



The remarkable effect of the coexisting arsenite and arsenate species ratios on arsenic removal by manganese oxide



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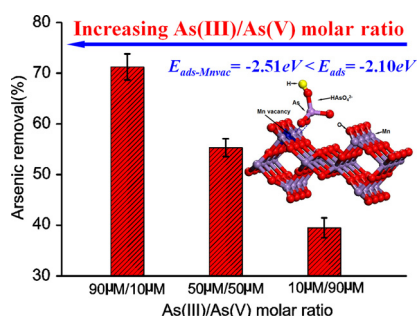
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HIGHLIGHTS

- The adsorption performance of manganese oxide in treating arsenic wastewater was investigated.
- The coexisting As(III)/As(V) molar ratio has a remarkable effect on arsenic removal by manganese oxide.
- Increasing the As(III)/As(V) molar ratio leads to a considerable increase of arsenic removal by manganese oxide.
- The origin of the molar ratio effect was studied by combining both the experimental and theoretical results.
- The formation of more Mn vacancy defects caused by As(III) oxidation makes the adsorption site more active.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:

Received 22 November 2016

Received in revised form 25 December 2016

Accepted 26 December 2016

Available online 27 December 2016

Keywords:

Arsenite

Arsenate

Adsorption

Manganese oxide

ABSTRACT

The adsorption performance of manganese oxide in treating arsenic wastewater that contained different As(III)/As(V) molar ratios was investigated, and the samples before and after their reactions were characterized by XRD, TEM, N₂ adsorption/desorption, SEM-EDS, FTIR, and XPS. The batch experimental results show that the coexisting molar ratio of As(III) and As(V) has a remarkable effect on arsenic removal by manganese oxide. Upon increasing the As(III)/As(V) molar ratio from 10 μM/90 μM to 50 μM/50 μM and 90 μM/10 μM, respectively, the total arsenic removal by manganese oxide significantly increased from 39.5% to 55.6% and 71.2%, respectively. The origin of the molar ratio effect was studied by combining both the experimental and theoretical results of the Mn²⁺ release detection, effect of Na₂SO₃-pretreatment on arsenic removal, and density functional theory (DFT) calculations. The results reveal that the highest arsenic removal by manganese oxide in an arsenic solution with the highest As(III)/As(V) molar ratio is attributed to the Mn²⁺ release caused by As(III) oxidation, forming more Mn vacancy defects, which makes the adsorption site more active, thus significantly promoting the adsorption performance of manganese oxide in arsenic removal.

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1. Introduction

The emission of arsenic-containing wastewater has become one of the most serious issues in the world because of its harm to human health and its destruction of the local ecological environment [1,2]. Among four oxidation states of arsenic species, arsenite[As(III)] and arsenate [As(V)] species are the predominant forms of arsenic that are present in aqueous environments, but their toxicity and adsorption affinity are significantly different, i.e., As(III) is more toxic and has a weaker affinity to adsorbents than As(V) [3]. It would be scientifically and technologically significant to develop highly efficient methods for both As(III) and As(V) arsenic sequestration. Oxidation/adsorption technology is regarded as one of the most promising methods for mixed arsenic species removal [4–6]. It is necessary to seek the integrated materials that exhibit highly efficient As(III) oxidation and As(V) adsorption for the simultaneous removal of As(III) and As(V) from arsenic-polluted groundwater.

Manganese oxide is one of the most extensively distributed natural adsorption materials, and it is frequently found in soils and Mn-rich ore deposits. Due to its high redox potential (E_0 ($\text{MnO}_2/\text{Mn}^{2+}$) = 1.22 V), manganese oxide has been widely investigated as an oxidant for the highly efficient oxidation of As(III) to As(V) [7–11], which is regarded as a vital step for reducing arsenic toxicity and facilitating arsenic immobilization. It is widely accepted that both As(III) oxidation and As(V) adsorption take place on the manganese oxide surface [9,12], and the influence of each one on the other has been observed in previous articles. For example, the adsorption of As(V) on manganese oxide surfaces can reportedly passivate the mineral surface [13], which is unfavorable to As(III) oxidation. In our previous report, we also found that the As(V) species at a high concentration adsorbed onto manganese oxide, clearly blocking the active site of manganese oxide and significantly inhibiting As(III) oxidation [14]. In addition, Manning et al. studied the behavior of As(III) oxidation on synthetic birnessite, and they found that As(III) oxidation causes an increase in As(V) adsorption on manganese oxide, which is attributed to the alteration of the manganese oxide surface that is caused by As(III) oxidation and the production of more fresh sites for As(V) adsorption [9]. These results indicate that the behavior of both As(III) oxidation and As(V) adsorption that are connected with one another should not be ignored, i.e., the coexisting ratio of As(III) and As(V) in arsenic-polluted water may have a considerable effect on arsenic removal by manganese oxide. However, to date, most reports have only focused on evaluating arsenic removal when an As(III) or As(V) species is alone [15–17], which do not represent real arsenic-polluted groundwater. To our knowledge, few researchers have investigated the effect of the coexisting ratios of As(III) and As(V) species on arsenic removal by manganese oxide. Due to the varying redox conditions in aqueous environments, the coexisting ratio of As(III) and As(V) also changes [18,19]. How and why the different As(III)/As(V) molar ratio in arsenic solution affects arsenic removal is still an open question.

