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

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1 **Abstract**

2 Ferrihydrite often precipitates with humic acid in natural ways, affecting the fate of lead ions,
3 the stabilization of humic acid and the aging process of ferrihydrite. A series of 2-line
4 ferrihydrite-humic (Fh-HA) acid with varying C loadings has been prepared, the morphology and
5 surface properties of Fh-HA organo-minerals have been characterized, the adsorption property of Pb
6 ions onto Fh-HA has been studied. The results indicated a strong interference of HA to ferrihydrite.
7 2-line Fh dominated mineral phase in all samples, but with increasing C/Fe molar ratios the
8 crystallinity gradually weakened, particles became smaller and SSA decreased significantly. The data
9 of Mössbauer spectra confirmed C loading changed the unit structure of ferrihydrite. Fh-HA
10 performed good adsorption properties to Pb(II): high efficiency and big capacity, especially
11 Fh-HA_2.0. pH had great effect on Lead uptake, the pH change not only affects the amounts of
12 competitive ions in solutions, but also the dissociation and protonation of functional groups on the
13 surface of Fh-HA. Sorption kinetics can be well modeled by a pseudo-second order model, and the
14 process was controlled by film and intraparticle adsorption simultaneously. The adsorption isotherms
15 can be well described by Freundlich isotherm model. The careful determination of Fe 2p, O 1s and
16 Pb 4f spectra before and after lead adsorption showed mononuclear bidentate or binuclear bidentate
17 ligands occurring on Fh-HA surface, forming stable inner-sphere complex. By comparison of
18 Mössbauer spectra and TEM images, it revealed a slower evolution of iron oxide/oxyhydroxide
19 phases in Fh-HA-Pb system compared to pure ferrihydrite with aging time, ferrihydrite transformed
20 to a combination of ferrihydrite, goethite and hematite phases. in this study, the determination of
21 C-Fe interaction, Pb fate influenced by Fh-HA and transformation of ferrihydrite would have a great

- 22 implication to application of Fh-HA precipitates in remediation for soil or groundwater polluted by
- 23 heavy metals.

Keywords: Ferrihydrite; Fh-HA precipitates; Lead; mechanism; transformation

24 **1.Introduction**

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

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

41 The widely distributed organic matter (NOM) always co-exists with iron (hydr)oxides by
42 complexation or coprecipitation(Bargar et al.,1997). Humic acid, as a typical representative for NOM,
43 contains of carboxyl, aromatic, phenolic functional groups that often closely associate with minerals
44 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) ($\geq 18 \text{ M}\Omega \text{ cm}$), CO_2 was rigorously excluded to prevent the formation of Pb(II)-carbonate aqueous complexes or precipitates. Stock solutions of FeCl_3 and $\text{Pb}(\text{NO}_3)_2$ 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 HNO_3 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

85 Cornell,1991). In brief, Fh was synthesized by hydrolysis of Fe^{3+} as $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ in ultrapure water,
86 rapidly adjust solution to pH ~ 7.5 using freshly prepared 1M NaOH, under vigorous stirring for 2 h,
87 subsequently was washed, centrifuged and freeze-dried. for Fh-HA coprecipitates, firstly, humic acid
88 soluble in sodium hydroxide was added and mixed with a previously prepared Fe^{3+} salt solution,
89 containing elevated initial C concentrations, then hydrolyzed and adjusted to pH ~ 7.5 , subsequently
90 operated in the same way as preparation procedure of Ferrihydrite. The five Fh-HA coprecipitates are
91 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
92 prepared Fh and Fh-HA were used as a standard for measurement and in all lead adsorption
93 experiments. Surface chemistry was characterized by XRD, TEM and BET.

