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► To cite this version:

Erwin A. Henry, Emmanuelle Montargès-Pelletier, Isabelle Bihannic, Céline Caillet, Jaafar Ghanbaja, et al.. Controlled assembly of heterogeneous aggregates of clay, iron hydr(oxydes) and polysaccharide. Applied Clay Science, 2022, 216, pp.106340. 10.1016/j.clay.2021.106340 . hal-03456217

HAL Id: hal-03456217

<https://hal.univ-lorraine.fr/hal-03456217v1>

Submitted on 10 Feb 2022

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Controlled assembly of heterogeneous aggregates of clay, iron hydr(oxydes) and polysaccharide: effects of preparation conditions.

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Abstract

The preparation of well-defined organo-mineral assemblies under controlled conditions is required to improve our understanding of the formation and surface reactivity of micrometric aggregates, ubiquitous in soils and continental aquatic media. We aim at investigating the building of organo-mineral assemblies with a specific focus on the assembly mode and its consequence on the final properties of the micrometric aggregates. In this work, the preparation and detailed characterization of clay-size aggregates composed of a clay mineral (illite), organic polymer (Dextran polysaccharide) and iron (hydr)oxide are reported, with a focus on the structural organisation of the generated aggregates. A step-by-step strategy was developed, and three sets of clay-size composites were prepared with illite particles as a starting material. In two first steps, two distinct sets of two-component composites were obtained according to different procedures. Illite-iron (hydr)oxide composites were obtained by alkaline hydrolysis of iron in the presence of illite particles, and illite-Dextran aggregates were obtained through the addition of Dextran polysaccharide to an illite suspension. In a third step, three-component micro-aggregates were obtained by subsequent addition of Dextran to suspensions containing the formed illite-iron (hydr)oxide composite. The so-prepared 2- and 3- component aggregates were investigated by electrophoresis, electron microscopy, X-ray absorption and FTIR spectroscopies. For materials containing Dextran, electrophoretic mobility measurements evidenced variations of surface charge, combined with an increase of aggregate size highlighted by dynamic light scattering. Electron microscopy and EXAFS at iron K-edge evidenced the precipitation of nanoparticles of iron (hydr)oxide onto clay mineral surfaces. FTIR data in transmission and diffuse reflectance modes supported not only the adsorption of Dextran but also the preferential localization of Dextran at the external surfaces of the aggregates. All in all, data collected on the two- and three-component materials demonstrated that the presence of iron (hydr)oxide nanoparticles on the surface of illite strongly modified the organization of organic and mineral constituents.

1. Introduction

Colloids and microparticles are ubiquitous in natural systems, soils and surface waters, and play a key role in the contaminant dynamics (organic, metallic and/or biological) through e.g. adsorption phenomena (Warren and Zimmermann, 1994; Buffle et al., 1998; Mavrocordatos et al., 2007; Wilkinson and Lead, 2007; Walling, 2013; Vindedahl et al., 2016). Those natural entities display a multiphasic character, with organic, mineral and biological components whose organization and spatial distribution obviously affect their surface properties (Mavrocordatos et al., 2007; Vindedahl et al., 2016). The physico-chemical and adsorption properties of the building units composing environmental particles, such as clay minerals, iron (hydr)oxides or humics, have been investigated extensively (Rey-Castro et al., 2009; Tertre et al., 2009; Churakov and Dähn, 2012). Whereas this abundant literature is of major interest for the understanding and prediction of e.g., contaminant behaviour, there remains a true need for addressing how complexity and heterogeneity of these clay-size composites affect their reactivity compared to those inferred from separate consideration of components contribution. Several

46 publications report the study of clay-composites (Nachtegaal and Sparks, 2004; Sipos et al., 2008, 2018; Moon
47 and Peacock, 2012; Du et al., 2016, 2018; Sowers et al., 2018a) but information is missing about the way the
48 different constituents are organized within the clay-size aggregates, which prevents the firm drawing of
49 mechanistic conclusions on reactivity features. A condition for deriving generic information on the relationship
50 between reactivity and heterogeneity of composite organo-mineral particles is, first, to have at disposal well-
51 defined organo-mineral assemblies whose structure and composition are fully addressed from the molecular to
52 colloidal scale.

53 Accordingly, we aim at building clay-size aggregates and investigating the influence of the preparation
54 mode on their external properties. Thus, we report below the preparation and characterization of two-component
55 and three-component aggregates with two minerals (illite and iron (hydr)oxide) and one organic constituent
56 (polysaccharide). Those assemblies will be referred to as binary or ternary aggregates depending on the number
57 of components used to prepare them. The selection of these building components is motivated by the
58 predominance of illite particles in the clay mineralogy of river SPM (Le Meur, 2016; Le Meur et al., 2017), the
59 targeted natural particles. Iron (hydr)oxide coatings were commonly reported in soil micro-aggregates
60 (Goldberg, 1989; Colombo and Torrent, 1991; Kleber et al., 2007; Totsche et al., 2018; Gao et al., 2020; Krause
61 et al., 2020) and were also evidenced in river suspended particulate matter (SPM) (Le Meur, 2016). Those
62 poorly crystalline iron (hydr)oxides are known to play a crucial role in the formation of micro-aggregates, as
63 cementing agents (Totsche et al. 2018) and also in the interactions between mineral and organic constituents
64 in soils (Vindedahl et al., 2016; Sowers et al., 2018a; Adhikari et al., 2019). Accordingly, to build mineral
65 assemblies that most adequately reflect the complex physicochemical composition of natural river particles, we
66 considered iron (hydr)oxide as a component to be included in our model aggregates. Recalling that iron
67 (hydr)oxide is supposedly poorly crystalline under natural conditions, pure iron oxide and iron hydr(oxide)
68 minerals such as goethite, lepidocrocite or ferrihydrite were not considered. Instead, the “addition of iron
69 (hydr)oxide” step in our synthesis protocol was performed as a controlled precipitation of iron (hydr)oxide in the
70 presence of illite particles, thereby enhancing the precipitation reaction rate due to the overall surface area of
71 dispersed illite particles. The preparation of illite-iron (hydr)oxide composites was based on the hydrolysis of
72 iron salt in the presence of illite particles with or without late addition of organic polymer. Numerous studies
73 reported the precipitation of ferrihydrite or ferrihydrite precursors in the presence of different salts and/or
74 different ligands, with cation substitution (Mikutta and Kretzschmar, 2008; Cismasu et al., 2012, 2014; Hofmann
75 et al., 2013; Guénet et al., 2017; Adhikari et al., 2019; Beauvois et al., 2020) or in the presence of montmorillonite
76 (Green-Pedersen and Pind, 2000; Yuan et al., 2008; Borgnino et al., 2009). To favour the formation of
77 nanoparticulate iron (hydr)oxides, closely associated to the clay minerals, relatively low concentrations of iron
78 were used. The efficient control of iron hydr(oxide) nanoparticle formation onto the clay mineral surfaces
79 constitutes the first key point of this work. Due to the key role played by organic matter in the formation of
80 aggregates in soils and rivers, acting as gluing agent (Lai et al., 2018; Totsche et al., 2018), the third component
81 had to be organic. In line with observations on particulate organic matter (Le Meur et al., 2017), a polysaccharidic
82 polymer group was selected to mimic the organic constituent of our model aggregates. A neutral and relatively
83 simple polymer was selected to promote the occurrence of hydrophobic interactions which are recurrently
84 advanced to explain the reactivity of complex organo-mineral assemblies (Laird, 2001; Claret et al., 2002; Chenu
85 et al., 2009; Hong et al., 2015; Gao et al., 2020). Dextran was selected as it was possible to vary the molecular
86 weight of this organic molecule. We avoided the use of natural organic matter or humic acids as representative
87 of the organic component in our micro-aggregates. This choice is motivated by a step-by-step strategy leading
88 to a gradual and controlled increase in the complexity of the structure of the investigated assemblies. This option

89 is obviously far more complex to be achieved if using e.g. natural organic matter whose intrinsic reactivity
90 properties are still controverted in literature (Town et al., 2012; Du et al., 2016). Even for relatively simple organic
91 component as the one adopted in this work, the very order in the sequential addition of the various building units
92 entering the composition of the prepared aggregates was itself central question. Based on literature review (Gao
93 et al 2020) and observations of river SPM (Le Meur et al. 2017), we decided to prepare controlled organo-
94 mineral assemblies with late addition of organic matter, using a neutral polymer. The developments below detail
95 the preparation and the characterization of the resulting products, in particular the respective organization of
96 the organic and mineral components of the generated assemblies.

97 **2. Experimental**

98 **2.1. Pristine materials and chemicals**

99

100 **2.1.1. Clay minerals, illite.**

101 The clay mineral used for all syntheses is the Illite from Puy-en-Velay, with prior purification and size-
102 fractionation (Blachier et al., 2014). Purification was performed as follows: 40 g of clay were dispersed in one
103 Litre of 1M sodium acetate solution adjusted to pH 5 upon addition of acetic acid 0.1 M. The suspension was
104 heated to 80°C for 2 h, shaken during 12 h, and subsequently centrifuged for 20 min at 25 700 g (13000 rpm).
105 The centrifuged paste was then re-dispersed in a sodium chloride solution (NaCl 1M) for 12 h to saturate the
106 exchangeable sites with sodium and centrifuged twice for 20 min at 25 700 g. The resulting paste was then re-
107 dispersed in ultrapure water for 12 h. Thus, the clay suspension was dialyzed to remove ions in excess
108 (Spectra/Por® Membrane MWCO 50 kD). Dialysis was carried out until conductivity of the external solution was
109 lower than 10 $\mu\text{S cm}^{-1}$. The dialyzed suspension was then centrifuged for 1 h at 25 700 g. The formed solid was
110 subdivided according to two distinct fractions: the bottom, greyish, fraction was referred to as size fraction 2,
111 the upper fraction, a greenish gel, was referred to as size fraction 3. In this work, only the gel fraction was
112 considered, frozen and freeze-dried prior to synthesis experiments. X-Ray Diffraction (XRD) patterns obtained
113 on pristine Illite evidenced the presence of impurities such as quartz and kaolinite clays (Data available on
114 ORDAR repository <https://doi.org/10.24396/ORDAR-28>). Those minerals were almost totally removed with
115 purification as shown by the XRD patterns obtained for the different size fractions. Size fraction 3 was noticeably
116 homogeneous in terms of mineralogy and particle size. Cation Exchange Capacity (CEC) was determined using
117 the cobalti-hexamine method (Ciesielski and Sterckeman, 1997). After exchange with cobalt hexamine and
118 analysis with UV-Visible Spectrophotometer (UV2501-PC Shimadzu), the CEC was estimated to 20 meq per
119 100g of dry matter. This value corresponds to the estimated number of sites available for cationic exchange on
120 clay surface. For all experiments, illite particles were dispersed for 4 hours at ambient temperature in 100 mL
121 of ultra-pure water to obtain a final concentration of 200 mg L⁻¹. This clay concentration is consistent with the
122 measured solid contents in river waters (Le Meur et al., 2016) and allowed us to perform multiple
123 characterization measurements.

124 **2.1.2. Chemical products**

125 Fe(NO₃)₃·9H₂O (quality: 0.9999) and KOH pellets from Aldrich were used for the preparation of clay-composites.
126 The polymer is a polysaccharide, a Dextran from Leuconostoc ssp., with molar mass 6000 g mol⁻¹, purchased
127 from BioChemika (Supplementary Material SM-1). This is a relatively small polymer, constituted of about 33
128 sugar units, considering the molar mass of glucose (180.56 g mol⁻¹). Its Stoke radius is around 2 nm. For this
129 molar mass range, Dextran molecules are supposed to behave as expandable coil. Dextran solutions were
130 prepared at final concentrations 1.67 and 16.67 $\mu\text{mol L}^{-1}$ (respectively 10 and 100 mg L⁻¹) with 5.10⁻⁴ M of CaCl₂

131 2H₂O (Prolabo, quality: 0.99). In the particular case of illite-Dextran composites, the addition of calcium was
132 mandatory to obtain the formation of aggregates. Without calcium addition, the illite-Dextran suspension
133 remained stable even after 24h, and no size increase could be detected. The CaCl₂ concentration was selected
134 on the basis of river water analysis (Le Meur et al., 2016) and also on the basis of suspension stability at 1h and
135 24h after Dextran addition (data not shown).

136 2.2. Preparation protocols

137 Three types of clay-composites were prepared, (i) illite-Fe (hydr)oxide referred to as IFeH_R, R being the Fe/illite
138 ratio; (ii) illite-Dextran referred to as ID_x, x being the concentration of Dextran solution in mg L⁻¹ and (iii) illite-Fe
139 (hydr)oxide-Dextran referred to as IFeH_RD_x. A schematic presentation of the different preparation paths is
140 provided in Supplementary material (SM-2).

141 2.2.1. Preparation of illite-Fe (hydr)oxide clay-composites IFeH_R with R (the ratio iron/illite) = 0.2, 0.6 or

142 2. The main step of the preparation of illite-iron (hydr)oxide composites is the alkaline hydrolysis of iron salt (iron
143 nitrate) in the presence of illite particles. The forced alkaline hydrolysis method was adapted from that of
144 Schwertmann and Cornell (Schwertmann and Cornell, 1991). The resulting products are hereafter differentiated
145 according to the initial iron/illite ratio, R. This ratio was calculated as a function of the CEC value of illite, and
146 the amount of iron added to the clay suspension via:

$$147 \quad R = (C_{\text{I Fe}} V_{\text{Fe ad}}) / (C_{\text{I}} V_{\text{I}} \text{CEC}) \quad (1)$$

148 where $C_{\text{I Fe}}$ is the concentration of iron nitrate solution (10⁻⁴ M) expressed in meq of Fe per Litre and $V_{\text{Fe ad}}$ the
149 added volume of the iron nitrate solution ($V_{\text{Fe, ad}} = 2.7, 8$ and 26.7 mL for $R = 0.2, 0.6, 2$, respectively). C_{I} (0.2 g
150 L⁻¹) and V_{I} (100 mL) were the illite suspension concentration and volume, respectively. The CEC was measured
151 and estimated to 20 meq per 100 g of illite. For the three R ratios adopted, the Fe/illite mass ratios were
152 respectively 0.075, 0.22 and 0.75 mg Fe per g of illite. Experimental conditions were selected to promote the
153 precipitation of iron (hydr)oxide onto the clay mineral surfaces rather than in solution. Iron nitrate concentration
154 was fixed to 10⁻⁴ mol L⁻¹, KOH solution was set to 10⁻³ mol L⁻¹ to slow down hydrolysis kinetics. Such pH and
155 iron concentration conditions were expected to enhance the adsorption of either ferric cations or partially
156 hydrolysed iron species on the cationic exchange sites of illite particles. The Fe(NO₃)₃ solution and KOH solution
157 were simultaneously added to the illite suspension using a Metrohm TITRANDO 809 station. Such a procedure
158 allowed controlled and reproducible synthesis conditions. Initial clay suspension displayed a pH close to 6. Iron
159 solution (10⁻⁴M, pH = 3.5) was added to the illite suspension at a rate of 0.25 mL min⁻¹ until the desired Fe/illite
160 ratio R was reached (R= 0.2, 0.6 or 2). Simultaneously, KOH was added at a rate of 0.1 mL min⁻¹ until pH
161 reaches 7.5 (± 0.2). Titration curves were performed several times (twice for IFeH_{0.2} and IFeH₂, nine times for
162 IFeH_{0.6}), and displayed a good reproducibility Supplementary Material SM-3. Subsequently, the resulting
163 suspensions were washed by dialysis to remove salts in excess (Spectra/Por® Membrane MWCO 1 kD) until
164 the suspension conductivity was close to that of ultrapure water (<10 μS cm⁻¹). All rinsed precipitates were
165 then freeze-dried and stored at 20°C prior to further analyses.

166 2.2.2. Preparation of illite-Dextran aggregates (ID_x). A supplementary series of binary samples was prepared
167 to better evidence the influence of iron (hydr)oxides on the interactions between polymer and clay particles. For
168 that purpose, binary aggregates composed of illite and Dextran polymer were prepared by adding
169 simultaneously 50 mL of Dextran solution ($x = 10$ or 100 mg L⁻¹, i.e. 1.67 and 16.67 μmol L⁻¹ respectively) and
170 50 mL of CaCl₂.2H₂O solution to the illite suspension (200 mg L⁻¹). The mixture was stirred for 24 hours and
171 repeatedly dialysed (Spectra/Por® Membrane MWCO 1 kD) until the suspension conductivity was close to that
172 of ultrapure water (<10 μS cm⁻¹).

173 **2.2.3. Preparation of illite-iron (hydr)oxide-Dextran aggregates (three component composites) referred**
174 **to as IFeHRD_x.** The IFeHRD_x aggregates were prepared by addition of 50 mL of Dextran solution ($x = 10$ or 100
175 mg L^{-1}) and 50 mL of $5 \cdot 10^{-4}$ M $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ solution which contained a divalent ion promoting the aggregation of
176 IFeHR particles in suspension. The mixture was stirred for 24 hours and repeatedly dialysed (Spectra/Por®
177 Membrane MWCO 1 kD) until the suspension conductivity was close to that of ultrapure water ($< 10 \mu\text{S cm}^{-1}$).
178 Such a preparation procedure was adopted to obtain aggregates displaying the three constituents, i.e., illite,
179 iron (hydr)oxides and organic polymer. The addition method was also established based on reported models of
180 soil particle surfaces (see Gao et al. 2020 for instance).

