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Arsenic transformation and adsorption by iron hydroxide/manganese dioxide doped straw activated carbon



Ying Xiong*, Qiang Tong, Weijun Shan, Zhiqiang Xing, Yuejiao Wang, Siqu Wen, Zhenning Lou

College of Chemistry, Liaoning University, Shenyang 110036, PR China

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ABSTRACT

Iron hydroxide/manganese dioxide doped straw activated carbon was synthesized for As(III) adsorption. The Fe-Mn-SAC adsorbent has two advantages, on the one hand, the straw active carbon has a large surface area ($1360.99 \text{ m}^2 \text{ g}^{-1}$) for FeOOH and MnO_2 deposition, on the other hand, the manganese dioxide has oxidative property as a redox potential of $(\text{MnO}_2 + \text{H}^+)/\text{Mn}^{2+}$, which could convert As(III) into As(V). Combined with the arsenic species after reacting with Fe-Mn-SAC, the As(III) transformation and adsorption mechanism was discussed. H_2AsO_4^- oxidized from As(III) reacts with the Fe-Mn-SAC by electrostatic interaction, and unoxidized As(III) as H_3AsO_3 reacts with SAC and/or iron oxide surface by chelation effect. The adsorption was well-described by Langmuir isotherms model, and the adsorption capacity of As(III) was 75.82 mg g^{-1} at pH 3. Therefore, considering the straw as waste biomass material, the biosorbent (Fe-Mn-SAC) is promising to be exploited for applications in the treatment of industrial wastewaters containing a certain ratio of arsenic and germanium.

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1. Introduction

Arsenic is a ubiquitous, toxic and carcinogenic chemical element present in the environment, so arsenic removal from wastewater is a worldwide environmental issue. Long-term exposure to arsenic, which is known to be a human carcinogen, probably induces several types of cancer in organs, such as the skin, liver, bladder, and so on [1–4]. However, arsenic has its relatively high concentration in coal combustion or gasification fly ash, which is a source of valuable elements such as germanium [5]. Thus, recovery and separation of arsenic from germanium has become an urgent problem to be solved.

Arsenic is predominantly found as As(III) (H_2AsO_3^- , HAsO_3^{2-} and AsO_3^{3-}) and As(V) (H_2AsO_4^- , HAsO_4^{2-} and AsO_4^{3-}) in the solution. Usually, As(III) is known to be more toxic and more difficult to remove than As(V), due to react with $-\text{SH}$ groups present in proteins [6]. So that, the removed technologies of arsenite or arsenate ions from water sources include precipitation, membrane processes, and ion exchange. In recent years, among these potential adsorbents, such as manganese-modified activated carbon fiber, iron hydroxides modified activated carbon fiber,

iron hydroxide-doped granular activated carbon and other iron-containing substances have been widely focused on arsenic species removal [7–18]. For example, Luo et al. reported that synthesis of magnetite Fe_3O_4 -reduced graphite oxide- MnO_2 nanocomposites for arsenic removal was depended strongly on its pore volume and large surface area [11]. Mayo et al. reported that the efficiency of arsenic removal was depended strongly on Fe_3O_4 nanoparticles size, and the adsorption capacity increased with decreasing nanoparticles size from 300 nm to 12 nm [12]. MnO_2 was an effective oxidizing agent of As(III), while adsorption capacity of arsenic by MnO_2 was low. Consequently, numerous researchers had combined Fe_3O_4 or MnO_2 with active carbon, resin [13], and carbon nanotube [14] to resolve the above problem.

Active carbon has a high surface area, mechanical stability, and surface functional groups which could provide a good support for other adsorbents [15]. Recently, active carbon-based materials have been a research hot in composite materials. Rangel-Mendez et al. had reported that the modified activated carbons with iron hydro (oxide) nanoparticles were applied to remove arsenic. The results of this study show that iron modified activated carbons are efficient adsorbents for arsenic at concentrations lower than $300 \mu\text{g L}^{-1}$ [16]. Sun et al. also reported that the maximum adsorption capacity of arsenic by manganese-modified activated carbon fiber was 23.77 mg g^{-1} [17]. Moreover, Cooper et al. reported that iron (hydr)oxide (FeOOH) nanoparticle-impregnated granu-

* Corresponding author.

E-mail address: xiongying_1977@hotmail.com (Y. Xiong).

lated activated carbons for arsenic removal was depended on –OH groups, but this adsorbent adsorption capacity of arsenic was very low [18]. In order to overcome above disadvantage, a novel adsorbent was developed to adsorb As(III) by combining the high surface area of straw activated carbon, the oxidation property of MnO₂, and functional group of FeOOH.

The objectives of this work are (i) synthesize and characterize of Fe-Mn-SAC, (ii) thermodynamics, kinetics, adsorption ability, and separation ability, (iii) the adsorption mechanism of arsenic on Fe-Mn-SAC.

2. Experimental

2.1. Materials

All chemicals and reagents were of analytical grade and dissolved in deionized water. Straw was collected from local cultivated areas. Nitric acid (HNO₃, 65%–68%), iron(III) chloride hexahydrate (FeCl₃·6H₂O), manganese sulfate monohydrate (MnSO₄·H₂O), potassium permanganate (KMnO₄), hydrochloric acid (HCl) and potassium hydroxide (KOH) were purchased from Sinopharm Chemical Reagent Co. Ltd (China). As(III) stock solution (1000 mg L⁻¹) was purchased from Xingcheng Chemical reagent factory of Liaoning province (China).

