



Tremendous effect of oxygen vacancy defects on the oxidation of arsenite to arsenate on cryptomelane-type manganese oxide



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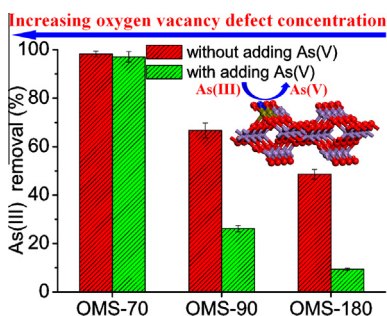
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HIGHLIGHTS

- The oxidation performance of As(III) on OMS-2 with different OVDs was investigated.
- Increasing the OVD reduces the unfavorable effect of As(V) adsorption on As(III) removal.
- The origin of the effect of OVDs on As(III) removal was experimentally and theoretically studied.
- The presence of OVD makes the adsorption of As(III) on OMS-2 more thermodynamically favorable.
- The OVD in OMS-2 accelerates the charge transfer from As(III) to Mn atom.

GRAPHICAL ABSTRACT



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ABSTRACT

Manganese oxide as a benign and low-cost oxidant has been widely investigated for the oxidation of As(III) to As(V), but its As(III) oxidation rate is easily hindered due to the thermodynamically favorable adsorption of the As(V) species produced and coexisting ions. Herein, we develop a novel strategy of tremendously increasing the As(III) oxidation activity via tuning the concentration of oxygen vacancy defects (OVD) in cryptomelane-type manganese oxides (OMS-2). The result of the batch experiment of the As(III) oxidation on OMS-2 shows that increasing the concentration of oxygen vacancy defects in OMS-2 remarkably increases the specific As(III) oxidation rate from 0.12 to 0.22 $\mu\text{mol m}^{-2} \text{min}^{-1}$, and dramatically reduces the unfavorable effect of the As(V) adsorption on the As(III) oxidation activity. The origin of the tremendous effect of OVD in OMS-2 on the As(III) oxidation activity is experimentally and theoretically investigated by the adsorption of the As(III) and As(V) species on OMS-2, the point of zero charge (pH_{PZC}), the evolution of the concentration of Mn^{2+} ions dissolved in the solution, and density functional theory (DFT) calculations. The results reveal that the presence of OVD in OMS-2 not only makes the adsorption of As(III) on OMS-2 more thermodynamically favorable, but also accelerates the charge transfer from As(III) to Mn atom, thus significantly improving the As(III) oxidation activity.

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1. Introduction

Arsenic, as one of the most toxic elements, has four oxidation states including arsine (−3), arsenic (0), arsenite (+3), and arsenate (+5). Among them, arsenite [As(III)] and arsenate [As(V)] are the two dominant arsenic species that coexist in polluted groundwater, and the former is more poisonous and less adsorbed by adsorbents than the later [1]. Therefore, the pre-oxidation of As(III) to As(V) is regarded as a necessary process for the efficient removal of the arsenic species prior to the treatment by adsorption or coprecipitation [2–5]. Chemical oxidants, such as ozone [6], chlorine [7], and hydrogen peroxide [5,8,9], have been widely used for the pre-oxidation of As(III) to As(V) [10]. But the utilization of these oxidants leads to the generation of toxic byproducts [11]. It is highly desirable to avoid such case by using other appropriate oxidants instead of the chemical oxidants [12].

Manganese oxide, which is environmentally benign and possesses high redox potential of E_0 ($\text{MnO}_2/\text{Mn}^{2+}$) = 1.224 V and E_0 ($\text{Mn}^{3+}/\text{Mn}^{2+}$) = 1.542 V, has been regarded as one of the most promising oxidants for the pre-oxidation of As(III) to As(V) [13–18]. In the process of the pre-oxidation, manganese oxide not only acts as an oxidant for the oxidation of As(III) to As(V), but also acts as an adsorbent for the arsenic species [14]. The experimental and theoretical results reveal that the adsorption of As(V) on the surface of manganese oxide is thermodynamically favorable as compared to As(III) [19,20]. In addition, in groundwater, the widespread coexisting competitive ions like phosphate also easily adsorb onto the mineral surface. This results in the decrease of the As(III) oxidation rate due to the occupation of the surface active sites of manganese oxide by the produced As(V) and coexisting ions, which passivates its surface and blocks the As(III) oxidation [21]. This means that the unfavorable effect of As(V) and coexisting ions on the As(III) oxidation is inevitable. The unfavorable effect of As(V) and coexisting ions could be only reduced by improving its As(III) oxidation rate. Up to now, several strategies have been developed to improve the oxidation activity of manganese oxides for the As(III) removal. The first strategy involves in increasing specific surface area and/or decreasing particle size by synthesizing micro-/nano-structured manganese oxides with urchin-like and dandelion-like morphology [22,23]. The second strategy involves in promoting its surface redox potential by the substitution of Mn in the framework of birnessite-type manganese oxides with Co^{2+} [24]. The third strategy involves in controlling the oxidation reaction condition by adjusting the pH value, initial arsenite concentration, oxidant dosages [3], and adding other mineral materials [21,25].

