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Surface modifications at the oxide/water interface: implications for Cu binding, solution chemistry and chemical stability of iron oxide nanoparticles

Edwige Demangeat^a, Mathieu Pédrot^{a,*}, Aline Dia^a, Martine Bouhnik-Le-Coz^a, Mélanie Davranche^a
and Francisco Cabello-Hurtado^b

^a Univ. Rennes, CNRS, Géosciences Rennes - UMR 6118, 35000 Rennes, France

^b Univ. Rennes, CNRS, Ecobio - UMR 6553, 35000 Rennes, France

Abstract

The oxidation of magnetite into maghemite and its coating by natural organic constituents are common changes that affect the reactivity of iron oxide nanoparticles (IONP) in aqueous environments. Certain ubiquitous compounds such as humic acids (HA) and phosphatidylcholine (PC), displaying a high affinity for both copper (Cu) and IONP, could play a critical role in the interactions involved between both compounds. The adsorption of Cu onto four different IONP was studied: magnetite nanoparticles (magnNP), maghemite NP (maghNP), HA- and PC-coated magnetite NP (HA-magnNP and PC-magnNP, respectively). According to the results, the percentage of adsorbed Cu increases with increasing pH, irrespective of the IONP. Thus, protonation/deprotonation reactions are likely involved within Cu adsorption mechanism. Contrary to the other studied IONP, HA-magnNP favor Cu adsorption at most of the pH tested including acidic pH (pH = 3), suggesting that part of the active surface sites for Cu²⁺ were not grabbed by protons. The Freundlich adsorption isotherm of HA-magnNP provides the highest sorption constant K_F (bonding energy) and n value which supports a heterogeneous sorption process. The heterogeneous adsorption between HA-magnNP and Cu²⁺ can be explained by both the diversity of the binding sites HA procured and the formation of multidendate complexes between Cu²⁺ and some of the HA functional groups. Such favorable adsorption process was neither observed on PC-coated-magnNP nor on maghNP, whose behaviors were comparable to that of magnNP. On another hand, HA and PC coatings considerably reduced iron (Fe) dissolution from magnNP as compared with magnNP. It was suggested that HA and PC coatings either provided efficient shield against Fe leaching or fostered dissolved Fe re-adsorption onto the functional groups at the coated magnNP surfaces. Thus, this study can help to better understand

30 the complex interfacial reactions between cations-organic matter-colloidal surfaces which are
31 relevant in environmental and agricultural contexts.

32 This work showed that magnetite NP properties can be affected by surface modifications, which
33 drive NP chemical stability and Cu adsorption, thereby affecting the global water chemistry.

34 **Keywords:** *magnetite oxidation, surface coating, humic acid, phosphatidylcholine, copper*
35 *adsorption, copper speciation*

36 * Corresponding author: mathieu.pedrot@univ-rennes1.fr Phone (+33)2 23 2360 83

37 **Declarations of interest: none**

38 **1. Introduction**

39 For almost two decades, engineered nanoparticles (NP), one of many nanomaterials, have been
40 revolutionary tools to human kind. Due to their nano-scale size, NP displays a high surface to
41 volume ratio which provides them with promising properties in many areas ([Gupta and Gupta,](#)
42 [2005](#), [Afkhami et al, 2010](#), [Dabrowski et al., 2004](#)). More specifically, engineered iron oxide NP
43 (IONP) display high reactivity, magnetic properties and biocompatibility that allow their use in
44 many technical applications. Examples of these uses range from medical therapies ([Wu et al.,](#)
45 [2015](#), [Karimi et al., 2013](#)), imaging and recording technologies to remediation methods and
46 agricultural practices ([Sabbatini et al., 2010](#), [Khot et al., 2012](#)). The application of iron
47 nanoparticles (IONP) for soils and water remediation, in particular, has been explored for a few
48 decades and several studies have highlighted the affinity of metals and metalloids for these
49 objects ([Wang et al., 2012](#), [Ahmed et al., 2013](#), [Pan et al., 2010](#)).

