



The oxidative transformation of sodium arsenite at the interface of α -MnO₂ and water

Xiu-juan Li^{a,b,d}, Cheng-shuai Liu^b, Fang-bai Li^{b,*}, Yong-tao Li^{c,**}, Li-jia Zhang^{b,c},
Chuan-ping Liu^b, Yong-zhang Zhou^a

^a Guangzhou Institute of Geochemistry, Chinese Academy of Sciences, Guangzhou 510640, PR China

^b Guangdong Key Laboratory of Agricultural Environment Pollution Integrated Control, Guangdong Institute of Eco-Environmental and Soil Sciences, Guangzhou 510650, PR China

^c College of Natural Resources and Environment, South China Agricultural University, Guangzhou 510642, China

^d Graduate University of Chinese Academy of Sciences, Beijing 100039, PR China

ARTICLE INFO

Article history:

Received 10 December 2008

Received in revised form 8 May 2009

Accepted 30 August 2009

Available online 4 September 2009

Keywords:

Arsenite

Arsenate

Pyrolusite

Manganese oxide

Oxidation

ABSTRACT

Arsenite is acute contaminant to human health in soil and water environment. In this study, Pyrolusite (α -MnO₂) was used to investigate the oxidative transformation of arsenite into arsenate with batch experiments under different reaction conditions. The results showed that arsenite transformation occurred and was accompanied by the adsorption and fixation of both As(III) and As(V) on α -MnO₂. About 90% of sodium arsenite (10 mg/L) were transformed by α -MnO₂ under the conditions of 25 °C and pH 6.0, 36.6% of which was adsorbed and 28.9% fixed by α -MnO₂. Increased α -MnO₂ dosages promoted As(III) transformation rate and adsorption of arsenic species. The transformation rate and adsorption of arsenic species raised with increasing pH values of reaction solution from 4.7 to 8.0. The oxidation rate decreased and adsorbed As(III) and As(V) increased with increasing initial arsenite concentration. The enhancement on oxidative transformation of sodium arsenite may result from abundant active sites of α -MnO₂. Along with adsorption and fixation of arsenic species during the reaction, the crystal structure of α -MnO₂ did not change, but the surface turned petty and loosen. Our results demonstrated that α -MnO₂ has important potential in arsenic transformation and removal as the environmentally friendly natural oxidant in soil and surface water.

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1. Introduction

As a contaminant released from metallic ores, industrial and agricultural effluents, arsenic is a toxic element for human health. The exposure to arsenic often has deleterious effects and can cause a variety of adverse health effects, including dermal changes, respiratory, cardiovascular, gastrointestinal, genotoxic, mutagenic and carcinogenic effects, and also may interfere with the immune system [1–3]. The poisoning events incurred by arsenic have been often reported worldwide up to now. Thus, the removal and disinfection of arsenic species are important to human health. Understanding the fate and behavior of arsenic in soil and aquatic environment is essential for arsenic removal [4–6]. Arsenic is ubiquitous in the environment and has four oxidation states: 0 (arsenic), –3 (arsine), +3 (arsenite) and +5 (arsenate). The toxicity of arsenic depends strongly on its chemical forms. Two soluble inorganic

forms, arsenite [As(III)] and arsenate [As(V)], are toxic to biological systems, with arsenite considered more toxic than arsenate [4]. As(III) is a neutral species of H₃AsO₃ at neutral pH, while As(V) is the most stable species under aerobic conditions and normally exists as deprotonated oxyanions of arsenic acid H₂AsO₄[–] in solution of pH 4–10 [5]. Compared with As(V), As(III) has high mobility and weak adsorption in soils, and thereby is more poisonous [6].

The conventional arsenic removal procedures generally involve a pretreatment for arsenite oxidation, followed by adsorption or co-precipitation of formed arsenate with adsorbents or coagulants [7]. Although arsenite oxidation can be achieved by some oxidants, such as oxygen, ozone, hydrogen peroxide, chlorine, ferrous and TiO₂ [8,9], these oxidants are unfortunately not environment friendly. As comparisons, natural oxidants in recent years have received increasing attention for arsenite removal because they can form self-cleaning system after some adjustments [7]. Natural adsorbents, such as iron oxyhydroxide, iron ores and ferruginous manganese ore, have been received more attention for adsorption and degradation of arsenic [10–12].

Manganese, as the third most abundant transition metal in earth crust, is important to both biological and environmental processes [13]. Manganese oxides are naturally found in soils,

* Corresponding author. Tel.: +86 20 87024721; fax: +86 20 87024123.

** Corresponding author. Tel.: +86 20 85281812; fax: +86 20 85281812.

E-mail addresses: cefbli@soil.gd.cn, cefbli@hotmail.com (F.-b. Li), yongtao@scau.edu.cn (Y.-t. Li).

aquifers, oceanic and aquatic systems [14], and are considered as important natural oxidizing agents, with reductive half potentials of 1.50 and 1.23 V for MnOOH and MnO₂, respectively [15,16]. Manganese oxides were reported readily oxidizing many reduced organic/inorganic pollutants in aqueous environment, such as chromium [17] and arsenite [18].