181 **2.3. Methods of characterization**

182 **2.3.1. Size distribution and electrophoretic mobility measurements.** Electrophoretic mobilities (μ) and
183 particle size distribution were measured for the final suspension of ID_x and IFeHRD_x and for the final dialyzed
184 products in the case of illite and IFeHR. A Zetasizer NanoZS (Malvern Instruments, UK) with a 633 nm laser
185 source was used. For that purpose, one millilitre of final suspensions was placed in Malvern DTS1070 cells.
186 The apparatus is well suited for measuring size of particles with diameter in the range of 1 nm to 6 μm and for
187 monitoring electrophoretic mobility of particles with diameter from ca. 5 nm to 10 μm . The hydrodynamic
188 diameter of particles was measured using dynamic light scattering (DLS). The particle diffusion coefficient was
189 obtained from analysis of the autocorrelation of the scattered intensity measured at a 173° angle (back
190 scattering) and converted into a hydrodynamic diameter using Stokes-Einstein equation. Electrophoretic
191 mobility evaluation consisted in measuring velocity of charged particles in electrolyte suspension moving in a
192 capillary cell under application of a DC electric field by Electrophoretic Light Scattering (ELS) technique.
193 Zetasizer NanoZS device uses the M3-PALS procedure, combining Phase Analysis Light Scattering and a
194 Mixed-Mode Measurement (M3). Using PALS, the particle velocity is obtained from the phase shift between
195 light scattered by moving particles and a reference beam. The M3 technique, which combines two successive
196 sequences of fast field reversal and slow field reversal, respectively, allows to overcome effects due to electro-
197 osmosis that is generated by the coupling between hydrodynamics and surface charge of the capillary. Results
198 were reported in the form of particle size distribution and electropherograms. In the developments that follow,
199 electrophoretic mobility data were not converted into zeta-potential using e.g. standard Smoluchowski equation.
200 The concept of zeta-potential makes physical sense for the only ideal scenario where particles are impermeable
201 to ions and fluid flow. However, considering the permeability of soft particles such as the polysaccharide
202 macromolecules used in this work, the concept of potential zeta cannot be applied (Duval et al., 2005, 2006;
203 Duval, 2007; Martin et al., 2015).

204 **2.3.2. Fourier Transform Infrared Spectroscopy (FTIR).** FTIR spectra were collected on freeze-dried samples
205 in Transmission (Tr) and Diffuse Reflectance (RD) modes using a Bruker Vector 22 FTIR spectrometer at a
206 resolution of 4 cm^{-1} , in the $400\text{-}4000 \text{ cm}^{-1}$ range. Samples were prepared from 1 mg of freeze-dried suspensions
207 and were either deposited on a sheet of aluminium foil (for diffuse reflectance mode) or mixed with 199 mg KBr
208 and pelletized (for transmission mode). Baseline-corrections were applied to collected spectra. An adjustment
209 of the signals has been made for their better visualization and qualitative interpretation.

210 **2.3.3. Transmission Electronic Microscopy (TEM) and Scanning Transmission Electron Microscopy**
211 **(STEM).** Samples for electron microscopy were prepared as follows: few dozens of μL of suspension was
212 sampled and air-dried on a carbon-coated copper grid (200 mesh/ $100 \mu\text{m}$) placed on a clamp. TEM and STEM
213 investigations were performed at the Centre for Microscopies, Microprobes and Metallography (CC3M, Institut
214 Jean Lamour, Nancy, France). As a first step, particles were investigated with a Philips CM200 TEM operated

215 at 200 kV. Beside transmission images, elemental composition of individual particles was determined using
216 Energy Dispersive X-ray spectroscopy (EDXS) by means of a PGT (Princeton Gamma-Tech) spectrometer. The
217 analyses were carried out in nanoprobe mode with a probe diameter of 50 nm.
218 High resolution transmission electron microscopy and scanning transmission electron microscopy (HRTEM and
219 STEM) investigations were carried out using a JEM - ARM 200F Cold FEG TEM/STEM operating at 200 kV and
220 equipped with a spherical aberration probe and image correctors (point resolution 0.12 nm in TEM mode and
221 0.078 nm in STEM mode). Images were recorded in Bright Field (BF) and High Angle Angular Dark Field modes
222 (HAADF). EDXS spectra were recorded by means of a Centurio Jeol spectrometer (SDD) mounted on ARM
223 200F. The analyses were carried out in STEM mode with 1 nm probe diameter. The ratio between atomic
224 percentages was estimated for semi-quantitative analysis. The Cliff Lorimer factors k , were determined using
225 standards and were kept constant for each analysis.

226 **2.3.4. X-ray absorption spectroscopy at Fe K-edge**

227 To investigate the iron species resulting from alkaline hydrolysis of iron salt in presence of illite particles, X-ray
228 absorption spectroscopy experiments at iron K-edge were conducted on SAMBA beamline (SOLEIL, France).
229 XAS spectra were collected in transmission and fluorescence modes at low temperature using a liquid He
230 cryostat 25K, with a Si(111) double crystal monochromator. Fe-illite composites were scanned at SAMBA in fly
231 scan mode from 7000 to 8000 eV with 0.5 eV steps, at a velocity of 60 eVsec⁻¹, counting 0.08 sec per point.
232 Samples were ground and pelletized before XAS measurements. XANES and EXAFS data were reduced using
233 standard normalization procedures performed with the ATHENA and ARTEMIS programmes (Ravel and
234 Newville, 2005). The spectra were background subtracted and normalized. A spline function was adopted to fit
235 through the absorption envelope and then subtracted from each spectrum. To transform data from energy space
236 E (eV) to wave vector space k (Å⁻¹), E_0 edge energy was chosen in the higher part of the edge step, at 7112 eV.
237 The resulting $\chi(k)$ function was weighted by k^3 to avoid oscillations damping at high k values.

238

239 **3. Results and discussion:**

240 **3.1. First series of binary clay-composites, illite-iron (hydr)oxide, IFeH_R.**

241 **3.1.1. Electrophoretic mobility and size of IFeH_R aggregates.**

242 Figure 1 reports size and electrophoretic mobility (μ) obtained for the iron-clay composites IFeH_R as
243 well as for the pristine illite clay particles. The analyses of pristine illite suspension showed particle sizes ranging
244 between 60 and 500 nm with a maximum at 164 nm. For the three samples IFeH_{0.2}, IFeH_{0.6} and IFeH₂, particle
245 size distribution did not show drastic modification, thus evidencing that a large fraction of the clay platelets
246 remained in suspension. For the three values of R considered in this work, clay particles aggregation was not
247 evidenced as the size distribution patterns are similar to that obtained for illite particles. Indeed, only IFeH_{0.2} and
248 IFeH₂ samples presented a weak contribution of larger particles (size in the μm range). Concerning
249 electrophoretic mobility measurements, the pristine illite particles displayed a rather broad distribution in μ
250 values. The most frequent electrophoretic mobility value was $-3.5 \times 10^{-8} \text{ m}^2 \text{ V}^{-1} \text{ s}^{-1}$. This value had already been
251 measured in low ionic strength solution (5 mM) (Beene et al., 1991; Sondi et al., 1996) and is mainly related to
252 the permanent charge of the illite layers, and to a lesser extent, to the terminal groups located on the lateral
253 edges (Thomas et al., 1999). For iron-illite samples, the electrophoretic mobility shifted to less negative values.
254 This shift goes from -3.5 to $-2.8 \times 10^{-8} \text{ m}^2 \text{ V}^{-1} \text{ s}^{-1}$ for IFeH_{0.2}, to $-2.6 \times 10^{-8} \text{ m}^2 \text{ V}^{-1} \text{ s}^{-1}$ for IFeH_{0.6} and to -2.4×10^{-8}
255 $\text{m}^2 \text{ V}^{-1} \text{ s}^{-1}$ for IFeH₂. This small but representative shift reflected the adsorption of hydrolysed Fe compounds on
256 the cation exchange sites of illite. However, as the electrophoretic mobility of the iron-illite aggregates was of

257 the same order of magnitude as that of illite, the surface charge of the iron-clay composites remained dominated
258 by the structural and permanent charge contribution of illite (Thomas et al., 1999).

259 **3.1.2. Identification of iron species in IFeH_R clay-composites.**

260 X-ray Absorption spectroscopy at Fe K-edge, Transmission Electron Microscopy (TEM and HRTEM), and
261 Scanning Transmission Electron Microscopy (STEM) were used to investigate iron species. Figure 2 presents
262 EXAFS data obtained at Fe-K edge for the illite-FeH_R samples. XANES spectra are provided as supplementary
263 material (SM-4). The EXAFS curves are dominated by the signal of oxygen atoms, constituting the first
264 coordination sphere, octahedrally coordinated to Fe. All EXAFS curves display similar features, with three
265 oscillations centred at 4, 6.5 and 8.5 Å⁻¹. However, some differences can be observed between illite samples
266 and FeH. The latter sample, resulting from the alkaline hydrolysis of a dilute solution of Fe(NO₃)₃, provides
267 EXAFS signal attributed to ferrihydrite or precursors of ferrihydrite (Hofmann et al., 2013; Beauvois et al., 2020).
268 The oscillation at 8.5 Å⁻¹ is less intense for FeH than for illite and IFeH_R samples. On the opposite, the shoulder
269 at 7.5 Å⁻¹ is more intense for FeH and reflects certainly the presence of iron atoms in the second coordination
270 sphere. FeH sample provided relatively noisy signal due to the low amount of available sample for the
271 measurement. IFeH_R signals are all dominated by the illite contribution, without noticeable contributions of
272 adsorbed Fe species.

273 Figure 3 displays selected micrographs obtained by HRTEM for pristine illite, and for the three illite-iron
274 (hydr)oxide clay-composites, IFeH_{0.2}, IFeH_{0.6} and IFeH₂ (supplementary images are presented in supplementary
275 material SM-5). For pristine illite, individualized illite particles with well-defined edges could be observed. Most
276 of the illite particles displayed their basal faces but some of them displayed the lateral faces, showing series of
277 aluminosilicate layers (clearly visible with 200k magnification). The size distribution of illite particles derived from
278 microscopy measurements (from 50 to 150 nm) agreed with the median hydrodynamic size reported in Figure
279 1. At 100k magnification (Figure 3, left images), some Fe nanoparticles with a stronger electron contrast could
280 be detected for IFeH_{0.6} and IFeH₂. Their presence of nanoparticles on the basal surfaces of illite for IFeH_{0.6} and
281 IFeH₂ samples is confirmed with higher magnification images (250 k). Again, Fe particles could not be detected
282 on IFeH_{0.2}. Size distribution of Fe nanoparticles was rather heterogeneous as some of them were clearly visible
283 at 100k magnification while most of those particles appeared only with higher magnification at 250 k. From those
284 250k images, the diameter of these Fe nanoparticles for IFeH_{0.6} and IFeH₂ was estimated to be 5.6 ± 0.7 nm
285 and 7.2 ± 1.7 nm, respectively. High magnification images also evidenced a drastic modification of illite particle
286 aspect with increasing Fe/illite ratio. Indeed, the edges of clay minerals became less and less defined and the
287 particles displayed a lumpy appearance due to iron precipitation. The presence of the nano-FeH on illite surfaces
288 indicated that the growth of iron (hydr)oxide had occurred on the illite surfaces and that the nucleation of iron
289 (hydr)oxide was constrained by the presence of illite particles. With increasing Fe/illite ratio, iron precipitation
290 could occur not only on basal surfaces but also on lateral sites, which would explain the loss of definition of illite
291 edges.

292 FeH_R samples were also analysed in STEM mode, providing Bright Field (BF) and High-Angle Annular
293 Dark-Field (HAADF) images (Figure 4). In HAADF mode, the increase in brightness indicated an increase in
294 atomic number (Z contrast, increase of electronic density) due to the presence of iron (hydr)oxide particles. Both
295 BF and HAADF modes revealed the presence of nanometric entities at the surface of the clay platelets for all
296 IFeH_R samples including IFeH_{0.2}. The detected Fe entities displayed a mean size of 2 nm (± 0.5 nm) for the
297 IFeH_{0.2} and IFeH_{0.6} samples. In the case of IFeH₂, two sets of particles could be evidenced, one with a similar
298 mean size of 2 nm, and another set of particles with a mean size of 8 nm (±1 nm).

299 The Fe/Si atomic ratio was estimated from EDXS data obtained on CM200 microscope. For IFeH_{0.2},
300 IFeH_{0.6} and IFeH₂, this ratio was 0.102 ±0.01 ,0.097±0.01 and 0.107±0.01, respectively, calculated from 10, 14
301 and 3 analyses respectively. Those Fe/Si atomic ratios do not show a clear trend with the increase of initial
302 Fe/illite ratio and finally are close to that obtained for the pristine illite particles (0.095±0.01, 6 analyses). Even
303 though Fe nanoparticles could be observed from TEM or STEM images, the atomic percentage of iron did not
304 increase significantly. The size range of these Fe nanoparticles prevented their detection by classical TEM and
305 associated EDXS. The nanoprobe used for EDXS was set between 50 and 100 nm, about ten times larger than
306 the nanoparticles of iron (hydr)oxide. This explains why the illite signal predominates the EDXS spectra.
307 Supplementary EDXS data obtained on the HRTEM microscope using a smaller nanoprobe (few nanometres),
308 demonstrated more clearly the increase in Fe/Si ratio (≥0.10) for IFeH_{0.2} and IFeH_{0.6} samples (see table in SM-
309 5), thereby confirming the presence of nanoparticles of iron-hydr(oxide). None of the EDXS spectra obtained
310 on both microscopes evidenced the presence of isolated iron hydr(oxide) for the three samples IFeH_{0.2}, IFeH_{0.6}
311 and IFeH₂. Both images and EDXS data obtained on ARM microscope demonstrated the formation of nanoFeH
312 onto the surface of illite, and the size limitation demonstrated that the formation of iron (hydr)oxide was
313 constrained by the interaction with the clay surface. The presence of surface hydroxyl groups, acted as ligands
314 in solution (Lartiges et al., 2019 and references therein). The titration of iron solution in the presence of an
315 organic and/or mineral component had already shown that hydrolysis and nucleation of iron in solution were
316 limited by these components, which explained the formation of iron (hydr)oxides of nanometer size (Mikutta and
317 Kretzschmar, 2008; Guénet et al., 2017; Lartiges et al., 2019; Beauvois et al., 2020). The interaction of iron
318 species with illite surface (via electrostatic interactions with the exchangeable sites, and with lateral hydroxyl
319 groups) had reduced the OH substitution and had prevented the formation of larger Fe (hydr)oxide particles.
320

321 **3.1.2. Influence of illite surface on the hydrolysis of iron.**

322 Previous publications reported the synthesis and characterization of hybrid particles based on montmorillonite
323 and iron oxides (Ferreiro et al., 1995; Green-Pedersen and Pind, 2000; Ji et al., 2004; Borgnino et al., 2009).
324 Borgnino and Green-Pedersen produced Fe-clay using a similar method, by alkaline hydrolysis of ferric salt in
325 the presence of clay particles. Although they display similar features, illite and montmorillonite presents a
326 different lateral/basal surface ratio, and different cation exchange capacities (CEC). Illite particles are thicker,
327 and their basal plane is less extended, the CEC of illite is about five times lower than that of montmorillonite.
328 Such differences strongly enhanced the interactions of iron with OH groups from the lateral edges of illite
329 particles. This point was demonstrated for high iron/illite ratios, as a modification of edge appearance was
330 evidenced (HRTEM, Figure 3).-Three mechanisms can be envisaged for iron hydrolysis in the presence of clay
331 particles: either (1) alkaline hydrolysis of iron, nucleation in solution and formation of nanoFeH in bulk solution
332 followed by adsorption on the Illite particles, or (2) adsorption of partially hydrolysed Fe(III) cations (with excess
333 charge ranging from +1 to +3) and/or Fe-oligomers on the illite particles, followed by nucleation and formation
334 of nanoFeH, or (3) concomitant occurrence of these two latter reactions. The exact nature of the adsorbed Fe
335 species during the titration needs to be debated. Supplementary material (SM-3) shows the three titration curves
336 obtained respectively for IFeH_{0.2}, IFeH_{0.6} and IFeH₂. The titration curves showing pH evolution as a function of
337 the addition of KOH are rather similar. Illite particles appear to be the main OH consumers in the second part of
338 the titration curve. Such an observation tends to support that the Fe species were already hydrolysed in solution
339 prior to adsorption onto clay illite. However, the similarity of the titration curves, irrespectively of the iron
340 concentration, could also be explained by the low amount of iron added in solution, insufficient to impact on the
341 form of the titration curve.

342 To conclude, the synthesis conditions of IFeH_{0.2} have enhanced the formation of iron oligomers in solution before
343 adsorption of iron species onto the clay surface, and subsequent nucleation and formation of nanoparticles of
344 iron (hydr)oxide, nanoFeH, have further occurred onto the clay basal surfaces.

345 For the higher Fe/illite ratios tested, R=0.6 or 2, there is a questioning about the formation process of iron
346 (hydr)oxide. The presence of lateral nanoFeH could result from either the hydrolysis of pre-adsorbed iron or
347 the adsorption of nanoFeH. The formation of covalent bonds between Fe atoms and the octahedral sheet of
348 illite have prevented the hydrolysis, i.e. the replacement of H₂O molecules by OH, and might have prevented
349 the olation and oxolation reactions that lead to the formation of nanoFeH. Then, we assumed that the lateral
350 nanoFeH were formed in solution and were finally adsorbed on the illite edges.

