

Arsenite sorption and oxidation by synthetic birnessite

N. Wang, C. Liang, L. Du and H. Cui

ABSTRACT

Arsenite (As(III)) is a more toxic form of inorganic arsenic and its removal from drinking water is less effective compared with arsenate (As(V)). In the present study, synthetic birnessite (δ -MnO₂) was used to investigate the oxidative transformation of arsenite into arsenate using batch experiments under different reaction conditions. Results showed that arsenite transformation occurred and was accompanied by the sorption and fixation of both As(III) and As(V) on δ -MnO₂. Approximately 90% of the arsenite (1.0 mg/L) was transformed by δ -MnO₂ at 25 °C and pH 6.0, 49% of which was sorbed and 10% fixed by δ -MnO₂. Increased δ -MnO₂ dosages promoted the transformation rate of As(III) and sorption of As species. As pH increased from a very low value (pH 2.0), the amount of As(III) oxidized by the tested δ -MnO₂ initially decreased, then negatively peaked at pH 4.0, and eventually increased remarkably. At the same time, the oxidation of As(III) by δ -MnO₂ had a buffering effect on the pH variation in the solution; the oxidation rate decreased and sorbed As(III) and As(V) increased with the increase in initial arsenite concentration. These findings are of great significance in improving our understanding of As geochemical cycling and in controlling As contamination.

Key words | As(III), As(V), birnessite, manganese oxide, oxidation, sorption

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INTRODUCTION

Arsenic (As) is both ubiquitous in the environment and potentially toxic to humans. Arsenic contamination is a worldwide problem, especially in developing countries where a significant percentage of the population depends on groundwater for drinking. Mineral dissolution, use of arsenical pesticides, disposal of fly ash, mine drainage, and geothermal discharge elevate concentrations of As in soils and waters. Epidemiological studies have shown a significant increase in the risks of lung, bladder, skin, liver, and other cancers associated with high levels of arsenate (As(V)) in drinking water (Katsoyiannis *et al.* 2002). Based on the impact on human health, the World Health Organization (WHO), the United States Environmental Protection Agency (USEPA), Taiwan, and the European Union have been required to lower the Maximum Allowable Concentration (MAC) in drinking water from 50 to 10 µg/L (Thirunavukkarasu *et al.* 2002). Several other countries suffering from arsenate contamination of drinking water will, nonetheless, be forced to review their standards.

Removal of dissolved arsenic from natural groundwaters is linked to the chemistry of arsenite (As(III)) and As(V) compounds and so, to their relative distribution, influenced by pH and redox conditions. Predominance diagrams (i.e., pe–pH plots) are available in the published literature (Van Elteren *et al.* 2002).

Many different methods, such as precipitation coprecipitation (Meng *et al.* 2002), adsorption onto activated carbon (Pattanayak *et al.* 2000), lime softening (Wang & Reardon 2001), and ion exchange (Guenegou *et al.* 1998) have been used for arsenic removal. However, fixed bed treatment systems, such as adsorption, are receiving increasing attention for arsenic removal in small-scale treatment systems due to their simplicity, ease of operation and handling, regeneration capacity, and sludge-free operation.

Several media are able to remove arsenic from water, particularly natural oxides, which oxidizes As(III) to As(V) and adsorb the As(V). Among them, manganese and iron (hydr) oxides are often used (Pierce & Moore 1982; Hsia *et al.* 1994;

Farquhar *et al.* 2002). Birnessite is a kind of ubiquitous hydrous-layered Mn oxide (phyllosilicate) found in geological environments. Usually occurring as fine-grained particles, birnessite exhibits high reactivity and is widely involved in a series of geochemical processes. Due to its mixed valences, large surface area, and low point of zero charge (Mohan & Pittman 2007; Lee *et al.* 2011), the synthetic birnessite, δ -MnO₂, which resembles the naturally occurring mineral birnessite, is posited to result in faster oxidation of As(III), compared with the α and β modifications of MnO₂. However, the exact effect of the synthetic birnessite on arsenic sorption and transformation is, to date, still to be examined.

The objectives of this study were therefore to investigate the feasibility of oxidative transformations of As(III) by δ -MnO₂. The factors that influence the oxidative transformations of As(III), such as reaction time, δ -MnO₂ dosage, pH, and initial concentration were investigated to elucidate the oxidative efficacy and the reactive mechanisms of As(III) on the δ -MnO₂ surface.

MATERIALS AND METHODS

Chemicals

All reagents were of analytical grade and purchased from Sinopharm Chemical Reagent Co., China. All the chemicals were used without further purification and the solutions were prepared with double distilled water.