However, oxidative transformation of arsenite is a complicated process because the reaction occurred both in solution and on surface of oxidants [19]. Similarly the different valents of arsenic(III and V) exist both in solution and on surface of oxidants, and some of them can even enter the structure of oxidant and be fixed as a part of the oxidant permanently [20]. However, systematic information about the oxidative transformation of arsenite species is yet not enough. Therefore, our aim was to investigate the effect of α -MnO₂, one of the most stable natural manganese oxides, on oxidative transformation of arsenite, based on different initial arsenite concentrations, α -MnO₂ dosages and pHs. The special focus was on the different states of arsenic species that occurred homogeneously in the reaction solution or heterogeneously on the surface and in the structure of α -MnO₂ during arsenite transformation process. The changes in morphologies and structures of α -MnO₂ during reaction were also studied to explore the reaction mechanisms.

2. Materials and methods

2.1. Chemicals

Sodium arsenite, analytical grade, was purchased from Aldrich (Milwaukee, WI, USA). The standard solution of 1000 mg/L As(V) stock solution was from National Analysis Center for Iron and Steel, China. All of other reagents were analytical grade and purchased from Guangzhou Chemical Co., China. All the chemicals were used without further purification and the solutions were prepared with high purity water obtained from a Milli-Q system to the required concentration and then stored in a refrigerator at 5 °C before used. A mixture of 5 mL 5% (w/v) ascorbic acid and 5 mL 5% (w/v) sulfocarbamide, and 10 mL of 5 M hydrochloric acid were employed to reduce As(V) to As(III), when analyzing arsenic species in 25 mL solution. A 5.0 g/L potassium tetrahydroborate solution dissolved in 20.0 g/L potassium hydroxide solution prepared daily was used to generate the corresponding arsenic hydrides when being pumped to the Atomic Fluorescence Spectrometry (AFS) instrument. Argon (>99.9%) was used as carrier gas (500 mL/min) to dry the formed hydride.

2.2. α -MnO₂ preparation and characterization

α -MnO₂ was prepared from 10.0 g MnCO₃, which was dissolved with 40 mL of 9 M H₂SO₄, and then diluted to 120 mL. The solution was stirred continually when 200 mL of 0.232 M KMnO₄ was added dropwise, and then maintained in water bath at 85 °C for 2 h. After being cooled down to room temperature naturally, the reaction suspensions were filtrated and the residue on filter was washed with high purity water to pH 7.0. After being sintered at 110 °C for 24 h and then skived and sieved with 1 mm mesh sieves, α -MnO₂ powders were obtained [21].

The synthetic manganese dioxide was characterized by the methods including the X-ray powder diffraction (XRD) and the Brunauer–Emmett–Teller (BET). The XRD characterization of α -MnO₂ was recorded on a Rigaku D/Max-III A diffract meter at room temperature, operated at 30 kV and 30 mA with a Cu K α radiation ($\lambda = 0.154$ nm). The BET surface area and the total pore volume of α -MnO₂ were measured by the BET method in which N₂ adsorption at 77 K was applied and Carlo Erba Sorptometer was used [22]. The

average size of α -MnO₂ was determined by the Scherrer formula with its (1 1 0) peak [23].

2.3. Experimental procedures

Transformations of arsenic species were conducted by adding given dosage of α -MnO₂ into 20 mL of aqueous sodium arsenite solution in a batch of 50 mL plastic bottles with appropriate plastic septa and cover. The experiment was performed on a shaker with the velocity of 200 rpm. At the given specific time intervals, the reaction samples were withdrawn and then immediately filtrated through a 0.45 μ m membrane filter, and the concentrations of different arsenic species in the filtrates were analyzed. The effect of initial arsenite concentration on the transformation by 1.0 g/L α -MnO₂ was performed with respective 2.5, 5.0, 10.0, and 20.0 mg/L sodium arsenite at 25 °C and pH 6.0. The effect of α -MnO₂ dosage on 10 mg/L arsenite transformation was conducted using 0.5, 1.0, 3.0, and 5.0 g/L α -MnO₂ as the oxidants at 25 °C and pH 6.0. The effect of reaction pH on 10 mg/L arsenite transformation by 1.0 g/L α -MnO₂ was performed with buffer solutions of pH 4.7, 6.0 and 8.0 at 25 °C. The buffer solutions were prepared as described in Table 1.

During the transformation process, arsenic species existed as three forms: (1) most was dissolved in solutions; (2) some was adsorbed on α -MnO₂, and the arsenic-treated α -MnO₂ (0.02 g) can be extracted with 20 mL of 0.1 M aqueous sodium hydroxide for 24 h [24] (compared with other extraction reagents NaF [25], NaHCO₃, and HCl [26], NaOH is the most effective extraction reagent of arsenic species from α -MnO₂. Data not presented); (3) some was fixed in the structure of α -MnO₂ and cannot be extracted with the same NaOH solution. The three kinds of arsenic species were named as As-dissolved, As-adsorbed, and As-fixed, respectively. The fixed arsenic was calculated by the difference between the concentration of the total added arsenic and the aqueous portion and the As-adsorbed portion.