351 All in all, regardless their precise formation mechanism, the status of iron species adsorbed onto the illite
352 particles was dominated by nanoFeH forms as evidenced by STEM observations, and this conclusion held for
353 all IFeH_R samples. One supplementary concluding remark about the illite-FeH composites is the moderate
354 modification of their size and electrophoretic mobility (compared to illite). As mentioned above, the Fe/illite ratio
355 used for our experiments was not sufficient to shield the repulsive interactions between negatively charged illite
356 platelets (Beene et al., 1991; Lin et al., 2017). Then, iron hydr(oxide) particles present in the IFeH_R are closely
357 associated with illite particles, forming size-reduced particles covering the illite surface.

358 **3.2. Illite-Dextran aggregates, ID_x.**

359 To evidence the influence of iron coatings on the interactions between clay particles and the organic polymer
360 Dextran, a second set of clay-composites was prepared without iron (hydr)oxide, using only illite and Dextran.
361 Dextran concentrations from 1.67 and to 16.67 μmol L⁻¹ were selected to produce illite-Dextran aggregates. The
362 endmembers of this sample series are referred to as ID₁₀ and ID₁₀₀, respectively. Dextran was always added
363 simultaneously with CaCl₂ as preliminary tests demonstrated that Dextran alone was not able to flocculate the
364 illite particles (those tests were based on the monitoring of the turbidity of the suspension, data not shown).
365 Figure 6 compares size and μ distributions obtained after the addition of both Dextran and CaCl₂. The same
366 measurements were performed after the addition of CaCl₂ alone. CaCl₂ addition caused a clear and well-marked
367 increase in particle size distribution (supplementary material SM-6). The size distribution was shifted towards
368 higher values, with a broad band centred in 1718 μm. Moreover, there was a weak contribution of smaller
369 particles, with a broad band centred at 250 nm. The electrophoretic mobility of illite particles after CaCl₂ addition
370 was further shifted towards lesser negative values, with a central value at $-1 \times 10^{-8} \text{ m}^2 \text{ V}^{-1} \text{ s}^{-1}$. The presence of
371 Ca²⁺ in solution screened the repulsive interactions between negatively charged illite particles. Such an
372 electrostatic screening was already reported in numerous publications (Jellander et al., 1988; Jiang et al., 2012;
373 Kloster and Avena, 2015 and references therein). The illite-Dextran aggregates (Figure 5) displayed similar size
374 distribution and electrokinetic properties compared to those obtained after addition of CaCl₂. Any increase in
375 Dextran concentration did not bring any modification to the resulting size and μ distributions. Modifications of
376 size and electrophoretic mobility of illite upon addition of Dextran and Ca²⁺ were mainly explained by the
377 shielding of clay charge, due to the saturation of illite exchange sites by divalent cations. Furthermore, the
378 addition of divalent cations was leading to a shift of μ to a value close to that of Dextran, thus minimizing the
379 range of eventual modifications of electrokinetic properties because of sole Dextran adsorption to illite particles.
380 Therefore, at this stage, we could not conclude on the occurrence and type of interactions between Dextran and
381 illite particles.

382 To monitor Dextran content, FTIR spectra were collected in two measurement modes, transmission (Tr), and
383 diffuse reflectance (DR) (Figure 6). The former provides quantitative chemical information on the whole illite-
384 Dextran aggregate (ID_x) and the relative contents of mineral and organic components. The latter is particularly

385 sensitive to surface composition (about few nanometres are estimated to be probed with this technique
386 considering the water content of samples) (Milosevic and Berets, 2002; Madejová, 2003; Armaroli et al., 2004).
387 Figure 6 presents the high wavenumber range of the FTIR spectra. The low wavenumber range of those spectra
388 are presented as supplementary material (SM-7). In transmission mode (Figure 6 top graph), the vibration bands
389 of illite (ν_{OH} 3698 and 3620 cm^{-1}) were visible for each of the samples tested and so were the bands
390 corresponding to Dextran (ν_{CH_2} 2954 and 2930 ν_{CH} 2890 and 2855 cm^{-1}). The intensity of the bands assigned
391 to Dextran is low for ID₁₀ sample and Dextran signature in the 1500-1000 cm^{-1} wavenumber range is hardly
392 detected (SM-7). With increasing Dextran concentration (ID₁₀₀), Dextran vibration bands increase in intensity,
393 in line with expectation. These FTIR spectra were acquired for three distinct series of ID_x samples with x initially
394 fixed to 5, 10, 20, 50 and 100, providing reproducible results. To estimate the illite/Dextran ratio, the ratios of
395 intensity bands respectively centred in 3698 and 2930 cm^{-1} were calculated. This ratio decreases from 3.05 to
396 0.71 for ID₁₀ and ID₁₀₀. Beside intensity, the stretching vibration bands of alkyl groups (ν_{CH_2} and ν_{CH} , 3000-2800
397 cm^{-1}) were modified for ID₁₀ sample. Those stretching vibrations are clearly separated for ID₁₀ whereas pure
398 Dextran displays a broad band centred in 2930 cm^{-1} and a shoulder at 2890 cm^{-1} (Figure 6 and supplementary
399 material SM-1). Such modifications of Dextran signal were assigned to interactions with illite surface (through
400 Ca^{2+} bridges). Previous experiments on Dextran-montmorillonite aggregates had also revealed a close
401 association of polymer with clay mineral surfaces (Labille et al., 2005) and experiments on humic adsorption
402 with different loads of Ca had also evidenced the crucial role of Ca (Kloster and Avena, 2015).
403 For ID₁₀₀ the splitting of the ν_{CH} and ν_{CH_2} bands is no longer observed, and the Dextran signal is basically similar
404 to that of pure Dextran. This observation is further confirmed upon inspection of the spectra in the low
405 wavenumber range. At such high Dextran concentrations, majority of the polymer chains did not interact with
406 the illite minerals and bulk Dextran phase showed up in the aggregate.
407 In diffuse reflectance mode (Figure 6, bottom graph), the vibration bands of illite are present and so are the
408 bands corresponding to Dextran. We observed for ID₁₀ the same shift of the ν_{CH} band as in transmission mode,
409 showing a modification of vibration bands of the polymer due to interactions between Dextran and the surface
410 of illite particles. For ID₁₀₀, the intensity of the Dextran peaks increased with no deviation of the bands in the
411 stretching vibration range (ν_{CH_2} 2930 cm^{-1} and ν_{CH} 2890 cm^{-1}). The absence of peak modification in the stretching
412 vibration range (ν_{CH_2} 2930 cm^{-1} and ν_{CH} 2890 cm^{-1}) in diffuse reflectance mode was reported in the literature for
413 other organo-clay mixtures (Webb et al., 1986; Mpofu et al., 2004). ID₁₀₀ FTIR spectra evidenced the presence
414 of Dextran on the surface of aggregates with low or no interaction with illite.
415 While Transmission FTIR spectra showed that Dextran was present within the aggregates and was in interaction
416 with the clay platelets, Diffuse Reflectance spectra evidenced that Dextran and illite were both present at the
417 surface of aggregates. Although the Dextran content is low for ID₁₀ (roughly estimated between 5 and 10% from
418 a linear combination of transmission spectra of Dextran and illite), Diffuse Reflectance spectrum confirmed the
419 presence of the polymer on the external surface of the aggregates. Since ID₁₀ FTIR-DR spectrum evidenced
420 the contribution of illite, we concluded that few illite particles remained as pristine illite, i.e. without Dextran. The
421 average diameter of Dextran, which is assumed to be cylindrical under the conditions of aggregate preparation,
422 is about 2-3 nm. Illite particles display a length of about 87 ± 25 nm, a width of about 58 ± 13 nm and a thickness
423 of 18 ± 7 nm (from TEM and HRTEM data). Dextran entities are smaller than illite particles and cover only partially
424 the surfaces of the clay platelets. For ID₁₀₀, the relatively high amount of adsorbed Dextran was evidenced by
425 transmission and explained the absence of shift of Dextran vibration bands in diffuse reflectance mode. Dextran
426 contribution to FTIR spectrum was roughly estimated to 50 % through the same method based on linear

427 combination of referenced spectra. With these results at hand, the now-demonstrated presence of Dextran at
428 the surface of illite particles is unseen in the size and electrokinetic measurements (Figure 5).

429 To explain the apparent low contribution of Dextran in the ID₁₀ FTIR signal, the micrometric size of aggregates
430 should be considered. Diffuse Reflectance spectra demonstrated the position of Dextran at the external surface
431 of aggregates. Thus, it can be concluded that those illite-Dextran aggregates display a dense core mainly
432 constituted of illite platelets, aggregated by Ca²⁺ ions. It can also be concluded that the Dextran molecules are
433 loosely attached to the surface, through Ca²⁺ bridges as it was suggested for montmorillonites (Labille, 2003;
434 Labille et al., 2005). In the case of swelling clays such as montmorillonite, multivalent cations reduce the energy
435 barrier separating montmorillonite particles. For illite particles, displaying a charge density twice higher than that
436 of montmorillonite layers, similar reactions were enhanced by Ca²⁺ (Jiang et al., 2012; Kloster and Avena, 2015;
437 Lin et al., 2017). Ca²⁺ ions occupy exchange sites on the surface of illite minerals and finally allow the adsorption
438 of Dextran simultaneously on several particles via weak interactions between the OH groups of Dextran and the
439 water molecules of the hydration sphere of the Ca²⁺ cations.

440 **3.3. Ternary aggregates, illite-Iron (hydr)oxide-Dextran IFeH_RD_x:**

441 Two series of IFeH_RD_x aggregates were respectively prepared from IFeH_{0.6} and IFeH₂ clay-composites. Figure
442 7 reports the results of size and electrophoretic mobility distributions for IFeH_{0.6}D_x samples and compares them
443 with data collected for the binary sample IFeH_{0.6}. Here, the addition of CaCl₂ and Dextran caused an increase
444 in particle size, similarly to what was observed for ID_x aggregates (Figure 5).

445 The particle size of IFeH_{0.6}D₁₀ ranges between 100 nm and 3 μm with a maximum at 955 nm, showing a clear
446 aggregation of illite-FeH particles. Increasing the amount of added Dextran leads to two populations of
447 aggregates, relatively large aggregates with size in the 0.4-3 μm range and smaller ones in the 100-400 nm
448 range. The electrophoretic properties of IFeH_{0.6} are modified upon addition of CaCl₂ and Dextran. There is
449 indeed a clear shift in mobility towards lesser negative values. The mobility distribution is centred around -1.6 x
450 10⁻⁸ m² V⁻¹ s⁻¹ for IFeH_{0.6}D₁₀ instead of -2.6 x 10⁻⁸ m² V⁻¹ s⁻¹ for IFeH_{0.6}. Addition of larger amount of Dextran to
451 IFeH_{0.6} results in a similar shift, except that the distribution of μ values for the resulting IFeH_{0.6}D₁₀₀ product is
452 now centred at -1.8 x 10⁻⁸ m² V⁻¹ s⁻¹, and it is broader than that for IFeH_{0.6}D₁₀.

453 Overall, the addition of CaCl₂ and Dextran to IFeH_{0.6} did not provoke the formation of large aggregates as we
454 could observe for the systems illite+Ca²⁺ or ID_x samples, and the shift in mobility was less pronounced than that
455 observed when CaCl₂ and Dextran were added to Illite alone (Figure 5). Last, the increase in Dextran
456 concentration leads to smaller particles as the curve displays a clear contribution centred at 210 nm. It is
457 therefore apparent that the presence of iron nanoparticles on the illite surfaces modified their surface reactivity.
458 The addition of CaCl₂ and Dextran to IFeH_{0.6} and IFeH₂ samples was followed by FTIR in Transmission and
459 Diffuse Reflectance modes (Figure 8). To unravel the influence of nanoFeH on Dextran adsorption and on the
460 respective organization of Dextran and clay platelets within the formed assemblies, two sets of aggregates
461 prepared from IFeH_{0.6} and IFeH₂ were considered.

462 FTIR spectra collected for ID₁₀, IFeH_{0.6}D₁₀ and IFeH₀₂D₁₀ samples (top graphs), all prepared with a Dextran
463 concentration set at 10 mg L⁻¹, are presented on Figure 8 in both transmission and diffuse reflectance modes
464 (low range of FTIR spectra are presented in figure SM-7B) Those spectra revealed the vibration bands of illite
465 and Dextran in the stretching domain. With increasing iron content (IFeH₂D₁₀, Figure 8 curve c), the vibration
466 bands of illite (ν_{OH} 3620 cm⁻¹) became less visible while vibration bands of Dextran are more intense. Moreover,
467 the sample IFeH₂D₁₀ exhibited a higher amount of water than in IFeH_{0.6}D₁₀, as judged by the broad and intense
468 stretching band of OH centred at 3400 cm⁻¹. This higher amount of water in the sample related to the higher

469 content of Dextran. For the three samples analysed, the stretching vibration bands of alkyl groups (3000-2800
470 cm^{-1} range) appeared in the form of separated bands, centred at 2954, 2930 and 2890 cm^{-1} . However, the
471 splitting of these signatures was as pronounced as that identified for IFeH_{0.6}D₁₀. To quantify the influence of
472 nanoFeH on Dextran adsorption, intensities ratios were calculated. The intensity ratio I_{3698}/I_{2930} compared the
473 contribution of illite and Dextran to the signal and this ratio decreased from ID₁₀ to IFeH_{0.6}D₁₀ and IFeH₂D₁₀, with
474 the respective values 3.05, 1.49 and 0.77. Although these intensity ratios cannot be used for an exact
475 quantification of Dextran content or of the illite/Dextran ratio, the calculation of such intensity ratios was useful
476 to compare the different samples.

477 The Diffuse Reflectance spectra (bottom graph in Figure 8) revealed the same trend between the three samples,
478 demonstrating that the presence of iron particles had modified Dextran adsorption. Indeed, IFeH_{0.6}D₁₀ spectrum
479 showed that the amount of Dextran in the external zone of the aggregates is higher than for ID₁₀. However, the
480 contribution of illite bands to the DR-FTIR signal suggested, similarly to ID₁₀, that the surface of illite particles
481 was partially visible and not covered by Dextran. Also, the splitting of the stretching bands of Dextran was even
482 more marked in DR than in Transmission mode, thus suggesting a stronger interaction between mineral entities
483 and Dextran OH groups.

484 For ternary aggregates built from IFeH₂ (Figure 8 spectrum c), the presence of Dextran in the external region of
485 aggregates was clearly unravelled from the Transmission and Diffuse Reflectance FTIR spectra. The stretching
486 bands of Dextran (2800-3000 cm^{-1}) were no longer separated for IFeH₂D₁₀, therefore suggesting that a major
487 proportion of Dextran chains did not experience interactions with the mineral surfaces. The comparison between
488 IFeH_{0.6}D₁₀ and IFeH₂D₁₀ spectra showed that the increase in amount of iron hydr(oxide) nanoparticles enhanced
489 the insertion of Dextran within the aggregates. In addition, the presence of iron nanoparticles also impacted on
490 the spatial distributions of clays and polysaccharide units in the aggregates. The differences between IFeH_{0.6}D₁₀
491 and IFeH₂D₁₀ spectra were more pronounced in diffuse reflectance mode than in transmission mode. As far as
492 the aggregates were concerned, the adsorption of Dextran was not only enhanced by nanoFeH, but its location
493 was also shifted towards the outer surface of the aggregates.

494 Similar spectra with higher concentration in Dextran (100 mg L⁻¹) can be found in supplementary material (figure
495 SM-8). For the samples prepared with a higher concentration of Dextran (100 mg/L) the vibration bands of illite
496 OH groups were hardly detected. Moreover, the intensity ratio I_{3698}/I_{2930} reflecting the respective contributions
497 of illite and Dextran signals basically decreased if compared to that for the previous series of aggregates
498 prepared with 10 mg/L Dextran: this ratio was further slightly decreasing from ID₁₀₀ to IFeH_{0.6}D₁₀₀ and IFeH₂D₁₀₀,
499 with the respective values 0.71, 0.57 and 0.5. In addition, in transmission mode the vibration bands of Dextran
500 in the stretching region were split for IFeH_{0.6}D₁₀₀ and IFeH₂D₁₀₀, which supported that OH groups carried by the
501 polymer were constrained through interactions with illite surface and/or nanoFeH entities. This splitting was not
502 observed for ID₁₀₀ and disappeared in Diffuse Reflectance mode for all IFeH_RD₁₀₀ samples. Moreover, the
503 Diffuse Reflectance spectra evidenced the fading away of illite signal, replaced by Dextran and associated
504 water. At sufficiently high polymer concentrations (100 mg L⁻¹), iron particles appeared to have no influence on
505 the adsorption and on the organization of Dextran within the aggregates, suggesting that the nano-Fe adsorption
506 sites for Dextran were saturated.

507 The above Diffuse Reflectance observations evidenced that the contribution of illite entities to FTIR signal was
508 significantly screened due to enhanced adsorbed amount of Dextran. These observations also indicated that
509 the higher the Dextran content was, the lower became the fraction of Dextran chains interacting with the mineral
510 surfaces.

511 **3.4. Influence of nanoFeH on illite-Dextran interactions**

512 The addition of Ca^{2+} and Dextran to illite-FeH aggregates did not produce similar results than the addition of
513 these components to bare illite particles. First, considering the size distributions and FTIR data (Figures 5 to 8)
514 the comparison between ID₁₀ and IFeH_{0.6}D₁₀ shows a reduction of aggregate size as well as an increase of the
515 Dextran/illite ratio for the latter system. Since Transmission FTIR collected the signal from the whole aggregate,
516 this apparent increase of Dextran content can be explained by the reduction of the aggregate size, i.e. the
517 contribution of the illite core is diminished and the signal from the peripheral part of the aggregates is enhanced.
518 The modifications in μ showed that the presence of nanoFeH reduced the interactions of Ca^{2+} with illite particles
519 (Figures 5 and 7). Indeed, without nanoFeH, μ was shifted by ca. $2.5 \times 10^{-8} \text{ m}^2 \text{ V}^{-1} \text{ s}^{-1}$, while it was only shifted
520 by $1 \times 10^{-8} \text{ m}^2 \text{ V}^{-1} \text{ s}^{-1}$ for samples exhibiting nanoFeH.