94 ***2.2 Lead adsorption experimental designs***

95 All Pb(II) adsorption experiments were processed at room temperature, and 0.01M NaNO_3 was
96 used as the background electrolyte. The affected factors such as pH, ionic strength, initial Pb (II)
97 concentrations and adsorbent dosage were introduced to the system separately to shed light on
98 adsorption occurring conditions. For each factor, reasonable value range and gradient were designed,
99 to determine the optimal adsorption aqueous environment. All samples are in triplicate. For
100 adsorption isotherms, the adsorption contained 6 g/L adsorbent and 0-16 mmol/L Pb(II). for
101 adsorption-desorption kinetics, common functions of combined effected factors were taken into
102 account. In the duration of this experiment, sampling time interval was set up, the supernatant was
103 collected during adsorption reaction at 15 min, 30 min, 60 min,120 min, 240 min and 1440 min. the
104 same sampling time interval for desorption, and the desorption was performed for two circles. All

105 finished processing suspensions were immediately allowed to equilibrate for 24 h at a shaker. To
106 remove adsorbent particles, the suspensions were centrifuged, the obtained supernatants were
107 purified through 0.22 μ m membrane filters. The Pb (II) concentration in supernatant was determined
108 using an atomic absorption spectroscopy after appropriate dilution (ZEEnitt700P Analytik Jena AG.,
109 Germany), and all residual dense paste was for analysis by XPS, Mössbauer Spectroscopy and TEM
110 equipped with Energy Dispersive X-ray spectroscopy (EDX).

111 ***2.3 XPS and Mössbauer Spectroscopy analysis***

112 X-ray photoelectron spectroscopy (XPS) is used to identify adsorbed species on the surfaces of
113 the Fh-HA. The XPS spectra of the precipitates that reacted and unreacted were determined by a
114 Kratos Axis spectrometer (Kratos Analytical, Manchester, UK), with application of monochromatic
115 Al K α -radiation with an excitation energy of 1486.7 eV. Survey spectra were acquired using a pass
116 energy of 160 eV and a step size of 1 eV. a high-resolution scan for O, C, Fe and Pb element were
117 acquired with a pass energy of 160 eV and a step size of 0.05 eV. All binding energies (BE) were
118 calibrated by reference to the C1s peak at 284.8 eV (Leone et al.,2006). The XPS spectra were fitted
119 and analyzed by means of curve fitting program Casaxps. Mössbauer spectra were measured in
120 transmission geometry employing a source of ^{57}Co in Rh and a sinusoidal velocity waveform. A Kr
121 proportional counter equipped with single channel analyzer windows, setting on both the 14.4 keV
122 photo peak and the escape peak was used to detect the 14.4 keV γ -rays. Mössbauer spectrometer
123 calibration was performed at room temperature using a standard SNP. For the given isomer shifts, to
124 eliminate contributions from the second order Doppler shifts, which are always in respect of the

125 ^{57}Co -Rh source keeping the same temperature as the absorber. The raw data were folded and the
126 geometry effect eliminated, and then least-square with Gaussian distributions of hyperfine
127 parameters. Further details of the distributions will be discussed in results and discussion section.
128

129 **3.Results and discussion**

130 ***3.1 surface and morphology***

131 Ferrihydrite displays nanometer sized particles in width and several microns in length. The SSA
132 of $\sim 300 \text{ m}^2/\text{g}$ determined for the 2-line ferrihydrite is supported by published data (Cornell et
133 al.,2003). All Fh-HA precipitates had much smaller SSA and porosity compared ferrihydrite (Table1),
134 In practice, the combined effect of charge stabilization and steric stabilization affect the final average
135 sizes of Fh-HA colloidal particles in soils and aqueous environment.

136 Fh and several Fe precipitates materials have similar N_2 adsorption edges. N_2 adsorption
137 capacity under low pressure is high, which agrees well with typical IV adsorption patterns, it is a
138 indicator that Fh and all Fh-HA samples are porous materials with mainly mesopores, small amount
139 of micropores, (Fig. 1), and the result is consistent with the pore size distribution. However, with
140 increasing C amount the N_2 -detectable mineral pore volume of Fe precipitates declined by up to 50%
141 compared to pure Fh.

142 The XRD of the synthetic ferrihydrite at $\sim 0.26 \text{ nm}$ and $\sim 0.15 \text{ nm}$ shows a characteristic peak of
143 2-L Fh (Fig. 2). Their diffuse shoulders are present in smaller peaks at 0.22 nm , 0.20 nm , 0.17 nm and
144 0.16 nm , which accords to standard JCPDS card no. 29-0712. For coprecipitates, differences in XRD

145 pattern get bigger with an increasing C/Fe molar ratio, two main peaks paralleled to Fh broaden and
146 some tiny peaks at 0.22 nm, 0.20 nm, 0.17nm and 0.16 nm weaken until finally disappear. The
147 change implied a strong interaction between Fh and HA, resulted in increasing disorder in the
148 anionic layers, indicative of formation of crossed small chains of Fe octahedra units in the
149 precipitation process (Xiu et al.,2018). The degree of structural deformation ferrihydrite was largely
150 affected by composition and amount of loaded HA (Eusterhues et al.,2011).

