Adsorption and Coprecipitation of As(V) from Aqueous Solutions by Manganese Dioxide

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Abstract：The effects of solution pH and initial concentration on adsorption and coprecipitation of As(V) from aqueous solutions by manganese dioxide [MnO_2] for 50d and 1120d were studied. The XRD, FT-IR and SEM results indicated that there was only slight difference between the MnO_2 adsorbents before and after adsorption, but their crystal structure had not changed. For the initial As(V) concentration C_o=0.1 or 1.0 mmol/L, the adsorption efficiency of As(V) onto MnO_2 decreased with the increasing pH when pH from 2.0 to 12.0. For the initial As(V) concentration C_o=0.01 mmol/L, the adsorption efficiency exceeded 95% at pH 2-8 after 50d or 1120d reaction, but the As(V) concentration in the solution after adsorption for 1120d was higher than that for 50d.

Keywords: ***Arsenic; manganese dioxide; Adsorption; Coprecipitation***

1 Introduction

Arsenic compounds are ubiquitous in the environment and potentially toxic to human. Arsenate pollution is mainly caused by natural and human activity. Water is one of the most important media through which arsenate enters into the human body [1,2].

Arsenic is regulated in drinking water and a maximum allowable limit, known as a maximum contaminant level (MCL), has been set for it. For many years, the maximum contaminant level was 50μg/L (ppb). Some people who drink water containing arsenic in excess of the MCL over many years could experience skin damage or problems with their circulatory system and may have an increased risk of getting cancer.

recommended maximum contaminant level (MCL) of arsenic in drinking water 10μg/L in 1993 [3]. The U. S. Environmental Protection Agency (EPA) decided to lower the MCL to 10μg/L in 2006. Meanwhile, this value also had been reduced from 50 to 10μg/L by China since 2007.

Appropriate purification techniques are required to meet these strict regulations. The treatment progresses for arsenic wastewater mainly include coagulation-precipitation, ion exchange, membrane filtration and adsorption [4]. Adsorption process was generally applied in water purification and wastewater treatment for its lower cost, better commercial availability and less environmental impact. The adsorbents mainly include activated carbons, α-Al_2O_3, montmorillonite modified with polymeric Al/Fe, MnO_2 , amberlite resins loaded metal(III) and so on [5,6].

Some studies had been carried on the adsorption and desorption mechanisms of manganese dioxide to arsenic recent years [7,8]. In solution, arsenic forms a series of aqueous complexes, the precipitation, dissolution, adsorption and desorption of these aqueous As species would control the stability of arsenic in water system. Unfortunately, little research had been reported about the mechanism of adsorption and its transformation to precipitation. Roman et al. (2003) firstly mentioned that the transformation from arsenic adsorption to desorption was continuous, but he did not studied deeply [9].

The objective of this study is to illustrate the mechanism of adsorption and coprecipitation for arsenic(V) on manganese dioxide by means of batch adsorption experiments. Especially, the effects of initial arsenic(V) concentration and solution pH on the adsorption were experimentally studied.

Ⅱ Materials and methods

A Materials

The reagents MnO_2 and As_2O_5, bought from National Medicine Group, Shanghai, China, were used as adsorbent manganese dioxide and adsorbate As(V), respectively. All the chemicals were of analytical grade.

B Batch Experiments

Firstly, 4.458g MnO_2 was weighed in a series of 50mL polyethylene bottles. And then, 50mL solutions of different As(V) concentration (0.001 mmol/L ~ 100 mmol/L), which were adjusted to a certain pH with 0.1 mol/L NaOH or HNO_3, were quickly added into these

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bottles. They were then sealed with capsules, shaken for about 2 minutes per day and stored at 25°C. The pH was adjusted to the desired value frequently according to its drift. After 50 days or 1120 days, the pH values of the solutions in the bottles were measured. Simultaneously 10.0 mL samples were extracted from each bottle and filtered through a 0.20 μm filter into a vial, and then diluted and stabilized with 0.2% (V/V) HNO_3 in 100mL volumetric flasks. The batch adsorption experiments with different initial As(V) concentrations (0.001, 0.005, 0.01, 0.05, 0.1, 0.5, 1.0, 5.0, 10, 50, 100, 500 and 1000 mmol/L) and different pH values (2-12) were carried out.