50 Sorption reactions with both organic and inorganic compounds play a key role in the
51 transport and fate of many trace elements in natural systems ([Ye et al., 2017](#)). Binding of metals
52 on oxide minerals, in particular, involves predominantly electrostatic interaction (non-specific
53 sorption) or chemical interaction (specific sorption) ([Smith, 1999](#)). According to [Hu et al.,](#)
54 [\(2006\)](#), metal ion sorption onto magnetite has been shown to involve both electrostatic attraction
55 and ligand exchange at various pH conditions. In aqueous environments, IONP are amphoteric
56 solids that become charged in response to the (de)protonation reactions of the Fe-OH surface
57 sites ([Pang et al., 2007](#)). Consequently, dissolved cationic species are attracted to IONP at pH
58 values higher than their pH_{zpc} (point of zero charge), where the surfaces of the IONP are

59 negatively charged. In fact, the mechanisms responsible for IONP and metal interactions are
60 dependent upon several geochemical parameters such as pH, ionic strength, temperature and soil
61 solution chemistry including the initial metal concentration and the adsorbent (IONP)
62 concentration (Stumm, 1992; Smith, 1999). To take into account the role of these parameters and
63 describe the resulting binding mechanisms of cations (or protons) onto oxide mineral surfaces,
64 surface complexation models are implemented based on similar principles (sorption of ions
65 occurs at specific coordination sites; sorption equations are described by mass law equations;
66 sorption of ions control solid surface charge; electrostatic effects on ions binding are considered)
67 (Smith, 1999).

68 The physico-chemical properties of IONP also do play a key role in cation adsorption
69 processes (Parkinson, 2016). These intrinsic properties are likely modified when IONP are
70 released in natural environments because of the numerous transformations that IONP undergo
71 and the interactions that occur with natural constituents and living organisms (Joo and Zhao,
72 2017, Amde et al., 2017). Phase transformations, affecting the whole mineral structure, can stem
73 from dissolution, precipitation, oxidation-reduction reactions, photochemical transformations or
74 other internal structural changes (Tang and Lo, 2013, Löhr et al., 2017). In addition, co-
75 precipitation, sorption and certain biotransformations can also affect the interactions occurring at
76 the surfaces of the IONP and thus modify their reactivity as well as the behavior of some
77 constituents, such as metal speciation (Nowack and Bucheli, 2007).

78 Once released into the ecosystems, IONP may be coated with organic substances due to
79 the pervasiveness of these compounds in natural areas (Tang et al., 2014). As part of the
80 dissolved organic matter, humic acids (HA), consist of a complex, heterogeneous arrangement of
81 high- to low-molecular weight species exhibiting different water solubilities and reactivities.
82 Hence, HA displays a high affinity for magnetite, and the adsorption of HA onto magnetite NP
83 has been proven to largely impact the physicochemical properties of iron oxides such as their
84 colloidal stability (Illés and Tombacz, 2006, Ghosh et al., 2011, Hadju et al., 2009, Grillo et al.,
85 2015, Tombacz et al., 2013, Demangeat et al., 2018) and also, their interactions with soil solution
86 species including several metals (Vindedahl et al., 2016, Davranche et al., 2013, Yu et al., 2018).
87 Indeed, HA contain metal-binding functional groups (such as carboxylates, phenols, amines,
88 thiols) with binding affinities and ligand densities that range several orders of magnitude.
89 Phospholipids, another ubiquitous family of compounds, are also commonly found in natural

90 waters. Phosphatidylcholine (PC), in particular, is a major component of living organisms and it
91 is largely employed in the agro-industry (Brown et al., 1999). Therefore, it is expected that
92 phosphatidylcholine can cover the surfaces of the IONP in surface waters and possibly, interfere
93 in the interactions between the metals and the IONP (Debnath et al., 2010). PC likely form lipid
94 bilayers onto mineral surfaces in aqueous mediums because of their amphiphilic character and
95 they can form various structures depending on the properties of these molecules (Mulder et al.,
96 2006, Giri et al., 2005). Therefore, PC coating can impact the surface structure of the IONP and
97 the ensuing interactions between the coated surface and metal ions mainly via electrostatic
98 interactions (Solis-Calero et al., 2015). In addition to surface coatings, magnetite is also
99 chemically unstable. The oxidation of magnetite NP into maghemite NP likely induces structural
100 and chemical changes which are of great concern towards contaminant interactions, including
101 metal adsorption (Frison et al., 2013, Gorski et al., 2010, Hu et al., 2005).