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

165 3.2 Mössbauer spectra analysis

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

180 3.3 Isotherms

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

185 3. The Langmuir isotherm is given as:

186
$$q_e = \frac{K_L q_m C_e}{1 + K_L C_e} \quad (1)$$

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

190
$$q_e = K_F C_E^{1/n} \quad (2)$$

191 where K_F and n are related to the adsorption capacity and the adsorption intensity, respectively.

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

205 3.4 Kinetics

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

$$209 \ln(q_e - q_t) = \ln q_e - k_1 t \quad (3)$$

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

$$212 \frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (4)$$

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

$$214 q_t = k_i(t^{0.5}) + C \quad (5)$$

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

216 The tested parameters can be seen from Table 4, a good R^2 was obtained for the
217 pseudo-second-order kinetic model compared to the other two models. This means that Pb(II)
218 adsorption properties onto Fh-HA is more in line with the pseudo-second-order rate expression,
219 which indicates the ions concentration at the adsorbent surface determines the Pb(II) adsorption rate.
220 Obviously, during the whole adsorption process, two phases involved: for fast and slow stages (0-2
221 and 2-24 h, respectively). The two-stage plot suggests Pb adsorption process proceeds by surface
222 adsorption and intraparticle adsorption (Xiu et al.,2018), a boundary layer effect for the initial stage
223 while pore diffusion for the second stage (Vadivelan et al.,2005). The actual rate-controlling step
224 involved in the adsorption can be determined by the calculation of adsorption dynamics, the
225 following equation was employed,

$$F = 1 - \frac{6}{\pi^2} \exp(-Bt) \quad (6)$$

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:

$$Bt = -\ln(1 - F) - 0.4799 \quad (7)$$

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 $Pb(II)$ amount desorbed increased in sequence of the amount of $Pb(II)$ retention in Fh-HAs, as expected, but the differences among adsorption amount were not dramatic. As expected, the $Pb(II)$ desorption decreased as pH increased. However, compared with adsorption stage, 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 $Pb(II)$ adsorption but slow and small desorption indicate a easily accessible sites with strong affinity for Pb ions on Fh-HAs. When initial $Pb(II)$ concentrations and 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-HAs 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_{7/2-5/2} line-shape of lead-oxygen compounds and Pb-metal bond (Zatsepin et al.,2017), indicating that the Pb ions was embedded into the Fh-HAs 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 2p_{3/2} 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

(Tan et al.,2008). 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 functional groups on iron oxide surface at PH 7: oxygens are triply, doubly, and singly bonded to Fe atoms, form $[Fe_{Fe}^{Fe} > O^{-1/2}]$, $[Fe_{Fe}^{Fe} > OH]$ and $[Fe-OH_2^{+1/2}]$ sites respectively. Considering when Pb (II) ions bind to $[Fe_{Fe}^{Fe} > OH]$ sites, Pb are not able to competitively replace H^+ due to strongly bonded H^+ . Pb (II) ions adsorb on ferrihydrite follow the following reactions:

Generally, for the above reactions, which predominates depends on the distributions and density of $[Fe_{Fe}^{Fe} > O^{-1/2}]$ and $[Fe-OH_2^{+1/2}]$ 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

308 bidentate complexes, the extremely low Pb desorption amount agrees well the result. In addition,
309 humic acid can improve morphology stability of ferrihydrite by inhibiting crystalline growth and
310 mineral transformation. The present research conclude that low molecular organic ligands adsorbed
311 to nucleation sites resulted in a slower crystallization of ferrihydrite (Liu et al.,2003). Therefore, HA
312 coprecipitated with Ferrihydrite can be used as efficient and stable adsorbent for Pb ions. At the
313 molecular level, the octahedral Fe^{3+} distorted in the presence of humic acid and resulted in new
314 geometric structure, the TEM with SAED images provide concerning proof for the assumption.
315 Mineral transformation occurred on Fh with aging time, from poorly ordered state to more crystalline
316 state, yielded goethite or hematite. However, which phase will be predominant in final product of
317 ferrihydrite transformation has not been determined, considering that the measurement conducted
318 before aging process finished. A few researches have indicated a close link between transformation
319 product and pH condition during aging process of ferrihydrite (Kim et al.,2014).