The strategy via tuning the oxygen vacancy defects (OVDs) of metal oxides has attracted attention for improving their catalytic oxidation performance for environmental purification [26–28]. For example, in our previous work, we prepared cryptomelane-type manganese oxides (OMS-2) with tunable OVD concentration via a facile hydrothermal redox reaction method, and found that the catalytic activity of OMS-2 for benzene oxidation was significantly enhanced by increasing OVD concentration [26]. Herein, OMS-2 nanorods with different OVD concentration are utilized for the oxidation of As(III) to As(V). It is found for the first time that the OVD in OMS-2 has a tremendous effect on the oxidation of As(III) to As(V). Increasing the concentration of the OVD in OMS-2 not only tremendously increases the As(III) oxidation rate, but also dramatically reduces the unfavorable effect of the As(V) and coexisting ions like phosphate, Fe^{2+} , and Mn^{2+} ions on the As(III) removal. We reveal the origin of the OVD effect of OMS-2 on the As(III) oxidation performance by combining the evidence of the experimental result and the density functional theory (DFT) calculation.

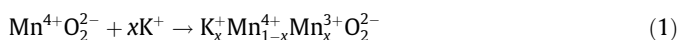
2. Experimental section

2.1. Sample preparation

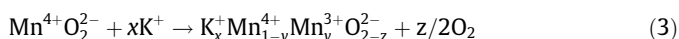
OMS-2 nanorods with the different OVD concentration were prepared by a facile hydrothermal redox reaction between $\text{Mn}(\text{NO}_3)_2$ and KMnO_4 with the $\text{Mn}(\text{NO}_3)_2/\text{KMnO}_4$ molar ratio of 2 at temperature of 70, 90, and 180 °C, respectively. The detailed preparation procedure was described in our previous work [26].

2.2. The relatively oxygen vacancy defect (OVD) calculation

The calculation method of relatively oxygen vacancy defect (OVD) concentration is based on that all the OMS-2 samples have the same cryptomelane structure and there is no other manganese oxide phase observed in XRD patterns [26]. The Mn 2p_{3/2} XPS spectra analysis shows that the mixed valence Mn atoms in all the samples are presence in the form of Mn^{3+} and Mn^{4+} . Therefore, the presence of Mn^{3+} in the sample may arise from the K^+ cations located in the tunnel of OMS-2 or the oxygen vacancies generated to maintain the electrostatic balance [26,29].



The overall reaction can be written as follows.



where z represents the relative oxygen vacancy concentration and is equal to $(1 - x - y)/2$. According to the above formula, the relative oxygen vacancy concentration of the OMS-2 samples can be calculated by combining both K/Mn atomic ratio and $\text{Mn}^{3+}/\text{Mn}^{4+}$ atomic ratio.

2.3. Batch experimental procedures

The batch experiment of As(III) oxidation and As(V) adsorption on the OMS-2 samples was conducted on a rotary oscillator with a velocity of 160 rpm in a water bath at 25 °C. The simulative As(III) wastewater concentration, prepared by diluting appropriate NaAsO_2 stock solution into a 1000 mL glass vessel using buffer solution of pH 6, is 0.1 mmol L^{−1}. 0.050 g of the OMS-2 sample was added into 50 mL of the As(III) solution in a 100 mL Erlenmeyer flask. In the process of the As(III) oxidation, 2.0 mL of the mixtures was taken out from the solution at intervals, mingled with 6.0 mL distilled water in a 10 mL centrifuge tube, and centrifuged in a centrifugal apparatus with a rotate speed of 5000 rpm for 10 min. The concentration of As(V), total As, As(III), and Mn^{2+} in the solution obtained by the centrifugation was analyzed. The effect of coexisting As(V), phosphate, Mn^{2+} , and Fe^{2+} ions on As(III) removal was conducted by respectively adding 0.1 mmol L^{−1} of NaHAsO_4 , NaH_2PO_4 , $\text{Mn}(\text{NO}_3)_2$, and FeCl_2 into the solution during the reaction of 0.1 mmol L^{−1} As(III) and 1.0 g L^{−1} OMS-2 at pH 6. The effect of OMS-2 dosages on 0.1 mmol L^{−1} As(III) removal was performed using 0.2, 0.4, 0.6, 0.8, and 1.0 g L^{−1} OMS-70 at pH 6. In order to investigate the effect of pH value on the As(III) oxidation, The buffer solutions of pH 4.7, 6.0 and 9.16 were respectively prepared as follows: (1) pH 4.7: 18.0 g of sodium acetate and 9.8 mL of acetic acid were dissolved into the 1000 mL distilled water at 25 °C. (2) pH 6.0: 54.6 g of sodium acetate and 20 mL of acetic acid (1 mol L^{−1}) were dissolved into the 500 mL distilled water at 25 °C. (3) pH 9.16: 1.06 g of sodium carbonate and 7.56 g of sodium bicarbonate were dissolved into the 1000 mL distilled water at 25 °C. We measured the change of pH

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