δ -MnO₂ preparation and characterization

The δ -MnO₂ was prepared by adding 0.070 mol/L MnSO₄ to 0.050 mol/L KMnO₄ solution dropwise with vigorous stirring. The solution was stirred continually for 6 h, aged for 30 min, dried at 80 °C, ground, and sieved until δ -MnO₂ powders were obtained (Tian & Qiao 2004). The synthetic Mn dioxide was characterized using scanning electron microscopy (SEM).

Experimental procedures

Batch sorption and transformation of As(III) were conducted by adding specified dosages of δ -MnO₂ into 25 mL of sodium

arsenite solution in 50 mL stoppered centrifuge tubes. The pH values were adjusted using 1 mol/L HNO₃ or NaOH solution. Adequate amounts of NaNO₃ were added to maintain an ionic strength of 0.1 mol/L. The experiment was performed in a shaker at 200 rpm velocity, the reaction samples were withdrawn and centrifuged at 4,000 rpm for 15 min, and then the supernatants were filtrated through a 0.45 μ m membrane filter to analyze the concentrations of different As species in the filtrates. Effect of reaction time on the sorption and transformation by 0.2 g/L δ -MnO₂ was performed using 1.0 mg/L sodium arsenite at 25 °C and pH 6.0. The effect of initial arsenite concentration on the sorption and transformation by 0.2 g/L δ -MnO₂ was performed using 1.0, 5.0, 10.0, and 15.0 mg/L sodium arsenite at 25 °C and pH 6.0. The effect of δ -MnO₂ dosage on the sorption and transformation arsenite (1.0 mg/L) was conducted using 0.2, 0.4, 1.0, and 2.0 g/L δ -MnO₂ as sorbents at 25 °C and pH 6.0. The effect of reaction pH on the sorption and transformation arsenite (1.0 mg/L) by 0.2 g/L δ -MnO₂ was performed using a series of solutions with initial pH at 3.0–9.0. The reaction solutions were capped and shaken for 2.5, 5, 10, 20, 30, 45, 60, 90 min, respectively. At designated time intervals, the reaction samples were withdrawn and centrifuged at 4,000 rpm for 15 min, and then the supernatants were filtrated through a 0.45 μ m membrane filter to determine the amounts of total arsenic and As(III). Twenty-five milliliters of 0.01 mol/L NaOH solution as desorption agent was added into the residues to desorb arsenic adsorbed on the δ -MnO₂ after washing two to three times with double distilled water. The reaction solutions were shaken at 25 °C for 2 h, and then centrifuged at 4,000 rpm for 15 min. The supernatants were also collected to examine the concentrations of total arsenic and As(III) adsorbed. The total amount of As(V) from the double treatments was regarded as the amount of As(III) oxidized.

During the transformation process, As species existed in three forms: (1) most were dissolved in solution; (2) some were sorbed on δ -MnO₂ and the As-treated δ -MnO₂ could be extracted with 25 mL of 0.01 mol/L NaOH for 2 h (Mohan & Pittman 2007); and (3) some were fixed in the structure of δ -MnO₂ and could not be extracted with the same NaOH solution. The three types of As species were As-dissolved, As-sorbed, and As-undesorbed, respectively. The undesorbed As was calculated as the difference between

the concentration of the total added As and the aqueous portion and the As-sorbed portion.

Analytical methods

Anion-exchange column (PRP-X100) was used to separate As(III) from As(V). The filtrate was assayed for total arsenic and As(III) by hydride generation-atomic fluorescence spectrometry (HG-AFS) using AFS-230a (Beijing JiTian Analytical Instrument Co. Ltd, China). Thus the concentrations of total dissolved As, dissolved As(III), total adsorbed As, and adsorbed As(III) were measured directly. The dissolved As(V) was calculated by the difference between the concentration of the total added arsenic and the dissolved As(III); the adsorbed As(V) was calculated by the difference between the concentration of the total adsorbed arsenic and the adsorbed As(III); the undesorbed arsenic was calculated by the difference between the concentration of the total added arsenic and the aqueous portion and the As-adsorbed portion.

The redox potential of the solution was measured between platinum and Ag/AgCl electrode pair with a voltmeter. The potential was read approximately 3 min after dipping the electrodes into the sample solution.

Mn(II) produced in the solution was determined via flame atomic absorption spectrophotometer (WFX-130, Beijing Rayleigh Analytical Instrument Co., China).

The sample aliquots were diluted to appropriate concentration prior to analysis. All analyses were performed in triplicate.

RESULTS AND DISCUSSION

Characterization of δ -MnO₂

Birnessite, the most common Mn oxide mineral in soils, is composed of layers of edge-sharing MnO₆ octahedra separated by a layer of water molecules (Post & Veblen 1990). As shown in Figure 1, the SEM image of the synthesized δ -MnO₂ shows poor crystalline characteristics. It consisted of cluster or ball-like aggregates. The balls were actually randomly stacked as thin plates in high multiples (Feng *et al.* 2006).