320 **4.Conclusions**

321 This paper discussed the coprecipitation properties of Fh with humic acid using some
322 techniques and Mössbauer spectra, further explored the mechanism of Pb adsorption onto Fh-HAs
323 and distinguished the changes and aging of Fh and Fh-HA before and after metal ions adsorbed.
324 Mössbauer and other characterization techniques results show that even small concentration of HA
325 have a clear impact on surface, size and structural properties on ferrihydrite. With increasing C/Fe,
326 the interaction between HA and ferrihydrite is increasing, and stronger turbulence to early Fe^{3+}
327 octahedra structure. HA coprecipitated with HA affects the fate and mobility of lead ions in soils and

328 water. The presence of HA results in increase in the available sites on the Fh surfaces and generates a
329 higher negative surface charge, thereby possess a good dispersion in any interface and increase the
330 Pb adsorption. Pb exhibits pH-dependent adsorption behavior and the maximum usually occur at
331 neutral and alkaline pH.

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

340 **Appendix A. Supplementary data**

341 The following are the Supplementary data to this article:

342 **Declarations**

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

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

346 Availability of data and materials: All data generated or analysed during this study are included
347 in this published article [and its supplementary information files].

348 Competing interests: The authors declare that they have no known competing financial interests
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359

360 **References**

361 Abdelwaheb M, Jebali K, Dhaouadi H, Dridi-Dhaouadi S (2019) Adsorption of nitrate, phosphate,
362 nickel and lead on soils: Risk of groundwater contamination. *Ecotoxicology and Environmental*
363 *Safety* 179:182-187.

364 Bancroft G(1974)*Mössbauer Spectroscopy: An Introduction for Inorganic Chemists and Geochemists*,
365 Halsted Press, New York, *Quaternary Research*. 4 (2): 232.

366 Bargar JR, Brown GE, Parks GA (1997) Surface complexation of Pb(II) at oxide-water interfaces: I.
 367 XAFS and bond-valence determination of mononuclear and polynuclear Pb(II) sorption products
 368 on aluminum oxides. *Geochimica et Cosmochimica Acta* 61(13):2617-2637.

369 Bargar JR, Jr GEB, Parks GA (1997) Surface complexation of Pb (II) at oxide-water interfaces: II.
 370 XAFS and bond-valence determination of mononuclear Pb (II) sorption products and surface
 371 functional groups on iron oxides. *Geochim. Cosmochim. Acta* 61(13):2639-2652.

372 Baskaralingam P, Pulikesi M, Elango D, Ramamurthi V, Sivanesan S (2006) Adsorption of acid dye
 373 onto organobentonite. *Journal of Hazardous Materials* 128:138-144.

374 Cardile CM (1988) Tetrahedral Fe^{3+} in ferrihydrite- Fe^{57} Mössbauer spectroscopic evidence. *Clays Clay*
 375 *Miner* 36:537–539.

376 Chen H, Wang A (2007) Kinetic and isothermal studies of lead ion adsorption onto palygorskite clay.
 377 *Journal of Colloid & Interface Science* 307(2):309-316.

378 Chen H, Wang A (2007) Kinetic and isothermal studies of lead ion adsorption onto palygorskite clay.
 379 *Journal of Colloid & Interface Science* 307(2):309-316.

380 Chen WQ, Lu ZH, Xiao BH, Gu PC, Yao W, Xing JL, Asiri AM, Alamry KA, Wang XG, Wang
 381 SH (2019) Enhanced removal of lead ions from aqueous solution by iron oxide nanomaterials with
 382 cobalt and nickel doping. *Journal of Cleaner Production* 211:1250-1258.

383 Cornell RM (2004) *The Iron Oxides: Structure, Properties, Reactions, Occurrences and Uses*, Second
 384 Edition.

385 Cornell RM, Schwertmann U (2004) *Introduction to the Iron Oxide// The Iron Oxides: Structure,*
 386 *Properties, Reactions, Occurrences and Uses, Second Edition.*

387 Cornell RM, Schwertmann U(1979)Influence of organic-anions on the crystallization of ferrihydrite.
 388 Clays Clay Miner 27:402–410.