102 IONP interactions with metals are relevant towards many applications because of the
103 ensuing environmental and societal impacts (Kah, 2015). Many studies have focused on the
104 adsorption capacity between some IONP and certain metals with the aim to investigate the
105 potential of some new depollution means or to precise the limits of such environmental
106 applications. However, although the effects related to the properties of the medium are often
107 investigated to decipher the adsorption process itself, their impacts on the behavior and fate of
108 IONP are frequently neglected despite their relevance towards several other mechanisms (such
109 as, NP dissolution, metal co-precipitation, etc.). Besides, much interest should be given to the
110 interactions between IONP and copper (Cu) since these compounds are of increasing concern in
111 various sectors whether it is for industrial, agricultural or environmental purposes (Li et al., 2016,
112 Adrees et al., 2015). Significant quantities of iron (in the form of IONP) along with dissolved
113 copper are released into the acidic waters coming from mining wastes and acid mine drainage
114 (Mohan et al., 2006, Otero-Farina et al., 2015). Besides, the use of pesticides, fungicides,
115 wastewater irrigation and other industrial effluents (related to petroleum refining, electroplating,
116 foundries) also result in high concentrations of copper in soils and waters (Mohan et al., 2006;
117 Adrees et al., 2015). In these mediums, toxic level of Cu most often hampers sustainable
118 agriculture as well as food and health safety (Adrees et al., 2015). In this frame, several studies
119 have shown the potential of IONP to remove Cu^{2+} from aqueous solutions as well as the effects
120 of HA coating onto magnetite nanoparticles reactivity (Christl and Kretzschmar, 2001; Liu et al.,

121 [2008](#)). However, the impacts of IONP/Cu interactions on the nanoparticle stability and on the
122 solution chemistry (especially Cu speciation) still raise a number of questions that are rarely
123 tackled.

124 In the present study, the adsorption capacity of four different IONP was investigated
125 using increasing amounts of Cu. The IONP included magnetite NP (magnNP), its oxidized form
126 maghemite (maghNP), magnetite NP coated with humic acid (HA-magnNP) and magnetite NP
127 coated with phosphatidylcholine (PC-magnNP). Thus, the scenario tested in this study is intended
128 to: (i) identify the physico-chemical modifications induced by oxidation and by two different
129 surface coatings on magnNP, (ii) decipher how these modifications are involved regards to
130 magnNP chemical stability (dissolution rate), (iii) and how they can drive Cu adsorption at the
131 surface of the IONP, and, (iv) provide insights into the relationships that possibly exist between
132 IONP dissolution, IONP reactivity and their colloidal stability.

133

134 **2. Materials and methods**

135

2.1. IONP

136

2.1.1. Synthesis procedures

137 **Magnetite** (Fe_3O_4) NP were synthesized following the method of [Khalafalla and Reimers \(1980\)](#)
138 [and Massart \(1981\)](#) using $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ and $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ salts.

139 **Maghemite** ($\gamma\text{-Fe}_2\text{O}_3$) NP were prepared based on the method of [Zasonska et al. \(2016\)](#), by
140 oxidizing the magnetite nanoparticles.

141 **Coatings of magnetite** NP were performed using HA (Elliott Soil Humic Acid Standard IV -
142 IHSS) and PC (1, 2-bis (10, 12-tricosadiynoyl)-sn-glycero-3-phosphocholine – Avanti Polar
143 Lipid, CAS Registry Number: 76078-28-9).

144 A precise description of the synthesis procedures of IONP is located in the Supporting
145 Information file (**SI-A**).

146

2.1.2. Characterization

147 **High Resolution Transmission Electron Microscopy** (HR-TEM) was conducted with a
148 JEOL2100F electron microscope (voltage 200 kV) magnNP, maghNP, HA-magnNP and PC-
149 magnNP.

150 **Multipoint N₂-Brunauer Emmett Teller (BET)** technique was carried out on magnNP and
151 maghNP using a Coulter (SA 3100) analyzer to measure the surface area of the IONP. BET
152 analyses were not performed on HA- and PC- magnNP because the coated molecules were shown
153 to contain highly narrow microporosity, which adsorbs no N₂ at 77K (Liu et al., 2008, Fu et al.,
154 2015).

155 **Attenuated Total Reflectance-Fourier Transform InfraRed (ATR-FTIR)** was performed on
156 magnNP, maghNP, HA-magnNP and PC-magnNP samples in the 650 - 3700 cm⁻¹ region using
157 an IS50 Nicolet spectrometer.

158
159 **Fe(II)/Fe(III) ratio** of magnNP and maghNP were determined by the measure of dissolved Fe(II)
160 and Fe(III) concentrations, after acid digestion, using the 1.10 phenanthroline colorimetric
161 method (AFNOR NF T90-017) (Komadel and Stucki, 1988).

162 The pH-dependent **surface charge (pH_{zpc})** of magnetite was determined by potentiometric acid-
163 base titration using a self-developed titration system with two titrators (794 Basic Titrino -
164 Metrohm).