521 The presence of nanoFeH on the basal surfaces of illites diminished the effect of Ca^{2+} , reduced the screening
522 effect and limited the flocculation reaction. Diffuse reflectance spectra evidenced an external positioning of
523 Dextran (Figure 9), but the polymer did not modify the electrophoretic mobility. As it was previously suggested
524 by measurements on ID_x aggregates, calcium adsorption on the clay minerals mainly governs the end
525 electrokinetic properties of the aggregates.

526 The splitting of the size distribution pattern observed for IFeH_{0.6}D₁₀₀ (Figure 6) can be explained by the
527 amount of Dextran integrated within the aggregates, itself depending on the amount of nanoFeH on the clay
528 surface. We can apply the same reasoning as for IFeH_{0.6}D₁₀. Indeed, the formation of sub-micrometric
529 aggregates (centred in 250 nm) with higher Dextran content strongly suggests that Dextran adsorption was
530 promoted by nanoFeH. The smaller size of aggregates can be explained by the heterogeneous distribution of
531 nanoFeH on illite surface as shown by TEM images. NanoFeH particles occupied cation exchange sites and
532 reduced the electrostatic interaction of Ca^{2+} cations with illite particles.

533 The apparent higher amount of adsorbed Dextran is related to the presence of nanoFeH on the surface of illite
534 platelets, which leads to the following questions: what is the exact mechanism of aggregate formation and what
535 is the exact role played by nanoFeH? The affinity of iron oxides for organic matter was reported in numerous
536 studies (Reinhardt and Wilkinson, 2004; Cloy et al., 2014; Vindedahl et al., 2016; Sowers et al., 2018b), so that
537 it is likely that the presence of nanoFeH enhanced Dextran adsorption. For Fe-montmorillonite hetero-
538 aggregates (Ji et al., 2004), it was suggested that the presence of FeH reduced the charge and electric field of
539 clay particles. Such a reduction of clay mineral charge reduced the repulsive forces acting between illite and
540 Dextran molecules, thereby promoted Dextran adsorption. Such an explanation might not be accepted for the
541 current case of illite-nanoFeH aggregates for two reasons. First, the charge density of the illite particles is twice
542 higher than that of montmorillonite, and second because the ratio iron/clay used for our study was far lower than
543 that of Ji et al.

544 Supported by these results obtained on three different types of aggregates, different assembly schemes
545 can be proposed (Figure 9). Binary aggregates ID₁₀ appear as large aggregates or large Ca-illite flocs with low
546 electrophoretic mobility values (in magnitude) due to the significant screening exerted by Ca^{2+} ions. They display
547 a rather low amount of Dextran as revealed by FTIR. The polymer interacts with the mineral surfaces through
548 Ca^{2+} bridges and shows preferential localization on the external surface of the Ca-illite flocs.

549 Ternary aggregates IFeH_{0.6}D₁₀ and IFeH_{0.6}D₁₀₀ display different properties. The presence of iron oxy-
550 hydroxide nanoparticles on the surface of the illite particles not only diminished the adsorption of Ca^{2+} and
551 subsequently limited the floc growth but also enhanced the adsorption of Dextran. IFeH_{0.6}D₁₀ is constituted of
552 aggregates of 900 nm size, with a charge that is screened by Ca^{2+} adsorption. The Dextran content is slightly
553 higher than for ID₁₀ and as for ID₁₀ sample, the polymer shows interaction with mineral entities (nanoFeH or

554 illite). Increasing Dextran concentration (IFeH_{0.6}D₁₀₀) lead to aggregates of similar size. Supplementary Dextran
555 molecules in the periphery of the aggregates did not develop interactions with mineral entities (FTIR data on
556 Figure 8 and SM-8). Furthermore, IFeH_{0.6}D₁₀₀ sample displayed additional smaller aggregates with higher
557 Dextran content. The presence of these smaller aggregates can be explained by the heterogeneous distribution
558 of nanoFeH. Illite platelets with a denser Fe coating may adsorb higher amounts of Dextran, limiting the
559 interactions with other clay platelets.

560 **4. Conclusions:**

561 Our main objective was to prepare and characterize ternary aggregates built from the addition of an
562 organic polymer, a neutral polysaccharide, to a suspension of illite particles coated by iron (hydr)oxide
563 nanoparticles. To understand the spatial assembly of the three components and highlight the influence of iron
564 coating, we analysed three distinct types of aggregates based on the modification of clay particles through the
565 addition of iron coating and/or Dextran to illite suspension. Such a step-by-step investigation of binary and
566 ternary aggregates was particularly relevant to explore the respective organizations of the different components
567 involved in the formed organo-mineral composites. In addition, the combination of electrokinetic and
568 spectroscopic data has been proven fruitful to elaborate assumptions regarding the way organic and mineral
569 components interact. Two main results can be highlighted:

570 - the formation of nanoFeH onto illite particles could be evidenced, and such illite-FeH aggregates were
571 synthesized under pH conditions close to neutrality with use of relatively low concentrations of both iron and
572 clay minerals. The preparation conditions were selected to be more realistic -from an environmental perspective-
573 than those adopted in previously published reports.

574 - the interactions between clay minerals and a neutral polysaccharide were shown to be favoured by
575 the presence of nanoFeH.

576 Our study further sheds light on the processes driving hydrolysis of iron in the presence of clay minerals. We
577 indeed evidenced the role of illite particles in the nucleation mechanism of ferrihydrite. This work on iron-clay
578 composites should be completed by a systematic investigation of the influence of layer charge (density and
579 localisation), or the influence of the clay shape and size. Moreover, to mimic the complex structure of natural
580 aggregates as found in river SPM, the use of more complex organic representatives like humic or fulvic acids
581 should be carried out. Also, considering the diversity of organic molecules in environmental media, the use of
582 several organic materials for the preparation of clay-based aggregates should be the next step. Our results are
583 based on the recourse to different characterization techniques but call for supplementary investigations. In the
584 future, larger amounts of clay composites will be prepared to investigate the surface properties using gas probes
585 to determine surface area and pore volume distribution. Finally, these preliminary works on ternary aggregates
586 pave the way for more complex systems, including further investigations of the aggregates formation and
587 reactivity.

588 **Acknowledgements:**

589 This study is part of a Ph.D. work financially supported by the French Administrative Region Grand-Est
590 and by the French Ministry of Higher Education and Research. This work was performed with the financial
591 support of the Zone Atelier Moselle (ZAM), belonging to the French Zones Ateliers Network (RZA) driven by
592 CNRS INEE institute. We are very grateful to Jaafar GHANBAJA and Sylvie MIGOT from Institut Jean Lamour
593 in Nancy (France) for their strong support for Transmission Electron Microscopy. We thank Delphine
594 VANTELON (SOLEIL) and Martine MALLET (LCPME) for their constructive discussions about this Ph.D. work.
595 We also acknowledge SOLEIL for provision of synchrotron radiation facilities, and we would like to thank

596 Gauthier LANDROT for assistance in using beamline SAMBA. We are grateful to Manuel PELLETIER (LIEC)
597 for his constructive comments on FTIR interpretation and to Christophe GAUTHIER (LIEC) for his help in running
598 XAS experiments at SAMBA beamline. We also thank the reviewers for their constructive comments on this
599 manuscript.

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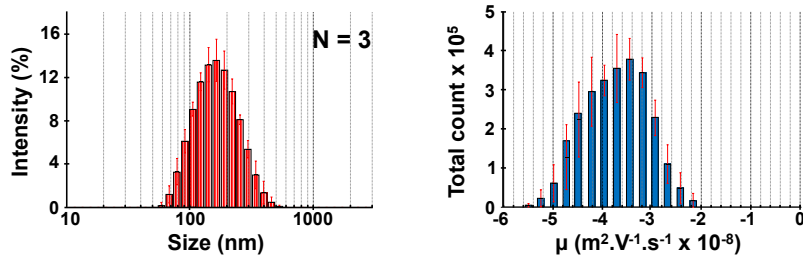
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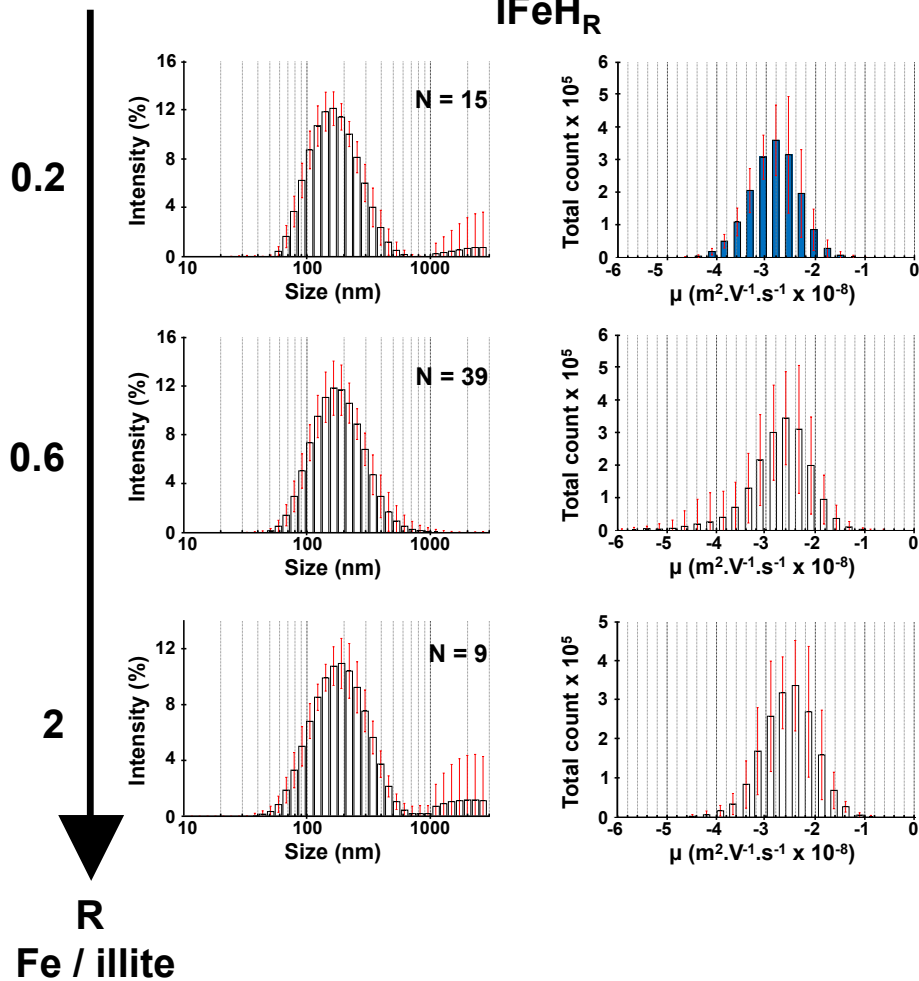
797 **FIGURE CAPTIONS**

- 798 Figure 1: Iron-illite aggregates IFeH_R. Size distribution (nm) (red histogram) and electrophoretic mobility μ (m^2
799 $\text{V}^{-1} \text{s}^{-1} \times 10^{-8}$) (blue histogram) of illite particles for different initial Fe/illite ratios $R = 0.2, 0.6$ and 2 . (N:
800 number of replicates). Conditions of synthesis: $[\text{Fe}(\text{NO}_3)_3] = 10^{-4}\text{M}$; $[\text{KOH}] = 10^{-3}\text{M}$; addition rate of iron
801 nitrate: 0.25 mL min^{-1} ; addition rate of KOH: 0.1 mL min^{-1} ; initial concentration of illite suspension: 200 mg
802 L^{-1} , initial volume of illite suspension 100 mL . The pH of all suspensions analysed after dialysis is 5.7 .
803
- 804 Figure 2 : X-ray absorption spectroscopy at Fe-K edge. EXAFS oscillations from Illite (a), IFeH_{0.6} (b), IFeH₂
805 (c) and FeH (d). The latter sample was synthesized in the same conditions as the others but without illite
806 particles.
807
- 808 Figure 3: High Resolution Transmission Electron Microscopy (HRTEM) images of illite, illite-Fe (hydr)oxide
809 with the ratio iron/illite = $0.2, 0.6$ or 2 (IFeH_{0.2}, IFeH_{0.6} and IFeH₂ respectively) at two magnifications (100k
810 and 200k for illite, 100k and 250k for IFeH_{0.2}, IFeH_{0.6} and IFeH₂). id: ill-defined edges; nanoFeH: nano
811 iron (hydr)oxide For IFeH_{0.6}, the black square indicates the region corresponding to the second picture on
812 the right, obtained at 250k .
813
- 814 Figure 4: Bright Field (BF) and High-Angle Annular Dark-Field (HAADF) scanning transmission electron
815 microscopy (STEM) images of illite-Fe (hydr)oxide with the ratio iron/illite = $0.2, 0.6$ or 2 (IFeH_{0.2}, IFeH_{0.6}
816 and IFeH₂ respectively). (IFeH_{0.2}: 2M magnification; IFeH_{0.6} and IFeH₂: 1.2M magnification).
817
- 818 Figure 5: Illite-dextran aggregates ID_x. Size distribution (nm) (red histogram) and electrophoretic mobility μ (m^2
819 $\text{V}^{-1} \text{s}^{-1} \times 10^{-8}$) (blue histogram) of illite particles for two different initial concentrations of dextran ($x = 10$
820 and 100 mg L^{-1} or 1.67 and $16.67 \mu\text{mol L}^{-1}$, respectively). (N: number of replicates). Initial concentration of
821 illite suspension: 200 mg L^{-1} , initial volume of illite suspension 50 mL . Initial concentration of $\text{CaCl}_2 = 5.10^{-4}$
822 M . The pH of all suspensions analysed after dialysis is 5.7 . The green curve represents the
823 electrophoretic mobility of dextran.
824
- 825 Figure 6: Fourier-transform infrared spectra of illite-dextran aggregates ID_x. (above) Transmission mode (Tr)
826 and (below) Diffuse Reflectance mode (DR) spectra: illite (a), dextran (b), illite-dextran aggregates ID₁₀ (c)
827 and ID₁₀₀ (d). Spectra have been corrected by the baseline of the device. An adjustment of the signal
828 intensity has been made for their better visualization and qualitative interpretation.
829
- 830 Figure 7: Illite-Fe (hydr)oxide-dextran aggregates. Size distribution (nm) (red histogram) and electrophoretic
831 mobility μ ($\text{m}^2 \text{V}^{-1} \text{s}^{-1} \times 10^{-8}$) (blue histogram) of illite particles for initial Fe/illite ratios $R = 0.6$ and two
832 different initial concentrations of dextran (1.67 and $16.67 \mu\text{mol L}^{-1}$) (N: number of replicates). $[\text{Fe}(\text{NO}_3)_3]$
833 $= 10^{-4}\text{M}$; $[\text{KOH}] = 10^{-3}\text{M}$; addition rate of iron nitrate: 0.25 mL min^{-1} ; addition rate of KOH: 0.1 mL min^{-1} ;
834 initial concentration of illite suspension: 200 mg L^{-1} , initial volume of illite suspension 100 mL . Initial
835 concentration of $\text{CaCl}_2 = 5.10^{-4}\text{M}$. The pH of all suspensions analysed after dialysis is 5.7 . The green line
836 represents the electrophoretic mobility of dextran.
837
- 838 Figure 8: Fourier-Transform Infrared spectra of ternary illite-Fe (hydr)oxide-dextran aggregates IFeH_RD₁₀ –
839 Transmission (top graph) and Diffuse Reflectance (bottom graph) spectra of ID₁₀ (a), IFeH_{0.6}D₁₀ (b),
840 IFeH₂D₁₀ (c). Spectra have been corrected by the baseline of the device but are not normalized. An
841 adjustment of the spectrum intensity was performed for a better visualization and qualitative
842 interpretation.
843
- 844 Figure 9: Scheme of the binary illite-dextran (ID₁₀) and ternary illite-Fe (hydr)oxide-dextran (IFeH_{0.6}D₁₀ and
845 IFeH_{0.6}D₁₀₀) aggregates. The illite-dextran samples ID₁₀ can be represented as large aggregates with a
846 core mainly constituted of clay minerals, flocculated by the addition of calcium ions. The large size of this
847 aggregate can be an interpretation key of FTIR data obtained in transmission, suggesting a relatively low
848 content of polymer associated to these aggregates. The second and third schemes presents IFeH_{0.6}D₁₀
849 and IFeH_{0.6}D₁₀₀ samples. Those samples are represented as smaller aggregates. The presence of
850 nanoFeH on illite surface limited the adsorption of Ca^{2+} on exchangeable cationic sites of clay particles
851 and finally stabilized small size flocs. The presence of the nanoFeH also promoted the adsorption of
852 dextran. The higher concentration of dextran lead to a second population of smaller aggregates.
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Illite (R = 0)

