Determination Of Interactions Of Ferrihydrite-Humic Acid-Pb(II) System

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Title: Determination of interactions of Ferrihydrite-Humic acid-Pb(Ⅱ) system

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Abstract

Ferrihydrite often precipitates with humic acid in natural ways, affecting the fate of lead ions, the stabilization of humic acid and the aging process of ferrihydrite. A series of 2-line ferrihydrite-humic (Fh-HA) acid with varying C loadings has been prepared, the morphology and surface properties of Fh-HA organo-minerals have been characterized, the adsorption property of Pb ions onto Fh-HA has been studied. The results indicated a strong interference of HA to ferrihydrite. 2-line Fh dominated mineral phase in all samples, but with increasing C/Fe molar ratios the crystallinity gradually weakened, particles became smaller and SSA decreased significantly. The data of Mössbauer spectra confirmed C loading changed the unit structure of ferrihydrite. Fh-HA performed good adsorption properties to Pb(II): high efficiency and big capacity, especially Fh-HA_2.0. pH had great effect on Lead uptake, the pH change not only affects the amounts of competitive ions in solutions, but also the dissociation and protonation of functional groups on the surface of Fh-HA. Sorption kinetics can be well modeled by a pseudo-second order model, and the process was controlled by film and intraparticle adsorption simultaneously. The adsorption isotherms can be well described by Freundlich isotherm model. The careful determination of Fe 2p, O 1s and Pb 4f spectra before and after lead adsorption showed mononuclear bidentate or binuclear bidentate ligands occurring on Fh-HA surface, forming stable inner-sphere complex. By comparison of Mössbauer spectra and TEM images, it revealed a slower evolution of iron oxide/oxyhydroxide phases in Fh-HA-Pb system compared to pure ferrihydrite with aging time, ferrihydrite transformed to a combination of ferrihydrite, goethite and hematite phases. in this study, the determination of C-Fe interaction, Pb fate influenced by Fh-HA and transformation of ferrihydrite would have a great
implication to application of Fh-HA precipitates in remediation for soil or groundwater polluted by heavy metals.

Keywords: Ferrihydrite; Fh-HA precipitates; Lead; mechanism; transformation
1. Introduction

Lead (Pb) is present at elevated concentrations in air, soils and aquatic environment, its
emission from a variety of anthropogenic sources, including municipal and industrial waste, metal
mining and processing and agricultural activities (Pan et al., 2012). Various lead origins make it be the
most often encountered metals to groundwater and soils (Abdelwaheb et al., 2019). The Pb
concentration in some soil samples in China was up to 1386 mg/kg (Wang et al., 2019). As a
non-degradable pollutant, Pb has a high mobility, bioavailability and toxicity (Turner et al., 2019).
Accumulating exposure of lead poses existing and potential risk and threat to human health and
ecological safety (Zhang et al., 2019), its toxicity ranks very high (the second) in the official
report (http://www.arsdr.cdc.gov/spl).

Ferrihydrite (Fh), as poorly ordered Fe minerals, distributed in soils, sediments and some
aquatic environments ubiquitously (Cornell et al., 2004), is the precursor of some crystalline iron
oxides. Naturally, Fh can adsorb metal ions and organic molecules effectively because of cooperation
effect of a large specific area and a high reactivity (Cornell et al., 2004). Freshly formed ferrihydrite is
mostly efficient adsorbent known for Pb, As, Cu, Zn sequestration (Zhu et al., 2010), affecting their
fate and mobility in the aqueous phase. It plays an important role in wastewater treatment and
remediation activities (Kragovi´c et al., 2017; Chen et al., 2019).

The widely distributed organic matter (NOM) always co-exists with iron (hydr)oxides by
complexation or coprecipitation (Bargar et al., 1997). Humic acid, as a typical representative for NOM,
contains of carboxyl, aromatic, phenolic functional groups that often closely associate with minerals
through hydroxyl groups, form organo-mineral composites (Fortin et al., 2005). C loadings can
change surface and structure properties of iron (hydr)oxides, for ferrihydrite, a new negative charge
surface and more available sites formed by coprecipitation with humic acid, thereby affects the
adsorption properties of Pb(II) onto ferrihydrite (Tiberg et al., 2016). HA has been found to inhibit
and retard crystallization and transformation processes (Cornell et al., 1979; Gustafsson et al., 2007),
altering geochemical reactivity of ferrihydrite. It is reported that in coprecipitation, amount of C
loading can significantly alter XRD patterns and Mössbauer spectrum of ferrihydrite, and the
maximum achieved C loading is limited, 170 mg C and 318 mg C per g ferrihydrite are achieved
respectively in some previous researches (Eusterhues et al., 2008; Kaiser et al., 2007). Based on this, it
is necessary to set proper C/Fe ratio range of the initial solution in synthesis of Fh-HA coprecipitates
experiments. Fe (O, OH)$_6$ octahedron is characteristic structural unit in all Fe (hydr)oxides, the
chains formed by the unit are cross-linked at corners of octahedron to neighbor chains. However, the
specific Fe arrangement in ferrihydrite structure is still under discussion. Furrer and Stumm reported
that when the humic acid adsorbs onto the iron hydroxides, the bidentate ligand with two oxygen
donors of the HA reacts with Fe hydroxides under acidic condition (Furrer et al., 1986).