2.4. Analytical methods

Arsenic species were analyzed on the spectroscopy equipment (AF-610A, Beijing Rayleigh Analytical Instrument Co. Ltd., China) on the basis of Hydrid Generation-Atomic Fluorescence Spectrometry (HG-AFS). It was reported that As(V) can react with KBH₄ at a lower reaction kinetic than As(III) [27]. Thus, the signal produced by the pentavalent species depends on the hydride generation conditions and it represented around 50–70% of signal produced by trivalent species [28]. Similar to the method that using a series of proportional equations to determine arsenic species in the same sample by HG-AFS [27,29], measurements of As(III) and As(V) by HG-AFS were conducted at two different experimental conditions in this study, which allowing us to establish two independent proportional equations for the measurement of each sample. It should be the fluorescence intensity obtained in each case that is proportional to the

Table 1
The buffer solutions with different pH values.

pH values	Preparation methods
4.7	Dissolved 18 g sodium acetate and 9.8 mL acetic acid in water, and then the solution was diluted to 1000 mL
6.0	Dissolve 54.6 g sodium acetate, and 1 M acetic acid 20 mL in water, and then the solution was diluted to 500 mL
8.0	Mixed 0.57 g borax and 22.94 g calcium chloride with 800 mL water, and after adjusted the pH to 8.0 with 2.5 mL 1 M hydrochloric acid, the solution was diluted to 1000 mL

concentration of As(III) and As(V) as:

$$C_{(A)} = [\text{As(III)}] + [\text{As(V)}] \quad (1)$$

$$C_{(B)} = [\text{As(III)}] + 0.5[\text{As(V)}] \quad (2)$$

In condition (A), an additional mixture of 5 mL ascorbic acid (5%, w/v), 5 mL sulfocarbamide (5%, w/v) and 10 mL of 5 M HCl was added into 0.5 mL obtained sample before HG-AFS measurement in order to reduce As(V) to As(III). The determined concentration is that of the total arsenic. In condition (B), the As solution sample (0.5 mL) was only treated with 10 mL of 5 M HCl, and the determined concentration refers to As(III) and half part of As(V) [29]. Mn(II) produced in the solution was determined by 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 duplicate.

2.5. Surface characterization of α -MnO₂ before and after arsenite reaction

The reaction suspensions were centrifuged immediately and α -MnO₂ was collected after 24 h of reaction of 1.0 g/L α -MnO₂ with 40.0 mg/L arsenite at 25 °C and pH 6.0. After being extracted with 0.1 M aqueous sodium hydroxide for 24 h and washed with high purity water for another 24 h, the collected α -MnO₂ was vacuum-freeze dried with a lyophilizer (FD-1D-50, Beijing, China), and then characterized with scanning electron microscopy, energy-dispersive X-ray spectrometry (SEM-EDX) and Fourier transform infrared spectroscopy (FTIR). α -MnO₂ samples before reaction were also characterized by the same methods. SEM was conducted on a secondary electron detector (Leica, tereoscan 440), and EDX was also obtained through the SEM equipped with a link analyzer (Oxford, ISIS-300) to determine the amount of elements on the surface. FTIR spectra were collected on a Fourier transformation infrared spectrometer (EQUINOX 55, Bruker, Germany).

3. Results and discussion

3.1. Structure property of prepared manganese oxide

The XRD graphs of standard α -MnO₂ and the prepared sample, as shown in Fig. 1, confirmed that the prepared sample had all seven peaks of (1 1 0), (2 0 0), (3 1 0), (2 1 1), (3 2 1), (4 1 1) and (5 2 1),

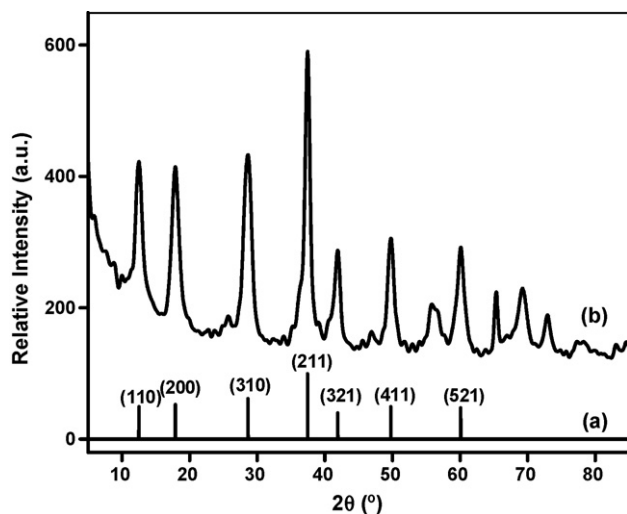


Fig. 1. The standard XRD pattern of α -MnO₂ (a) and the XRD pattern of prepared α -MnO₂ (b).