2.2. Preparation of iron hydroxide/manganese dioxide doped straw activated carbon

2.2.1. Preparation of straw activated carbon (SAC)

The straw (6 g) was grinded into powder and put into a tube furnace at 350 °C (at a heating rate 10 °C min⁻¹), and it was kept for 2 h in the tube furnace, then cooled down to the room temperature. According to the mass ratio of 1: 3, 18 g KOH and 50 mL deionized water was added, then mixed for 30 min, dried at 80 °C for 2.5 h in the vacuum drying oven. After that, it was put into the tube furnace at 800 °C (at a heating rate 15 °C min⁻¹), and it was kept for 1 h in the tube furnace, and cooled to the room temperature. Finally, the powder was mixed with 500 mL of 5% HCl for 30 min, and washed and dried to produce the straw activated carbon (SAC), the yield of which is 93%. At the same conditions, the potassium hydroxide was not added in the synthetic process, which is called straw activated carbon treating without KOH (WK-SAC).

2.2.2. Preparation of Fe-Mn-SAC

The synthetic steps of iron hydroxide/manganese dioxide doped straw activated carbon adsorbent were schematically presented in Fig. 1. Five grams of straw activated carbon was mixed with 100 mL of 68% nitric acid for 1 h at room temperature. Then, the oxidized straw activated carbon was washed thoroughly with distilled water in order to remove residual acid. The acidic straw activated carbon was mixed with 150 mL of 0.05 mol L⁻¹ FeCl₃ and 40 mL of 3 mol L⁻¹ HCl, and stirred for 22 h at room temperature followed by heating at 100 °C for 6.8 h. Then, iron hydroxide doped straw activated carbon (Fe-SAC) was filtered, washed followed by drying at 80 °C for 24 h. In order to doping manganese dioxide into the Fe-SAC, 5.0 g of MnSO₄·H₂O and 5.0 g of Fe-SAC were put into 150 mL deionized water, and vigorously stirred at 80 °C for 15 min with water cooled condenser. According to the mass ratio of MnSO₄·H₂O and KMnO₄ as 1: 1, 5.0 g of KMnO₄ and 10 g of KOH dissolved in deionized water (150 mL) were put into the obtained mixture solution, then it was refluxed for 1.5 h. Finally, the product was filtered, washed to neutrality, and dried at 50 °C. The iron hydroxide/manganese dioxide doped straw activated carbon is abbreviated hereafter as Fe-Mn-SAC. The yield of the Fe-Mn-SAC was above 90%.

2.3. Determination of the acidic surface functional group

Boehm titration method was used to determine the acidic surface functional groups on the adsorbents before and after modification. These experimental methods have been reported in our previous work [19,20].

2.4. Batch adsorption, regeneration and reuse of adsorbent studies

Equilibrium adsorption experiments were conducted at 303 K by shaking 10 mg of adsorbent (Fe-Mn-SAC) and 10 mL of 20 mg L⁻¹ As (III) solution for 24 h. The pH range of the aqueous solution was from 1 to 12 adjusted by hydrochloric acid (HCl) or ammonium hydroxide (NH₃·H₂O). The initial and residual concentrations of As(III) were directly measured by ICP-AES. The specific amount of adsorbed As(III) per unit mass of the adsorbent was calculated by mass balance as Eq. (1).

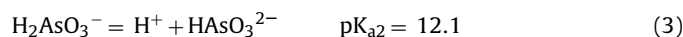
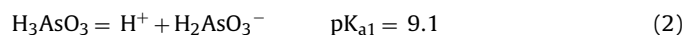
$$q_e = \frac{(C_0 - C_e)}{W} \times V \quad (1)$$

where C₀ (mg·L⁻¹) is the initial concentration of As(III), C_e (mg L⁻¹) stands for the equilibrium concentration measured after adsorption, q_e (mg g⁻¹) is the equilibrium adsorption capacity, V (mL) is the volume of As(III) solution, and W (mg) is the amount of adsorbent used in the experiments. Reproducibility of all data was confirmed by repeating the same experiment in duplicate.

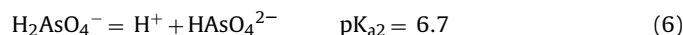
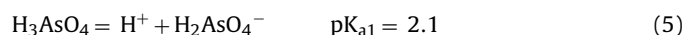
Three continuous adsorption and regeneration cycles were carried out. After the adsorption of As(III) on the Fe-Mn-SAC adsorbent, 20 mg of the adsorbent loaded arsenite was mixed with 20 mL of 0.05% NaOH solution and shaken for 24 h, then filtered. The remaining total concentrations of arsenic were measured by ICP-AES, in which the concentrations of As(V) was measured by UV/Vis spectrophotometer and the concentrations of As(III) was calculated by subtracting the amount of As(V) from the total arsenic.

2.5. Distribution of arsenic

Speciation of arsenite plays an important role, which affects As(III) adsorption capacity by chemical adsorption method. Because As(III) could be converted into As(V) by using the Fe-Mn-SAC adsorbent, both of the distribution of As(III) and As(V) at different pH were discussed. The oxyanions of As(III) and As(V) formed inner-sphere complexes, including bidentate binuclear complexes and monodentate mono-nuclear complexes. Distributing equation of As(III) is as follows:



Distributing equation of As(V) is as follows:



Arsenate and arsenite exist as oxoanions [21], and a picture of their calculated chemical speciation based on their stability constants is shown in Fig. 2. Existing forms of As(III) include neutral H₃AsO₃ in the case of pH < 10, and anionic H₂AsO₃⁻ in the pH range of 9–12, HAsO₃²⁻ in the pH range of 12–14, and AsO₃³⁻ in the case of pH > 14, respectively. Compared with As(III), existing forms of As(V) contain H₂AsO₄⁻, HAsO₄²⁻ and AsO₄³⁻ when pH range is from 2 to

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