165 More information about these characterization techniques can be found in the SI file (SI-A).

166 **2.2. Batch reactions**

167 The adsorption experiments investigated the affinity of copper (Cu) for bare magnetite NP
168 (magnNP), HA coated magnetite NP (HA-magnNP), PC coated magnetite NP (PC-magnNP) and
169 maghemite NP (maghNP). Three experiments were conducted to investigate: (i) the Cu
170 adsorption kinetics, (ii) the effect of pH on the Cu adsorption capacity and (iii) the Cu adsorption
171 capacity for the four IONP studied.

172 **2.2.1. Experimental set-up**

173 Copper adsorption kinetic experiments were conducted to determine the equilibration time
174 prior to the Cu adsorption experiments, performed at different pH values and variable Cu

175 concentrations. The kinetic experiments were performed in triplicate for each IONP in a $0.5 \pm$
176 0.05 g L^{-1} solution (400 mL) at $\text{pH} = 6$ with constant $\text{Cu} = 0.05 \text{ mM}$. The solutions were shaken
177 for 48 h and for each replicate, 10 samples were collected through time. The accurate total Cu
178 and IONP concentrations were controlled for each experiment. Major- and trace-element
179 concentrations were determined by ICP-MS (Agilent 7700x) as described in [Demangeat et al.](#)
180 [\(2018\)](#) and using SLRS-5 geostandard ([Yéghicheyan et al., 2013](#)). Other aliquots were filtered
181 using ultrafiltration units (2 kDa, cellulose nitrate membranes) and the TE concentrations of the
182 filtrate were determined as the dissolved fractions. Thus, dissolved Cu ($< 2 \text{ kDa}$) was considered
183 as non-adsorbed Cu and dissolved Fe was monitored to highlight possible Fe dissolution, which
184 was expected to occur at acidic pH. The results showed that equilibration was achieved within 15
185 min. All of the following experiments, which lasted several hours, were therefore performed at
186 equilibrium.

187 To investigate the effect of pH on the Cu adsorption capacity of the IONP, the initial Cu
188 concentration was set at 0.05 mM by diluting a 250 mg L^{-1} Cu stock solution in tubes containing
189 20 mL of 0.5 g L^{-1} IONP suspension. The pH was adjusted using 0.1 M NaOH or HCl to reach
190 the targeted pH (pH 3, 4, 5, 6 and 7). In the last experiment, Cu was added to 20 mL of 0.5 g L^{-1}
191 IONP suspension in appropriate amounts to obtain concentrations of $\text{Cu} = 0.5 \text{ mM}$, $\text{Cu} = 0.1 \text{ mM}$,
192 $\text{Cu} = 0.05 \text{ mM}$, $\text{Cu} = 0.01 \text{ mM}$ and $\text{Cu} = 0.005 \text{ mM}$. The pH was adjusted to $\text{pH} = 6 \pm 0.1$ using
193 0.1 M NaOH . Experiments were performed in triplicate for each IONP. After shaking under
194 anaerobic conditions for 18 h, each sample was split into two aliquots to perform the total and
195 dissolved ICP-MS analyses, as previously described.

196 **2.2.2. Adsorption studies**

197 The amount of adsorbed Cu on the four investigated IONP was calculated according to
198 the following equation:

$$199 \text{ Removal efficiency (\%)} = C_0 - C_e / C_0 * 100 \quad (1)$$

200 where C_0 (mg L^{-1}) and C_e (mg L^{-1}) are the initial dissolved Cu concentrations and dissolved
201 concentrations of metal ions after adsorption, respectively. The equilibrium adsorption capacity,
202 Q_e (mg g^{-1}) represents the adsorbed Cu per g of IONP and was calculated using the following
203 mass balance equation:

204 $Q_e = (C_0 - C_e)V/m$ (2)

205 where V (L) is the sample volume, and m (g) is the mass of adsorbent.

206 To parameterize the adsorption behavior of Cu^{2+} onto the IONP, the Langmuir and
207 Freundlich isotherms were employed. Several mathematical models exist to describe the
208 adsorption of molecules and diverse materials onto solid surfaces, and the choice depends on the
209 characteristics of the studied system (Sheng et al., 2010). Langmuir and Freundlich models are
210 commonly used to describe metal ion adsorption equilibrium onto mineral surfaces (Sheng et al.,
211 2010, Panneerselvam et al., 2011, Mamindy-Pajany et al., 2011). The Langmuir model is adapted
212 to describe dynamic equilibrium adsorption processes, assuming that uptake of metal ions occurs
213 on a homogeneous surface by monolayer adsorption and that no interaction exists between the
214 sorbed species. The Langmuir equation is expressed as:

215 $C_e/Q_e = 1/(Q^\circ \cdot b) + C_e/Q^\circ$ (3)

216 where C_e is the concentration of the solute at equilibrium (mg L^{-1}), Q_e is the mass of the
217 contaminant adsorbed per unit weight of the adsorbent (mg g^{-1}), Q° (mg g^{-1}) and b (L mg^{-1}) are
218 constants related to the adsorption capacity and energy of adsorption, respectively.