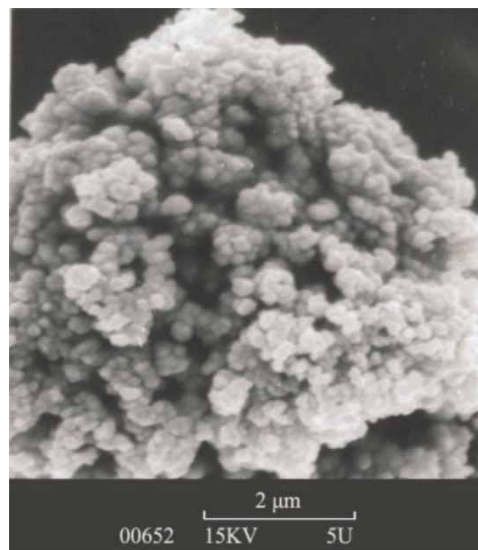


Figure 1 | SEM micrograph of δ -MnO₂.

Oxidative transformation of sodium arsenite with δ -MnO₂

As shown in Figure 2(a), the total As and As(III) in solution decreased sharply at the early reaction stage and turned slowly to a plateau at the later stage. The decrease in total As concentration of the solution could be ascribed to sorption on δ -MnO₂, which was confirmed by the increased sorbed As during the reaction period as shown in Figure 2(b). For As(III), both sorption and oxidative transformation mechanisms by δ -MnO₂ compensated for the decrease. The removal rate at 90 min was 89.4%. Furthermore, solid δ -MnO₂ was reduced to Mn(II) ions in the reaction solution which occurred with the As(III) oxidation reaction, with some slightly dissolved into solutions and some more sorbed onto δ -MnO₂ (Stone & Ulrich 1989). Figure 2(a) shows that the dissolved Mn(II) in the solution was approximately 0.05% of the total Mn species at the 90-min reaction, and may be more in the structure of δ -MnO₂ (Stone & Ulrich 1989).

All As(III) transformations in the solution via oxidation and sorption processes were completed almost within 90 min. The reaction between As(III) and Mn oxide was considerably fast during the first 20 min, which corresponded to approximately 90% of the removal. It has been reported that the surface layer of covalently bonded As(V) can form on the reacted δ -MnO₂ surface, which limits the further reaction of

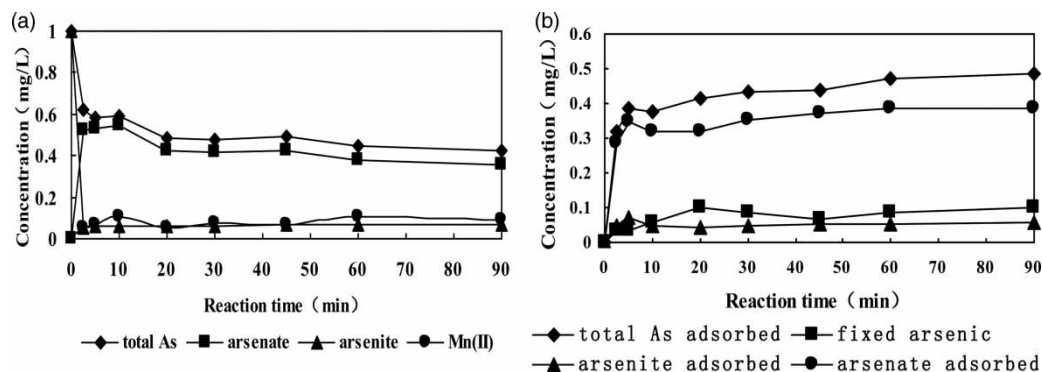


Figure 2 | Concentrations of (a) dissolved As species and Mn(II) in the solution and (b) sorbed exchangeable As species.

δ -MnO₂ with As(III) (Manning *et al.* 2002; Tournassat *et al.* 2002). Moreover, the redox potential in the solution decreased gradually with reaction time (298.4, 281.4, 276.1, 271.7, 267.3, 262.0, 254.2, and 249.6 mV for reaction time 2.5, 5, 10, 20, 30, 45, 60, and 90 min, respectively) due to the generation of Mn(II), which decreased the reaction rate. The inhibited reaction may also be attributed to the reduced reactive surface of δ -MnO₂ by the sorption of reaction products (Klausen *et al.* 1997).

The As(V) concentration in the solution increased in the first 20 min and gradually decreased (Figure 2(a)). The increase in As(V) concentration in the solution is ascribed to As(III) oxidation, whereas the gradual decrease is caused by the simultaneous sorption and fixation on δ -MnO₂ (Wang *et al.* 2008). The faster oxidation rate than the sorption and fixation rates at the initial stage led to the increase in As(V) concentration. The As(V) concentration decreased gradually because of the decreased oxidation rate as discussed above and the relatively faster sorption and fixation rates in the later reaction stage.