389 Cornell RM, Schwertmann U(2003)The Iron Oxides, seconded.

390 Ding Z, Fu F, Dionysiou DD, Tang B(2018)Coadsorption and subsequent redox conversion behaviors
 391 of As (III) and Cr (VI) on Al-containing ferrihydrite. Environmental Pollution 235 : 660-669.

392 Eusterhues K, Rennert T, Knicke H, Kogel-Knabner I, Totsche KU, Schwertmann
 393 U(2011)Fractionation of organic matter due to reaction with ferrihydrite: coprecipitation versus
 394 adsorption. Environ. Sci. Technol 45:527–533.

395 Eusterhues K, Wagner FE, Häusler W(2008) Characterization of Ferrihydrite-Soil Organic Matter
 396 Coprecipitates by X-ray Diffraction and Mössbauer Spectroscopy. Environmental Science &
 397 Technology 42(21) :7891-7897.

398 Fortin D, Langley S (2005) Formation and occurrence of biogenic iron-rich minerals. Earth Science
 399 Reviews 72(1-2):1-19.

400 Furrer G, Stumm W(1986) The coordination chemistry of weathering: I. Dissolution kinetics of δ –
 401 Al_2O_3 and BeO. Geochimica Et Cosmochimica Acta 50(9):1847-1860.

402 Grosvenor AP, Kobe BA, McIntyre NS, Tougaard S, Lennard WN (2004) Use of QUASES™/XPS
 403 measurements to determine the oxide composition and thickness on an iron substrate. Surface and
 404 Interface Analysis 36(7):632-639.

405 Gupta SS, Bhattacharyya KG (2006) Adsorption of Ni (II) on clays, Journal of Colloid & Interface
 406 Science. 295(1):21-32.

407 Gustafsson JP, Persson I, Kleja DB, Van Schaik JWJ (2007) Binding of iron(III) to organic soils:
 408 EXAFS spectroscopy and chemical equilibrium modeling. *Environ Sci Technol* 41:1232–1237.
 409 Janney DE, Cowley JM, Buseck PR(2000)Structure of synthetic 2-line ferrihydrite by electron
 410 microdiffraction. *Am. Mineral* 85:1180–1187.
 411 Kaiser K, Mikutta R, Guggenberger G(2007) Increased Stability of Organic Matter Sorbed to
 412 Ferrihydrite and Goethite on Aging. *Soil Science Society of America Journal*. 71(3):711.
 413 Kim SO, Lee WC, Cho HG, Lee BT, Lee PK, Choi SH (2014) Equilibria, kinetics, and spectroscopic
 414 analyses on the uptake of aqueous arsenite by two-line ferrihydrite. *Environ. Technol* 35
 415 (3):251-261
 416 Kragović M, Daković A, Marković M(2017) Removal of Lead and Cadmium Ions from Aqueous
 417 Solution by Using Natural and Modified Zeolite. *Advanced Science Letters* 23(6):5862-5865.
 418 Lei T, Yuzhen L, Yang L, Wu P X, Shi Z Q (2018) Pb (II) and Cu (II) Adsorption and Desorption
 419 Kinetics on Ferrihydrite with Different Morphologies. *Soil Science Society of America Journal*
 420 82(1): 96-105.
 421 Leone L, Loring J, Sjöberg S, Persson P, Shchukarev A(2006)Surface characterization of the
 422 gram-positive bacteria *Bacillus subtilis* – an XPS study. *Surf. Interface Anal* 38 202–205.
 423 Liu C, Huang PM (2003) Kinetics of lead adsorption by iron oxides formed under the influence of
 424 citrate. *Geochim. Cosmochim. Acta* 67:1045–1054.
 425 Lu Y, Hu S, Wang Z, Ding Y, Lu G, Lin Z, Shi ZQ(2019)Ferrihydrite transformation under the impact
 426 of humic acid and Pb: Kinetics, nano-scale mechanisms, and implications for C and Pb dynamics.
 427 *Environmental science. Nano*.

428 Mikutta C, Mikutta R, Bonneville S, Wagner F, Voegelin A, Christl I, Kretzschmar R (2008) Synthetic
 429 coprecipitates of exopolysaccharides and ferrihydrite. Part I: Characterization, *Geochimica et*
 430 *Cosmochimica Acta* 72(4):1111-1127.