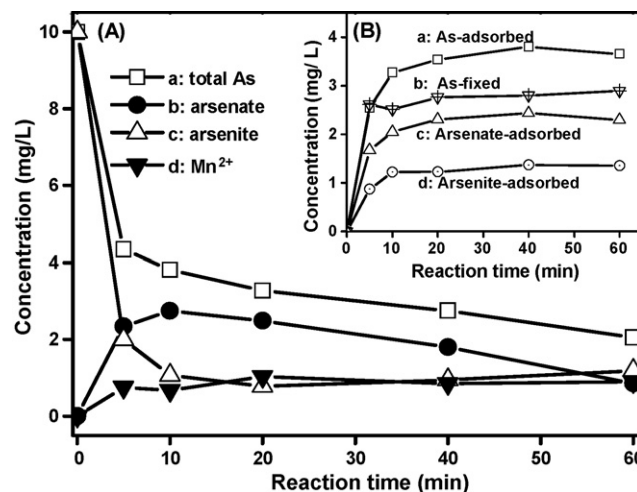


Fig. 2. The concentration of the arsenic species and Mn(II) in the solution (A), and the concentration of adsorbed exchangeable arsenic species (B) during the transformation process of 10 mg/L sodium arsenite by 1.0 g/L α -MnO₂ at pH 6.0 and 25 °C.

which were attributed to α -MnO₂ (JCPDS 44-0141) [30]. The average size of α -MnO₂ was determined using the Scherrer formula with its (1 1 0) peak to be 12.5 nm [23]. The specific surface area was 100.9 m²/g and the total pore volume was 0.156 cm³/g.

3.2. Oxidative transformation of sodium arsenite with α -MnO₂

Transformation kinetics of arsenic species (As-dissolved) were shown in Fig. 2A at 10.0 mg/L initial As(III) concentration, 1.0 g/L α -MnO₂ dosage, 25 °C and the reaction pH 6.0 maintained by buffer solution. The results in Fig. 2A showed that the total arsenic and As(III) in solution decreased sharply at early reaction stage, and then turned slowly to a plateau at the later stage. These results indicated that the oxidation of sodium arsenite by α -MnO₂ did not follow the pseudo-first-order kinetics well. The decrease in total arsenic concentration in the solution was ascribed to the adsorption and fixation on α -MnO₂, which was confirmed by the increased adsorbed arsenic during the reaction period as shown in Fig. 2B. As for As(III), both of adsorption and oxidative transformation mechanisms by α -MnO₂ compensated for the decrease and the removal rate at 60 min was 88.07%. Furthermore, solid α -MnO₂ was found to be reduced to Mn(II) ions in the reaction solution accompanied As(III) oxidation reaction, with some slightly dissolved into solutions and some more adsorbed onto α -MnO₂ [31]. According to Fig. 2A, the dissolved Mn(II) in the solution accounted for about 0.09% of total manganese species at 60 min of reaction, and more may be in the structure of α -MnO₂ [31]. The result also indicated that the dosage of 1.0 g/L α -MnO₂ was enough for the complete oxidation of 20 mL of 10.0 mg/L sodium arsenite as used in the study.

All of As(III) transformations in the solution by oxidation and adsorption processes occurred almost within 60 min. The reaction between As(III) and manganese oxide was considerably fast at the first 20 min, which responds for about 90% of the As(III) removal. It has been reported that the surface layer of covalently bound As(V) can form on the reacted α -MnO₂ surface, which limited further reaction of α -MnO₂ with As(III) [32,33]. Moreover, the redox potential in the solution decreased gradually along with the reaction time owing to the generation of Mn(II), which decreased the reaction rate. The inhibited reaction may also be attributed to the reduced reactive surface of α -MnO₂ by the adsorption of reaction products [34].

As(V) concentration in solution increased at the first 10 min and then decreased gradually (Fig. 2A). The increase of As(V) in solution was ascribed to oxidation of As(III), while the gradual decrease was caused by the simultaneous adsorption and fixation on α -MnO₂ [19]. The faster oxidation rate than the adsorption and fixation rate at the initial stage led to the increase of As(V). Then due to the decreased oxidation rate as discussed above and the relatively faster adsorption and fixation rate in the later reaction stage, As(V) concentration decreased gradually.

The adsorbed and fixed arsenic species on α -MnO₂ was determined to further study the removal behavior of manganese oxide at the same reaction process (Fig. 2B). According to Fig. 2B, the adsorbed arsenic species, As(III) and As(V), increased gradually up to 3.66, 1.36 and 2.30 mg/L, respectively in 60 min of reaction, which suggested 36.6% of total added As(III) can be adsorbed by α -MnO₂. It indicated that the adsorption occurred throughout the reaction process and it was also an important pathway for arsenic removal together with the oxidative transformation. Apart from the species discussed above, some of arsenic cannot be extracted by sodium hydroxide. The result indicated that arsenic may be permanently fixed inside the structure of α -MnO₂ and had little environmental toxicity. As indicated by line 'b' in Fig. 2B, the concentration of fixed arsenic in α -MnO₂ increased quickly at the initial reaction stage, and then kept constant at the concentration of about 2.89 mg/L in the later stage, which suggested that about 28.9% of added total As(III) can be fixed. It may indicate that the fixing speed was rapid when arsenic species contacted α -MnO₂ and the fixing sites for arsenic in the structure of α -MnO₂ were limited.