The sorbed and undesorbed As species on δ -MnO₂ were determined to further study the removal behavior of Mn oxide in the same reaction process. Figure 2(b) shows that the sorbed total As species increased gradually. It indicates that the sorption occurred throughout the reaction process and was an important pathway for As removal together with the oxidative transformation. Apart from the species discussed above, some As cannot be extracted by NaOH solution. This result indicates that As may be permanently fixed inside the structure of δ -MnO₂ and has little environmental toxicity. As indicated in Figure 2(b), the sorbed amount of undesorbed As in δ -MnO₂ increased quickly at the initial

reaction stage, and remained constant in the later stage. It may indicate that the fixing speed was rapid when the As species comes into contact with δ -MnO₂, and that the fixing sites for As in the structure of δ -MnO₂ were limited.

Factors affecting sodium arsenite oxidative transformation

Effect of δ -MnO₂ dosages

Concentrations of the different As species were determined to evaluate the arsenite transformation and the distribution of As species in the current study.

The results show that increasing δ -MnO₂ increases the transformation rate of sodium arsenite as indicated in Figure 3(a). With relatively high dosages of δ -MnO₂ (1.0 and 2.0 g/L), As(III) was efficiently removed, and the removal rates of As(III) at 90 min were 94.9 and 97.9%, respectively. Lower removal percentages of 79.9 and 84.8% were obtained at dosages of 0.2 and 0.4 g/L δ -MnO₂, respectively. The concentrations of the dissolved and sorbed As(V) and the undesorbed As all increased in the first 20 min. After that, the dissolved and sorbed As(V) increased initially and later decreased, but the undesorbed As exhibited the opposite behavior by decreasing first and increasing later. The redox reaction between Mn oxides and As(III) occurred at the interface of minerals and solution. Sorption of As(III) and desorption of As(V) on the surface of MnO₂ are two steps in the reaction before and after the electron transfer from As(III) to the MnO₂, respectively (Oscarson & Huang 1983). Sorption of As(III) on the surface of Mn oxides would enhance the oxidation of

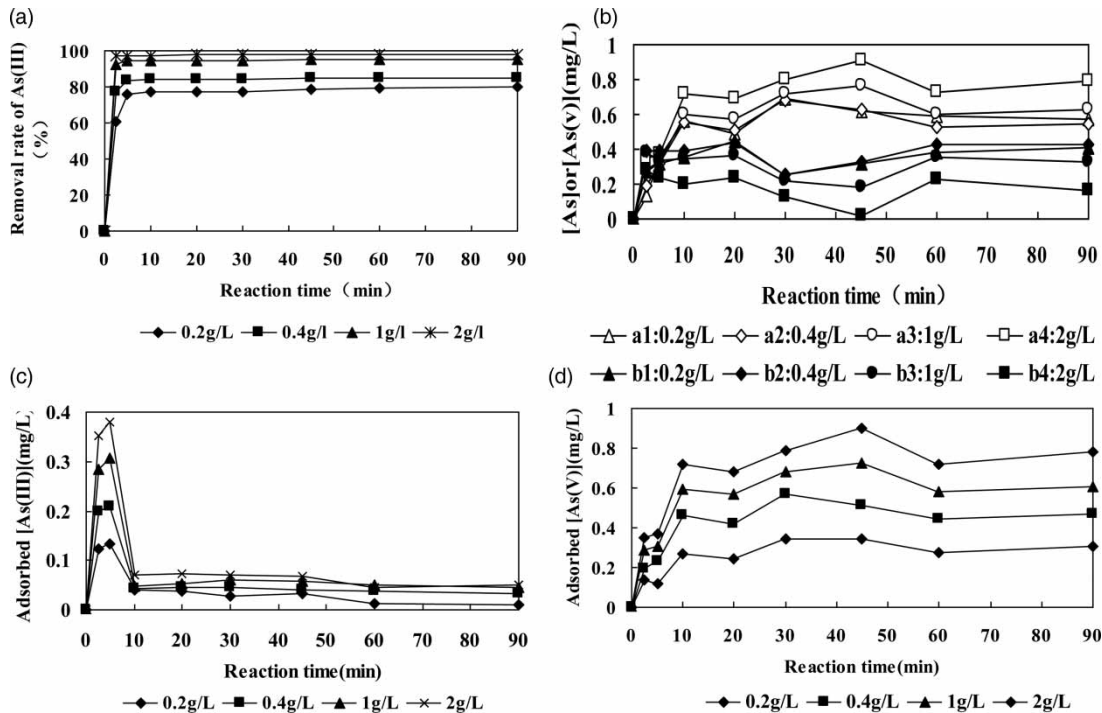


Figure 3 | Effect of δ -MnO₂ dosage on the transformation of arsenite: (a) removal rates of As(III); (b) different formations of formed total As and As(V) (a – As(V) dissolved and sorbed, b – As undersorbed); (c) concentrations of sorbed exchangeable As(III); and (d) As(V) on δ -MnO₂.

