Chemical Engineering Journal 331 (2018) 492–500

Contents lists available at ScienceDirect

Chemical Engineering Journal

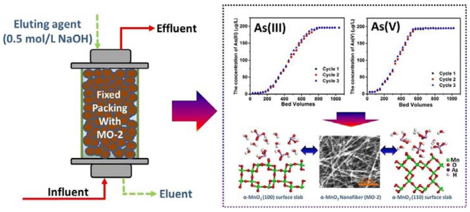
journal homepage: www.elsevier.com/locate/cej

Arsenic adsorption on α-MnO_2 nanofibers and the significance of (1 0 0) facet as compared with (1 1 0)

Jinming Luo[a,b,c], Xiaoyang Meng[c], John Crittenden[c], Jiuhui Qu[a], Chengzhi Hu[a,*], Huijuan Liu[a], Ping Peng[d]

[a] *Key Laboratory of Drinking Water Science and Technology, Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences, Beijing 100085, China*
[b] *University of Chinese Academy of Sciences, Beijing 100049, China*
[c] *Brook Byers Institute for Sustainable Systems and School of Civil and Environmental Engineering, Georgia Institute of Technology, 828 West Peachtree Street, Atlanta, GA 30332, United States*
[d] *School of Materials Science and Engineering, Hunan University, Hunan 410082, China*

GRAPHICAL ABSTRACT



ARTICLE INFO

Keywords:
Arsenic
Adsorption
α-MnO_2
(1 1 0)
(1 0 0)

ABSTRACT

The adsorption behavior of arsenic (As) on specific crystalline phases of manganese dioxide (MnO_2) remains unclear. In this study, we evaluated the ability of α-MnO_2 nanofibers (MO-2) to remove both arsenite (As(III)) and arsenate (As(V)), using experimental and computational methods. The maximum adsorption capacity values of As(III) and As(V) on MO-2 were 117.72 and 60.19 mg/g, respectively, which is higher than values reported for α-MnO_2, β-MnO_2 and γ-MnO_2. In particular, because MO-2 has much higher adsorption capacity for As(III) than As(V), it can be effectively applied in removal of As(III) from groundwater, and a pre-oxidation process is not required. Fixed-bed tests showed that about 800 mL As(III)- or 480 mL As(V)-contaminated water could be treated before breakthrough, and MO-2 can be effectively regenerated using only 12 mL of eluent. This means we can concentrate the As(III) and As(V) by factors of 66.6 and 40.0, respectively. According to density functional theory (DFT) calculations, As(III) and As(V) form stable complexes on (1 0 0) and (1 1 0) of α-MnO_2. Moreover, the surface complexes of As(III) and As(V) on (1 0 0) are more stable than (1 1 0). Electron transfer from As(III) on (1 0 0) is greater than (1 1 0). These phenomenon are may due to the fact that (1 0 0) has lower surface energy than (1 1 0). Partial density of state (PDOS) analysis further confirmed that As(III, V) are chemisorbed on MO-2, which agreed with the Dubinin-Radushkevich model.

1. Introduction

Heavy metals contamination in water, especially arsenic (As), has become a worldwide problem in recent decades. Arsenic can cause many human ailments and diseases, including kidney disease, reproductive failure, central nervous system, liver and brain damage [1]. Drinking water is the major exposure pathway for As that can affect humans, and causes serious health risk in many parts of the world, such

---

[*] Corresponding author.
E-mail address: czhu@rcees.ac.cn (C. Hu).

http://dx.doi.org/10.1016/j.cej.2017.08.123
Received 3 July 2017; Received in revised form 28 August 2017; Accepted 28 August 2017

as Argentina, Bangladesh, Chile, China, Hungary, India (West Bengal), Mexico, Romania, Taiwan, Vietnam, many parts of the USA, Nepal, Myanmar and Cambodia [2–5]. As a result, the United States Environmental Protection Agency (USEPA) has decreased the maximum contaminant level (MCL) of As from 50 μg/L to 10 μg/L in drinking water, because of the severe negative impact of As on human health [6].

Nowadays, adsorption has been recognized as the most appropriate and effective technique for As removal from water, due to its high efficiency, simplicity of operation, and low cost [7–9]. Meanwhile, adsorption technique is especially useful for treating lower concentrations of As and has commonly been suggested as a polishing step for drinking water purifications [10,11]. Many adsorbents have been synthesized and proposed for As removal, including metal oxide/activated carbon [12,13], biochar [14], biomass sorbents [15], and organic polymers [16]. However, the adsorption capacities of the reported adsorbents were relatively low, and the understanding of intrinsic adsorption mechanism is still very limited. In natural water, arsenic mainly exists as the arsenite (As(III)) and arsenate (As(V)). As(III) has higher mobility and toxicity than As(V), and is commonly present in ground water [17]. Many studies have only focused on the removal of one As species (i.e. As(III) or As(V)) from water via adsorption [18–22]. Meanwhile, many reported adsorbents exhibit higher adsorption capacity for As(V) than As(III), and conventional iron-based adsorption technologies require the oxidation of As(III) to As(V) because the adsorption capacity for As (III) is much lower than for As(V) [23–27]. Accordingly, we have focused on the synthesis of a highly effective adsorbent to simultaneously remove As(III) and As(V) from aqueous solution, especially for As(III). Combining with the systematically adsorption mechanism analysis of As on the adsorbent.

