



Evaluation of the ability of ferrihydrite to bind heavy metal ions: Based on formation environment, adsorption reversibility and ageing



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ARTICLE INFO

Article history:

Available online 31 March 2014

Editorial handling by M. Kersten

ABSTRACT

Binding ability of heavy metal ions on the surface of environmental minerals may greatly affect the local chemical properties, long-range interactions, surface reactivity, and bioavailability of metal ions in the aquatic environment. In this work, three ferrihydrites (Fh-1, Fh-2 and Fh-3) were prepared by different clearly defined procedures. Among them, the formation condition of Fh-3 is close to that of ferrihydrite in natural environment. The adsorption characteristics of the Cu(II) ions on the three ferrihydrites were investigated. The affinity of three ferrihydrites to Cu(II) ions was evaluated based on pH-sorption edge curves, Langmuir and Freundlich model parameters, adsorption–desorption isotherms and ageing of ferrihydrite adsorbed Cu(II). The results indicate that the maximum adsorption capacity for Cu(II) was found to be 8.74, 13.33 and 14.39 mg g⁻¹ for Fh-1, Fh-2 and Fh-3, respectively. Fh-2 and Fh-3 have stronger affinity than Fh-1 to adsorb Cu(II) ions. The experimental data were well fitted by double layer surface complexation model. The sorption differences of Cu(II) on the three Fhs were investigated by results gained from the simulation.

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1. Introduction

Ferrihydrite (Fh) is one of the distinct minerals in the family of oxides, hydroxides and oxyhydroxides of Fe, which occurs naturally and can also be easily synthesized. It is frequently used for sorbents because of its extremely high surface area, adsorption capacity and content of reactive surface groups (Filip et al., 2007; Gustafsson et al., 2009). Studies of heavy metal adsorption on Fh have followed two main lines. One is the measurement of the extent to which Fh removes the heavy metal ions from a solution. The other is spectroscopic investigation to determine the structure of the surface complexes formed through adsorption. Some of the early work relating to the adsorption of various adsorbate (e.g. cations, anions and organic species) on Fh is summarized by Jambor and Dutrizac (1998). Up to now, studies of the adsorption of organic or inorganic pollutants on Fh are still paid more attention. For instance, to determine key factors controlling the kinetics, Scheinost et al. (2001) measured Cu and Pb uptake as a function of Fh morphology, reaction temperature and metal competition over a period of 2 months. Cu and Pb were found to be bound to the ferrihydrite surface by formation of edge-sharing inner-sphere

sorption complexes. Song et al. (2008) investigated the effect of H₂Lp (phthalic acid) on Cu²⁺ and Cd²⁺ adsorption by Fh and gained insight into the structure and significance of ternary complexes on Fh. The results indicate that ternary complex structures on both Fh and goethite are either the same or similar. Those cations having large adsorption constants also have large equilibrium constants for ternary complex formation. According to research results reported by Arai (2008), the reactivity and surface speciation of Ni are sensitive to the crystallinity of iron oxyhydroxides. Fritzsche et al. (2011) studied the association of As with Fh colloids in the effluent from water-saturated soil columns run under anoxic conditions. No subsequent release of As from the Fh colloids was observed despite the presence of some (in)organic species known to compete with As for adsorption on Fh.

Despite the existence of many ion-sorption studies on Fh, to our knowledge, experimental data for Fh sorbent systems are typically reported based on a single preparation procedure, which was reported by Cornell and Schwertmann (2003). Briefly, alkaline solution was added into Fe(III) solution to adjust the pH to 7–8. In this process, the formation of Fh went through a pH change from acidic to neutral. Beyond that, Fh often occurs in many environments under circumneutral to alkaline conditions (Dold, 2003; Jambor and Dutrizac, 1998). When the effect of modifying the procedure for preparation of Fh was tested, significant changes in its microstructure and physico-chemical properties were observed (Liu et al., 2010).

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In this paper, Cu(II) ion was used as a adsorbate and three Fhs prepared by different clearly defined procedures as adsorbents. The adsorption characteristics of the Cu(II) ions on the three Fhs were investigated. The ability of three Fhs to bind Cu(II) ions was evaluated based on adsorption–desorption isotherms and ageing data of Fh adsorbed Cu(II).

2. Materials and methods

2.1. Preparation and characterization of Fh

Fh was prepared using three different procedures. All reagents used were of the analytical grade. The three procedures have been described in reference (Liu et al., 2010). Briefly, in procedure 1 Fh was prepared by the addition of $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ to DI water to obtain a specified iron concentration (0.5 mol L^{-1}). NaOH solution (6.0 mol L^{-1}) was added until the pH stabilized at 7.0. This procedure is consistent with that reported by Cornell and Schwertmann (2003). The suspension was centrifuged, washed with DI water and then dried at 40°C for 10 days. This product was called Fh-1. Procedure 2: The mixing procedure of Fe(III) and NaOH solutions was the reverse of that described in procedure 1. This product was called Fh-2. Procedure 3: Fe(III) and NaOH solutions were simultaneously added to a certain volume of water until the Fe(III) solution was exhausted. The drip rate of the two solutions was controlled by maintaining pH 7. The deposit obtained was called Fh-3. The formation condition of Fh-3 is close to that of Fh in natural environment. All samples were two-line Fh, which was ascertained by their X-ray diffraction pattern.