As(III), whereas sorption of As(V) would block sorption and subsequent oxidation of As(III) because of the limited sorption sites on the surface of δ -MnO₂. Thus, As(V) was released from the surface to the solution. In this process, a part of undersorbed As was also released to the solution (Scott & Morgan 1995). Furthermore, a high dosage of δ -MnO₂ can provide more specific sorption sites to fix more As(V). A period of 45 min was needed for the concentration of undersorbed As to reach the minimum value with relatively high dosages of δ -MnO₂ (1.0 and 2.0 g/L), whereas less time was needed with 0.2 and 0.4 g/L δ -MnO₂. On the other hand, the concentrations of the dissolved and sorbed As(V) increased gradually with decreasing undersorbed As, and more time was needed to reach the maximum value at high dosages of δ -MnO₂. The concentrations of the dissolved and sorbed As(V) reached the maximum value indicating that most of the As(III) added was oxidized to As(V). When the concentration of the undersorbed As reached the minimum value, the specific sorption was in a dominant position; the released As(V) in solution was again sorbed and fixed in the structure of δ -MnO₂ (Tournassat *et al.* 2002). The restored specific sorption increased anew the

concentration of undersorbed arsenic and the dissolved and sorbed As(V) decreased accordingly. However, at the same dosage, the concentration of the dissolved and sorbed As(V) was higher than that of the undersorbed As in the whole reaction process, indicating that the oxidation of As(III) is the main process. The formed As(V) increased with increasing dosage because of the more oxidation sites available, and the trend became more obvious with higher dosages. Hence, with lower oxide loading, the undersorbed As(V) concentration was higher, and the dissolved and sorbed As(V) concentration was lower.

With the increase in δ -MnO₂ dosages, more As(V) and As(III) were sorbed. The sorbed As(III) increased sharply in the first 5 min and decreased to a plateau in the subsequent process. At the same time, the sorbed As(V) increased sharply in the first 10 min. The concentration of sorbed As(III) was far lower than sorbed As(V) with the same δ -MnO₂ dosage.

Higher δ -MnO₂ dosages can increase the oxidation rates of As(III). However, the oxidation efficiency per unit weight of δ -MnO₂ decreased with increasing δ -MnO₂ dosages. At 0.2, 0.4, 1.0, and 2.0 g/L δ -MnO₂, the oxidation efficiencies

were 4.57, 2.35, 0.98, and 0.39 mg/g, respectively. At a fixed volume reaction suspension, lower dosages of δ -MnO₂ can result in more sufficient contact between the added δ -MnO₂ and As(III).

Effect of initial concentration of sodium arsenite

The arsenite removal rates decreased when increasing the initial sodium arsenite concentration from 1.0 to 15.0 mg/L (Figure 4(a)). The transformation trend of the concentration of As(V) (the oxidation product) and the undesorbed As was in accordance with that of different dosages. The formed As(V) concentration sharply increased until it reached the maximum value at 45 min. Then, the concentration decreased gradually to a plateau. The concentration of undesorbed As decreased initially and then increased. In contrast to the higher concentration of formed As(V), the undesorbed As concentrations were lower. These findings further prove that oxidation of As(III) dominates the reactions.

For the sorbed exchangeable As species on the surface of δ -MnO₂ as shown in Figures 4(d) and 4(e), As(III) concentrations were lower than 0.07 mg/L at all initial arsenite concentrations. The concentration of sorbed As(III)

increased quickly in the initial stage and decreased gradually as the oxidation proceeded. Similarly, the sharply increased sorbed As(V) concentration indicates that As(III) can instantly be oxidized as soon as it is sorbed on δ -MnO₂. For As(V), the combined process of both sorbed As(III) oxidation and the As(V) sorption resulted in increased As(V) throughout the reaction process.

