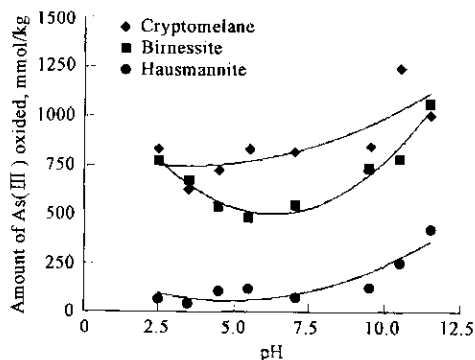

Fig.4 Relation between As(III) oxidized by different Mn oxides and pH
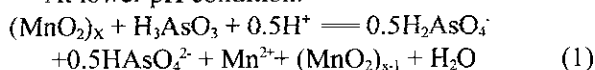The ionic strength of background electrolyte KCl is 0.1 mol/L and the added As(III) is 16 mmol/L

produced during the reaction and pH decreased after reaction. That is to say oxidation of As (III) by Mn oxides had a buffering effect on the pH in the solution. Variation of pH after oxidation is shown in Table 2.

pH across a range of 2.0—9.0 before reaction for birnessite and cryptomelane transferred to a narrow range of 6—8.

Under different pH conditions, different reaction

Table 2 Variation of pH after oxidation of As(III) with Mn oxides

Sample and period	pH							
Before reaction	2.00	3.00	4.00	5.00	6.00	7.00	8.00	9.00
After reaction with birnessite	6.01	6.78	6.80	6.85	6.97	7.05	7.19	8.02
After reaction with cryptomelane	6.23	6.69	6.76	6.94	7.01	7.11	7.27	7.68
After reaction with hausmannite	5.26	5.83	6.09	6.33	6.83	7.24	7.44	8.54

processes due to variation of species of reactants and products may be present. It was reported that birnessite was transformed to MnO at pH 7.0(Neibitt *et al.*, 1998). The main states of As (III) and As(V) could be thought to be H_3AsO_3, $H_2AsO_4^-$ and $HAsO_4^{2-}$ across the experimental pH range based on their acid disassociation constants. Thus, if $(MnO_2)_x$ was used to denote Mn oxides, birnessite or cryptomelane, the oxidation reactions at lower and higher pH range between As(III) and the Mn oxides could be expressed as follows, respectively.

At lower pH condition:
$(MnO_2)_x + H_3AsO_3 + 0.5H^+ = 0.5H_2AsO_4^-$
$+0.5HAsO_4^{2-} + Mn^{2+} + (MnO_2)_{x-1} + H_2O$ (1)
At higher pH condition:
$(MnO_2)_x + H_3AsO_3 = 0.5H_2AsO_4^- + 0.5HAsO_4^{2-}$
$+1.5H^+ + (MnO_2)_{x-1} \cdot MnO$ (2)
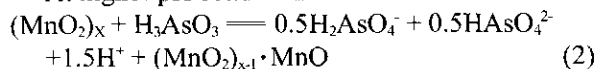
In above equations, $0.5H_2AsO_4^- + 0.5HAsO_4^{2-}$ represented the produced As(V). As shown in Fig.5, the ratio of $H_2AsO_4^-$ to $HAsO_4^{2-}$ varied with pH. When pH was increased, the concentration of $HAsO_4^{2-}$ increased and that of $H_2AsO_4^-$ decreased. At a lower pH, oxidation of As(III) occurred following Equation (1), pH increased after reaction due to consumption of H^+. As pH was increased from a lower value, the reaction of Equation (1) would apparently be restrained, and the oxidation amount of As(III) was gradually decreased. The lower the initial pH was, the more increment pH would appear after reaction, resulting from more H^+ consumed due to reaction and balance of $0.5H_2AsO_4^-$ and $0.5HAsO_4^{2-}$ at lower pH. When pH was higher in alkali medium, oxidation of As(III) occurred following Equation (2), pH decreased after reaction due to production of H^+. As pH was increased, the reaction of Equation (2) would apparently be promoted, and the oxidation amount of As (III) was rapidly increased. The higher the initial pH was, the more decrement pH would occur after reaction, resulting from more H^+ produced due to reaction and balance of $0.5H_2AsO_4^-$ and $0.5HAsO_4^{2-}$ at higher pH. From equations, 1.5 times of more H^+ was produced in alkaline medium than that consumed in acid medium. Moreover as pH was increased, more