The manganese and arsenic concentrations were determined by Atomic Absorption Spectrometer (PE AAnalyst 700). The solid fractions were extracted via filtration, washed with ethanol and pure water, oven-dried at 50°C and then characterized using X-ray Diffractometer (XRD, X'Pert PRO) and Fourier Transformed Infrared Spectrophotometer (FT-IR, Nicolet Nexus 470). The morphology was analyzed by Scanning Electron Microscopy (SEM, Jeol JSM-6380LV).

III RESULTS AND DISCUSSION

A XRD, FT-IR and SEM characterization

The XRD results of MnO_2 before and after adsorption were shown in Figure 1. The solids were all well crystallized. The higher intensity peaks were located at 28.70°, 37.31° , 40.98 °, 42.76°, 44.61° , 56.59° and 65.00° of 2θ values with slight variation before and after adsorption in aqueous solutions with different initial As(V) concentration, but the crystal structure of the adsorbent had not changed.

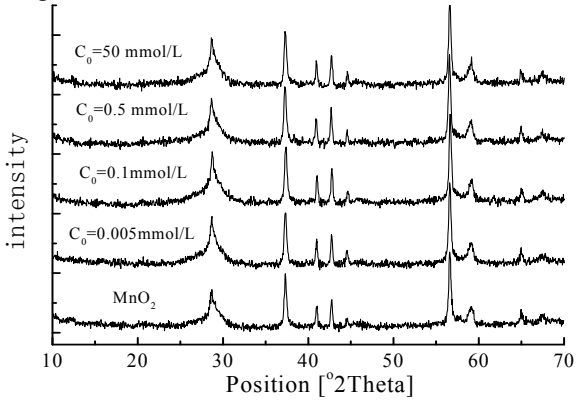

Fig 1 XRD spectra of the manganese dioxide before and after adsorption at pH 3

The FT-IR spectra of MnO_2 before and after adsorption of As(V) were shown in Figure 2. There was a Mn-OH bend at 1089.6 cm^{-1}, which is the typical band for hydration MnO_2 [10]. The band intensities at 2360.48 cm^{-1}, 1089.60cm^{-1} and 611.33 cm^{-1} increased with the increasing in the initial As(V) concentrations. The band at 611.33 cm^{-1} shifted to 607.48 cm^{-1} after the adsorption with the initial As(V) concentration of 0.5 mmol/L.

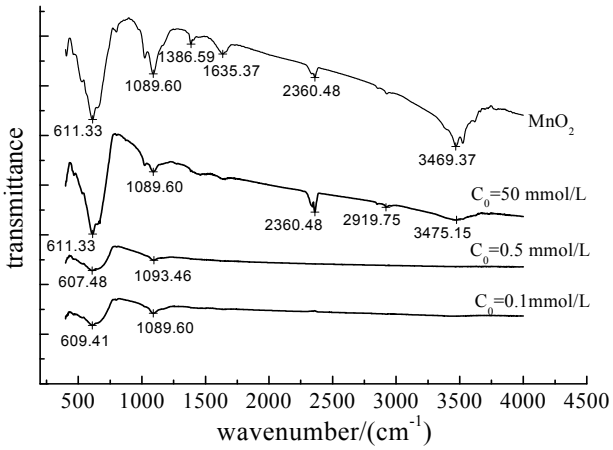

Fig 2 IR spectrum the manganese dioxide before and after adsorption at pH 3

The SEM results indicate that the crystal structure of MnO_2 was unchanged, but the morphology of MnO_2 changed greatly after the adsorption of As(V) on its surface (Figure 3). The MnO_2 particles had the shape of a cube with clear-cut edges and corners. But after the adsorption reaction, their edges and corners became rounded.

B Effect of pH on the As(V) adsorption

The adsorption efficiencies of As(V) on MnO_2 for 50d and 1120d were shown in Figure 4. The initial As(V) concentration C_o was 1.0, 0.1 and 0.01 mmol/L. For C_o=1 mmol/L, the adsorption efficiencies were all less than 30% after 50d or 1120d adsorption at pH 2.0-12.0. The optimum adsorption pH was about 2.0. When pH>2, the adsorption efficiency decreased with the pH increasing. For C_o=0.1 mmol/L, the adsorption efficiency increased obviously, which exceeded 50% at pH 2-8 after 50d reaction and at pH 2-7 after 1120d reaction. For C_o=0.01 mmol/L, the adsorption efficiency increased obviously, even exceeded 95% at pH 2-8 after 50d or 1120d reaction.When pH>8, the adsorption efficiency decreased rapidly with the pH increasing. The adsorption behavior of As(V) was related to its species in solution. The predominant As(V) species were H_3AsO_4 (pH<2), $H_2AsO_4^-$ (pH 2-7), $HAsO_4^{2-}$ (pH 7-11) and AsO_4^{3-} (pH>12). The main chemical equations in the solution could be described as following:

In the weak acidic aqueous solution:

$$M(OH_2)_2^+ + H_2AsO_4^- \rightarrow MO_2(H)As(OH)_2 \qquad (1)$$

In the neutral and weak alkaline aqueous solution:

$$M(OH_2)_2^- + HAsO_4^{2-} \rightarrow MO_2As(O)OH^- \qquad (2)$$

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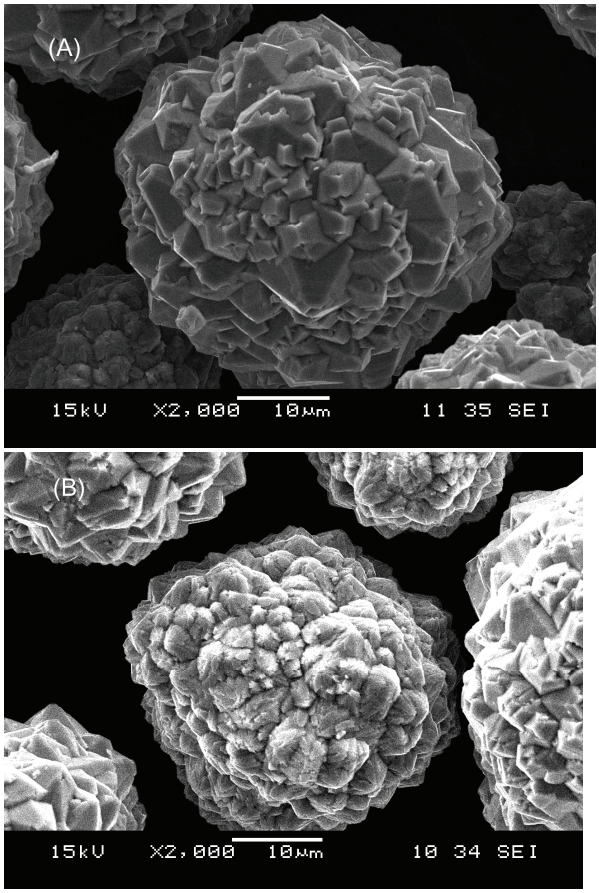

Figure 3 SEM images of MnO_2 before (A) and after (B) adsorption at pH=3.

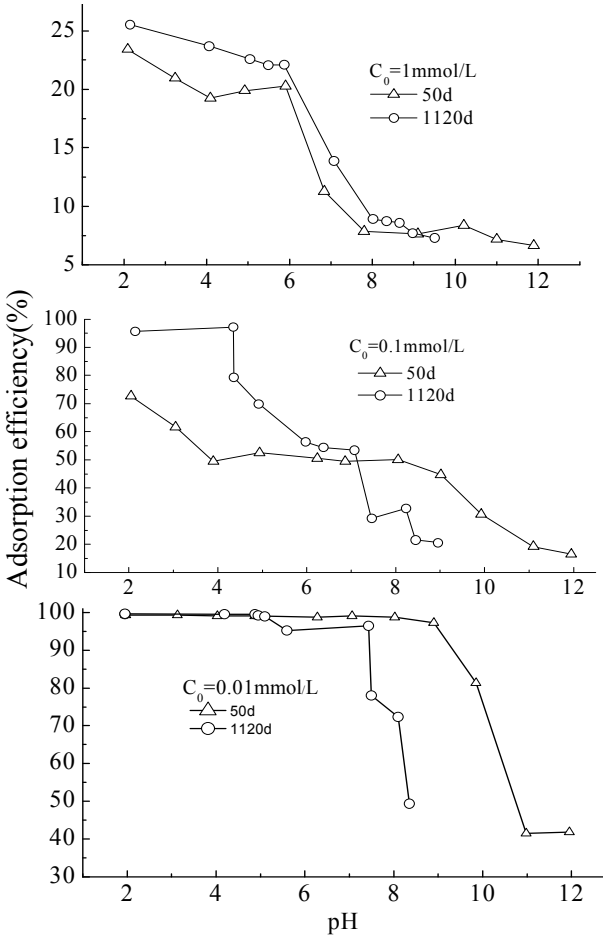

Fig 4 Effect of pH and initial concentration on As(V) adsorption on MnO_2

MnO_2 is amphoteric compound whose pH point of zero charge (pHPZC) was approximately 2.4 [11,12]. In solution, MnO_2 shows positive or negative electricity while pH < pHPZC or > pHPZC, respectively. In the optimum adsorption pH 2.0-4.0, $H_2AsO_4^-$ is the predominant species and MnO_2 is positive, which is in favor of the As(V) adsorption.