Among the existing researches (Ding et al., 2018; Lu et al., 2019; Lei et al., 2018; Chen et
al., 2007), it is noted that the interaction of Fh-HA-Pb system and the effect of associated HA and Pb
on geochemical reactivity of ferrihydrite on the molecular scale has received little attention. To
facilitate the dearth of regarding knowledge, the possible change of Fh-HA coprecipitates with varied
C loadings (C to Fe molar ratio is 0.5, 1.0, 1.5, 2.0, 2.5) has been examined, we elucidate physical
and structural properties of Fh-HA by means of X-ray diffraction (XRD), Transmission electron
microscope (TEM) and BET and Mössbauer spectra. Batch experiments have been conducted to
analyze Pb sorption behavior onto Fh-HA. Thermal and kinetic models were constructed based on detailed reaction data to describe Pb(II) transport in water-mineral interface. The molecular structure, bonding characteristic, and compositions of Pb(II) complexes, and the acid/base properties has also been determined to characterize the interactions of Fh-HA-Pb ternary system combined with a series of techniques such as XPS, Mössbauer Spectroscopy. The findings of this work could provide a better understanding of the Pb mobility and fate affected by Fh-HA in contaminated environment, also facilitate our knowledge about the way ferrihydrite transformed when humic acid introduced and Pb adsorbed.

2. Materials and methods

All reagents and chemicals were of analytical grade, all solutions were prepared using deionized water (DIW) (≥18 MΩ cm), CO₂ was rigorously excluded to prevent the formation of Pb(II)-carbonate aqueous complexes or precipitates. Stock solutions of FeCl₃ and Pb(NO₃)₂ were made by dissolving metal salts in DIW. HA was purchased from XIYA (1415-93-6. Shandong, China), and was dissolved with 0.4 M NaOH. The total C content in HA was measured at 61.98wt%. Glassware used for all synthesis steps was rinsed in DIW; soaked in 0.1 M HNO₃ for at least 24 h; triple-rinsed in DIW.

2.1 Synthesis of Fh-HA coprecipitates

Pure two-line ferrihydrite (Fh) and five Fh-HA coprecipitates (0.5, 1.0, 1.5, 2.0 and 2.5) were prepared according to the procedures adapted from Schwertmann and Cornell. (Schwertmann and
Cornell, 1991). In brief, Fh was synthesized by hydrolysis of Fe$^{3+}$ as FeCl$_3$ • 6H$_2$O in ultrapure water, rapidly adjust solution to pH ~7.5 using freshly prepared 1M NaOH, under vigorous stirring for 2 h, subsequently was washed, centrifuged and freeze-dried. For Fh-HA coprecipitates, firstly, humic acid soluble in sodium hydroxide was added and mixed with a previously prepared Fe$^{3+}$ salt solution, containing elevated initial C concentrations, then hydrolyzed and adjusted to pH ~7.5, subsequently operated in the same way as preparation procedure of Ferrihydrite. The five Fh-HA coprecipitates are termed hereafter as C/Fe$_{0.5}$, C/Fe$_{1.0}$, C/Fe$_{1.5}$, C/Fe$_{2.0}$ and C/Fe$_{2.5}$ accordingly. All freshly prepared Fh and Fh-HA were used as a standard for measurement and in all lead adsorption experiments. Surface chemistry was characterized by XRD, TEM and BET.

2.2 Lead adsorption experimental designs

All Pb(II) adsorption experiments were processed at room temperature, and 0.01M NaNO$_3$ was used as the background electrolyte. The affected factors such as pH, ionic strength, initial Pb (II) concentrations and adsorbent dosage were introduced to the system separately to shed light on adsorption occurring conditions. For each factor, reasonable value range and gradient were designed, to determine the optimal adsorption aqueous environment. All samples are in triplicate. For adsorption isotherms, the adsorption contained 6 g/L adsorbent and 0-16 mmol/L Pb(II). For adsorption-desorption kinetics, common functions of combined effected factors were taken into account. In the duration of this experiment, sampling time interval was set up, the supernatant was collected during adsorption reaction at 15 min, 30 min, 60 min, 120 min, 240 min and 1440 min. the same sampling time interval for desorption, and the desorption was performed for two circles. All
finished processing suspensions were immediately allowed to equilibrate for 24 h at a shaker. To remove adsorbent particles, the suspensions were centrifuged, the obtained supernatants were purified through 0.22 um membrane filters. The Pb (II) concentration in supernatant was determined using an atomic absorption spectroscopy after appropriate dilution (ZEnitt700P Analytik Jena AG., Germany), and all residual dense paste was for analysis by XPS, Mössbauer Spectroscopy and TEM equipped with Energy Dispersive X-ray spectroscopy (EDX).