negative charge on the surface of Mn oxides would promote oxidation of As(III) due to stronger effect on transferring yielded As(V) from the surface to the solution. Therefore, increase of pH in alkaline condition had more significant influence on As (III) oxidation by Mn oxides than that in acid condition. As for hausmannite, pH may have similar mechanism to influence oxidation of As(III) from its similar curve in shape to those of birnessite and cryptomelane(Fig.4), although hausmannite had different Mn AOS and composition. In addition, disproportionation of hausmannite preferably occurred in acid condition(Feng *et al.*, 2005) may partly account for variation of pH after reaction.
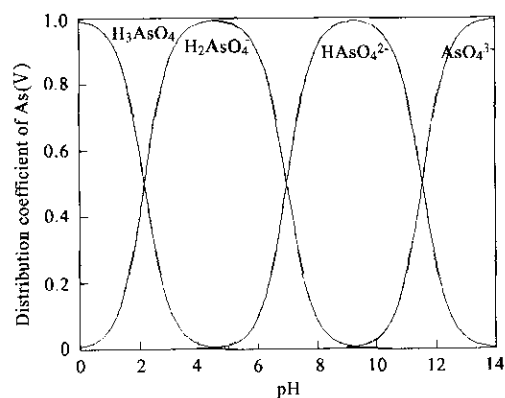

Fig.5 Curve of As(V) species distribution versus pH

2.4 Effects of ion strength on oxidation of As(III) by different Mn oxides

Fig.6 shows relationship between oxidation of As (III) for three Mn oxides and ion strength. The amount of As(III) oxidized by birnessite and cryptomelane decreased with ion strength, and was significantly negatively correlative with ion strength. When ion strength increased from 0 to 2 mol/L KCl, the oxidation amount of As (III) for birnessite and cryptomelane decreased from 695.5 and 632.9 to 567.2 and 408.9 mmol/kg, respectively. However ion strength had little effect on oxidation of As(III) by hausmannite.

When ion strength increased at pH 5.5, according to Gouy-Chapman formula the surface negative charge
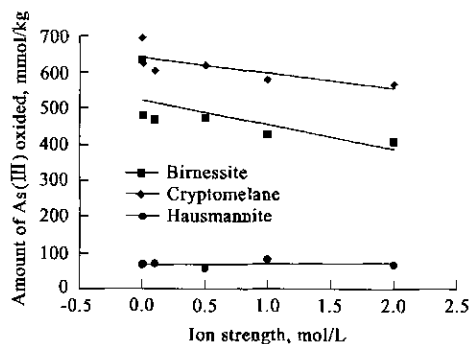
Fig.6 Relation between As(III) oxidized by different Mn oxides and ion strength
The solution pH is 5.5, and the added As(III) is 16 mmol/L

Fig.7 Relation between As (III) oxidized by different Mn oxides and concentration of tartaric acid
The solution pH is 5.5, ionic strength of background electrolyte KCl is 0.1 mol/L, and the added As(III) is 16 mmol/L

of birnessite and cryptomelane slightly increased, being advantageous to oxidation of As(III). On the other hand, the added Cl would compete with As(III) to be adsorbed on Mn oxide surface (Chen and Fang, 1998; Jackson and Miller, 2000). This would occupy part of oxidative sites on the surface and restrain oxidation of As(III). Because the ion strength had not great influence on the amount of surface negative charge relative to a great deal of total charge on the Mn oxide surface, the combined result of the two opposite effects of ion strength was promotion of As (III) oxidation with increase of ion strength. The Ion strength had different effects on oxidation of As (III) by hausmannite, indicating other mechanism may exist.