C Effect of initial As(V) concentration

The relationships between the initial As(V) concentrations and the As(V) concentrations after adsorption at pH=3, 7 and 12 were illustrated in Figure 5.

When the initial As(V) concentrations were lower than 0.01 mmol/L, the As(V) concentrations in the solutions after adsorption for 50d and 1120d at pH=3.0, near the pK_{a1} (2.24) of H_3AsO_4, were lower than those at pH=7 and pH=12. The electrostatic attraction between positive Mn species and negative As(V) species was the main adsorption mechanism.

When the initial As(V) concentrations were higher than 0.01 mmol/L, the As(V) concentrations in the solutions after adsorption for 50d and 1120d at different pH (3, 7 or 12) were approximately similar to each other. Except for electrostatic action, the diffusion might be another controlled mechanism in solutions of high As(V) concentrations .

The As(V) concentration in the solution after adsorption for 1120d was lower than that for 50d, especially for the adsorption with low initial As(V) concentration at pH<3. This means that the adsorbent MnO_2 after adsorption was suitable for direct disposal for long term to avoid the release of arsenic into water environment.

IV CONCLUSIONS

The XRD spectra, FT-IR spectra and SEM morphology of MnO_2 had slight differences before and after adsorption in aqueous solutions with different initial As(V) concentration, but the crystal structure of the adsorbent had not changed.

The adsorption efficiency of As(V) onto MnO_2 decreased with the increasing pH. When pH=2-8, the ad-

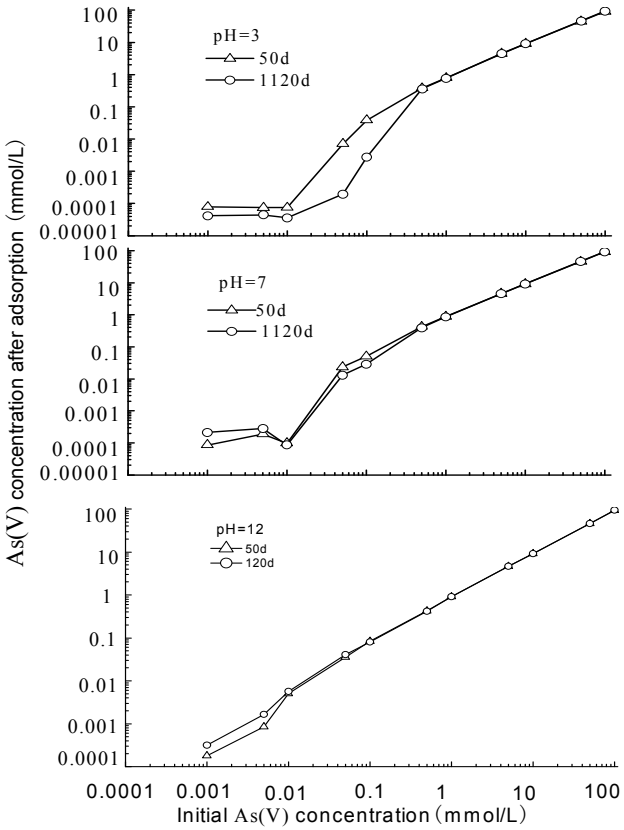

Figure 5 Relationship between the initial As(V) concentration and the As(V) concentration after As(V) adsorption on MnO_2

sorption efficiency changed little for the initial As(V) concentrations of 0.01mmol/L, but decreased significantly for the initial As(V) concentration of 0.1 and 1.0 mmol/L. When pH>8, the adsorption efficiency decreased with the increasing pH.

For the initial As(V) concentration C_o=0.01 mmol/L, the adsorption efficiency exceeded 95% at pH 2-8 after 50d or 1120d reaction. The As(V) concentration in the solution after adsorption for 1120d were lower than that for 50d, especially for the adsorption with low initial As(V) concentration at pH<3.0.

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