Ferruginous oxides/hydroxides have also been used to remove arsenic. As reported previously, ferruginous manganese ore can remove about 99% of arsenic from real groundwater samples [35], and for the mine waste effluent iron hydroxide even can remove the residual concentrations of arsenic close to the drinking water standard proposed by the World Health Organization (10 μ g/L) [36]. Compared with ferruginous oxides and iron hydroxide, α -MnO₂ may be not a so efficient removal reagent as Ferruginous oxides/hydroxides. However, manganese dioxides are important natural oxidants and it can oxidize As(III) into As(V) together with the adsorption and fixation processes to decrease the toxicity of arsenic, and also it can oxidize As(III) efficiently in shorter time.

3.3. Factors affecting sodium arsenite oxidative transformation

3.3.1. The effect of the initial concentration of sodium arsenite

The sum of arsenic species both in the solutions and adsorbed on α -MnO₂, the fixed total As, and the adsorbed exchangeable arsenic species on α -MnO₂ were used to evaluate the arsenite transformation and the distribution of arsenic species in the following studies. Increasing initial sodium arsenite concentration from 2.5 to 20.0 mg/L, the arsenite removal rates decreased from 99.2% to 87.9% (Fig. 3A). The concentration of As(V) (the oxidation product) increased from 1.99 to 11.04 mg/L in 60 min of reaction with increasing initial sodium arsenite concentration from 2.5 to 20.0 mg/L (Fig. 3B). As to the adsorbed exchangeable arsenic species on the surface of α -MnO₂ as shown in Fig. 3C and 3D, As(III) concentrations were lower than 1.40 mg/L at all initial arsenite concentrations, while As(V) increased quickly in initial stage and then to around 1.78, 2.37, 1.89, and 4.00 mg/L with the initial arsenite concentrations of 2.5, 5.0, 10.0, and 20.0 mg/L. The results indicated that As(III) could instantly be oxidized as soon as it was adsorbed on α -MnO₂. As for As(V), the combined process of both oxidation of adsorbed As(III) and the adsorption of As(V) resulted in increased As(V) throughout the reaction process. The fixed arsenic species increased with the increasing initial concentration of As(III). When the initial concentrations of As(III) were 2.5, 5.0, 10.0, and 20.0 mg/L,

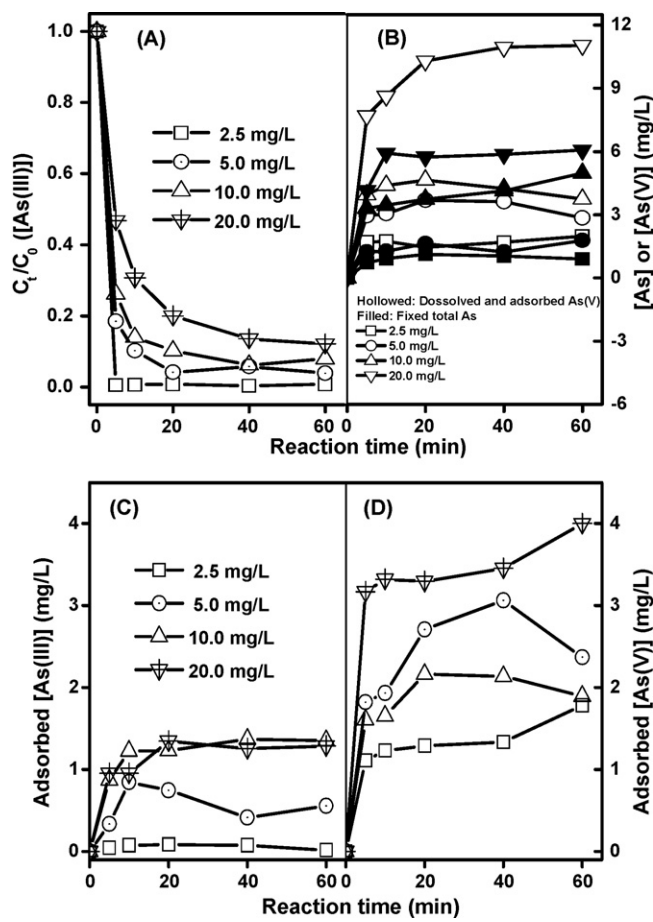


Fig. 3. The effect of the initial concentration of sodium arsenite on the transformation by 1.0 g/L α -MnO₂ at 25 °C and pH 6.0: the removal rates of As(III) (A), the formed different formations of total As and As(V) (B), the concentrations of adsorbed exchangeable As(III) (C) and As(V) (D) on α -MnO₂.

the fixed total As was obtained with 0.90, 1.78, 4.97, and 6.07 mg/L (Fig. 3B).

With increased initial concentration of sodium arsenite, elevated dissolved Mn(II) amount was formed. According to Fig. 4, concentration of formed Mn(II) increased from 0.31 to 3.05 mg/L

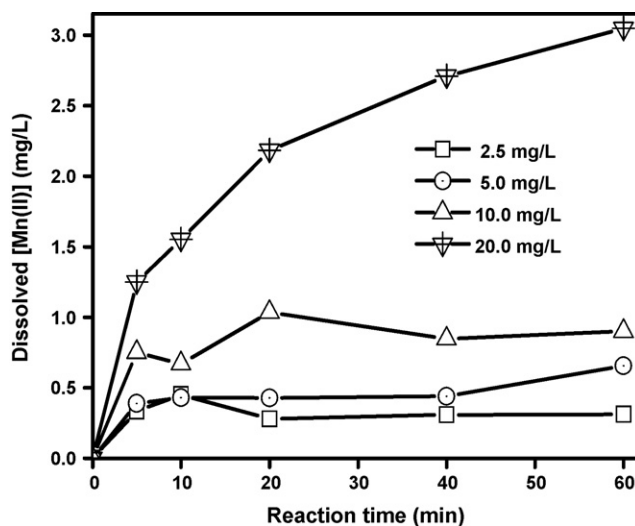


Fig. 4. The concentration of released Mn(II) in the reaction solutions with the reaction conditions as in Fig. 3.