2.3 XPS and Mössbauer Spectroscopy analysis

X-ray photoelectron spectroscopy (XPS) is used to identify adsorbed species on the surfaces of the Fh-HA. The XPS spectra of the precipitates that reacted and unreacted were determined by a Kratos Axis spectrometer (Kratos Analytical, Manchester, UK), with application of monochromatic Al Kα-radiation with an excitation energy of 1486.7 eV. Survey spectra were acquired using a pass energy of 160 eV and a step size of 1 eV. a high-resolution scan for O, C, Fe and Pb element were acquired with a pass energy of 160 eV and a step size of 0.05 eV. All binding energies (BE) were calibrated by reference to the C1s peak at 284.8 eV (Leone et al.,2006). The XPS spectra were fitted and analyzed by means of curve fitting program Casaxps. Mössbauer spectra were measured in transmission geometry employing a source of $^{57}$Co in Rh and a sinusoidal velocity waveform. A Kr proportional counter equipped with single channel analyzer windows, setting on both the 14.4 keV photo peak and the escape peak was used to detect the 14.4 keV γ-rays. Mössbauer spectrometer calibration was performed at room temperature using a standard SNP. For the given isomer shifts, to eliminate contributions from the second order Doppler shifts, which are always in respect of the
$^{57}$Co–Rh source keeping the same temperature as the absorber. The raw data were folded and the geometry effect eliminated, and then least-square with Gaussian distributions of hyperfine parameters. Further details of the distributions will be discussed in results and discussion section.

3. Results and discussion

3.1 Surface and morphology

Ferrihydrite displays nanometer sized particles in width and several microns in length. The SSA of ~300 m$^2$/g determined for the 2-line ferrihydrite is supported by published data (Cornell et al., 2003). All Fh-HA precipitates had much smaller SSA and porosity compared ferrihydrite (Table 1), In practice, the combined effect of charge stabilization and steric stabilization affect the final average sizes of Fh-HA colloidal particles in soils and aqueous environment.

Fh and several Fe precipitates materials have similar N$_2$ adsorption edges. N$_2$ adsorption capacity under low pressure is high, which agrees well with typical IV adsorption patterns, it is a indicator that Fh and all Fh-HA samples are porous materials with mainly mesopores, small amount of micropores, (Fig. 1), and the result is consistent with the pore size distribution. However, with increasing C amount the N$_2$-detectable mineral pore volume of Fe precipitates declined by up to 50% compared to pure Fh.

The XRD of the synthetic ferrihydrite at ~0.26 nm and ~0.15 nm shows a characteristic peak of 2-L Fh (Fig. 2). Their diffuse shoulders are present in smaller peaks at 0.22 nm, 0.20 nm, 0.17 nm and 0.16 nm, which accords to standard JCPDS card no. 29-0712. For coprecipitates, differences in XRD
pattern get bigger with an increasing C/Fe molar ratio, two main peaks paralleled to Fh broaden and some tiny peaks at 0.22 nm, 0.20 nm, 0.17nm and 0.16 nm weaken until finally disappear. The change implied a strong interaction between Fh and HA, resulted in increasing disorder in the anionic layers, indicative of formation of crossed small chains of Fe octahedra units in the precipitation process (Xiu et al., 2018). The degree of structural deformation ferrihydrite was largely affected by composition and amount of loaded HA (Eusterhues et al., 2011).

TEM images and corresponding selected area electron diffraction (SAED) patterns of the six samples are given in Fig. 3. Fh forms aggregates with no surface roughness, a spherical geometry with hexgonal edges and consists of particles ~3-5 nm in diameter. This coincides with the measured SSA of ~310 m² g⁻¹ (Table1). It has been reported that the developed hexagonally shaped particles are indicator of Fh with higher structural order (Mikutta et al., 2008). While smaller particles formed in the presence of HA in spite of its smaller SSA, it can be explained by the formation of denser aggregates by the associated HA resulted in a reduced accessibility for N₂, thus less surface was detected. The SAED pattern of all samples is indexed to the (110), (112) and (115) planes of ferrihydrite (Janney et al., 2000). With increasing C loading, the corresponding SAED shows less distinct diffused rings. The images combined with XRD analysis, showed the shape of sample particle either in hexagonal (Fh) or spherical shape (Fh-HA) with a size of 2-4 nm, more C loadings, less ordered. In summary, our analyses confirmed that 2-line ferrihydrite was prominent mineral phase in coprecipitates, C loadings affected and changed the surface properties, phase as well as the morphology.
3.2 Mössbauer spectra analysis