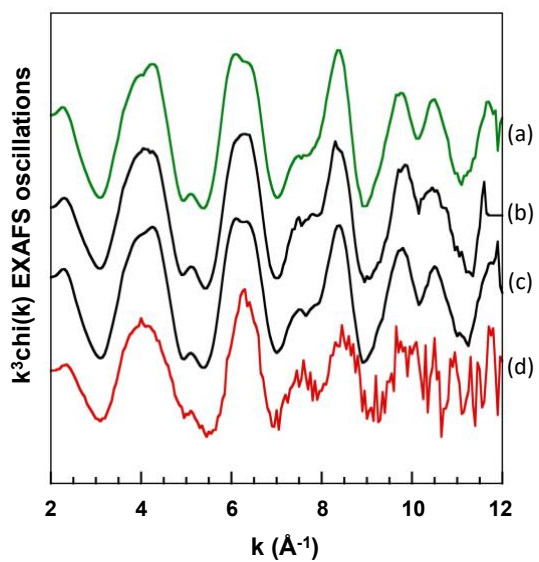


IFeH_R



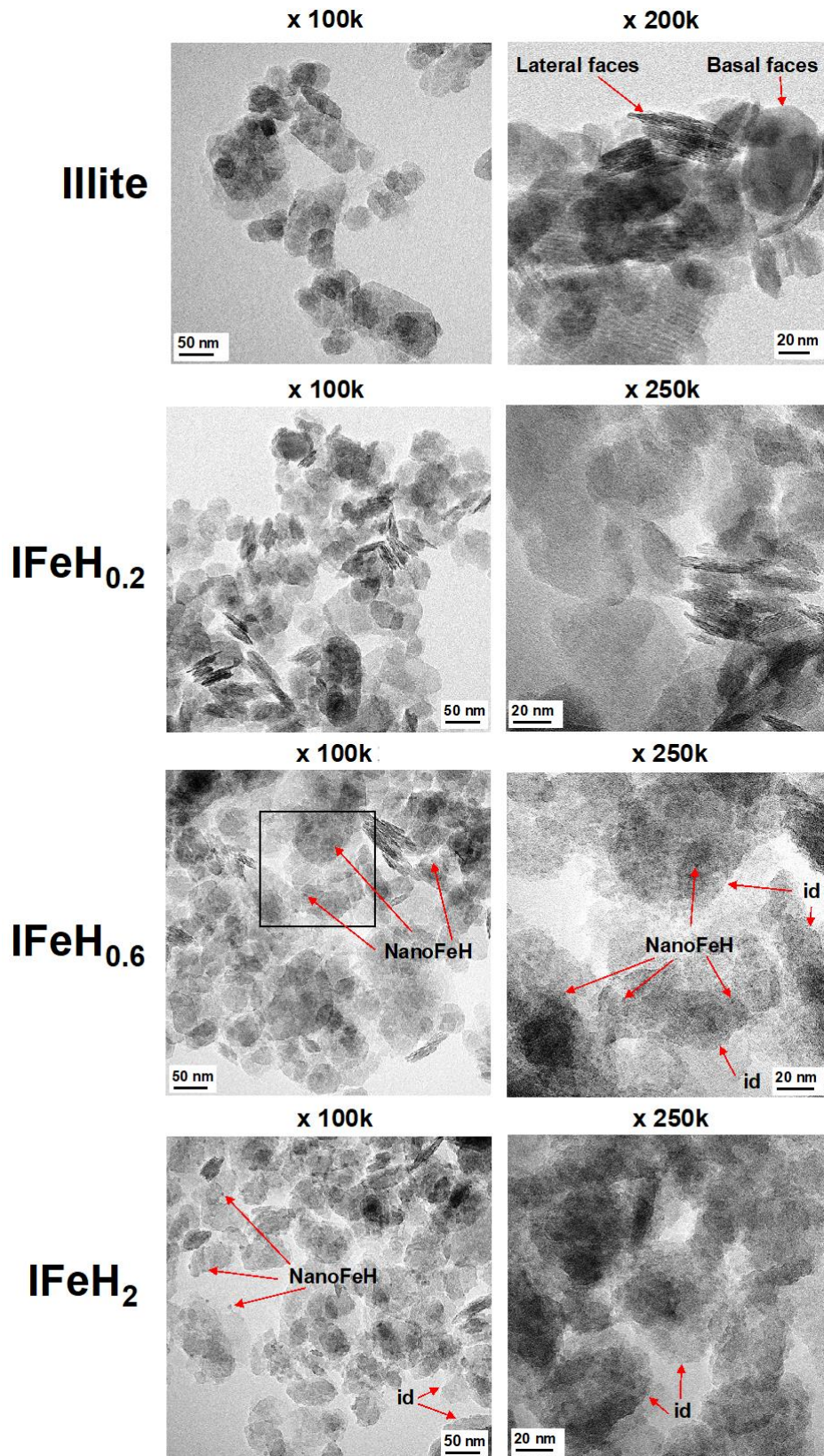
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Figure 1: Iron-illite aggregates IFeH_R. Size distribution (nm) (red histogram) and electrophoretic mobility μ ($\text{m}^2 \text{V}^{-1} \text{s}^{-1} \times 10^{-8}$) (blue histogram) of illite particles for different initial Fe/illite ratios $R = 0.2, 0.6$ and 2 . (N: number of replicates). Conditions of synthesis: $[\text{Fe}(\text{NO}_3)_3] = 10^{-4} \text{M}$; $[\text{KOH}] = 10^{-3} \text{M}$; addition rate of iron nitrate: 0.25 mL min^{-1} ; addition rate of KOH: 0.1 mL min^{-1} ; initial concentration of illite suspension: 200 mg L^{-1} , initial volume of illite suspension 100 mL . The pH of all suspensions analysed after dialysis is 5.7 .



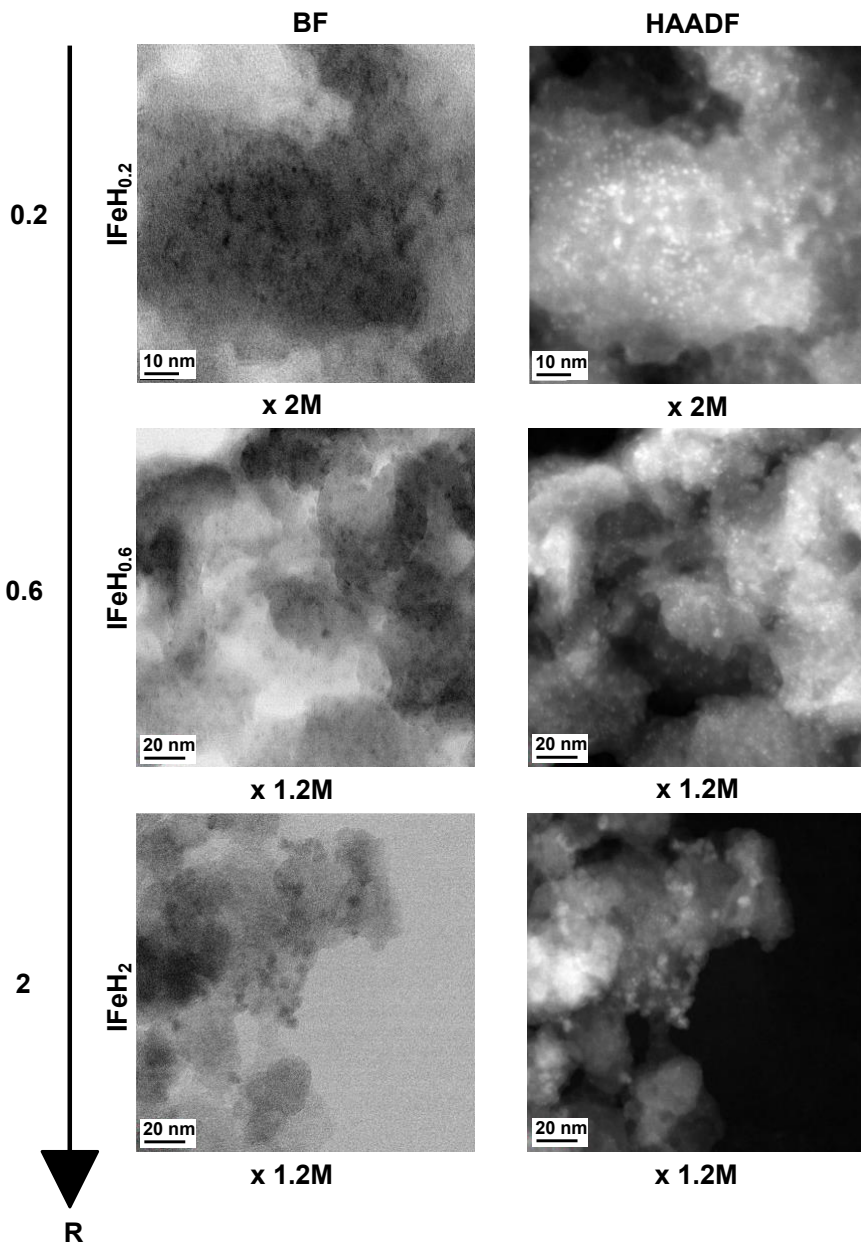
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Figure 2: X-ray absorption spectroscopy at Fe-K edge. EXAFS oscillations from Illite (a), IFeH_{0.6} (b), IFeH₂ (c) and FeH (d). The latter sample was synthesized in the same conditions as the others but without illite particles.



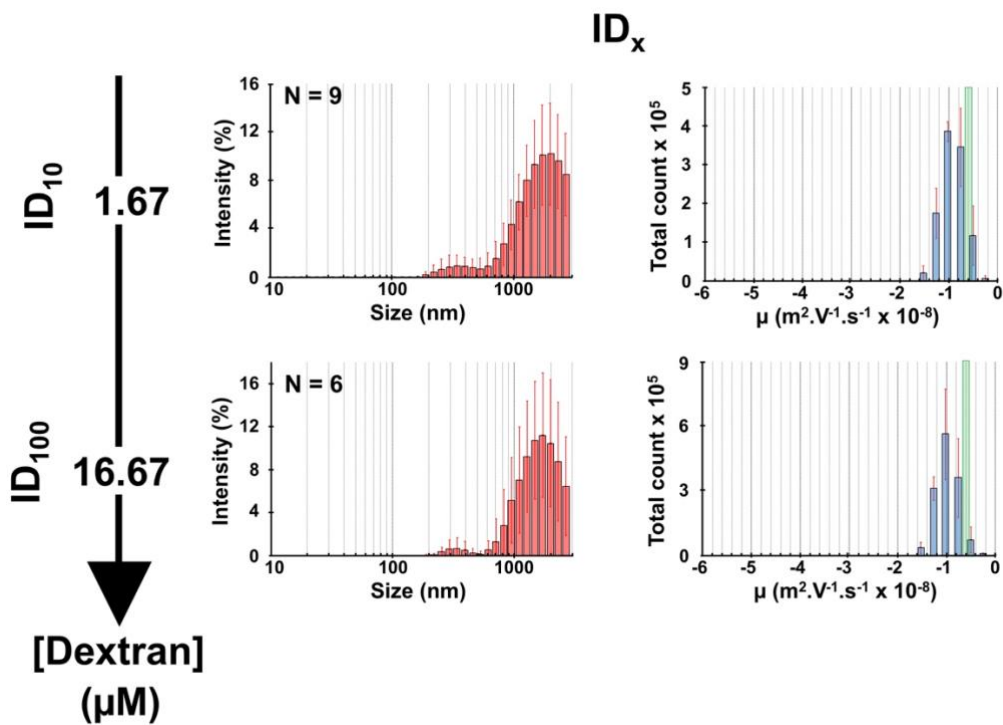
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Figure 3: High Resolution Transmission Electron Microscopy (HRTEM) images of illite, illite-Fe (hydr)oxide with the ratio iron/illite = 0.2, 0.6 or 2 (IFeH_{0.2}, IFeH_{0.6} and IFeH₂ respectively) at two magnifications (100k and 200k for illite, 100k and 250k for IFeH_{0.2}, IFeH_{0.6} and IFeH₂). id: ill-defined edges; nanoFeH: nano iron (hydr)oxide For IFeH_{0.6}, the black square indicates the region corresponding to the second picture on the right, obtained at 250k.



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Figure 4: Bright Field (BF) and High-Angle Annular Dark-Field (HAADF) scanning transmission electron microscopy (STEM) images of illite-Fe (hydr)oxide with the ratio iron/illite = 0.2, 0.6 or 2 ($\text{IFeH}_{0.2}$, $\text{IFeH}_{0.6}$ and IFeH_2 respectively). ($\text{IFeH}_{0.2}$: 2M magnification; $\text{IFeH}_{0.6}$ and IFeH_2 : 1.2M magnification).



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Figure 5: Illite-dextran aggregates ID_x . Size distribution (nm) (red histogram) and electrophoretic mobility μ ($m^2 V^{-1} s^{-1} \times 10^{-8}$) (blue histogram) of illite particles for two different initial concentrations of dextran ($x = 10$ and 100 mg L^{-1} or 1.67 and $16.67 \mu\text{mol L}^{-1}$, respectively). (N: number of replicates). Initial concentration of illite suspension: 200 mg L^{-1} , initial volume of illite suspension 50 mL . Initial concentration of $\text{CaCl}_2 = 5.10^{-4} \text{ M}$. The pH of all suspensions analysed after dialysis is 5.7 . The green curve represents the electrophoretic mobility of dextran.

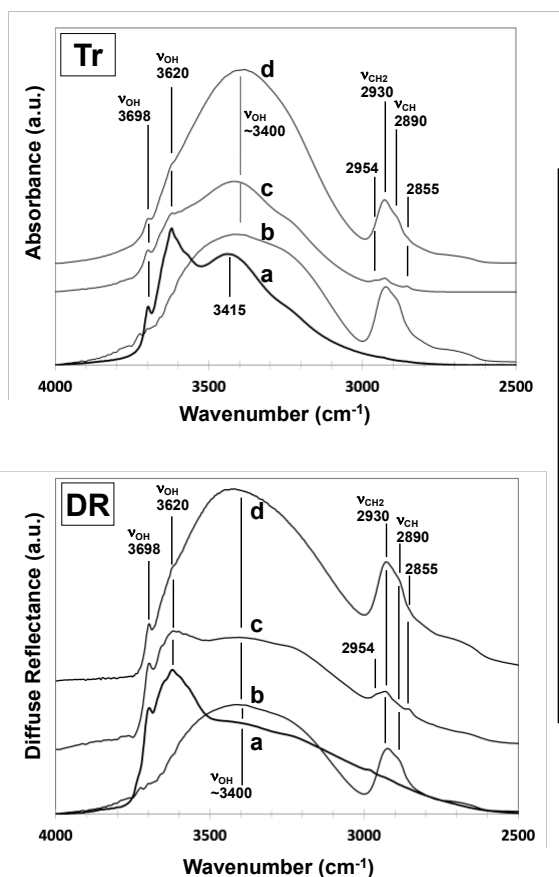
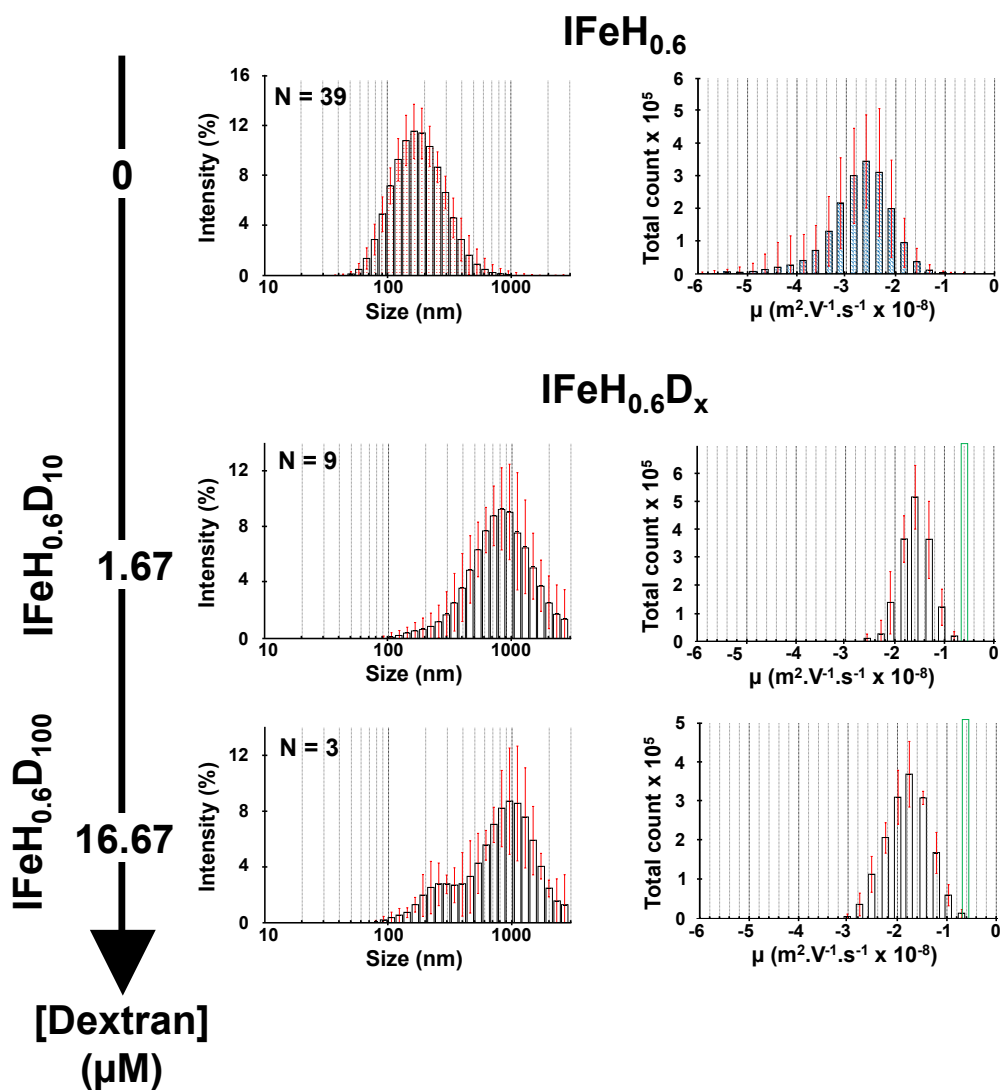


Figure 6: Fourier-transform infrared spectra of illite-dextran aggregates ID_x . (above) Transmission mode (Tr) and (below) Diffuse Reflectance mode (DR) spectra: illite (a), dextran (b), illite-dextran aggregates ID_{10} (c) and ID_{100} (d). Spectra have been corrected by the baseline of the device. An adjustment of the signal intensity has been made for their better visualization and qualitative interpretation.