219 The Freundlich isotherm describes non-ideal and reversible adsorption. It is commonly used for
220 adsorbents having irregular surface or for single solute systems within a define concentration
221 range (Shaker and Albishri, 2014). The model assumes multilayer adsorption, meaning that
222 different adsorption sites with different adsorption energy exist at the surface of the solid,
223 characterized by non-uniform distribution of adsorption heat and affinities over a heterogeneous
224 surface (Sigg et al, 2011). The Freundlich isotherm is represented as follows:

225 $Q_e = K_F \times [C_e]^{1/n}$ (4)

226 where C_e is the concentration of the solute at equilibrium (mg L^{-1}), Q_e is the mass of the
227 contaminant adsorbed per unit weight of the adsorbent (mg g^{-1}), K_F and n are Freundlich
228 constants which relate to the adsorption capacity and to the degree of dependence of adsorption at
229 equilibrium concentration, respectively. When it is expressed in the logarithmic form, Equation
230 (4) gives:

231 $\log Q_e = \log K_F + (1/n) \log C_e$ (5)

232 The adsorption data were plotted according to Equation (3) (Langmuir model) and (5)
233 (Freundlich model) using the Cu concentrations obtained in triplicates in the last experiment. The
234 adsorbent concentrations in the solutions were equal to 0.5 g L^{-1} and the pH was adjusted to pH =
235 6.

236 **2.3. Cu speciation**

237 Copper speciation in the presence of IONP was investigated using Visual Minteq 3.1. In
238 particular, the concentration of the different Cu species was calculated relative to the pH in our
239 experimental conditions (21 °C, 0.005 M NaCl). The model considered the presence of IONP
240 (0.5 g L^{-1}) including the properties of IONP determined from the BET analyses and
241 potentiometric titration (i.e. number of adsorption sites, pK_{a1} and pK_{a2}). From the potentiometric
242 titration experiment conducted at NaCl = 0.005 M, we calculated $\text{pK}_{a1}=4.6$ and $\text{pK}_{a2}=7.8$ for
243 magnNP. For maghNP, $\text{pK}_{a1}=5.4$ and $\text{pK}_{a2}=9.3$ were estimated from literature considering
244 maghemite nanoparticles with similar properties as those used in this study (Jarbling et al., 2005).
245 The surface site density of IONP, $N_s = 1.59 \pm 0.05$ sites per nm^2 was calculated from
246 potentiometric titration of magnNP based on the Granplot method (Jolstera et al., 2012, Cheng et
247 al., 2018). The obtained value is close to those found in previous works using the same method
248 (Jolstera et al., 2012, Cheng et al., 2018, Lucas et al., 2007). The stability constant was deduced
249 from the best fit obtained between experimental data and modelled data at $\log K=0.6$.

250 The sorption constant was fitted using the experimental datasets of the adsorption isotherm
251 experiments. The best fit was validated by the calculation of the RMSE. Calculations were
252 performed at pH values ranging from 3 to 8 to obtain the concentrations of the significant Cu
253 species (Cu^{2+} , CuOH^+ , $\text{Cu}(\text{OH})_2(\text{aq})$, $\text{Cu}(\text{OH})_3^{3-}$, $\text{Cu}_3(\text{OH})_4^{2+}$, $\text{Cu}(\text{OH})_2(\text{s})$) as well as the
254 saturation index of the possible Cu solids ($\text{Cu}(\text{OH})_2(\text{s})$, Tenorite). The adsorption of Cu onto HA-
255 magnNP and PC-magnNP was not modeled because Visual Minteq3.1 considers HA and PC as
256 additional ligands instead of surface materials.