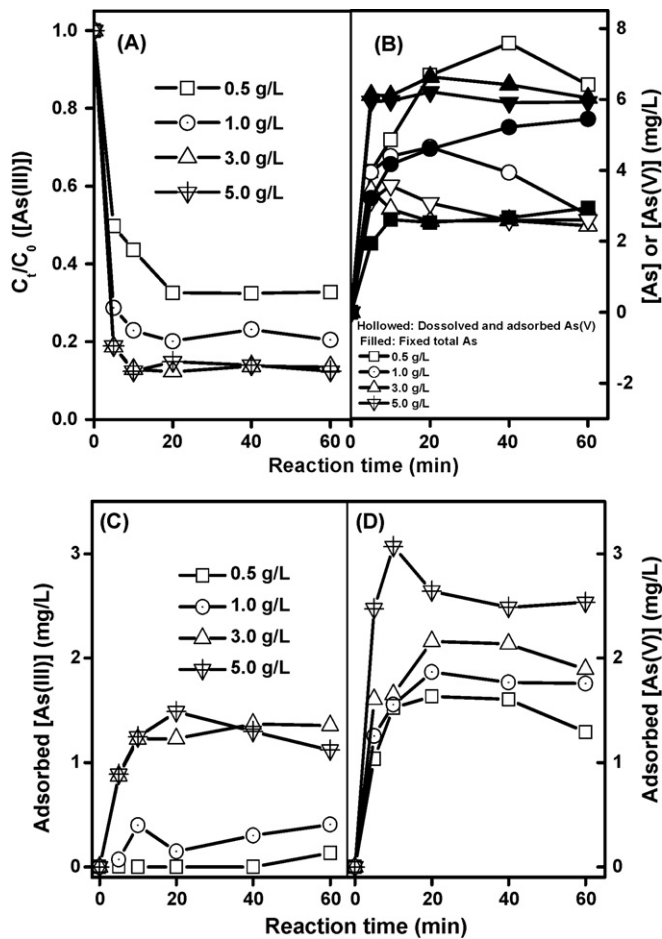


Fig. 5. The effect of α -MnO₂ dosage on the transformation of 10 mg/L sodium arsenite at 25 °C and pH 6.0: the removal rates of As(III) (A), the formed different formation of total As and As(V) (B), the concentrations of adsorbed exchangeable As(III) (C) and As(V) (D) on α -MnO₂.

when the initial concentration of arsenite increased from 2.5 to 20.0 mg/L. The formed Mn(II) can occupy the reactive sites on α -MnO₂ surface and may also limit the reaction between Mn(IV) and arsenite, leading to a lower transformation rate.

3.3.2. The effect of α -MnO₂ dosages

Four α -MnO₂ dosages were employed to determine the influence of dosages on the transformation of 10 mg/L sodium arsenite at 25 °C and pH 6.0 as shown in Fig. 5. The results showed that increasing α -MnO₂ obviously increased the transformation rate of sodium arsenite as indicated by Fig. 5A. With relatively high dosage of α -MnO₂ (3.0 and 5.0 g/L), As(III) was efficiently removed and the removal rates of As(III) at 60 min were 86.5% and 87.6%, respectively, whereas obtained lower removal rates of 67.2% and 69.5% when with 0.5 and 1.0 g/L α -MnO₂, respectively. However, the formed As(V) did not increase with the increased α -MnO₂ dosages (Fig. 5B). This may be attributed to the fixing of arsenic in the structure of α -MnO₂ as discussed in Section 3.2. Being fixed by α -MnO₂ may also cause the decrease in formed As(V) and the final fixed arsenic increased from 21.49% to 58.23% with increasing α -MnO₂ dosage from 0.5 to 5.0 g/L (Fig. 5B). Higher dosages of α -MnO₂ can adsorb more arsenic species as indicated by Fig. 5C and 5D. With increased α -MnO₂ dosages, more As(V) and As(III) were adsorbed, and the concentration of adsorbed As(III) was far lower than adsorbed As(V) when with the same α -MnO₂ dosage. Furthermore, as indicated by Fig. 5B, when with lower dosage of α -MnO₂, the fixed As(V) was fewer than when with higher dosage due to