431 Pan k, Wang WX(2012) Trace metal contamination in estuarine and coastal environments in China.
 432 *Sci Total Environ* 421:3–16.

433 Reichenberg D(1953) Properties of Ion-Exchange Resins in Relation to their Structure. III. Kinetics of
 434 Exchange, *Journal of the American Chemical Society*. 75(3):589-597.

435 Tan XL, Wang XK, Geckeis H, Rabung T(2008) Sorption of Eu (III) on humic acid or fulvic acid
 436 bound to hydrous alumina studied by SEM-EDS, XPS, TRLFS, and batch techniques. *Environ.*
 437 *Sci. Technol* 42(17):6532-6537.

438 Tian L, Shi Z, Lu Y, Dohnalkova A, Lin Z, Dang Z(2017) Kinetics of cation and oxyanion adsorption
 439 and desorption on ferrihydrite: Roles of ferrihydrite binding sites and a unified model. *Environ.*
 440 *Sci. Technol* 51 (18):10605-10614.

441 Tiberg C, Gustafsson JP (2016) Phosphate effects on cadmium (II) sorption to ferrihydrite. *Journal of*
 442 *Colloid and Interface Science* 471:103-111.

443 Turner A(2019) Lead pollution of coastal sediments by ceramic waste. *Marine Pollution Bulletin*
 444 138:171-176.

445 Vadivelan VK(2005) Vasanth Kumar, Equilibrium, kinetics, mechanism, and process design for the
 446 sorption of methylene blue onto rice husk. *Colloid Interface Sci* 286(1):90-100.

447 Wang S, Li H, Xu L (2006) Application of zeolite MCM-22 for basic dye removal from wastewater.
 448 *Journal of Colloid and Interface Science* 295(1):71-78.

449 Wang XQ, Han ZX, Wang W, Zhang BM, Wu H, Nie LS, Zhou J, Chi QH, Xu SF, Liu HL, Liu DS,
 450 Liu QQ (2019) Continental-scale geochemical survey of lead (Pb) in mainland China's
 451 pedosphere: Concentration, spatial distribution and influences. *Applied Geochemistry* 100:55-63.
 452 Xiu W, Guo H, Zhou X, Richard B. W, Michael K(2018) Change of arsenite adsorption mechanism
 453 during aging of 2-line ferrihydrite in the absence of oxygen. *Applied Geochemistry* 88:149-157.
 454 Xiu W, Guo HM, Zhou XQ, Wanty RB, Kersten M (2018) Change of arsenite adsorption mechanism
 455 during aging of 2-line ferrihydrite in the absence of oxygen. *Applied Geochemistry* B
 456 88:149-157.
 457 Zatsepin DA, Boukhvalov DW, Gavrilov NV, Kurmaev EZ, Zatsepin AF, Cui L, Shur VY, Esin AA
 458 (2017) XPS-and-DFT analyses of the Pb 4f — Zn 3s and Pb 5d — O 2s overlapped ambiguity
 459 contributions to the final electronic structure of bulk and thin-film Pb-modulated zincite. *Applied*
 460 *Surface Science* 405:129-136.
 461 Zhang LL, Verweij RA, Van Gestel CAM(2019) Effect of soil properties on Pb bioavailability and
 462 toxicity to the soil invertebrate *Enchytraeus crypticus*. *Chemosphere* 217:9-17.
 463 Zhu J, Pigna M, Cozzolino V, Caporale AG, Violante A(2010) Competitive sorption of copper (II),
 464 chromium (III) and lead (II) on ferrihydrite and two organomineral complexes. *Geoderma*
 465 159(3-4):409-416.
 466

Table 1. Specific surface areas and pore sizes measured by N₂-accessible BET method

Sample	SSA (m ² g ⁻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 δ (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

Table 3. Parameters of adsorption isotherms of Pb(II) on Fh-HA at different pHs

	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 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 $\langle\Delta E_Q\rangle$ (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.

($[C/Fe_{2.0}] = 6 \text{ g L}^{-1}$; $[NaNO_3] = 0.1 \text{ M}$)

Fig.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)

Fig. 7. Bt 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.

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

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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.