Manganese (Mn) is one of the most abundant and widespread elements on earth, and it is non-toxic and inexpensive. Moreover, Mn-oxides have a strong affinity toward metal ions due to their large specific surface areas, typically in the range of 50–300 m^2/g [28,29]. Among Mn-oxide adsorbents, manganese dioxide (MnO_2) is one of the most stable Mn-oxides under ambient conditions. In recent decades, there has been great interest in using MnO_2 as an adsorbent for the removal of various heavy metals from aquatic systems, including Cr (VI), Pb(II), Cd(II), and Zn(II) [30–33]. In addition, α-MnO_2 has shown great advantages as a catalyst in phenol degradation [34] and carbon monoxide oxidation [35]. It has also been shown that it can be used to synthesize highly efficient supercapacitor electrodes [36]. Nevertheless, to the best of our knowledge, systematic studies of the removal of As (III) and As(V) from water using α-MnO_2 are still very limited.

Quantum chemical calculations, such as density functional theory (DFT), have been applied to investigate geochemical processes, including interactions between adsorbents and adsorbates [37–41], especially between As and other metal oxides or metal hydroxyl compounds. By using DFT calculations, Yan et al. have determined adsorption surface complexes of As(V) on the rutile (1 1 0) surface, and confirmed As(V) bound in an inner-sphere fashion with the edge/corner-sharing tridentate (ECT) complex is the most favorable adsorption configuration [42]. Meanwhile, He et al. have identified that the adsorption of As(V) on TiO_2 surfaces involved not only chemical bond but also H-bond, especially at low pH. And both monodentate and bidentate complexes were formed between As(V) and TiO_2 surfaces [43]. Oliveira et al. have proposed mechanisms for As(III) on gibbsite-γ-Al $(OH)_3$ using DFT calculations, which confirmed that As(III) is not adsorbed via an acid/base, but by a non-dissociative mechanism in which O–H bonds are not being broken [44]. While the adsorption surface complexes between As and Mn-oxides and its intrinsic mechanisms are seldom studied. Only Zhu et al. have investigated the interaction between As(III, V) and Mn-oxides by using DFT calculations [45]; and Hou et al. have elucidated the effect of oxygen vacancy defects on the oxidation of As(III) to As(V) on cryptomelane-type manganese oxides using both experimental and computational results (DFT calculations) [46]. To the best of our knowledge, the adsorption mechanism of As(III, V) on different facets of typical MnO_2 (i.e. α-MnO_2) have not been extensively studied via DFT calculations.

In this study, the adsorption behavior of As(III, V) onto α-MnO_2 nanofibers (MO-2) was comprehensively studied in both varies experimental methods and theoretical calculations (i.e. DFT calculations). MO-2 has shown great performance on As removal, and the adsorption capacity on As(III) and As(V) were 117.72 and 60.19 mg/g, respectively. Noteworthy, the adsorption ability of MO-2 on As(III) is nearly two times higher than As(V), which can be effectively applied in removal of As(III) from groundwater, and a pre-oxidation process is not required. Meanwhile, the adsorption mechanisms of As(III, V) on two different facets in α-MnO_2, including (1 1 0) and (1 0 0), were further identified. The present work provides an efficient Mn oxide-related adsorbent which applicable for As removal from aqueous solutions.

2. Materials and methods

2.1. Chemicals and materials

All chemicals were analytical grade and used without further purification. The stock solutions of As(III) and As(V) with the concentration of 500 mg/L were prepared in deionized (DI) water using sodium arsenate ($Na_2HAsO_4 \cdot 12H_2O$) and sodium arsenite ($NaAsO_2$). Graphite powder, ethanol, potassium hydroxide (KOH), and potassium permanganate ($KMnO_4$) were used for the synthesis of α-MnO_2 nanofibers. The α-MnO_2 nanofibers were prepared by a hydrothermal method, and the synthesis procedure was detailed in the Supporting Information, Section 1.

2.2. Characterization

The crystalline phase samples were analyzed using X-ray diffraction (XRD, Rigaku UltimaIV) using graphite monochromatized Cu-Ka (λ = 1.5406 Å) radiation. X-ray photoelectron spectroscopy (XPS) measurements were carried out with a VG Escalab 250 spectrometer that was equipped with an Al anode (Al-$K\alpha$ = 1486.7 eV). The Brunauer-Emmett-Teller (BET) specific surface areas and porosity were determined by using nitrogen-sorption isotherms via a Micrometritics ASAP 2010 analyzer.

2.3. Adsorption experiments

As(III) and As(V) solutions (50 mL) with initial concentrations ranging from 10 to 270 mg/L were prepared by diluting the corresponding stock solutions with DI water. Batch experiments were used to determine the adsorption isotherms of As(III) and As(V). The adsorption isotherms for As(III) and As(V) at different temperatures (20, 30, 40 °C) were analyzed. The dosage of adsorbent for all the experiments was 0.5 g/L. The adsorption capacity (q_e) for As was calculated according to the following Eq. (1):

$$q_e = \frac{V\,(C_0 - C_e)}{m} \tag{1}$$

where q_e (mg/g) is the equilibrium adsorption capacity; C_0 and C_e (mg/L) are the initial and equilibrium concentrations of the adsorbate in solution, respectively; V is the volume (mL) of As solution; m is the mass (mg) of adsorbent used in the experiment. All the adsorption modeling equations can be found in Supporting Information, Section 2.

Fixed-bed column sorption experiments were carried out at ambient temperature using as-prepared MO-2 packed in fixed-bed columns. The influent concentration was 200 μg/L for both As(III) and As(V). The fixed bed was fed in down-flow mode using a peristaltic pump. 0.5 mol/L sodium hydroxide (NaOH) solution was used as the eluting agent for desorption. Then MO-2 was washed using DI water for the repeat use. The column parameters are summarized in Table S1.