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Co-adsorption of phosphate and zinc(II) on the surface of ferrihydrite

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HIGHLIGHTS

- Phosphate and Zn(II) exhibited a synergistic adsorption on Ferrihydrite.
- The effects of pH on the adsorption of the two contaminants were investigated.
- XPS and ATR-FTIR demonstrated ternary complexes were formed on Ferrihydrite.
- A phosphate-bridged ternary complexes model was proposed.

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ABSTRACT

Ferrihydrite (Fh) is of great importance in affecting the migration and transformation of heavy-metal cations and oxyanions. To advance the understanding of co-adsorption reactions on Fh surface, the co-adsorption of phosphate and Zn(II) from aqueous solution to a synthesized Fh was determined. The batch experiments demonstrated a synergistic adsorption of phosphate and Zn(II) on Fh. In the pH range of 3.5–6, the adsorption of the two contaminants showed strong pH dependence in the single solute adsorption systems, but the dependence alleviated in the simultaneous adsorption system. X-ray photoelectron spectroscopy (XPS) revealed that the chemical shifts of Zn $2p_{1/2}$ and Zn $2p_{3/2}$ binding energies were more significant than that of P 2p in the single and simultaneous adsorption systems. On the other side, in situ attenuated total reflectance Fourier transform infrared (ATR-FTIR) observed increased formation of outer- and inner-sphere complexes of phosphate in the simultaneous system. Thus, the synergistic adsorption of the two contaminants could be attributed to the formation of ternary complexes as well as electrostatic interactions, while surface precipitation could not be completely ruled out. On the basis of the results from both the batch adsorption experiments and structural characterization, these two contaminants were likely to form phosphate-bridged ternary complexes (≡Fe–P–Zn) in the simultaneous adsorption system.

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1. Introduction

Iron (oxyhydr)oxides which can be formed through the weathering of many kinds of rocks and iron based clays, are ubiquitous in the environment and play significant roles in geochemical process (Stipp et al., 2002; Pedersen et al., 2006). In the family of iron (oxyhydr)oxides, ferrihydrite (Fh) is considered as one of the most distinct minerals, as it is a precursor to other iron minerals such as goethite and hematite (Jambor and Dutrizac, 1998; Meng et al., 2014). Due to its extremely large surface area and chemically active surface groups, Fh shows strong capacity in the adsorption of heavy-metal cations and oxyanions and therefore has a close relationship with the geochemical cycling of these contaminants (Jambor and Dutrizac, 1998; Moon and Peacock, 2013). Furthermore, its abundance in the environment as well as easy availability and small toxicity also make it an excellent candidate in

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contaminant removal strategies (Hiemstra et al., 2009). Therefore, the interactions of Fh with heavy-metal cations and oxyanions have drawn significant concerns (Trivedi et al., 2004; Mallet et al., 2013), and the adsorption mechanisms of heavy-metal cations/oxyanions on Fh have been well studied, including ligand exchange (Mustafa et al., 2004; Das et al., 2013), electrostatic interactions (Fukushi et al., 2013), surface precipitation (Michael et al., 2013), etc.

On the other hand, oxyanions and heavy-metal cations often coexist in the environment, and their co-adsorption behaviors of the two species on geosorbents therefore have received great concerns as well (Diaz-Barrientos et al., 1990; Swedlund et al., 2003; Li et al., 2006). Prior studies revealed that the adsorption of heavy-metal cations (e.g. copper, cadmium, nickel and zinc) and oxyanions (e.g. phosphate, arsenate) on (oxyhydr)oxides can be either inhibited or promoted by each other (Krishnamurti et al., 1999; Jiang et al., 2013). Decreased adsorption may arise from the competition for coordination sites at the metal oxide surface, or the formation of a stable non-adsorbing cation–oxyanion complex in solution (Benjamin and Leckle, 1982; Theis and West, 1986). Promoted adsorption could be attributed to the reduced electrostatic repulsion during the co-adsorption of oppositely charged contaminants (Diaz-Barrientos et al., 1990; Collins et al., 1999) as well as the formation of surface precipitates (Vaca-Escobar et al., 2012) and surface ternary complexes (Ler and Stanforth, 2003; Jiang et al., 2013; Elzinga and Kretzschmar, 2013). The different adsorption behaviors probably can be attributed to the physicochemical properties of the adsorbents and the cation–anion pairs, solutions pH, and surface adsorption coverage, etc.