Effect of pH

The effect of pH values on the transformation of sodium arsenite was studied (Figure 5). After 90 min, the As(III) removal rate and the concentration of the sorbed As species decreased with increasing pH (2.0–9.0) (Figures 5(a), 5(d), and 5(e)). When the reaction occurred at higher pH values, As(III) easily formed flocculent deposition. It is difficult for As(III) to disperse to the surface of δ -MnO₂ because of the lower solubility of the deposition, thereby decreasing the sorbed As(III). Two mechanisms are probably involved in the sorption of As(V) by δ -MnO₂. One is the unspecific sorption that occurs between the charges on the surface and As(V) anions through electrostatic potential. The surface shows more negative charge with increasing pH, and electrostatic repulsion occurs between the surface negative charge

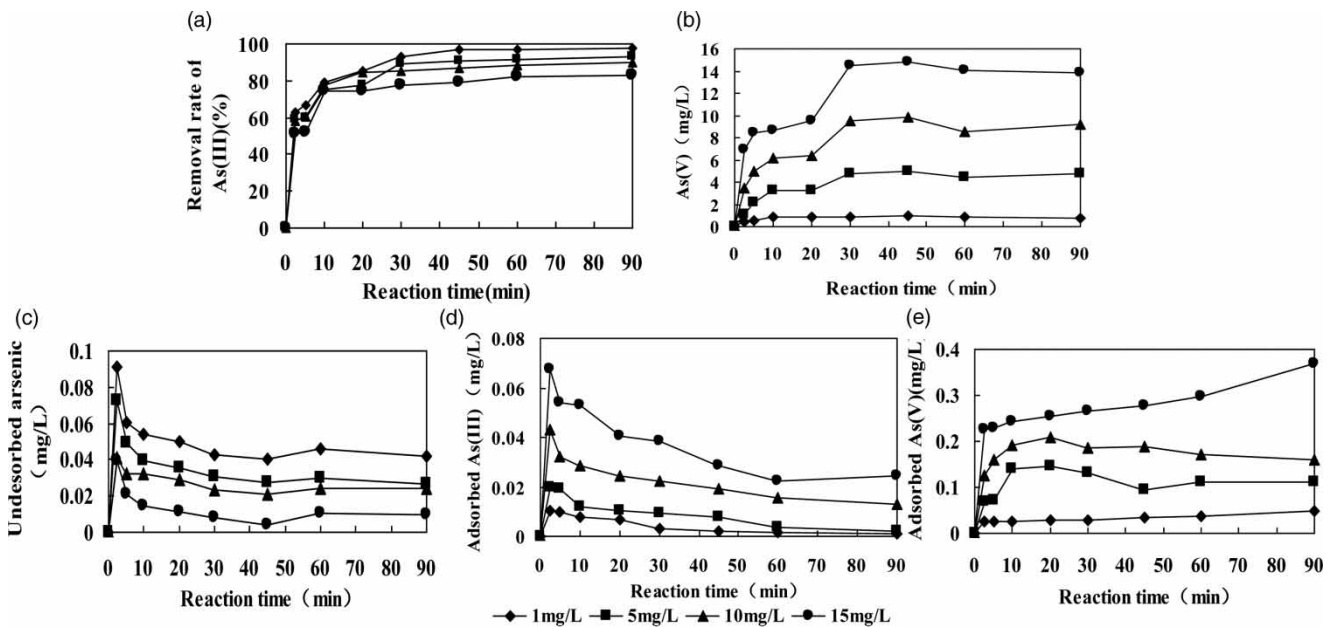


Figure 4 | Effect of initial concentration on the transformation of arsenite: (a) removal rates of As(III); (b) As(V) dissolved and sorbed; (c) As undesorbed; (d) concentrations of sorbed exchangeable As(III); and (e) As(V) on δ -MnO₂.