All spectra recorded at ambient temperature consist of a single, broadened electric quadrupole, possessing isomer shift (IS) of 0.36 mm s\(^{-1}\) (Fig. 4). The identical mean shift value for all samples is in accordance with the exclusive presence of high-spin Fe\(^{3+}\) in an octahedral oxygen environment (Eusterhues et al., 2008), considering trivalent Fe is in range of 0.24—0.54 mm s\(^{-1}\) (Bancroft et al., 1974; Cardile et al., 1988). Quadrupole splitting (Qs) was well fitted by an asymmetrical Gaussian distribution (Table 2). Increasing Qs value with increasing C/Fe implied affected spatial coordination of center Fe\(^{3+}\) and the octahedral structure around the center Fe atom increasingly distorted. Some research indicated that at 4.2 K the Mössbauer spectra showed a broaden sextet, and with C/Fe ratios increased, the mean magnetic hyperfine field decreased, this was ascribed to decreasing particle size and crystallinity. Mössbauer spectrum confirming the XRD results, both showed that the Fe compounds in all prepared samples was single ferrihydrite phase, without presence of goethite or hematite derivatives. C loading affected not only the surface properties and morphology of ferrihydrite, but also the microscopic geometric structure centered on iron atoms, more C loaded, stronger effect generated.

3.3 Isotherms

Uptake data of Pb (Ⅱ) adsorbed to coprecipitates isotherms at various pH are illustrated in Fig. 5. The Pb adsorption capacity increases evidently with the pH increased, particularly at pH 8, suggesting alkaline environment is favorable for Pb adsorption. The analysis of adsorption process applied Langmuir and Freundlich isotherm models, and all parameters of both models listed in Table
3. The Langmuir isotherm is given as:

\[ q_e = \frac{K_L q_m C_e}{1 + K_L C_e} \]  

where \( q_m \) (mmol g\(^{-1}\)) represents the maximum adsorption capacity; \( q_e \) (mmol g\(^{-1}\)) is the amount of adsorbed Pb per g of Fh-HA at equilibrium; and \( K_L \) is the Langmuir constant. The Freundlich isotherm is given as:

\[ q_e = K_F C_e^{1/n} \]  

where \( K_F \) and \( n \) are related to the adsorption capacity and the adsorption intensity, respectively.

One can see that Freundlich yields a better fitting than the Langmuir model at pH 4 and pH 6 by comparing \( R^2 \) values, while Langmuir model is better at pH 8, the best \( R^2 \) for Langmuir isotherm and Freundlich isotherm is 0.962 and 0.965, respectively, at investigated pHs. The change of pH not only affects the amounts of competitive ions in solutions, but also has a significant effect on the dissociation and protonation of functional groups on the surface of Fh-HA. According to Langmuir fitting, the adsorption capacity, \( q_m \) (mmol/g Fe), follows the order: pH8 > pH6 > pH4. The difference was normalized to their varying active sites density on surface, at higher pH, more proportion of carboxylic and phenolic groups in humic acid were dissociated, thus more sites are available to complex Pb ions. Moreover, the higher \( K_L \)-value and \( n \)-value in isotherm fittings at pH 8 indicating Fh-HA precipitates has stronger affinity for Pb (II) ions at higher pH, and the result coincides with that obtained in desorption experiment, in which Pb(II) is harder to desorb from Fh-HA at higher pH.

In summary, the isotherm results revealed that Pb adsorption occurs on heterogenous sites of Fh-HA, the acidic/base state have great effect on not only available sites, also the affinity to Pb ions.
3.4 Kinetics

It has been depicted in Fig. 6, three different kinetic models have been used to evaluate the adsorption kinetics of Pb(II) on Fh-HA precipitates. The pseudo-first order, pseudo-second order, and intraparticle diffusion formulas are given as (3), (4) and (5), respectively.

\[
\ln(q_e - q_t) = \ln q_e - k_1 t
\]

(3)

where \(q_t\) (mg L\(^{-1}\)) represents adsorption capacity at time \(t\) and \(k_1\) (h\(^{-1}\)) is the rate constant of the adsorption type.

\[
\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e}
\]

(4)

where \(k_2\) (L mg\(^{-1}\) g\(^{-1}\)) represents the rate constant of the pseudo-second-order adsorption.

\[
q_t = k_i (t^{0.5}) + C
\]

(5)

where \(k_i\) (mg L\(^{-1}\) h\(^{1/2}\)) represents the rate constant of intraparticle diffusion, \(C\) (mg L\(^{-1}\)) is a constant.

The tested parameters can be seen from Table 4, a good \(R^2\) was obtained for the pseudo-second-order kinetic model compared to the other two models. This means that Pb(II) adsorption properties onto Fh-HA is more in line with the pseudo-second-order rate expression, which indicates the ions concentration at the adsorbent surface determines the Pb(II) adsorption rate.