Hence, in this paper, different initial As(III)/As(V) molar ratios were employed to evaluate the arsenic adsorption performance of manganese oxide. For the first time, the different molar ratios of As(III)/As(V) that coexist in wastewater were found to affect arsenic removal markedly by manganese oxide. Increasing the As(III)/As(V) molar ratio leads to a considerable increase in arsenic removal. We also combined the experimental and theoretical results to reveal the origin of the As(III)/As(V) molar ratio effect on arsenic removal by manganese oxide.

2. Experimental section

2.1. Sample preparation

Manganese oxide was synthesized by performing a facile hydrothermal reaction between $\text{Mn}(\text{NO}_3)_2$ and KMnO_4 at 75 °C for 48 h. All the reagents used in this study were of analytical grade without further purification. The details of the preparation procedure, which were similar to those in our previous work, are as follows [20]. A 3.5190 g quantity of $\text{Mn}(\text{NO}_3)_2$ (50 wt.%) was dissolved into 80 mL of distilled water in a 100 mL beaker, and 3.1608 g of KMnO_4 was rapidly incorporated into the above solution under vigorous magnetic stirring so it would be thoroughly dissolved. The beaker was then sealed with plastic wrap and subsequently placed inside an electric heating oven set to 75 °C. After 48 h, the beaker was taken out from the oven and cooled to room temperature. Lastly, the resulting precipitates were filtered, washed with distilled water several times, and dried in the oven at 75 °C for 12 h.

2.2. Adsorption experimental procedures

The batch adsorption experiment for removing arsenic from wastewater containing different As(III)/As(V) molar ratios by using manganese oxide was conducted on a rotary oscillator with a velocity of 160 rpm in a water batch at 25 °C. Wastewater containing mixed As(III) and As(V) wastewater was prepared by diluting certain ratios of NaAsO_2 and $\text{NaH}_2\text{AsO}_4 \cdot 7\text{H}_2\text{O}$ stock solution into a 1000 mL glass vessel using an acetate acid/sodium acetate buffer solution with a pH of 6. The total arsenic concentration was 100 μM . The As(III)/As(V) molar ratios in simulated arsenic wastewater were prepared as 90 $\mu\text{M}/10 \mu\text{M}$, 70 $\mu\text{M}/30 \mu\text{M}$, 50 $\mu\text{M}/50 \mu\text{M}$, 30 $\mu\text{M}/70 \mu\text{M}$, and 10 $\mu\text{M}/90 \mu\text{M}$. A 0.050 g quantity of each sample was added to 50 mL of the arsenic solution in a 100 mL Erlenmeyer flask. After being stirred for 24 h, 8 mL of each suspension was taken from the bottle, transferred into a 10 mL centrifuge tube, and centrifuged in a centrifugal apparatus to separate the suspended particles from the solution. All the experiments were performed twice. The formula for calculating the total arsenic removal is as follows.

$$X = (\text{C}_0 - \text{C})/\text{C}_0 \times 100\% \quad (1)$$

where X represents the removal rate of the total arsenic, and C_0 and C are the initial and the residual arsenic concentrations following a reaction of 24 h, respectively, in mmol L^{-1} .

In order to evaluate the adsorption capacity of manganese oxide for arsenic removal, the adsorption isotherm was investigated by using adsorbent dosage of 1.0 g L^{-1} at 25 °C. Initial total arsenic concentrations were varied from 10 to 1000 μM at pH 6. The As(III)/As(V) molar ratio in all arsenic solutions was fixed at 90/10.

2.3. Analytical methods

The total As (As(III) + As(V)) content in solution was analyzed on a GFA-6880 graphite furnace atomic absorption spectrometer equipped with autosampler cups (SHIMADZU, Japan). The current of the As hollow cathode lamp is 12 mA. The As spectral line is 193.7 nm, and the spectral bandpass is 0.5 nm. The deuterium arc was used to correct the background. A 10 mg L^{-1} preparation of $\text{Pd}(\text{NO}_3)_2$ was used as a chemical modifier. A 10 μL volume of solution and 10 μL of chemical modifier were injected into the platform of a high-density graphite tube for analysis. The detailed graphite furnace heating program is shown in Table S1 (see supporting information). The Mn^{2+} concentration was measured

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