257

258 **3. Results and discussion**

259 **3.1. Impacts of oxidation and surface coating on magnNP**

260 **3.1.1. IONP physicochemical properties**

261 **Magnetite and maghemite.** As determined from the HR-TEM analyses (**SI-B**), maghNP were
262 spherical and had a mean diameter close to 7 ± 2 nm. Although the transformation of magnNP
263 into maghNP did not show any change in size, the BET measurements highlighted an increase in
264 the surface area from 115 ± 4 m² g⁻¹ before oxidation (magnNP) to 130 ± 4 m² g⁻¹ after oxidation
265 (maghNP). It has further been demonstrated that maghemite has a disordered crystal structure in
266 which vacancies could favor cation scavenging (Frison et al., 2013, Gorski et al., 2010). On
267 another hand, the Fe(II)/Fe(III) ratio of magnNP in the adsorption experiment decreased from
268 0.38 ± 0.02 at the beginning of the experiment to 0.34 ± 0.02 after the interaction, corresponding
269 to non-stoichiometric magnetites (Schwaminger et al., 2017, Lohdia et al., 2010). The
270 Fe(II)/Fe(III) ratio is worth considering as it has an influence on the interactions with the
271 surrounding dissolved species, as Fe(II) likely facilitates the transfer of electrons (Auffan et al.,
272 2008). In a previous study, we showed that after nine days Fe(II)/Fe(III) rapidly decreased to
273 Fe(II)/Fe(III) = 0.1 in aerobic conditions due to oxidation of magnetite into maghemite
274 (Demangeat et al., 2018). In the present study, the Fe(II)/Fe(III) ratio of maghNP was measured
275 at 0.05 ± 0.02 . Besides, the pHzpc of magnNP obtained from potentiometric titration experiment
276 gave a pHzpc=6.2 whereas the pHzpc of maghNP was determined at 7.35.

277 **HA- and PC- coated magnetite.** Neither HA nor PC coatings induced any significant size
278 change, indicating that the modifications occurred at the surface of magnNP (Fu et al., 2015,
279 Koesnarjadi et al., 2015). According to the obtained infrared spectra (**SI-C**), PC- and HA-
280 magnNP have bands of pure PC and HA, respectively, as well as bare magnNP, which support
281 the successful coating of PC and HA, respectively, onto the oxide surface (Niu et al., 2011). In
282 the spectra of Fe₃O₄-PC, as observed in pure PC sample, the absorption bands at 2849 cm⁻¹ and
283 2940 cm⁻¹ were assigned to symmetric and asymmetric methylene (CH₂) and methyl (CH₃)
284 vibrations, respectively (Debnath et al., 2010). The bands at 1272 cm⁻¹, 1088 cm⁻¹, 970 cm⁻¹ and
285 820 cm⁻¹ were attributed to the presence of PO₄³⁻ group onto magnetite surface (Debnath et al.,
286 2010), and those at 1470 cm⁻¹ and 1412 cm⁻¹ were ascribed to CH₂ scissoring. The anchoring of
287 PO₄³⁻ supports the successful coating of PC on magnNP surface, most likely via chemisorption,
288 which involves the covalent binding between the phosphate groups and the hydroxyl groups of
289 magnNP (Le et al., 2014). In the spectra of HA-magnNP, the band at ~1614 cm⁻¹ was attributed
290 to the sorption of carboxylates onto the magnetite surface. This absorption band likely resulted
291 from the shift, after its binding to the FeO, of the 1709 cm⁻¹ vibration band (C=O stretch of free

292 carboxylic acid) observed in pure HA spectra. The band at 1410 cm^{-1} could be related to COO^-
293 symmetric stretch (Demirel et al., 2006). HA is likely fractionated during its adsorption to the
294 magnNP and it has been demonstrated that low molecular weight, $-\text{O}$ and $-\text{N}$ rich functional
295 groups would preferentially adsorbed onto the IONP surface. These smaller size-fractions would
296 display enhanced probability for ligand-exchange reactions (Illès and Tombacz, 2004). Indeed,
297 the binding of carboxylate with the surface hydroxyl site of iron oxide has been reported to
298 involve ligand exchange mechanism (Liu et al., 2008, Maity and Agrawal, 2007). The surface
299 chemical modifications induced by HA and PC coatings to magnNP are relevant regards to the
300 numerous interactions occurring between IONP and the solution constituents, including metal
301 ions. Indeed, if the same sites for binding HA and metals are used, the binding of HA directly on
302 mineral surface may hamper metal sorption due to the site blockage and competition. If not, the
303 binding of HA at the IONP surface can become favorable to the uptake of metals because of the
304 complexation between HA and metals.

