



Coadsorption and subsequent redox conversion behaviors of As(III) and Cr(VI) on Al-containing ferrihydrite[☆]



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ABSTRACT

Naturally occurring ferrihydrite often contains various impurities, and Al is one of the most prominent impurities. However, little is known about how these impurities impact the physical and chemical properties of ferrihydrite with respect to metal(loid) adsorption. In this study, a series of Al-containing ferrihydrites were synthesized and exposed to a mixed solution containing As(III) and Cr(VI). The results showed that the two contaminants can be quickly adsorbed onto the surface of Al-containing ferrihydrite under acidic and neutral conditions. With the increase of Al molar percentage in ferrihydrites from 0 to 30, the adsorption capacity of As(III) decreased, whereas it increased for Cr(VI). On the other hand, with the increase of pH value from 3.0 to 11.0, the decreasing rate of As(III) was accelerated first, then slowed down, whereas the Cr(VI) decreasing rate slowed down dramatically. X-ray diffraction (XRD), Brunauer-Emmett-Teller (BET) analysis method, transmission electron microscopy (TEM) analysis, energy dispersive spectroscopy (EDS) mapping, Attenuated Total Reflectance Fourier Transform Infrared Spectroscopy (ATR-FTIR), and X-ray photoelectron spectroscopy (XPS) were employed to characterize Al-containing ferrihydrite. Interestingly, it was found that the redox transformation occurred between As(III) and Cr(VI) after the two contaminants were coadsorbed onto the surface of Al-containing ferrihydrite. The oxidation of As(III) to As(V) and reduction of Cr(VI) to Cr(III) would greatly lower the environmental hazard of the As(III) and Cr(VI).

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1. Introduction

Iron (hydr)oxides are often found in the natural environment, and they play an important role in the remediation of environmental contaminants (Zhou et al., 2014; Tang et al., 2017). Ferrihydrite is an environmentally important iron (hydr)oxides commonly found in soils, sediments, and often in areas contaminated by acid mine drainage (Jambor and Dutrizac, 1998; Michel et al., 2007). Due to its abundance in nature, high surface area and content of reactive surface groups (Filip et al., 2007; Meng et al., 2014), ferrihydrite plays an important role in affecting the migration and transformation of contaminants in aquatic environments through adsorption (Qi and Pichler, 2016), coprecipitation (Martin

et al., 2005), and redox reactions (Fortin and Langley, 2005). Ferrihydrite is a particularly effective adsorbent for both arsenic (Zhu et al., 2011) and heavy-metal ions (Karapinar, 2016), and hence, ferrihydrite is manufactured for use in wastewater treatment (Smith et al., 2012). However, in natural environments, ferrihydrite is rarely found as a pure phase and instead often contains foreign ions, especially Al (Adra et al., 2016). Al is the third most abundant element in the Earth's crust (Casey, 2006), and it is often found in the structure of Fe (hydr)oxides such as maghemite (up to 10 mol% Al), hematite (up to 18 mol% Al), and goethite (up to 33 mol% Al) (Cismasu et al., 2012). In the case of Al-containing ferrihydrite, it was reported that Al element can be incorporated in the ferrihydrite structure up to 30 mol% (Johnston and Chrysochoou, 2016). It has been shown that the occurrence of Al affects the physico-chemical properties of ferrihydrite, such as particle morphology and size, solubility, and redox (Cismasu et al., 2012, 2013; Johnston and Chrysochoou, 2016). Besides, with the increase of Al content from 0 to 13 mol%, bacterial Fe(III) reduction rates of Al-containing

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ferrihydrate significantly decreased (Ekstrom et al., 2010), which indicates that Al-containing ferrihydrate can exist in more stable forms in natural environment than pure ferrihydrate.

Due to the widespread occurrence and toxicity, arsenic and chromium are listed as priority hazardous substance by the United States Environmental Protection Agency (de Oliveira et al., 2014). Arsenic is mainly present in inorganic forms in natural water, and occurs as arsenite (As(III)) and arsenate (As(V)) (Sorg et al., 2014). As(III) is dominant in groundwater due to the anoxic condition, while As(V) is primarily present in well-oxygenated water. As(III) exists as an uncharged species (H_3AsO_3) at pH values below 9.2 and as H_2AsO_3^- at a pH range of 9.2–12.1, while As(V) often occurs as oxyanions (H_2AsO_4^- and HAsO_4^{2-}) in a pH range of about 2.1–11.9 (Smedley and Kinniburgh, 2002). Although both As(III) and As(V) are toxic and carcinogenic to human beings (Nordstrom, 2002), As(III) is considered much more toxic, more soluble, and more mobile than As(V) (Zhang et al., 2007). Chromium, another common contaminant, is involved in many industries including metallurgy, electroplating, leather tanning, dye and pigment (Kimbrough et al., 1999). In general, chromium exists in the environment as trivalent (Cr(III)) and hexavalent (Cr(VI)) species. The toxic Cr(VI) occurs mainly as oxyanions (HCrO_4^- and CrO_4^{2-}) at low concentration and pH higher than 3 (Kotaš and Stasicka, 2000), while Cr(III) is less toxic and can be effectively immobilized as the hydroxide ($\text{Cr}(\text{OH})_3$) in the pH range of ~6–11.5 (Cerkez et al., 2015). Cr(VI) is carcinogenic and mutagenic to human beings, and its toxicity is due to its high solubility in water and rapid permeability through biological membranes (Levina et al., 2003).