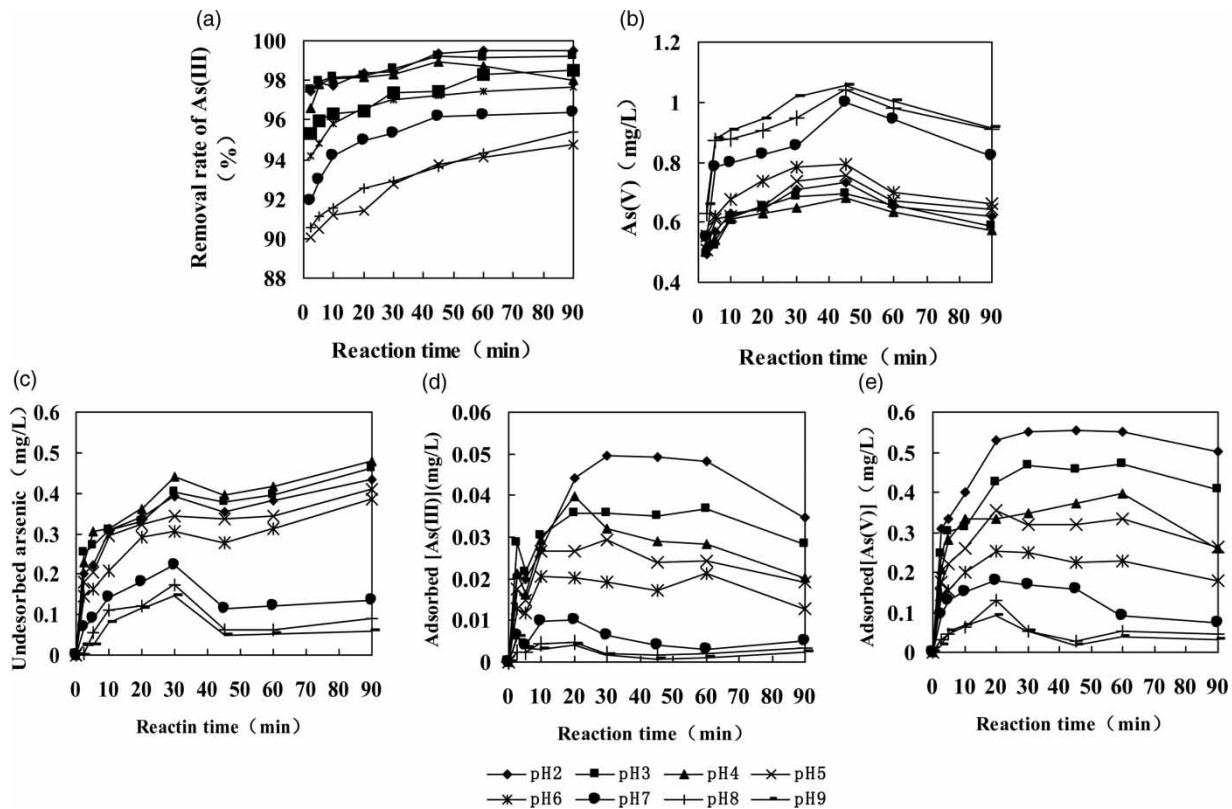


Figure 5 | Effect of pH on the transformation of arsenite: (a) removal rates of As(III); (b) dissolved and sorbed As(V); (c) As undesorbed; (d) concentrations of sorbed exchangeable As(III); and (e) As(V) on δ -MnO₂.

and As(V). The electrostatic repulsion becomes stronger with increasing surface negative charge. The other mechanism is the specific sorption of As(V) anions by δ -MnO₂ through ligand exchange. At lower pH values, the exchangeable Mn-OH₂⁺ is the main species on the surface of the oxide, which leads to more sorption quantity. With increasing pH, the dominant species gradually transforms to Mn-OH, which is not possible for the ligand exchange with arsenate anions. Furthermore, the competitive sorption may occur because of the increasing concentration of OH⁻. Both reasons can explain the reduction of the sorbed As(V). Therefore, both specific and unspecific sorption could be weakened and lead to the decrease of removal rate of total As.

When pH was increased from a very low value (pH 2.0), the dissolved and sorbed As(V) by δ -MnO₂ gradually decreased until it reached the minimum (pH 4.0), for example, the concentrations of dissolved and sorbed As(V) were 0.64, 0.61, 0.57 mg/L, respectively, from pH 2.0 to pH 4.0 at 90 min. While pH continually increased, the formed As(V) amount remarkably increased. Such effect

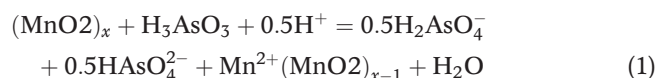
can be attributed to two opposing mechanisms. As pH increased, the oxidation ability of δ -MnO₂ is restrained; however, the reduction ability of As(III) was enhanced. In an acidic medium, the standard potentials for the half reactions (MnO₂ + H⁺)/Mn²⁺ and (H₃AsO₄ + H⁺)/H₃AsO₃ were 1.23 and 0.56 V; however, in alkaline medium, the standard potentials for the half reactions MnO₂/(Mn(OH)₂ + OH⁻) and AsO₄³⁻/(AsO₃³⁻ + OH⁻) were 0.1 and -0.71 V. The lowest potential of the reaction between Mn oxides and As(III) existed at a certain pH value, where the minimum oxidation of As(III) occurred. Mn oxides had a stronger tendency to oxidize As(III) in alkaline medium than in acidic medium, which is consistent with a previous report (Feng *et al.* 2006).

When the pH in the initial solution was at a lower value, H⁺ was consumed during the reaction, and pH increased after oxidation. In contrast, when pH was initially higher, H⁺ was produced during the reaction, and pH decreased after the reaction. That is to say, the oxidation of As(III) by Mn oxides had a buffering effect on the pH in the

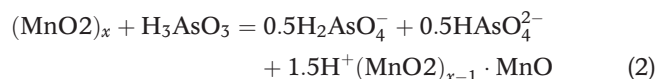
solution. The pH changed from 2.00, 3.00, 4.00, 5.00, 6.00, 7.00, 8.00, and 9.00 to 2.16, 3.50, 4.92, 6.40, 6.88, 7.11, 7.32, and 7.86 after oxidation.