305 **3.1.2. Chemical stability of IONP**

306 The increased Fe concentrations (dissolved Fe measurements) highlighted the preferential
307 dissolution of magnNP at acidic pH (**Table 1**). After 18 hours, dissolved Fe accounted for 1.5%
308 of the total Fe content in magnNP at $\text{pH} = 3$ and it decreased to 0.4% when the pH increased to
309 $\text{pH} = 4$. These values fall in the range of previously reported dissolved Fe concentrations in close
310 experimental conditions (Missana et al., 2009). However, the time of the experiment being much
311 shorter in our study compared with that of Missana et al. (2009), it appears that the dissolution
312 rate was much higher for the 7-nm-sized magnNP than for the 50-200 nm magnetite nanocrystals
313 of Missana's work. Previous studies have indeed highlighted that increased dissolution rate
314 preferentially occurred to smaller-sized particles (Mudunkotuwa and Grassian, 2011, Liu et al.,
315 2009). MaghNP displayed a lower amount of released Fe than magnNP, from 0.43% at $\text{pH} = 3$ to
316 0.09% at $\text{pH} = 4$. The decrease in released Fe between magnNP and maghNP stemmed from the
317 different compositions of both Fe oxides. While maghemite only contains Fe(III) in its structure,
318 magnetite (Fe_3O_4) also contains Fe(II), which is a much more soluble species than Fe(III)
319 (Jolstera et al., 2012, Maity and Agrawal, 2007). Therefore, magnetite is prone to higher Fe
320 leaching than maghemite, which has previously been observed (Jolstera et al., 2012). The
321 transformation of magnetite to maghemite stems from the solubilization of Fe(II). In our study,

322 the dissolved Fe concentrations were negligible for PC-magnNP and HA-magnNP at acidic pH,
323 suggesting that dissolution was almost ineffective at low pH values, and thus, that the
324 transformation of magnetite into maghemite was reduced in the presence of these organic
325 coatings. From these observations, we inferred that PC and HA yield comparable protecting
326 effects against IONP dissolution, probably related to the presence of an efficient barrier at the
327 surface of magnNP (Scherer and Neto, 2005, Lu et al., 2007). Nevertheless, another possibility is
328 that HA and PC surface coatings can provide binding sites to dissolved Fe (Peng et al., 2019,
329 Catrouillet et al., 2014). Re-adsorption of aqueous Fe would limit the measured total dissolved Fe
330 content, as observed from the ICP-MS measurements performed in the present study. Although
331 different modes of interaction have been proposed to explain the adsorption of HA and PC onto
332 magnNP, it is likely that several mechanisms are involved, and their relative contribution may
333 vary depending on the intrinsic properties of the organic molecules, those of magnNP and those
334 of the solution chemistry as well. In our study, the coating of magnNP by HA was performed at
335 basic condition in order to increase HA resistance to leaching. Although low pH promotes HA
336 attraction to positively charged iron oxide surface, the formation of specific surface complexes
337 onto mineral surfaces can effectively be achieved even if the oxide surfaces and the organic
338 molecules are both negatively charged (Aiken et al., 2011, Yu et al., 2018). At high pH, HA
339 exists in a rather linear or stretched structure which favors multiple sites binding with magnetite,
340 and by the same, reduce the Fe and HA leaching from HA-coated magnetite (Liu et al., 2008,
341 Grillo et al., 2015). According to Liu et al (2008), Fe and HA leaching would be negligible and
342 undergo only slight modification after 6 hours (0.03% and 1.3% respectively), 12 hours (0.07%
343 and 3.5% respectively) and 12 days (0.21% and 0.33% respectively). Results of this study were
344 based on the concentration of Fe and DOC in the supernatant obtained from the resuspension of
345 HA-coated magnetite NP in deionized water (constant pH = 6) over different periods of time. It is
346 corroborated to other studies, which showed that the leaching of HA from iron oxide is generally
347 negligible in tap waters and deionized waters (Gu et al., 1994).