Obviously, during the whole adsorption process, two phases involved: for fast and slow stages (0-2 and 2-24 h, respectively). The two-stage plot suggests Pb adsorption process proceeds by surface adsorption and intraparticle adsorption (Xiu et al., 2018), a boundary layer effect for the initial stage while pore diffusion for the second stage (Vadivelan et al., 2005). The actual rate-controlling step involved in the adsorption can be determined by the calculation of adsorption dynamics, the following equation was employed,
\[ F = 1 - \frac{6}{\pi^2} \exp(-Bt) \]  \hspace{1cm} (6)

where \( F \) is the fractional attainment of equilibrium at time \( t \) and \( Bt \) is a calculated mathematical function of \( F \) derived from Reichenberg’s table (Reichenberg et al., 1953). \( Bt \) can be given as:

\[ Bt = -\ln(1 - F) - 0.4799 \]  \hspace{1cm} (7)

Bt vs t as proposed by Eq. (7) and fitted and plotted in Fig. 7. The linearity can be used to distinguish which mechanism predominates, film diffusion or intraparticle diffusion, and to estimate which factor controls the adsorption kinetics. Based on the point proposed by S. Wang, et.al (2006), the intercept (C) was not zero and the plot is not a straight line passing through origin, which signify the film diffusion controlled the adsorption rate in whole process (Baskaralingam et al., 2006; Gupta et al., 2006; Wang et al., 2006). Based on the \( Bt \) values, two plotted portions implied different mechanisms, the \( R^2 \) value for 2-24 h is higher than that for the 0-2 h portion, suggesting that the intraparticle diffusion dominated when the adsorption time becomes longer (Chen et al., 2007).

### 3.5 Desorption

As shown in Fig. 8, in the desorption stage, the \( \text{Pb(II)} \) amount desorbed increased in sequence of the amount of \( \text{Pb(II)} \) retention in Fh-HAs, as expected, but the differences among adsorption amount were not dramatic. As expected, the \( \text{Pb(II)} \) desorption decreased as \( \text{pH} \) increased. However, compared with adsorption stage, \( \text{pH} \) had relatively small effect on the desorption stage because in re-adsorption reactions strong coordination influenced much in the overall desorption process. Quick and much \( \text{Pb(II)} \) adsorption but slow and small desorption indicate a easily accessible sites with strong affinity for \( \text{Pb} \) ions on Fh-HAs. When initial \( \text{Pb(II)} \) concentrations and \( \text{pH} \) decreased, the
desorption effect was more obvious, this can be explained by the significant contribution of medium
and strong sites to Pb(II) (Tian et al., 2017).

3.6 Mechanism of Pb complex formed and phase evolution of ferrihydrite

The interaction mechanism, types of complexes between Fh-HA and Pb(II) were determined by
XPS. As shown in Fig. 9(a), (b), survey spectra indicated as expected the presence of Fe, O,
adventitious carbon and Pb. The Pb 4f\(_{7/2-5/2}\) core-level spectra acquired after Pb adsorbed on Fh-HA
was presented in Fig. 9(d). Obviously, The spectra of the Pb 4f had two bands, both closely coincide
with standard spectra for α-Pb, the Pb 4f\(_{7/2-5/2}\) core-level spectra have high coincidence with the
regular double 4f\(_{7/2}\) line-shape of lead-oxygen compounds and Pb-metal bond (Zatsepin et
al., 2017), indicating that the Pb ions was embedded into the Fh-HA by bonding with oxygen in
functional groups on Fh-HA. For Fe 2p XPS spectra, Fe (III) species in iron (oxyhydr)oxides was
confirmed for it typical spectra mode, a maximum at ~711.2 eV for 2p3/2 core level and a broad
satellite peak at ~719 eV were observed (Fig. 9(c)) (Grosvenor et al., 2004). The careful comparison
of the position of the core level peak seemingly indicate a very slight shift toward higher binding
energy after Pb ions adsorbed. Thus, the assumption that the formation of Fe-O-Pb binding according
to spectra of Fe 2p and O1s is clearly confirmed here.

Through XPS peak separation and simulation, the main O 1s XPS spectra of the Fh-HA was
divided into three subpeaks (Fig. 10), every subpeak is for a component: ~529.9 eV is for oxygen in
the crystal lattice (Fe-O-Fe), ~531.5 eV is for oxygen forming bonds as Fe-O-H or Fe-O-Pb or
simply oxygen in the HA, and ~533.2 eV is for oxygen in carboxyl and phenolic groups in the HA
The component at ~531.5 eV was calculated and increased ~29% after Pb adsorption, while the components at ~531.5 eV and ~533.2 eV decreased. The change in the peak intensity and area is contributed by the surface -OH, O=C-O, and R-OH groups protonated and partly interact with Pb ions, implying inner-sphere complex between lead ions and Fh-HA formed. The result also proved C loading can promote heavy metal binding to Ferrihydrite.

When Pb (II) adsorbed on ferrihydrite, hematite or goethite, the Pb (II) ions have very similar coordination environments: distorted trigonal pyramidal coordination, with hydroxide ion ligands or surface oxygen ligands (Bargar et al., 1997). There are three types of functional groups on iron oxide surface at pH 7: oxygens are triply, doubly, and singly bonded to Fe atoms, form \([Fe^{Fe}_Fe>\text{O}^{1/2}]\), \([Fe^{Fe}_Fe>\text{OH}]\) and \([\text{Fe—OH}_2^{+1/2}]\) sites respectively. Considering when Pb (II) ions bind to \([Fe^{Fe}_Fe>\text{OH}]\) sites, Pb are not able to competitively replace H\(^+\) due to strongly bonded H\(^+\). Pb (II) ions adsorb on ferrihydrite follow the following reactions:

\[
\begin{align*}
(1) \quad & \text{Pb}^{2+}(aq) + [Fe^{Fe}_Fe>\text{O}^{1/2}]_2 + \text{H}_2\text{O} = [Fe^{Fe}_Fe>\text{O}]_2 \text{PbOH} + \text{H}^+ \\
(2) \quad & \text{Pb}^{2+}(aq) + [\text{Fe—OH}_2^{+1/2}] [Fe^{Fe}_Fe>\text{O}^{1/2}] + \text{H}_2\text{O} = [\text{Fe—OH}] [Fe^{Fe}_Fe>\text{O}] \text{PbOH} + 2\text{H}^+ \\
(3) \quad & \text{Pb}^{2+}(aq) + [\text{Fe—OH}_2^{+1/2}] + \text{H}_2\text{O} = [\text{Fe—(OH)}_2] \text{PbOH} + 3\text{H}^+ 
\end{align*}
\]

Generally, for the above reactions, which predominates depends on the distributions and density of \([Fe^{Fe}_Fe>\text{O}^{1/2}]\) and \([\text{Fe—OH}_2^{+1/2}]\) sites. Pb (II) ions are adsorbed to in edge-sharing manner on ferrihydrite, formed mononuclear sorption complex on FeO\(_6\) octahedra. The reactions and adsorbate species formed are illustrated in Fig. 13. The Mössbauer spectra of Fh-HA after Pb adsorbed is shown in Fig. 12. Based on the data (Table 5), the Fe remains in a stable trivalent state, but Fe unit structure changed compared that before Pb adsorption. Decreased Qs implied a more symmetrical Fe
unit structure. The original chemical bonds such as Fe-OH, R-COOH, R-OH were replaced by Fe-O-Pb, R-COO-Pb and R-O-Pb respectively, resulted in change of bond length, bond angle and bond energy. Based on the fact, the interaction between Pb(II) and Fh-HA is stronger than that between hydroxyl hydrogen and Fh-HA. In addition, site heterogeneity lead to the difference of complexation affinity and adsorption density, the combined effect contributed to the change of Fe unit structure.

The TEM images equipped with Energy Dispersive X-ray spectroscopy (EDX) of Fh-HA sample after Pb (II) sorption was determined. The element analysis from EDX (Fig.11(a)) agrees well with the XPS survey spectra. The TEM images shows the ferrihydrite has partly transformed, part converted to acicular goethite, part to spherical hematite particles as shown by arrows (Fig.11(b)). As given in Fig. 11(c), clear diffraction spots in The SAED pattern indicates the high crystallinity of goethite and hematite nanoparticles generated. A combination of TEM and SAED diffraction pattern suggests that with time the Fh sample has transformed and tend to be more crystalline phase. However, as showed in Fig. 11(d), (e), no obvious changes occurred on the TEM image and SAED pattern of Fh-HA precipitate sample, after a period of adsorption and desorption process, the ferrihydrite still dominated in mineral phase. The result implied the transformation of ferrihydrite has been inhibited when associated with HA.

It can be concluded that the Pb adsorption occurs on Fh, HA surface, or form Fh-HA-Pb ternary complex, this can explain why C loading in a certain range can enhance Pb sorption in spite of reduced SSA, new active sites from HA can balance the loss of SSA and even achieve a better complexation. Pb adsorbed on Fh-HA is expected to form steady mononuclear and binuclear
bidentate complexes, the extremely low Pb desorption amount agrees well the result. In addition, humic acid can improve morphology stability of ferrihydrite by inhibiting crystalline growth and mineral transformation. The present research conclude that low molecular organic ligands adsorbed to nucleation sites resulted in a slower crystallization of ferrihydrite (Liu et al., 2003). Therefore, HA coprecipitated with Ferrihydrite can be used as efficient and stable adsorbent for Pb ions. At the molecular level, the octahedral $\text{Fe}^{3+}$ distorted in the presence of humic acid and resulted in new geometric structure, the TEM with SAED images provide concerning proof for the assumption. Mineral transformation occurred on Fh with aging time, from poorly ordered state to more crystalline state, yielded goethite or hematite. However, which phase will be predominant in final product of ferrihydrite transformation has not been determined, considering that the measurement conducted before aging process finished. A few researches have indicated a close link between transformation product and pH condition during aging process of ferrihydrite (Kim et al., 2014).

4. Conclusions

This paper discussed the coprecipitation properties of Fh with humic acid using some techniques and Mössbauer spectra, further explored the mechanism of Pb adsorption onto Fh-HAs and distinguished the changes and aging of Fh and Fh-HA before and after metal ions adsorbed. Mössbauer and other characterization techniques results show that even small concentration of HA have a clear impact on surface, size and structural properties on ferrihydrite. With increasing C/Fe, the interaction between HA and ferrihydrite is increasing, and stronger turbulence to early $\text{Fe}^{3+}$ octahedra structure. HA coprecipitated with HA affects the fate and mobility of lead ions in soils and
The presence of HA results in increase in the available sites on the Fh surfaces and generates a higher negative surface charge, thereby possess a good dispersion in any interface and increase the Pb adsorption. Pb exhibits pH-dependent adsorption behavior and the maximum usually occur at neutral and alkaline pH.