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Figure 7: Illite-Fe (hydr)oxide-dextran aggregates. Size distribution (nm) (red histogram) and electrophoretic mobility μ ($\text{m}^2 \text{V}^{-1} \text{s}^{-1} \times 10^{-8}$) (blue histogram) of illite particles for initial Fe/illite ratios $R = 0.6$ and two different initial concentrations of dextran (1.67 and $16.67 \mu\text{mol L}^{-1}$) (N : number of replicates). $[\text{Fe}(\text{NO}_3)_3] = 10^{-4}\text{M}$; $[\text{KOH}] = 10^{-3}\text{M}$; addition rate of iron nitrate: 0.25 mL min^{-1} ; addition rate of KOH: 0.1 mL min^{-1} ; initial concentration of illite suspension: 200 mg L^{-1} , initial volume of illite suspension 100 mL . Initial concentration of $\text{CaCl}_2 = 5 \cdot 10^{-4}\text{M}$. The pH of all suspensions analysed after dialysis is 5.7 . The green line represents the electrophoretic mobility of dextran.

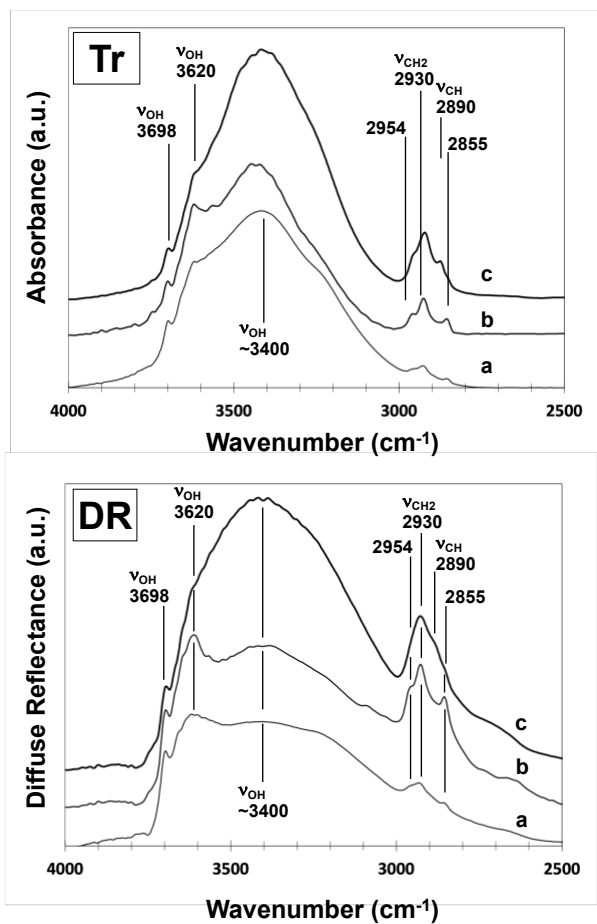
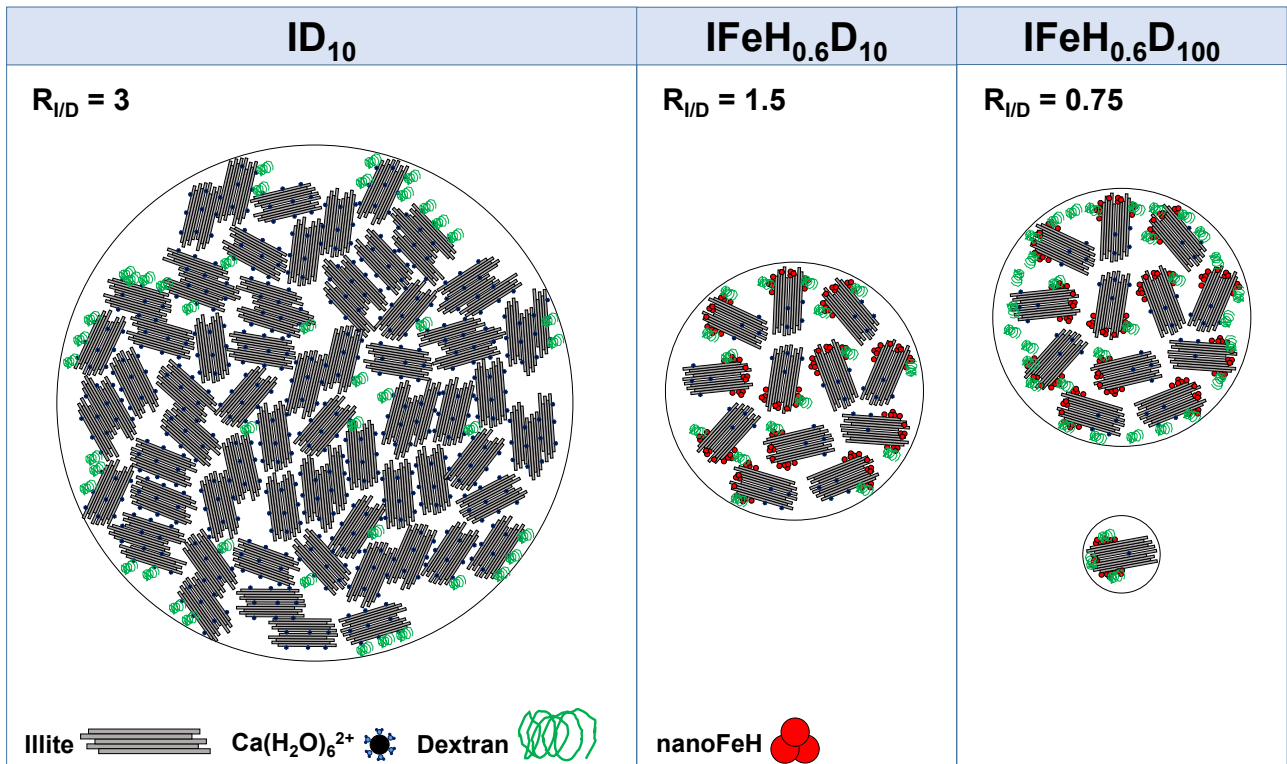


Figure 8: Fourier-Transform Infrared spectra of ternary illite-Fe (hydr)oxide-dextran aggregates IFeH_RD₁₀ – Transmission (top graph) and Diffuse Reflectance (bottom graph) spectra of ID₁₀ (a), IFeH_{0.6}D₁₀ (b), IFeH₂D₁₀ (c). Spectra have been corrected by the baseline of the device but are not normalized. An adjustment of the spectrum intensity was performed for a better visualization and qualitative interpretation.

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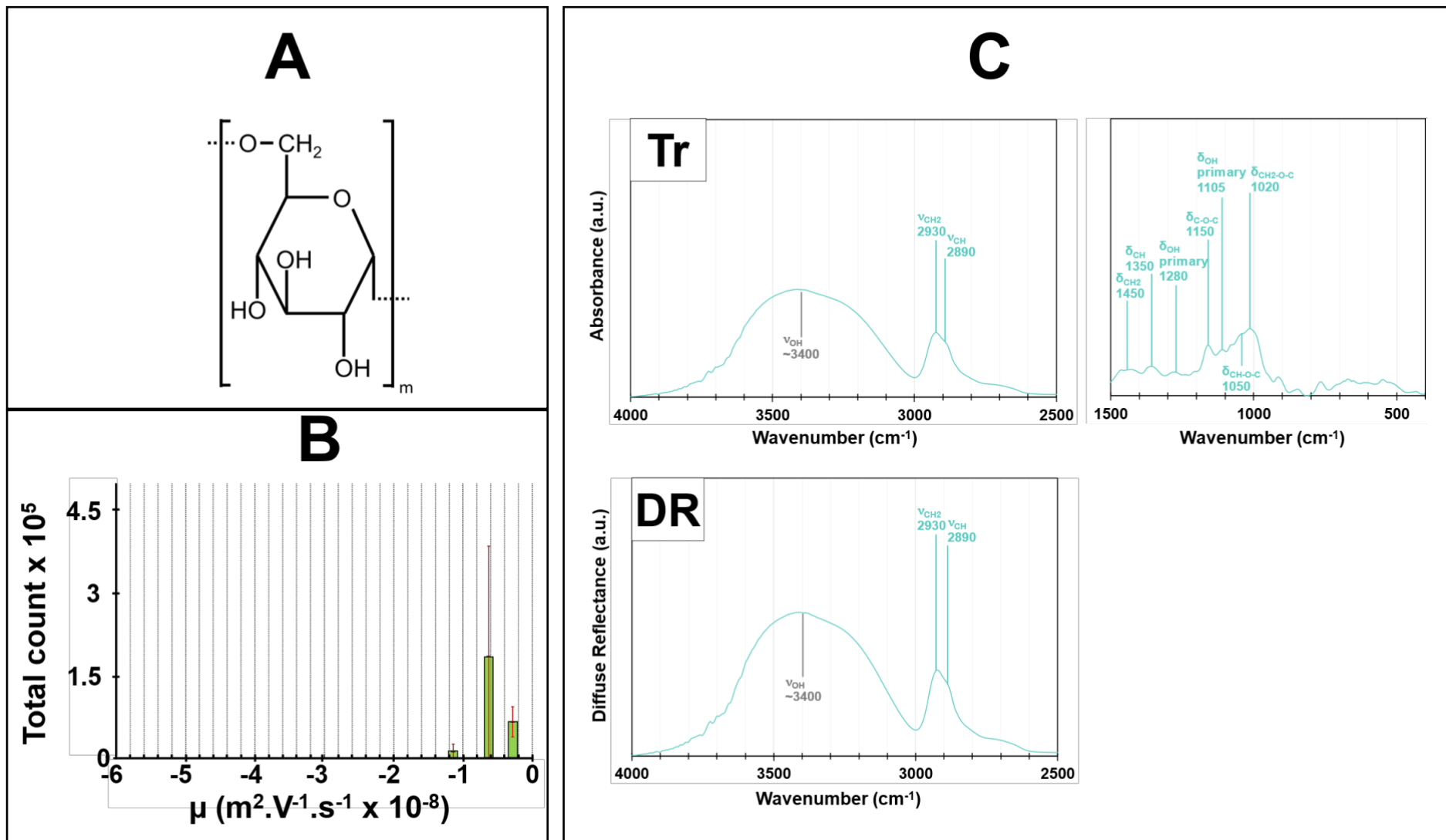


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Figure 9: Scheme of the binary illite-dextran (ID_{10}) and ternary illite-Fe (hydr)oxide-dextran ($IFeH_{0.6}D_{10}$ and $IFeH_{0.6}D_{100}$) aggregates. The illite-dextran samples ID_{10} can be represented as large aggregates with a core mainly consisted of clay minerals, flocculated by the addition of calcium ions. The large size of this aggregate can be an interpretation key of FTIR data obtained in transmission, suggesting a relatively low content of polymer associated to these aggregates. The second and third schemes present $IFeH_{0.6}D_{10}$ and $IFeH_{0.6}D_{100}$ samples. Those samples are represented as smaller aggregates. The presence of nanoFeH on illite surface limited the adsorption of Ca^{2+} on exchangeable cationic sites of clay particles and finally stabilized small size flocs. The presence of the nanoFeH also promoted the adsorption of dextran. The higher concentration of dextran led to a second population of smaller aggregates.

Supplementary Material 1: Dextran polymer, presentation and properties.

Figure SM-1: (A). Schema of Dextran unit. (B) Electrophoretic mobility μ ($\text{m}^2 \text{V}^{-1} \text{s}^{-1} \times 10^{-8}$) (green histogram) of Dextran, Dextran concentration 10 mg L^{-1} , CaCl_2 concentration $5 \cdot 10^{-4} \text{ M}$. (C) Fourier-transform infrared spectra of Dextran, transmission mode (Tr) and diffuse reflectance mode (DR) spectra. Spectra have been corrected by the baseline of the device. An adjustment of the signal intensity has been made for their better visualization and qualitative interpretation.



Supplementary Material 2: schematic presentation of the synthesis path of binary and ternary aggregates

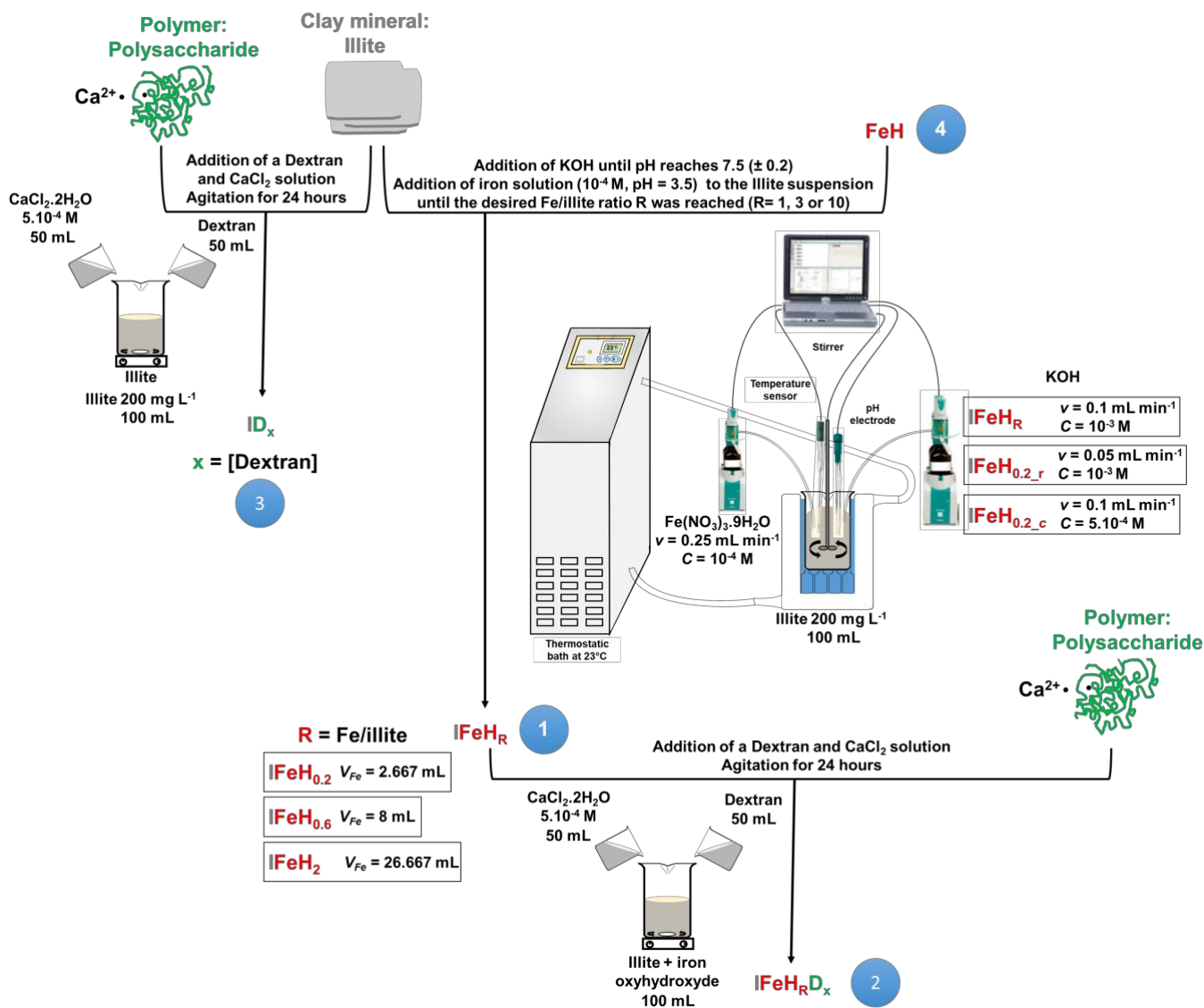


Figure SM-2: schematic presentation of synthesis protocols

1-Synthesis of Illite-Fe oxyhydroxide clay-composites IFeH_R ; iron/illite ratio R, where R = 0.2, 0.6 or 2. The main step of the synthesis of illite-iron oxyhydroxide aggregates is the alkaline hydrolysis of iron salt (iron nitrate) in the presence of illite particles and the resulting products are hereafter differentiated according to initial iron/illite ratio, denoted as R. This ratio was calculated as a function of the CEC value of illite and the amount of iron added to the clay suspension:

$$R = \frac{C_{i\text{Fe}} V_{\text{Fe ad}}}{C_i V_i \text{CEC}} \quad (1)$$

where $C_{i\text{Fe}}$ is the concentration of iron nitrate solution (10⁻⁴ M) and $V_{\text{Fe ad}}$ the added volume (2.7, 8 and 27 mL for R = 0.2, 0.6, 2 respectively). C_i (200 mg L⁻¹) and V_i (100 mL) were the Illite suspension concentration and volume, respectively. CEC (cation exchange capacity) was measured and estimated to 20 meq per 100g of illite.