Ferrihydrate is one of the most important mineral adsorbents to control the fate of As(III) and Cr(VI). Zhao et al. (2011) pointed out that As(III) can be adsorbed onto the surface of ferrihydrate and can be oxidized to As(V) by dissolved oxygen. Spectroscopic study indicated that Cr(VI) can form inner-sphere complexes on ferrihydrate (Johnston and Chrysochoou, 2012). In the environment, As(III) and Cr(VI) can be found in a variety of settings, including soil, groundwater, and many industrial wastewaters, especially in acid mine drainage (Le Hécho et al., 2003). Cerkez et al. (2015) used ferrihydrate as an adsorbent for simultaneous removal of As(III) and Cr(VI), and they observed a significant phenomenon that As(III) and Cr(VI) converted to lower toxicity species, As(V) and Cr(III). The overall redox reaction between As(III) and Cr(VI) can be described as Eq. (1).



However, when Al incorporated into ferrihydrate, how does Al-containing ferrihydrate interact with As(III) and Cr(VI)? Whether the incorporation of Al will affect the adsorption of As(III) and Cr(VI), as well as the redox conversion between the two contaminants? In this paper, further researches have been studied. A series of Al-containing ferrihydrates were prepared by co-precipitation, and were exposed to a mixed solution containing As(III) and Cr(VI). Batch experiments were carried out to examine the removal performance of As(III) and Cr(VI) by Al-containing ferrihydrate. The experimental parameters affecting the removal of As(III) and Cr(VI) by Al-containing ferrihydrate were investigated and the reaction mechanisms were discussed.

2. Materials and methods

2.1. Chemicals

All the chemicals were at least of analytical grade, and all solutions were prepared with deionized water. NaAsO_2 and $\text{K}_2\text{Cr}_2\text{O}_7$ were used to prepared As(III) and Cr(VI) stock solution,

respectively. Mixed solution of As(III) and Cr(VI) were freshly prepared.

2.2. Synthesis of Al-containing ferrihydrate

Al-containing ferrihydrate was synthesized according to a modified version of the method adopted by Cismasu et al. (2012). Briefly, stock solutions of $\text{Fe}(\text{NO}_3)_3$ and $\text{Al}(\text{NO}_3)_3$ were combined to obtain 100 mL solutions with a total concentration of $([\text{Fe}^{3+}] + [\text{Al}^{3+}])$ of 0.2 mol/L in proportions corresponding to 0, 10, 20, and 30 mol% Al, respectively. These solutions were adjusted to pH 7.5 by adding dropwise 1.0 mol/L NaOH under magnetic stirring. All suspensions were centrifuged after pH neutralization and the solids were washed repeatedly with deionized water to remove excess electrolytes. The washed materials were freeze-dried for 8 h before being ground into fine powders, and the final products were stored in 4 °C freezer. The Al-containing ferrihydrate samples obtained by this procedure had 0, 10, 20, and 30 mol% Al, and were referred to as Fh-Al-0, Fh-Al-10, Fh-Al-20, and Fh-Al-30, respectively. The morphologies of the four samples were observed by scanning electron microscopy (SEM) image analysis (Fig. S1).

2.3. Coexistence of As(III) and Cr(VI)

Defined amounts of As(III) and Cr(VI) stock solutions were added into a 500 mL conical flask, to obtain a mixed solution (200 mL) containing 150 $\mu\text{mol/L}$ As(III) and 100 $\mu\text{mol/L}$ Cr(VI). The initial pH of the mixed solutions were adjusted to the designated values (3.0, 7.0, and 11.0) with HCl solution (0.1–1 mol/L) or NaOH solution (0.1–1 mol/L). All conical flasks were shaken on a thermostatic shaker (120 ± 5 rpm) at 25 ± 1 °C. No acid or alkali was subsequently added to control the pH during the reaction. After 24 h, the residual concentrations of As(III) and Cr(VI) were determined.

2.4. Simultaneous removal of As(III) and Cr(VI)

Al-containing ferrihydrates with different Al content (1.5 g/L) were added into the mixed solutions (containing 150 $\mu\text{mol/L}$ As(III) and 100 $\mu\text{mol/L}$ Cr(VI)) at various initial pH values (3.0, 7.0, and 11.0). All the mixed solutions were shaken on a thermostatic shaker (120 ± 5 rpm) at 25 ± 1 °C. Appropriate amounts of suspensions were taken from the conical flask at 5, 10, 20, 30, 45, 60, 90, and 120 min of reaction, and the suspensions were filtered through a 0.45 μm membrane filter. The residual concentrations of As(III) and Cr(VI), as well as the possible generated As(V) and Cr(III) in the filtered solution were determined.

2.5. Adsorption isotherm

To obtain the adsorption isotherms, 0.1 g Al-containing ferrihydrates were exposed to 100 mL solutions ($\text{pH}_0 = 3.0$) containing different concentrations of As(III) or Cr(VI). Initial As(III) concentrations ranged from 300 to 1800 $\mu\text{mol/L}$, while initial Cr(VI) concentrations ranged from 400 to 4000 $\mu\text{mol/L}$. The mixtures were shaken on a thermostatic shaker (120 ± 5 rpm) at 25 ± 1 °C for 24 h. The equilibrium adsorption capacity (q_e) ($\mu\text{mol/g}$) for As(III) or Cr(VI) was calculated according to Eq. (2).

$$q_e = \frac{(C_0 - C_e)V}{m} \quad (2)$$

where C_0 ($\mu\text{mol/L}$) is the initial concentrations of As(III) or Cr(VI), and C_e ($\mu\text{mol/L}$) is the equilibrium concentrations of As(III) or Cr(VI), and V (L) is the volume of As(III) or Cr(VI) solutions, and m

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