In particular, the O1s XPS spectrum was investigated due to it consists of an effective molecular probe for sorption processes. A stable mononuclear and binuclear bidentate coordination between Pb ions and Fh-HAs formed. Aging process of ferrihydrite resulted in a mixed phase of ferrihydrite, goethite and hematite. HA inhibited the transformation of ferrihydrite and kept morphology stability relatively. The study revealed how the varying amount of HA affected the ferrihydrite structure, the excellent properties of Fh-HA to adsorb Pb ions, and transformation product in aging process. These observations and conclusions would have enlightenment to application of Fh-HA in Pb-contaminated sites.

Appendix A. Supplementary data

The following are the Supplementary data to this article:

Declarations

Ethics approval and consent to participate: This part does not applicable.

Consent for publication: Informed consent was obtained from all individual participants included in the study.

Availability of data and materials: All data generated or analysed during this study are included in this published article [and its supplementary information files].
Competing interests: The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Authors’ contributions: All authors contributed to the study conception and design. Material preparation, data collection and analysis were performed by Zhuanjun Zhao, Liwei Yao, Jie Li, Xiangbang Ma, Liangwei Han, Shuqi Guan and Zhiyuan Lin. The first draft of the manuscript was written by Zhuanjun Zhao, Liwei Yao and all authors commented on previous versions of the manuscript. All authors read and approved the final manuscript.

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Table 1. Specific surface areas and pore sizes measured by N\textsubscript{2}-accessible BET method

| Sample      | SSA (m\textsuperscript{2} g\textsuperscript{-1}) | Pore size (nm) | Zeta potential (mV) |
|-------------|-----------------------------------------------|----------------|---------------------|
| Fh          | 309.7                                         | 2.8043         | 51.93               |
| Fh-HA-0.5   | 258.9                                         | 2.8054         | 78.55               |
| Fh-HA-1.0   | 230.5                                         | 2.9927         | -33.33              |
| Fh-HA-1.5   | 196.6                                         | 2.9990         | -9.88               |
| Fh-HA-2.0   | 183.3                                         | 3.0500         | -40.3               |
| Fh-HA-2.5   | 140.8                                         | 3.1763         | -41.43              |
Table 2. Mössbauer parameters of ferrihydrite and coprecipitates determined from spectra collected at room temperature

| Sample     | Mean isomer shift $\delta$ (mm/s) | Mean quadrupole splitting $\langle \Delta E_Q \rangle$ (mm/s) |
|------------|----------------------------------|-------------------------------------------------------------|
| Fh         | 0.364                            | 0.774                                                       |
| C/Fe_0.5   | 0.366                            | 0.804                                                       |
| C/Fe_1.0   | 0.366                            | 0.811                                                       |
| C/Fe_1.5   | 0.368                            | 0.824                                                       |
| C/Fe_2.0   | 0.369                            | 0.873                                                       |
| C/Fe_2.5   | 0.364                            | 0.925                                                       |
|          | Freundlich |          | Langmuir |          |          |          |
|----------|------------|----------|----------|----------|----------|----------|
|          | $K_F$      | $n$      | $R^2$    | $qm$     | $K_L$    | $R^2$    |
| pH=4     | 0.444      | 0.965    | 0.952    | 2.216    | 2.074    | 0.952    |
| pH=6     | 0.570      | 1.141    | 0.965    | 2.247    | 2.263    | 0.962    |
| pH=8     | 1.991      | 1.287    | 0.849    | 2.692    | 2.513    | 0.859    |

*Table 3. Parameters of adsorption isotherms of Pb(II) on Fh-HA at different pHs*
Table 4. A comparison of pseudo-first-order, pseudo-second-order, and intraparticle diffusion kinetic model rate constants from experimental data.

| $C_0$ (mmol/L) | Pseudo-first-order | Pseudo-second-order | Intraparticle diffusion |
|----------------|--------------------|---------------------|-------------------------|
| $q_e$ (mg L$^{-1}$) | $k_1$ (h$^{-1}$) | $r^2$ | $q_e$ (mg L$^{-1}$) | $k_2$ (L mg$^{-1}$) | $r^2$ | $k_i$ (mg g$^{-1}$ h$^{-1/2}$) | C (mg L$^{-1}$) | $r^2$ |
| 0.5 | 100.96 | 8.2 | 0.999 | 101.38 | 0.92 | 0.999 | 1.47 | 98.63 | 0.764 |
| 1.0 | 199.36 | 5.4 | 0.995 | 202.88 | 0.10 | 0.998 | 10.97 | 181.77 | 0.526 |
| 2.0 | 331.61 | 2.7 | 0.985 | 313.62 | 4.51 | 0.911 | 63.45 | 225.02 | 0.697 |
| 4.0 | 476.08 | 3.1 | 0.989 | 456.34 | 1.29 | 0.944 | 73.37 | 354.36 | 0.711 |
| 8.0 | 1001.36 | 6.6 | 0.999 | 995.18 | 6.80 | 0.998 | 26.46 | 958.40 | 0.609 |
| 16.0 | 2471.23 | 9.2 | 0.999 | 2467.09 | 7.61 | 0.999 | 21.97 | 2436.55 | 0.790 |
Table 5. Mössbauer parameters of ferrihydrite and coprecipitates determined from spectra collected at room temperature