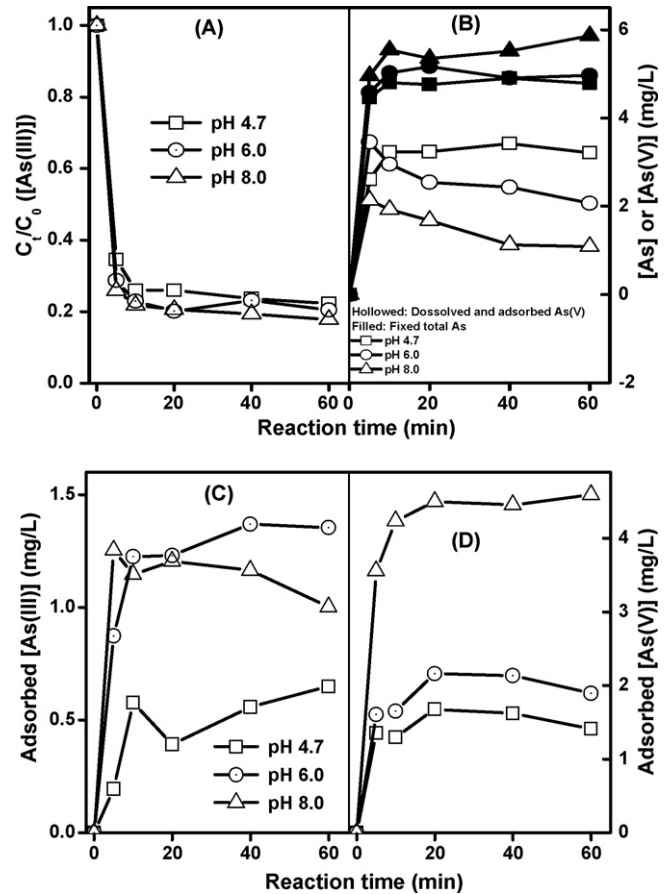


Fig. 6. The effect of pH on the transformation of 10 mg/L sodium arsenite by 1.0 g/L α -MnO₂ at 25 °C: the removal rates of As(III) (A), the formed different formation of total As and As(V) (B), the concentrations of adsorbed exchangeable As(III) (C) and As(V) (D) on α -MnO₂.

the fewer sites for fixation. So, when with lower oxide loading, the fixed As(V) was fewer, and accordingly the dissolved and adsorbed As(V) concentration was higher.

Higher α -MnO₂ dosages can increase the oxidation rates of As(III). However, the oxidation efficiency of per unit weight of α -MnO₂ decreased with the increasing α -MnO₂ dosages. When with 0.5, 1.0, 3.0, and 5.0 g/L α -MnO₂, the oxidation efficiencies were 0.33, 0.17, 0.06, and 0.03 mg/g/min, respectively. When at the fixed volume reaction suspension, lower dosages of α -MnO₂ can result in more sufficient contact for higher ratio of added α -MnO₂ with As(III), i.e. per unit amount of α -MnO₂ can contact more As(III), so as to oxidize more As(III).

3.3.3. The effect of pH

Effect of pH values on transformation of sodium arsenite was studied with 1.0 g/L α -MnO₂ and 20 mL of 10.0 mg/L sodium arsenite at 25 °C with pH values controlled by different buffer solutions (Fig. 6) (The ionic strength of the buffer solution was proven to have little effect on the reaction, and the results were not presented). After reaction for 60 min, As(III) removal rate slightly increased from 77.7% to 79.5% and 82.2% when with increasing pH values from 4.7 to 6.0 and 8.0 (Fig. 6A). When the reaction occurred in higher pH values, As(III) can be more easily adsorbed on the surface of α -MnO₂, which may be more electronic negatively when in higher pH condition, so as to result in higher transformation rate of As(III). The concentration of obtained dissolved and adsorbed As(V) decreased with the increasing pH values, while the concentration of fixed As(V) increased with increasing pH values (Fig. 6B).

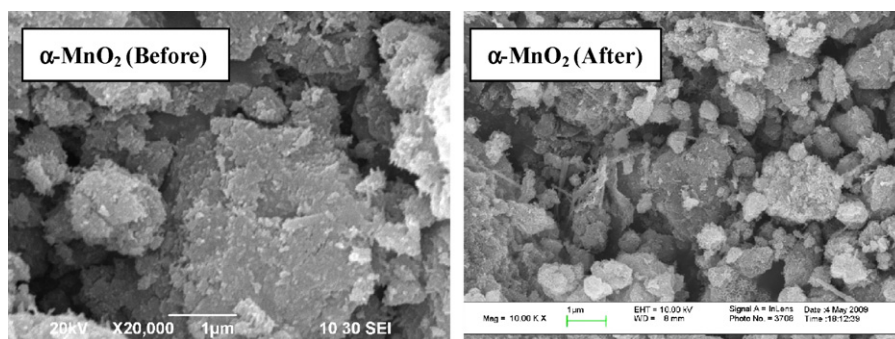


Fig. 7. The SEM images of α -MnO₂ before and after reaction with sodium arsenite for 24 h.

At more acidic reaction condition, more As(V) could be released and less would be fixed in the structure of α -MnO₂. The removal of As(III) may also be attributed to adsorption and precipitation of As(III) in the solutions with increased pH. As indicated by Fig. 6C and 6D with the results of adsorbed arsenic species, both of adsorbed As(III) and As(V) increased with higher reaction pH values. The fixed arsenic species also increased with 13.5%, 29.0% and 39.6% when the reaction pH was 4.7, 6.0 and 8.0, respectively.