The microstructure was characterized by a JEOL 2010 HRTEM. The specific surface area was evaluated by nitrogen adsorption–desorption isotherm measurements at 77 K (Micromeritics ASAP2020).

2.2. Adsorption experiments

Fh suspensions were pre-equilibrated in 0.1 mol L^{-1} NaCl solutions at desired pH values. Equilibrium pH was adjusted to the desired pH level (± 0.05 pH unit) by adding dilute solution of either HCl or NaOH. Calibration of respective pH was achieved by the addition of $<1 \text{ mL}$ of dilute HCl or NaOH solution, which did not significantly affect the ionic strength. Aliquots of these samples were transferred into a number of PP centrifuge tubes.

After obtaining the desired constant equilibrium pH for Fh suspension, $1.5\text{--}7.5 \text{ mL}$ of Cu(II) solution (200 mg L^{-1}) was added to a series of tubes, resulting in Cu concentrations varying from 10 to 50 mg L^{-1} . The pH of adsorption system was again adjusted to the desired pH rapidly. At the same time the total volume of the system was brought up to 30 mL . In the final suspensions, the dose of Fh is 7.0 g L^{-1} . The tubes were capped and equilibrated for 6 h on an isothermal shaker at $25 \pm 2^\circ\text{C}$. The solutions were centrifuged and filtered through a $0.22\text{-}\mu\text{m}$ membrane filter and the concentrations were determined by Polarized Zeeman 180-70 model Atomic Absorption Spectrometer (AAS). The amount of Cu(II) sorbed was calculated as the difference between initial and final solution concentrations.

2.3. Adsorption–desorption experiments

The adsorption experiment of Cu(II) ions on the three Fhs was conducted according to the above description. The desorption experiment of Cu(II) ions adsorbed on the three Fhs was conducted based on the method described by Yang et al. (2007). Briefly, desorption processes were conducted by removing 25 mL of the supernatant solution after centrifugation, then topping this up to

the original volume with NaCl stock solution and DI water. The preparation was maintained with shaking for 12 h and pH was adjusted to 5.5 thrice during this equilibrium time. After that, the solution was centrifuged and the amount of Cu(II) in the supernatant solution was measured. When calculating the amount of Cu(II) desorbed, the amount of Cu(II) in the residual (5 mL) volume was deducted. A second round of desorption was carried out using the same procedure to complete a two-step desorption.

2.4. Ageing experiments

The adsorption of Cu(II) ions on the three Fhs was conducted according to the above description. The suspensions with Cu(II) were held in closed bottles and aged at room temperature for a predetermined time varying from 5 to 1080 h. The suspensions were not stirred during ageing period. At given time, a certain volume of suspension was sampled, centrifuged, and subsequently filtered through a $0.22 \mu\text{m}$ Millipore filter to remove Fh. The concentrations of Cu(II) in the filtrates were measured by AAS.

3. Results and discussion

3.1. Characterization of three Fhs

TEM image and electron diffraction (ED) patterns of as-prepared the three samples are shown in Fig. 1. The three Fh particles are quasi-spherical. The average size of them is about 3–5 nm. ED patterns are weak diffraction rings, suggesting that crystallinity of the three Fhs is poor. The BET-specific surface areas of the three samples are 222.66, 224.38 and $257.42 \text{ m}^2 \text{ g}^{-1}$ for Fh-1, Fh-2 and Fh-3, respectively. These specific surface areas are slightly lower than the value reported in references probably because of high initial Fe concentration (Hiemstra and Van Riemsdijk, 2009; Davis and Leckie, 1978). Fig. 1 indicates that the particle size of Fh-3 is slightly less than that of Fh-1 and Fh-2, which makes Fh-3 have a larger specific surface area.

3.2. Adsorption of Cu(II) at different pHs

The pH of an aqueous solution is one of the most important controlling parameters in the heavy metal adsorption process. This study was carried out in a pH range 2–7. Fig. 2 presents the results of Cu(II) batch adsorption experiments on the three Fhs surfaces as a function of pH. As seen in Fig. 2, the adsorption of Cu(II) by the three Fhs was highly pH dependent, and the sorption efficiency increased sharply with an increasing pH level. At low pH levels, an excess H_3O^+ could compete with Cu(II), resulting in a low level of adsorbed Cu(II). With increasing pH value, the concentration of H^+ ions decreased, resulting in greater Cu(II) adsorption (Perez-Marin et al., 2007). Nonetheless, the differences among the three Fhs also cannot be ignored. The major inflection point occurs at about pH 4.5 in both Fh-2 and Fh-3 systems. The inflection point of the Cu(II) adsorption edge shifted to a higher pH in Fh-1 system. For identical experimental conditions, the position of the pH-sorption edge curves is characteristic of the affinity between the metal and the sorbent. The more the pH-sorption edge is shifted toward acidic pH, the stronger is the affinity between the metal and the sorbent (Guibaud et al., 2006; Wang et al., 2013). This could be quantified through the pH_{50} , pH value at which half of the added metal is sorbed. Of the three samples, the affinity between the metal and Fh-3 is the strongest. This conclusion will be further confirmed in the subsequent experiments. As seen in Fig. 1, the sorption efficiency at the same pH was ranked in the order Fh-3 > Fh-2 > Fh-1. Comparing with the concentration of total Cu(II) ($\sim 10^{-4} \text{ M}$) in the current system, the concentration of Fh is

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