| Sample | Mean isomer shift δ (mm/s) | Mean quadrupole splitting 〈ΔE_Q〉 (mm/s) |
|--------|-----------------------------|------------------------------------------|
| pH=4   | 0.352                       | 0.844                                    |
| pH=6   | 0.351                       | 0.834                                    |
| pH=8   | 0.377                       | 0.775                                    |
Fig. 1. N₂ adsorption-desorption isotherms and pore size distribution of Fh and Fh-HA samples
Fig. 2. Powder x-ray diffractograms of the ferrihydrite (Fh) and coprecipitates synthesized.

Figures in parentheses refer to the molar C/Fe ratio of the coprecipitates. All diffractograms were stacked by a constant value.
Fig. 3. Transmission electron micrographs of the ferrihydrite and coprecipitates used in this study: selected area electron (SAED) pattern are shown for all samples.
Fig. 4. Mössbauer spectra of Fh and Fh-HA coprecipitates taken at room temperature.
Fig. 5. Sorption isotherms of lead ions on Fh-HA coprecipitates at various pH.

\([\text{C}/\text{Fe}_{2.0}] = 6 \text{ g L}^{-1}; [\text{NaNO}_3] = 0.1 \text{ M}\)
Fig. 6. Kinetics of Pb adsorption on Fh-HAs and fitted by three adsorption models

\[ [\text{C/Fe}_{2.0}] = 6 \text{ g L}^{-1}, [\text{NaNO}_3] = 0.1 \text{ M} \]
Fig. 7. $B_t$ vs $t$ plot for Pb(II) adsorption onto Fh-HA coprecipitates
Fig. 8. A comparison of amount of Pb adsorbed and desorbed at various pH.
Fig. 9. (a) Survey spectra, (b) C 1s, (c) Fe (2p), (d) Pb (4f) spectra of Fh-HA samples after Pb(II) adsorption
Fig. 10. O (1s) XPS spectra of Fh-HA_2.0 coprecipitate before (a) and after (b) the binding of Pb(II) at pH 8.
Fig. 11. TEM images and SAED patterns of the Fh sample (b)(c) and Fh-HA_2.0 (d)(e) after Pb (II) adsorption equipped with (a) EDX mapping
Fig. 12. Mössbauer spectra of ferrihydrite taken at room temperature after Pb(II) adsorption at various pH.
Fig. 13. The reactions taking place during formation of Fh-HA coprecipitates, Pb(II) sorption on Fh-HA and evolution of ferrihydrite.
Figures

Figure 1

N2 adsorption-desorption isotherms and pore size distribution of Fh and Fh-HA samples
Figure 2

Powder x-ray diffractograms of the ferrihydrite (Fh) and coprecipitates synthesized. Figures in parentheses refer to the molar C/Fe ratio of the coprecipitates. All diffractograms were stacked by a constant value.
Figure 3

Transmission electron micrographs of the ferrihydrite and coprecipitates used in this study: selected area electron (SAED) pattern are shown for all samples.
Figure 4

Mössbauer spectra of Fh and Fh-HA coprecipitates taken at room temperature.
Figure 5
Sorption isotherms of lead ions on Fh-HA coprecipitates at various pH. ([C/Fe_2.0] =6 g L⁻¹; [NaNO₃] =0.1 M)

Figure 6
Kinetics of Pb adsorption on Fh-HAs and fitted by three adsorption models ([C/Fe_2.0] =6 g L⁻¹; [NaNO₃] =0.1 M)

Figure 7
Bt vs t plot for Pb(II) adsorption onto Fh-HA coprecipitates

Figure 8

A comparison of amount of Pb adsorbed and desorbed at various pH.
Figure 9

(a) Survey spectra, (b) C 1s, (c) Fe (2p), (d) Pb (4f) spectra of Fh-HA samples after Pb(II) adsorption

Figure 10

O (1s) XPS spectra of Fh-HA_2.0 coprecipitate before (a) and after (b) the binding of Pb(II) at pH 8
Figure 11

TEM images and SAED patterns of the Fh sample (b)(c) and Fh-HA_2.0 (d)(e) after Pb (Ⅰ) adsorption equipped with (a) EDX mapping.
Figure 12

Mössbauer spectra of ferrihydrite taken at room temperature after Pb(II) adsorption at various pH.
Figure 13

The reactions taking place during formation of Fh-HA coprecipitates, Pb(II) sorption on Fh-HA and evolution of ferrihydrite.