Under different pH conditions, different reaction processes resulting from the variation in 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) can be considered as H_3AsO_3 , H_2AsO_4^- , and $\text{H}_2\text{AsO}_4^{2-}$ across the experimental pH range based on their acid disassociation constants. Thus, if $(\text{MnO}_2)_x$ were used to denote Mn oxides, the oxidation reactions at the low and high pH ranges between As(III) and the Mn oxides can be expressed as follows (Feng *et al.* 2006):

At low pH:



At high pH:



In Equations (1) and (2), $0.5\text{H}_2\text{AsO}_4^- + 0.5\text{HAsO}_4^{2-}$ represents the produced As(V). As shown in Figure 6 (Feng *et al.* 2006), the ratio of H_2AsO_4^- to $\text{H}_2\text{AsO}_4^{2-}$ varies with pH. When pH was increased, the concentration of $\text{H}_2\text{AsO}_4^{2-}$ increased and that of H_2AsO_4^- decreased.

At low pH, the oxidation of As(III) occurred as Equation (1): pH increased after reaction due to H^+ consumption. As pH increased from a lower value, the reaction of Equation (1) would apparently be restrained, and the oxidation amount of As(III) gradually decreased. The lower the initial pH, the more increment the pH would show after reaction. This results from more H^+ consumed due to the reaction and the balance of $0.5\text{H}_2\text{AsO}_4^-$ and $0.5\text{H}_2\text{AsO}_4^{2-}$ at lower pH. When pH was higher, such as in alkali medium, the oxidation of As(III) tended to predominantly occur as Equation (2). As a result, pH decreased after reaction due to the release of H^+ . As pH increased, the reaction of Equation (2) would apparently be promoted, and the oxidation amount of As(III) rapidly

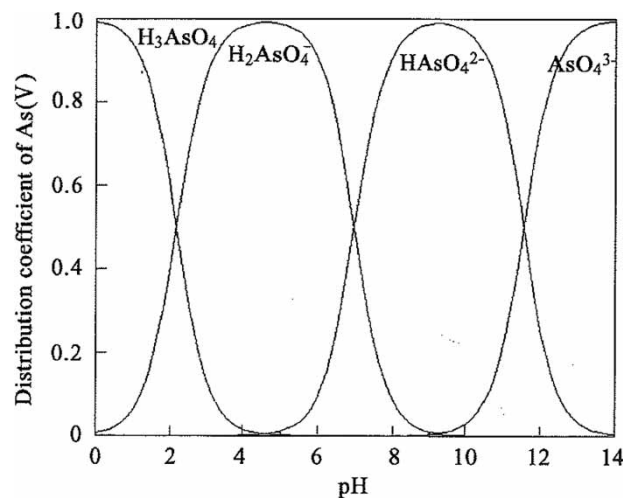


Figure 6 | Curves of As(V) species distribution versus pH.

increased. The higher the initial pH, the more decrement the pH would show after reaction, resulting from more H^+ produced due to the reaction and the balance of $0.5\text{H}_2\text{AsO}_4^-$ and $0.5\text{H}_2\text{AsO}_4^{2-}$ at higher pH. From the equations, 1.5 times more H^+ was produced in alkaline medium than that consumed in acidic medium. Moreover, as pH increased, more negative charges 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, pH increase in alkaline condition had a more significant influence on As(III) oxidation by Mn oxides than that in acid condition.

As discussed above, higher amounts of dissolved and sorbed As(V) were disadvantageous to the specific sorption of As. Thus, the transformation tendency of the undesorbed As was still in contrast to that of the dissolved and sorbed As(V) (Figure 5(c)). Consequently, the concentration of the undesorbed As increased at the lower pH range of 2.0–4.0, but decreased with increasing pH at the higher pH range of 5.0–9.0.

CONCLUSIONS

Arsenite was effectively transformed into arsenate both in the solution and on the surface of $\delta\text{-MnO}_2$. The oxidative transformation rate increased with high $\delta\text{-MnO}_2$ dosage and low initial concentration of arsenite. The sorption and

oxidation of As(III) were influenced by the initial pH value. When pH was increased from the very low value (pH 2.0), the amount of As(III) oxidized by the tested δ -MnO₂ initially decreased and then dropped at pH 4.0. While pH continually increased, the amount of As(III) oxidation by δ -MnO₂ remarkably increased. While the pH at 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. The oxidation processes at low and high pH range between As(III) and δ -MnO₂ can be expressed by different reaction equations because of the variation in pH effects and different species of products.

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