3.4. The change of structural properties of α -MnO₂ before and after reaction

Structure and surface morphologies of α -MnO₂ before and after reaction (with fixed arsenic species in the structure) for 24 h were studied by XRD, SEM-EDX, and FTIR characterization methods in order to further determine the behavior of arsenic species on α -MnO₂. XRD results (data not shown) suggested that the crystal structure of the manganese dioxide did not change during the reaction process. The relative atomic amount of arsenic was much lesser than that of manganese, and the reaction occurred primarily in the surface, which did not cause the obvious change of the crystal structure of α -MnO₂.

The SEM images of α -MnO₂ presented in Fig. 7 showed that synthesized α -MnO₂ powder was compact and appeared agglomerated particles. However, it appeared mellow and loose after 24 h of reaction with arsenite. After reaction with arsenite in the suspension, the surface of α -MnO₂ was reductively dissolved, and the formed Mn(II) and arsenic species were adsorbed. As shown in Table 2 with the EDX results, arsenic weight on the surface of α -MnO₂ increased from 0% to 1.31%.

The FTIR spectra of α -MnO₂ before and after reaction are presented in Fig. 8, which showed that the broad band around 3390 cm⁻¹ attributed to hydrogen-bonded hydroxyl groups of H–O and the band around 523 cm⁻¹ attributed to the Mn–O vibrations of MnO₆ octahedron in α -MnO₂ crystal did not vary. These results are attributed to unchanged structure of H–O and Mn–O, although some Mn(IV) was reductively released [37]. But the peaks at 523 cm⁻¹ have higher peak intensity and the 716 cm⁻¹ have weaker peak intensity than the peaks at the spectra of the untreated

Table 2
EDX results of α -MnO₂ before and after reaction with arsenite for 24 h.

Before reaction			After reaction		
Element	Weight (%)	Atomic (%)	Element	Weight (%)	Atomic (%)
O	40.71	55.23	O	28.15	58.42
K	4.48	3.86	K	4.03	3.54
Mn	54.90	40.98	Mn	66.51	37.69
As	-0.10	-0.07	As	1.31	0.44
Total	100.0	100.0	Total	100.0	100.0

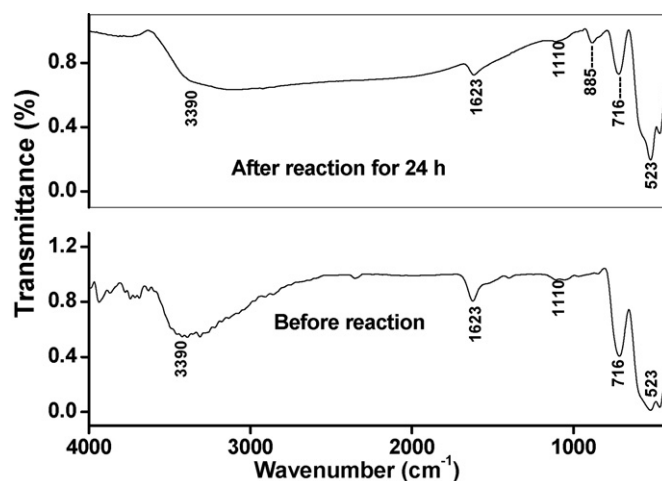


Fig. 8. The FTIR spectra of α -MnO₂ before and after reaction with sodium arsenite for 24 h.

sample. Furthermore, new bands at 885 cm⁻¹ in the FTIR spectra of α -MnO₂ were found after adsorption and reaction, which matched well with the stretching frequencies of As(V)–O bands in H₂AsO₄⁻ groups [38]. This further confirmed the adsorption and oxidative transformation of arsenite to arsenate on the surface of α -MnO₂.

The morphological results suggest that α -MnO₂ materials play an important role in arsenic removal as both efficient oxidizer and sorbent at near neutral pH condition. During the reaction occurred at the interface of manganese oxide and water, As(III) species can be adsorbed onto the surface and structure of MnO₂ followed by electron transfer from As(III) to Mn(IV), and then As(V) and Mn(II) were released into reaction solution. The majority of the oxidation products of As(V) were released into the solution and a certain fractions were adsorbed on the surface or fixed in the structure of α -MnO₂.

4. Conclusions

Sodium arsenite was effectively transformed into arsenate both in solution and on surface of α -MnO₂ and the oxidative transformation rate increased with high α -MnO₂ dosage and pH value, and low initial concentration of sodium arsenite. The increase of arsenic atomic percentage by SEM-EDX indicated that some of arsenic species were adsorbed and fixed by α -MnO₂ along with the reaction. With the arsenic species adsorbed and fixed on α -MnO₂, the surface of α -MnO₂ became looser and claviform shaped, and new FTIR peaks at 885 cm⁻¹ appeared, although the crystal structure of α -MnO₂ kept unchanged. The changes in morphologies and structures of α -MnO₂ during reaction disclosed the reaction process between arsenite and α -MnO₂.

Acknowledgements

The authors appreciate the financial support by the National Science Foundation of China (No. 40771105).

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