Experimental conditions were selected to favour the precipitation of iron oxyhydroxide onto the clay mineral surfaces rather than in solution. The $\text{Fe}(\text{NO}_3)_3$ solution and KOH solution were simultaneously added to the Illite suspension using a Metrohm TITRANDO 809 station. Such a procedure allows reproducible synthesis conditions. Initial clay suspension displays a pH close to 6. Iron solution (10^{-4} M, pH = 3.5) was added to the Illite suspension at a rate of 0.25 mL/min until the desired Fe/illite ratio R was reached (R= 0.2, 0.6 or 2). Simultaneously, KOH was added at a rate of 0.1 mL.min⁻¹ until pH reaches 7.5 (\pm 0.2). Iron nitrate concentration was fixed to 10^{-4} mol L⁻¹, KOH solution was also diluted to slow down hydrolysis kinetics, and the concentration was set to 10^{-3} mol L⁻¹. Such pH and iron concentration conditions were expected to enhance the adsorption of either ferric cations or partially hydrolysed iron species on the cationic exchange sites of illite particles. Titration curves were performed several times (twice for IFeH_{0.2} and IFeH₂, nine times for IFeH_{0.6}), and display a good reproducibility. Additional experiments were performed at lower KOH concentration ($5 \cdot 10^{-4}$ mol L⁻¹) or with lower KOH addition rate (0.05 mL min⁻¹) to check the influence of hydrolysis conditions (two supplementary titration curves are presented as supplementary material appendix C). Subsequently, the resulting suspensions were washed to remove salts in excess by dialysis (Spectra/Por® Membrane MWCO 1 kD) until the suspension conductivity was close to that of ultrapure water (<10 $\mu\text{S} \cdot \text{cm}^{-1}$). All rinsed precipitates were freeze-dried and stored at 20° C prior to analyses.

2-Preparation of aggregates Illite-Iron oxyhydroxide-Dextran referred to as IFeH_RD_x. The IFeH_RD_x aggregates were prepared by addition of 50 mL of Dextran solution ($x = 10$ or 100 mg L⁻¹) and 50 mL of $5 \cdot 10^{-4}$ M $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ solution in IFeH_R suspension. The mixture was stirred for 24 hours and repeatedly dialysed (Spectra/Por® Membrane MWCO 1 kD) until the suspension conductivity was close to that of ultrapure water (<10 $\mu\text{S} \cdot \text{cm}^{-1}$). Such a preparation procedure was selected in order to obtain aggregates displaying the three constituents, i.e., illite, iron oxyhydroxides and organic polymer. Indeed, other procedures were tested, and we could observe that when adding Dextran and Calcium solutions to illite suspension prior performing iron hydrolysis, the final products do not present organic polymer in their composition.

3-Preparation of illite-Dextran aggregates (ID_x). A supplementary series of binary samples were prepared to better evidence the influence of iron oxyhydroxides on the interactions between polymer and clay particles. Binary aggregates composed of illite and Dextran polymer were prepared by adding simultaneously 50 mL of Dextran solution ($x = 10$ or 100 mg L⁻¹, i.e. 1.67 and 16.67 $\mu\text{mol} \cdot \text{L}^{-1}$ respectively) and 50 mL of $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ solution to the Illite suspension ($200 \text{mg} \cdot \text{L}^{-1}$). The mixture was stirred for 24 hours and repeatedly dialysed (Spectra/Por® Membrane MWCO 1 kD) until the suspension conductivity was close to that of ultrapure water (<10 $\mu\text{S} \cdot \text{cm}^{-1}$).

4-FeH was prepared as IFeH₂ but without illite particles in the solution. This sample was then compared to IFeH_R samples through XAS spectroscopy.

The choice of the different concentrations was based on observations from natural aquatic media. Ca concentrations in continental river waters go from few mg L⁻¹ to several 200 mg L⁻¹. $5 \cdot 10^{-4}$ M of CaCl_2 corresponds to 20 mg L⁻¹ for Ca ions. The concentration of illite suspension was set to $100 \text{mg} \cdot \text{L}^{-1}$ or $200 \text{mg} \cdot \text{L}^{-1}$. These concentrations can be compared with solid content in river waters that is few mg L⁻¹ in low flow regime and can reach 200 or 300 mg L⁻¹ during high flow regime. Dextran concentration and iron (hydr)oxide content were varied and sometimes pushed to high values that were not particularly environmentally relevant, but were used to demonstrate the interactions between the different components.

Supplementary Material 3: Preparation of illite-iron (hydr)oxide clay composites, titration curves.

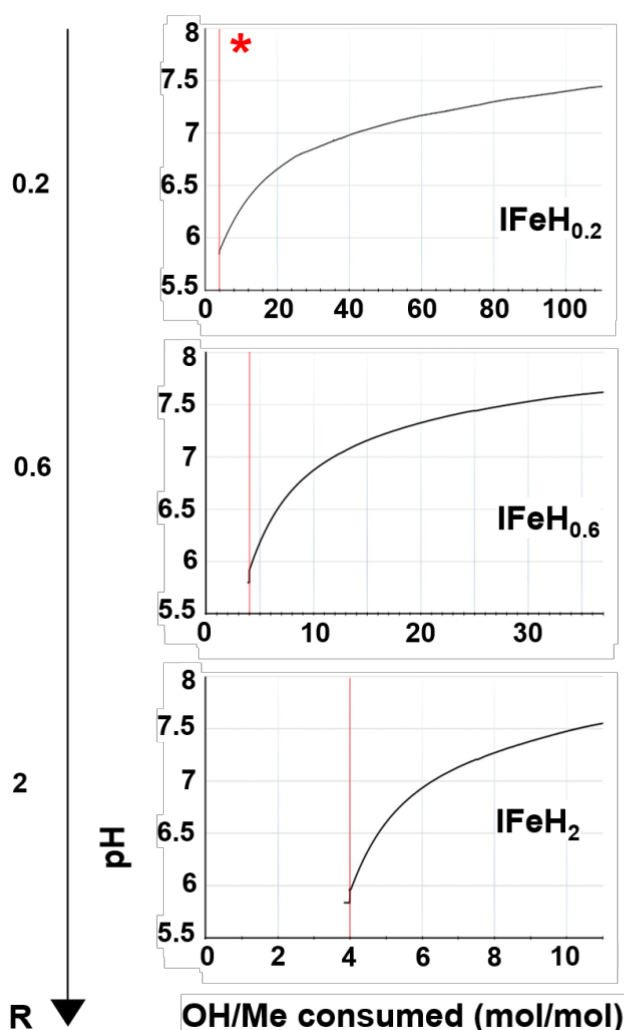


Figure SM-3: pH titration curves for three different initial Fe/illite ratios $R = 0.2, 0.6$ or 2 . Illite suspension: 200 mg L^{-1} , volume 100 mL . Initial pH value of illite suspension close to 5.7 ± 0.2 . Iron concentration in solution, $[\text{Fe}(\text{NO}_3)_3] = 10^{-4} \text{ M}$, the volume of iron solution was set to $2.7, 8$ and 27 mL for the three respective iron/illite ratios. The addition rate of iron nitrate was set to 0.25 mL min^{-1} and the KOH concentration was $[\text{KOH}] = 10^{-3} \text{ M}$, addition rate of KOH: 0.1 mL min^{-1} .

The formation of binary aggregates IFeH_R ($R = 0.2, 0.6$ or 2) was monitored via recording the evolution of the pH upon addition of $\text{Fe}(\text{NO}_3)_3$ and KOH solutions, hereafter denoted as pH titration curves. The first part of the titration curve (before the red line) corresponds to the step of Fe addition. The volume of iron solution to be added is from 2.7 to 27 mL . The higher was R , the higher was the volume of Fe solution to be added, and the longer was the time required for complete addition of Fe. In the first step of the hydrolysis, OH and Fe solution were added simultaneously. During this first step, the pH of the illite suspension slightly increased (from 5.86 to 5.88 for $\text{IFeH}_{0.2}$, from 5.8 to 5.92 for $\text{IFeH}_{0.6}$ and from 5.84 to 6.05 for IFeH_2). This increase in pH suggested that the amount of OH ligands in solution was always sufficient for the hydrolysis of iron cations to occur. As soon as the fixed volume of iron solution was added, there was a clear excess of OH in solution and the pH increased rapidly to c.a. 7.5 for all examined R conditions.

Supplementary Material 4: XANES spectra from IFeH_R samples

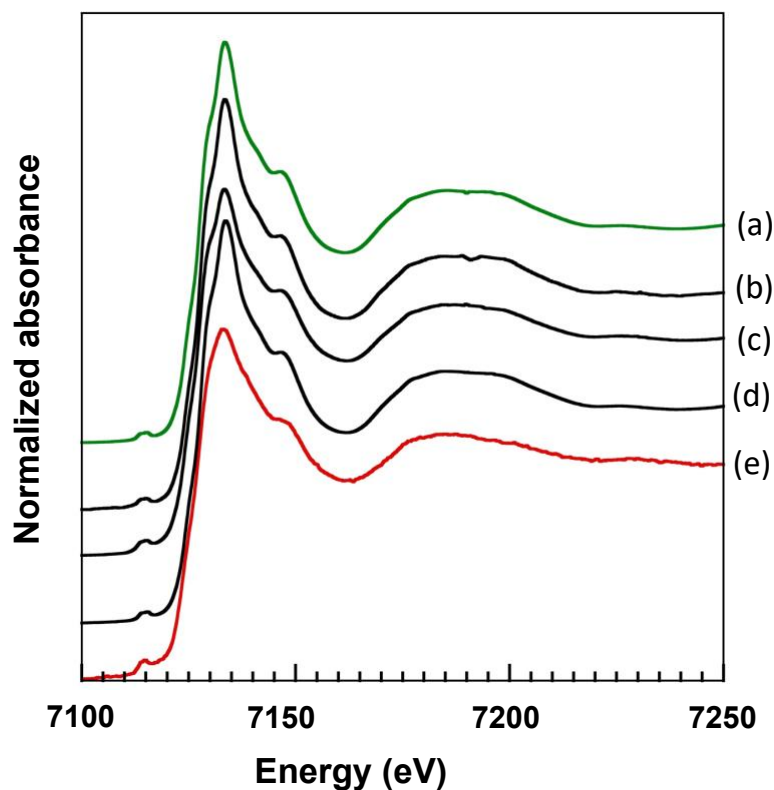


Figure SM-4: XANES spectra at Fe-K edge and from illite (a), IFeH_{0.2} (b), IFeH_{0.6} (c) IFeH₂ (d) and FeH (e). The latter sample was synthesized in the same conditions as the others but without illite particles.

The main absorption peak is relatively sharp for all illite bearing samples (curves a to d), while the FeH spectrum (curve e) displays a rather broad shape. The XANES curves of IFeHR samples are dominated by the signal of iron primarily inserted in the structure of illite (octahedral sheet). The contribution of adsorbed iron (hydr)oxide was not evidenced from these curves and no information about adsorbed iron species could be deduced.

Supplementary Material 5: TEM and HRTEM data on illite-iron oxyhydroxides composites.

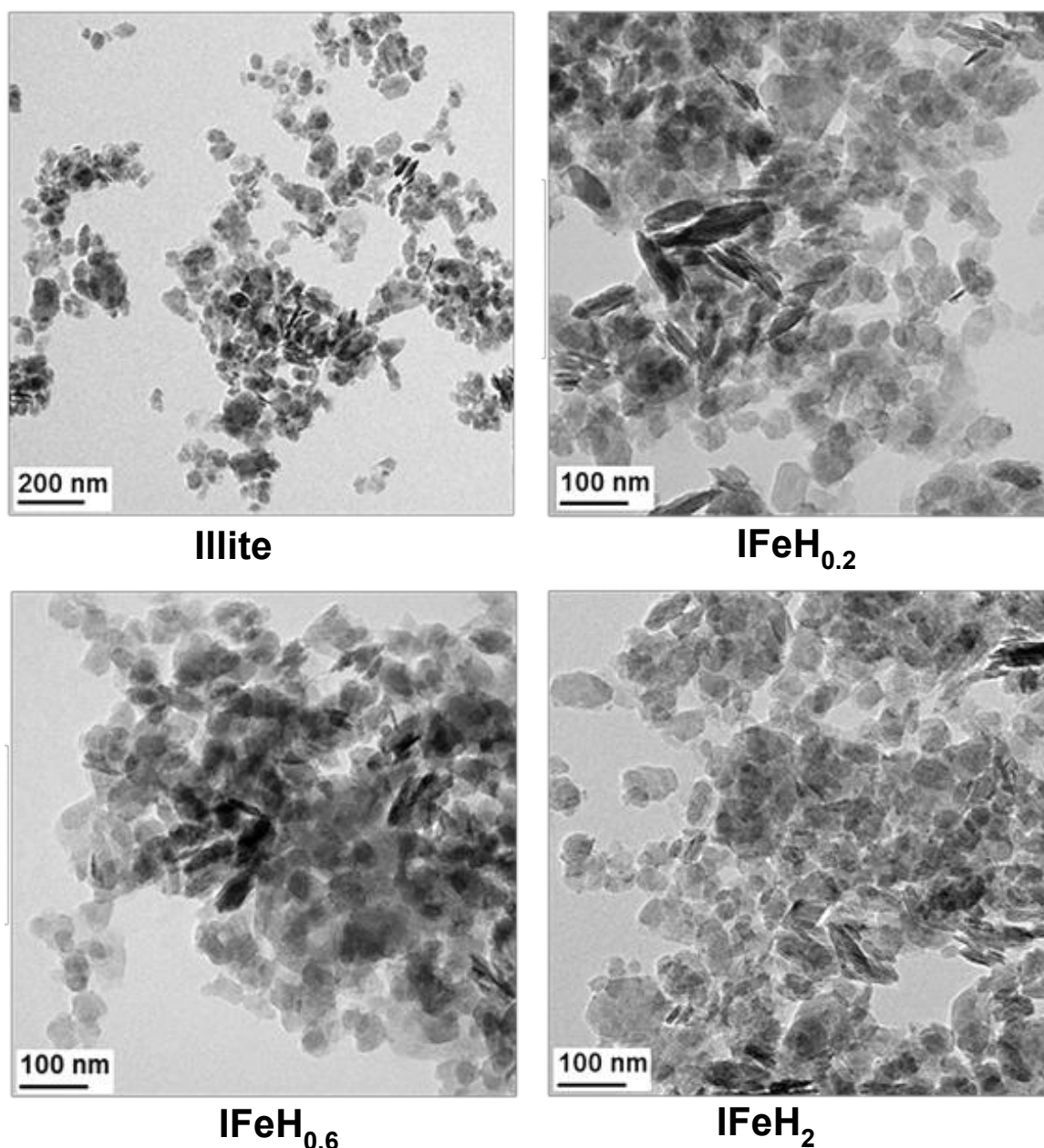


Figure SM-5: TEM micrographs obtained at low magnification for IFeH_{0.2}, IFeH_{0.6} and IFeH₂ (30k for Illite, 60k for IFeH_{0.2}, IFeH_{0.6} and for IFeH₂) of Illite,.

The TEM micrographs presented above were obtained on the ARM microscope at low magnifications (30 k for illite and 60 k for other samples IFeH_{0.2}, IFeH_{0.6} and IFeH₂). These large fields of view demonstrate the absence of individual micrometric iron (hydr)oxide phases.

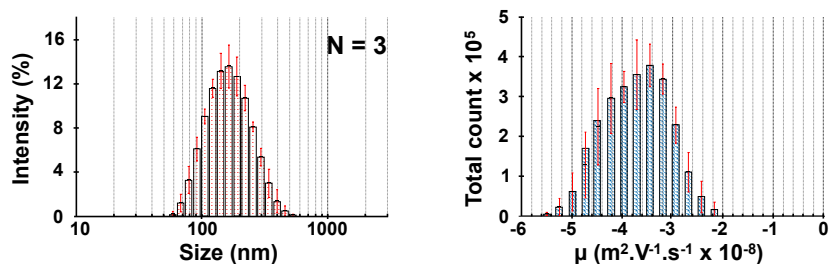
EDXS data were collected for two samples on HRTEM microscope using a nanoprobe of few nanometers (2-4 nm). The atomic percentages obtained for the different elements suggest that illite particles contributed to each EDXS spectrum. Furthermore, none of the collected spectra could evidence a large increase of iron atomic percentage. Iron/Silicium atomic ratios were calculated, and those ratios vary slightly within the 0.02-0.21 range. The lower ratios are assigned to bare illite particles.