Until now, most of the co-adsorption studies focused on goethite (α-FeOOH) (Wang and Xing, 2002; Kanematsu et al., 2013), hematite (α-Fe_2O_3) (Li et al., 2006), and clay minerals (Zhu et al., 2014), while Fh received less concern. The limited studies showed that oxyanions and heavy metal cations generally can be synergistically adsorbed on Fh (Swedlund et al., 2003; Song et al., 2008; Tiberg et al., 2013; Carabante et al., 2012). Swedlund et al. (2003) investigated the effect of SO_4 on the adsorption of Co(II), Pb(II), and Cd(II) on Fh and proposed the formation of cation-bridged ternary complexes. Tiberg et al. (2013) stated a similar mechanism in the co-adsorption of phosphate and Cu(II)/Pb(II) on Fh according to the results of EXAFS spectra and the CD-MUSIC model. However, Carabante et al. (2012) observed quite different results in the co-adsorption of arsenic and Zn(II) at pH/pD 8 on Fh, they believed the precipitation of zinc hydroxide carbonate followed by arsenate adsorption on it was the plausible mechanism for the synergistic adsorption. On the other hand, many studies quite often showed the formation of oxyanion-bridged ternary complexes on other geosorbents, particularly when phosphate and arsenate were used as the co-adsorption oxyanion (Zhao and Stanforth, 2001). As such, one might wonder whether the oxyanion-bridged ternary complexes can be formed on Fh as well. As the co-adsorption behavior of oxyanions and heavy metal cations is rather complex, it still needs extensive investigations.

In the present study, phosphate was chosen as oxyanion because it has a relatively high affinity to iron (oxyhydr)oxides and often reported to form oxyanion-bridged ternary complexes on geosorbents (Ler and Stanforth, 2003); Zn(II) was selected as heavy metal cation due to its relatively weak affinity to geosorbents (Zhou et al., 2002). One therefore may expect the formation of phosphate-bridged ternary complexes on Fh. Another reason for choosing the two contaminants was the wide distribution of phosphate and Zn(II) in the developing countries (e.g., in China), owing to the widespread applications of phosphate-containing fertilizers and Zn(II)-containing pesticides, as well as the industrial and mining activates related to them (Kabata-Pendias and Pendias, 2001; Lei et al., 2010). The mobility and accumulation of phosphate and Zn(II) in long term are likely to be affected by their surface interactions on the surface of geosorbents.

Batch adsorption experiments were carried out to examine the adsorption behaviors of phosphate and Zn(II) on Fh both in the single and simultaneous adsorption systems. Experimental data showed that phosphate and Zn(II) could be synergistically adsorbed on Fh; combining with the XPS and ATR-FTIR results, we hypothesized a phosphate-bridged ternary complexes model for the co-adsorption of the two contaminants on the surface of Fh.

2. Materials and methods

2.1. Materials

All glassware and plasticware were cleaned by soaking overnight in diluted HCl solution and washed in deionized water before the experiments. $FeCl_3$, NaOH, HCl, KH_2PO_4, and $ZnCl_2$ of analytical grade (purity >99%) were obtained from Shanghai Chemical Co., China, and used as received.

2.2. Preparation of Fh

Two-line Fh was synthesized in the laboratory as reported by Schwertmann and Cornell (1991) with slight modifications: $FeCl_3$ solution (1 M, 50 mL) was added into NaOH solution (6 M, 25 mL) dropwise with vigorous stirring by a magnetic stirrer until the pH stabilized at 7. The suspension was standing for 30 min and the precipitates were separated by centrifugation at 5000 rpm for 10 min. Thereafter, the precipitates was washed by deionized water to remove the electrolyte on the surface. The washed material was dried at 50 °C for 8 h before ground to pass a 100 mesh sieve and the final product was stored in 4 °C freezer.

2.3. Characterization of Fh

The X-ray diffraction (XRD) patterns of Fh before and after the adsorption of contaminants were recorded using a Bruker D8 ADVANCE X-ray diffractometer (Karlsruhe, German), operating at 40 kV and 40 mA with CuKa radiation. The patterns were recorded over the 2θ range of 10–80° at a scanning speed of 1°/min, thereupon, the characteristic peaks of Fh were available.

Nitrogen sorption–desorption isotherms at 77 K were determined by means of a NOVA 2200e Surface Area & Pore Size Analyzer from Quantachrome (Boynton Beach, Florida, USA), using samples that were previously degassed under vacuum at 100 °C for 12 h. The relative pressure (P/P_0) range of 0.05–0.35 was selected for the calculation of BET surface areas.

The zeta potentials of Fh under different pH were examined by Malvern, Zetasizer nano ZS Instrument (Malvern Instruments, UK). 0.75 mL finely dispersed Fh suspension with the ionic strength of 0.001 M and pH 5 were transferred into the zeta cell and an equilibration time of 2 min was needed prior to starting measurements.

2.4. Adsorption experiments

Two different adsorption systems were conducted in the experiments: (1) adsorption of a single contaminant on Fh (‘P’ system or ‘Zn’ system) and (2) simultaneous adsorption of two contaminants on Fh (‘P + Zn’ system). In the single systems, the adsorption of phosphate or Zn(II) on Fh was measured using the initial concentration of 0.081–5.2 mM for phosphate and 0.038–2.4 mM for Zn(II). In the ‘P + Zn’ system, the initial concentration of the one contaminant was set the same as that in the single adsorption systems; meanwhile, three concentrations of the coexisting

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