2.5 Effects of tartaric acid on oxidation of As(III) by different Mn oxides

Low-molecular-weight (LMW) organic acids occur widely in soils from the sources of secretion from plant roots and decomposition of plant residues (Xu et al., 2003). Their anions could influence interaction between soil active components and pollutants. In this study, tartaric acid was used as a LMW. Oxidation of As(III) by the Mn oxides with concentration of tartaric acid is shown in Fig.7. Birnessite possessed increasing oxidation amount of As(III) with increase of tartaric acid. While for cryptomelane and hausmannite, only concentration of tartaric acid was lower than 4 mmol/L, oxidation of As (III) gradually increased. Otherwise, oxidation of As(III) tend to decrease with tartaric acid.

When tartaric acid was present, two opposite effects may occur on the oxidation of As(III). The first is coordination effect. Tartaric acid could act as a ligand to coordinate with the yielded Mn^{2+} in solution and/or on the surface of Mn oxides. As a result, the concentration of Mn^{2+} in solution decreased and the oxidative sites had been occupied by Mn^{2+} released. Thus oxidation of As(III) could be promoted. Another is competitive adsorption effect. Tartaric acid would compete the oxidative sites on the Mn oxide surface with As(III) and As(V) through being adsorbed on the
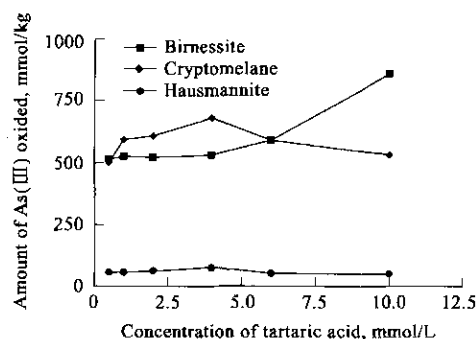
surface. Oxidation of As(III) was obviously impeded in this situation. The influence of tartaric acid may depended on such two effects. The disassociation constants of tartaric acid pK_{a1} and pK_{a2} were 3.04 and 4.37. Tartaric acid existed in anions states at pH 5.5, and birnessite was strongly negatively charged due to its lowest PZC. Thus competitive adsorption of tartaric acid on the surface of birnessite should be weak, and the main effect of tartaric acid may be coordination. Cryptomelane possessed relative low negative charge and hausmanite was positively charged at pH 5.5. Accordingly, competitive adsorption of tartaric acid on their surface was more significant. When concentration of tartaric acid was above 4 mmol/L, competitive adsorption effect of tartaric acid on oxidation of As (III) exceeded coordination effect. Otherwise coordination effect would be predominant. Therefore tartaric acid effect was associated with its concentration and surface properties of Mn oxides.

3 Conclusions

Three Mn oxides could actively oxidize As(III) to As(V), and greatly varied in their ability of oxidation. Cryptomelane exhibited the highest capacity of As(III) oxidation, followed by birnessite. Hausmannite had the lowest capacity of As (III) oxidation, and released more Mn^{2+} than cryptomelane and birnessite during the oxidation. The oxidation ability of the Mn oxides was associated with their structure, composition, crystallinity, and surface properties. The maximum amount of As (III) oxidation by cryptomelane, birnessite, and hausmannite was 824.2, 480.4 and 117.9 mmol/kg.

When pH was increased from the very low value, the amount of As (III) oxidized by the tested Mn oxides was firstly decreased, then negatively peaked in pH 3.0—6.5. While pH was continually increased, As (III) oxidation amount by the Mn oxides was remarkably increased. When pH in the initial solution was at a lower value, it increased after oxidation

reaction, while pH decreased after reaction when it was higher at the beginning. Upon pH effects and different species of products, the oxidation processes at lower and higher pH range between As(III) and Mn oxides could be expressed with different reaction equations.

The As (III) oxidized by birnessite and crypto-melane decreased with ion strength, and was strongly negatively correlated with ion strength. However ion strength had little influence on oxidation of As(III) by hausmannite. The presence and increase of tartaric acid promoted oxidation of As(III) by birnessite. As for cryptomelane and hausmannite, the produced As (V) increased with addition of tartaric acid when its concentration was below 4 mol/L, while the oxidized As(III) decreased when tartaric acid concentration was above 4 mol/L.

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