R		0.2								
Element (%)	O	60.2	59.8	57.3	57.1	57.8	61.6	63.8	60.7	58.3
	Mg	0.3	0.3	0.3	0.6	0.5	0.7	0.4	0.2	0.6
	Al	1.9	2.4	4.2	8.4	7.0	4.3	4.3	0.6	3.3
	Si	32.0	33.2	32.7	27.3	29.3	29.5	29.5	36.3	31.5
	K	0.9	0.5	0.5	0.7	0.4	0.5	0.5	0.8	0.8
	Fe	4.6	3.7	5.0	5.6	4.6	2.5	0.7	0.8	5.2
Fe/Si		0.14	0.11	0.15	0.21	0.16	0.08	0.02	0.02	0.17
R		0.6								
Element (%)	O	58.2	57.9	60.5	56.2	59.4	60.4	58.4	61.3	57.6
	Mg	1.9	2.3	3.1	2.6	1.2	2.3	2.8	3.1	0.8
	Al	8.6	7.8	9.0	6.7	11.8	10.6	4.8	7.7	5.6
	Si	25.2	25.7	22.7	24.9	22.7	23.3	28.4	23.4	26.0
	K	0.4	0.3	0.2	0.6	0.3	0.3	0.5	0.3	0.4
	Fe	2.9	1.9	2.4	2.5	1.6	1.5	3.9	2.2	2.6
Fe/Si		0.12	0.08	0.11	0.10	0.07	0.06	0.14	0.10	0.10

Table SM-5: Energy-Dispersive X-ray Spectroscopy (EDXS)-based elemental analysis expressed in percentage (O: Oxygen, Mg: Magnesium, Al: Aluminium, Si: Silicon, K: Potassium, Fe: iron) and ratio Fe/Si of $\text{IFeH}_{0.2}$ and $\text{IFeH}_{0.6}$ (eight analyses each).

Supplementary material 6: Influence of calcium on illite particle aggregation.

Illite (R = 0)



Illite + Ca²⁺ 5 x 10⁻⁴M

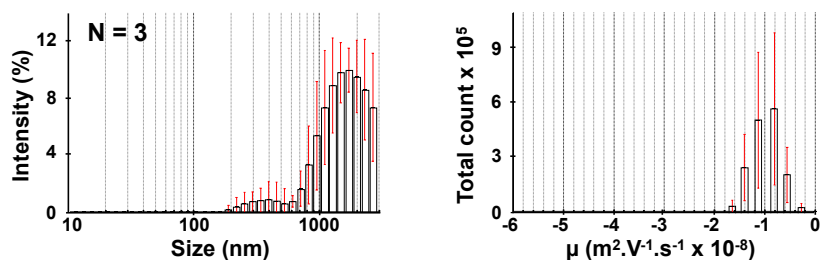


Figure SM-6: Illite-Ca aggregates. Size distribution (nm) (red curve) and electrophoretic mobility μ ($m^2 V^{-1} s^{-1} \times 10^{-8}$) (blue curve) of illite particles with and without calcium in solution (N : number of replicates). Concentration of illite suspension: 200 mg L^{-1} , initial volume of illite suspension 50mL . Initial concentration of $\text{CaCl}_2 = 5 \cdot 10^{-4}\text{M}$.

CaCl_2 addition caused a clear and well-marked increase in particle size distribution (Figure SM-6). The size distribution was shifted towards higher values, with a broad band centred in $1718 \mu\text{m}$. Moreover, there was a weak contribution of smaller particles, with a broad band centred at 250 nm . The electrophoretic mobility of illite particles after CaCl_2 addition was further shifted towards lesser negative values, with a central value at $-1 \times 10^{-8} \text{ m}^2 \text{ V}^{-1} \text{ s}^{-1}$. The presence of Ca^{2+} in solution screened the repulsive interactions between negatively charged illite particles. Such an electrostatic screening was already reported in numerous publications (Jellander et al., 1988; Jiang et al., 2012; Kloster and Avena, 2015 and references therein).

Supplementary material 7: FTIR spectra of binary and ternary aggregates.

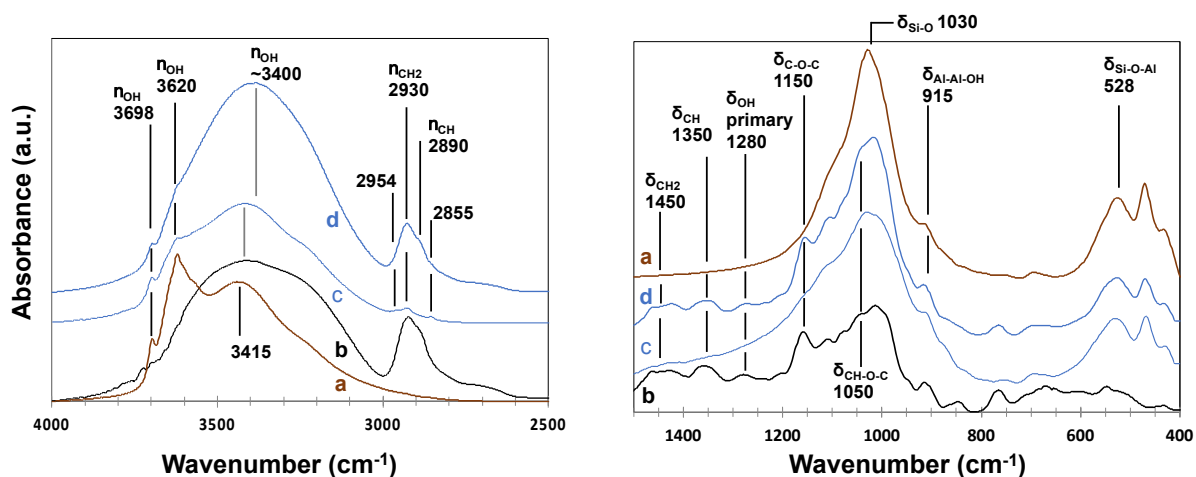


Figure SM-7A: Transmission FTIR spectra of ID_x aggregates, low wavenumber range. illite (a), dextran (b), illite-dextran aggregates ID₁₀ (c) and ID₁₀₀ (d). Spectra have been corrected by the baseline of the device. An adjustment of the signal intensity has been made for their better visualization and qualitative interpretation.

In transmission mode (Figure SM-7A), the vibration bands of illite ($\delta_{\text{Si-O}}$ 1030 cm^{-1} , $\delta_{\text{OH-Al-Al}}$ 915 cm^{-1} , $\delta_{\text{OH-Al-Fe}}$ 886 cm^{-1} , $\delta_{\text{Si-O}}$ 698 cm^{-1} , $\delta_{\text{OH-Al-Si}}$ 528 cm^{-1}) were visible for each of the samples tested and so were the bands corresponding to Dextran (ν_{CH_2} 2930 and δ_{CH_2} 1450 cm^{-1} , ν_{CH} 2890 and δ_{CH} 1350 cm^{-1} , δ_{OH} 1280 and 1105 cm^{-1} , $\delta_{\text{C-O-C}}$ 1150 cm^{-1} , $\delta_{\text{CH}_2\text{-O-C}}$ 1050 cm^{-1} , $\delta_{\text{CH-O-C}}$ 1020 cm^{-1}). The intensity of the bands assigned to Dextran was low for ID₁₀ sample and Dextran signature in the 1500-1000 cm^{-1} wavenumber range was hardly detected. With increasing Dextran concentration (ID₁₀₀), Dextran vibration bands increase in intensity, in line with expectation. Transmission FTIR spectra thus clearly show a strong increase in Dextran content of the formed aggregates from ID₁₀ to ID₁₀₀ samples. To quantify the Illite/Dextran ratio, we calculated the ratios of intensity bands respectively centred at 3698 and 2930 cm^{-1} . This ratio decreases from 3.05 to 0.71 for ID₁₀ and ID₁₀₀.

The stretching vibration bands of alkyl groups (ν_{CH_2} and ν_{CH} , 3000-2800 cm^{-1}) for pure Dextran are clearly modified for ID₁₀ sample. Indeed, for ID₁₀, the contributions of these stretching vibrations are clearly separated whereas pure Dextran displays a broad band centred at 2930 cm^{-1} and a shoulder at 2890 cm^{-1} . Such modifications of Dextran signal likely originate from its interactions with illite surface (through Ca^{2+} bridges). However, for ID₁₀₀ the aforementioned splitting of the ν_{CH} and ν_{CH_2} bands is no longer observed, and the Dextran signal is basically similar to that of pure Dextran. This observation was further confirmed upon inspection of the spectra in the low wavenumber range. We concluded that at such high Dextran concentrations, most the polymer chains do not interact with the illite surfaces and that bulk Dextran phase arises in the aggregate.

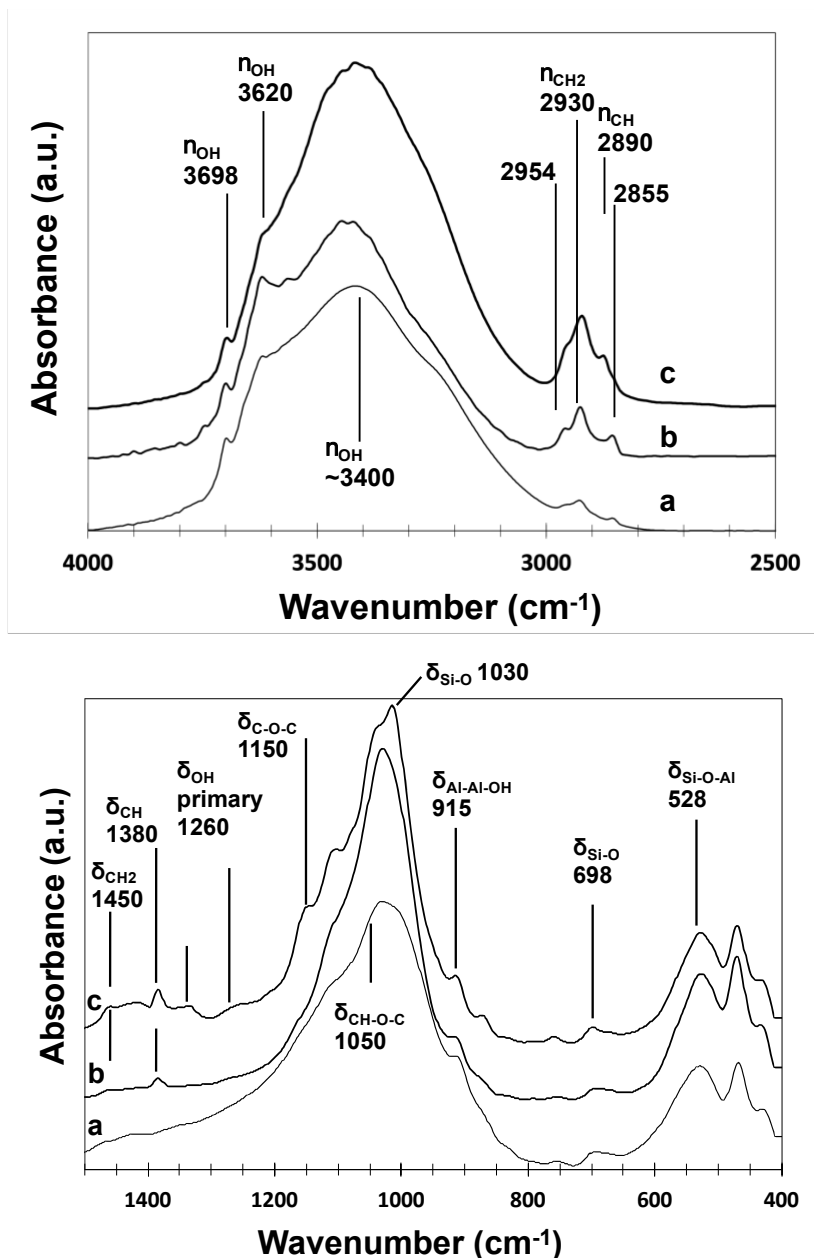


Figure SM-7B: Transmission FTIR spectra of ternary illite-Fe (hydr)oxide-dextran aggregates $IFeH_{0.6}D_{10}$ (b), $IFeH_2D_{10}$ (c) and ID_{10} (a). Spectra have been corrected by the baseline of the device but are not normalized. An adjustment (translation) of the signals was performed for a better visualization and qualitative interpretation.

Figure SM7-B presents the transmission FTIR spectra collected for ID_{10} and $IFeH_RD_{10}$ samples (Figure 9A, top graphs), all prepared with a Dextran concentration set at 10 mg L^{-1} . Those spectra reveal the vibration bands of Illite (ν_{OH} 3698 and 3620 cm^{-1} , δ_{Si-O} 1030 cm^{-1} , δ_{O-H-Al} 915 cm^{-1} , $\delta_{OH-Al-Fe}$ 886 cm^{-1} , δ_{Si-O} 698 cm^{-1} , $\delta_{Si-O-Al}$ 528 cm^{-1}) and Dextran in the stretching domain (ν_{CH_2} 2930 cm^{-1} and ν_{CH} 2890 cm^{-1}). In the spectral domain corresponding to molecular bending (from 1500 to 1000 cm^{-1}), the presence of Dextran is hardly detected for $IFeH_{0.6}D_{10}$, with a single peak at 1373 cm^{-1} that could be assigned to δ_{CH} . With increasing iron content ($IFeH_2D_{10}$, Figure 9A curve c), the vibration bands of Illite (ν_{OH} 3620 cm^{-1} and δ_{Si-O} 1030 cm^{-1}) become less visible while vibration bands of Dextran are more intense. Moreover, the sample $IFeH_2D_{10}$ exhibits a higher amount of water than in $IFeH_{0.6}D_{10}$, as judged by the broad and intense stretching band of OH centred at 3400 cm^{-1} . This higher amount of water Dextran in the sample relates to the higher content of Dextran. For the three samples analysed, the stretching vibration bands of alkyl groups (3000 - 2800 cm^{-1} range) appear in the form of separated bands, centred at 2954 , 2930 and 2890 cm^{-1} . However, the splitting of these signatures is as

pronounced as that identified for IFeH_{0.6}D₁₀. To quantify the influence of nanoFeH on Dextran adsorption, intensities ratios were calculated. The intensity ratio I_{3698}/I_{2930} compares the contribution of both illite, and Dextran signal and this ratio decreases from ID₁₀ to IFeH_{0.6}D₁₀ and IFeH₂D₁₀, with the respective values 3.05, 1.49 and 0.77.

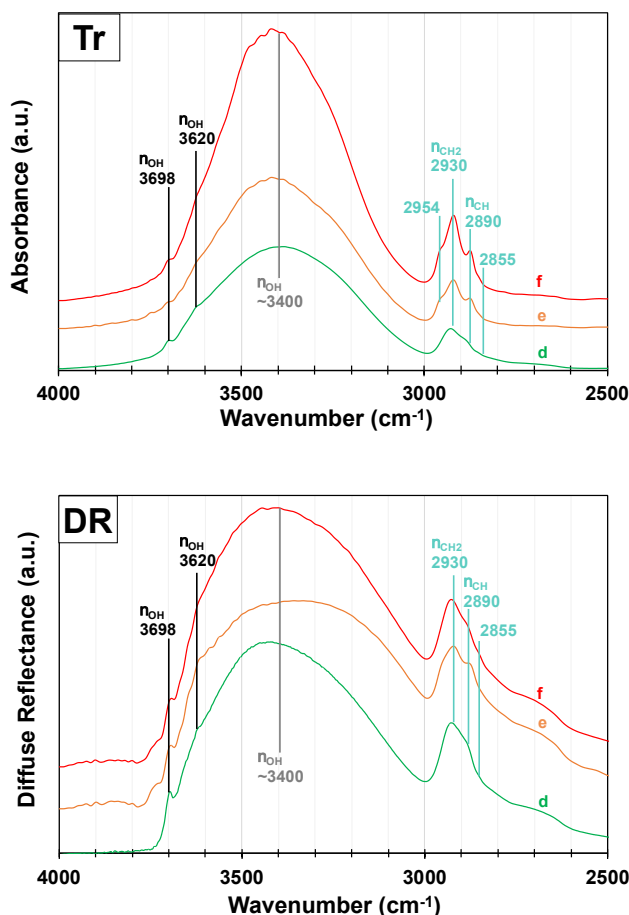


Figure SM-7C: Fourier-Transform Infrared spectra of ternary illite-Fe (hydr)oxide-dextran aggregates IFeH_RD₁₀₀ –Transmission (top graph) and Diffuse Reflectance (bottom graph) spectra of ID₁₀₀ (d), IFeH_{0.6}D₁₀₀ (e), IFeH₂D₁₀₀ (f). Spectra have been corrected by the baseline of the device but are not normalized. An adjustment (translation) of the signals was performed for a better visualization and qualitative interpretation.

Figure SM-7C presents FTIR spectra for the samples prepared with a higher concentration of Dextran (100 mg/L). In transmission mode (top graph), the vibrations of illite OH groups were hardly detected and the intensity ratio I_{3698}/I_{2930} reflecting the respective contributions of illite and Dextran signals basically decreased if compared to that for the previous series of aggregates prepared with 10 mg/L Dextran: this ratio was further slightly decreasing from ID₁₀₀ to IFeH_{0.6}D₁₀₀ and IFeH₂D₁₀₀, with the respective values 0.71, 0.57 and 0.5.

In addition, in transmission mode the vibration bands of Dextran in the stretching region were split for IFeH_{0.6}D₁₀₀ and IFeH₂D₁₀₀. This splitting demonstrates that OH groups of the polymer are constrained through interactions with illite surface and/or nanoFeH entities. This splitting was not observed for ID₁₀₀ and disappeared in Diffuse Reflectance mode for all IFeH_RD₁₀₀ samples. Moreover, the Diffuse Reflectance spectra evidenced the fading away of illite signal, replaced by Dextran and associated water (bottom graph). At sufficiently high polymer concentrations (100 mg L⁻¹), iron

particles appear to have no influence on the adsorption and on the organization of Dextran within the aggregates, suggesting that the nano-Fe adsorption sites for Dextran are saturated. The above diffuse reflectance observations evidenced that the contribution of illite entities to FTIR signal was significantly screened due to enhanced adsorbed amount of Dextran. These observations also indicated that the higher the Dextran content was, the lower became the fraction of Dextran chains interacting with the mineral surfaces.