348

349 **3.2. How do magnNP modifications constrain Cu adsorption?**

350 **3.2.1. Effects of pH on Cu adsorption**

351 **MagnNP.** For bare magnNP and Cu = 0.05 mM, the percentage of Cu adsorbed (Cu%
352 adsorbed) increased with the increasing pH (**Figure 1**). In compliance with the measured $pH_{zpc} =$

353 6.2, the Cu% adsorbed at $\text{pH} > \text{pH}_{\text{zpc}}$ (at pH 6 and 7) was high (almost 100% Cu adsorbed) as
354 compared to the weak Cu% adsorbed (<10% Cu adsorbed) at low pH (pH 3 and 4). At $\text{pH} >$
355 pH_{zpc} , the IONP surfaces became negatively charged resulting from deprotonation reactions. The
356 decreasing protons concentration at magnetite surface favors cation attraction and allows Cu^{2+} to
357 complex onto the FeO^- surface sites (Madden et al., 2006, Huang and Chen, 2009). According to
358 ATR-FTIR analyses performed on magnNP after Cu addition (Cu = 0.5 mM) (SI-D), the
359 adsorption of Cu onto magnNP was discernable by the vibration at 1350 cm^{-1} . This absorption
360 band was observed in the IR spectrum obtained for Cu in the solution, and in the IR spectrum of
361 magnNP/Cu at pH 5, 6, 7 and 8, whereas no absorption band was recorded at 1350 cm^{-1} in the IR
362 spectrum of bare magnNP (before Cu addition). On the contrary, the IR spectrum of magnNP/Cu
363 at pH 3.5 resembled that of magnNP before NP/Cu interaction, with no absorption band at 1350
364 cm^{-1} suggesting that no Cu was adsorbed on magnNP surface at pH 3.5. The broad band at $3150 -$
365 3400 cm^{-1} and the band at circa 1630 cm^{-1} are characteristic of, respectively, the stretching and
366 bending vibration of hydroxyl groups at the surface of magnNP (Maity and Agrawal, 2007,
367 Ahmad et al., 2012) and their intensity is clearly decreased with increasing pH as deprotonation
368 occurs and Cu^{2+} ions are adsorbed onto the surface of the adsorbent. ATR-FTIR results are
369 consistent with previous ICP-MS data, highlighting that Cu adsorption is favored at $\text{pH} \geq 5$ and
370 thus that protonation/deprotonation reaction is a major mechanism controlling Cu sorption onto
371 magnNP.

372 **MaghNP.** Cu adsorption onto maghNP followed the same trend as on magnNP, and Cu%
373 adsorbed increased with increasing pH. Therefore, magnetite and maghemite likely had similar
374 surface properties. In particular, as magnNP is not perfectly stoichiometric, it is suggested that its
375 surface is partially oxidized. Hence, fully oxidized maghemite and partially surface-oxidized-
376 magnetite displayed similar adsorption capacity for Cu. Furthermore, since no improvements in
377 Cu sorption onto maghemite were observed, the surface area increase observed after oxidation
378 did not enhance the adsorption of Cu, which was expected to increase. To address this issue,
379 Jarbling et al. (2005) proposed that the increased surface area was related to the microporous
380 surface structure of maghemite, which includes non-active surface sites. On another hand, surface
381 area determined by BET measurements was conducted at a favorable pH to form stable
382 maghemite suspension, whereas magnetite likely aggregated at the same pH. Thus, the surface
383 area of magnNP might have been lowered due to its aggregation during the measurements.

384 **PC-magnNP.** The results for PC-magnNP showed that Cu adsorption started from pH = 4
385 (4% Cu adsorbed) and reached its maximum at pH = 6 (100% Cu adsorbed), hence following the
386 same trend as for bare magnNP. In fact, PC anchoring did not modify the pH_{zpc} of magnNP in a
387 great extent as PC is electrically neutral at pH = 7. The pH-dependency of Cu adsorption onto
388 PC-magnNP may yet remain on the zwitterionic head group in PC (containing a positively
389 charged trimethylethanolammonium group and a negatively charged glycerophosphate group),
390 which likely created a dipole, impacted the surface hydration of the NP and thus the interaction
391 with Cu (Shinoda, 2016). In this frame, Cu could coordinate with the electronegative oxygen in
392 the carbonyl group deeper in the bilayer as was reported for Zn^{2+} (Alsop et al., 2016).
393 Furthermore, cation binding is expected to occur more or less close to the phosphate group (or to
394 the glycerol group) possibly depending on the size of the ion. Divalent Ca^{2+} was found to
395 coordinate and bind electrostatically with oxygen molecules on four adjacent lipid molecules,
396 whereas Mg^{2+} bound closer to the phosphate group and coordinated with water oxygens
397 (Melcrová et al., 2016). Thus, the PC coating does not necessarily represent a barrier to metal
398 cations and therefore Cu could bind to some of the PC functional groups. Nevertheless, it is still
399 difficult to specify the interaction between Cu and PC-magnNP as it is not known whether PC
400 encapsulated the whole surface of magnNP or if it formed patchy coatings around the magnNP
401 (leaving some of the magnNP surfaces lipid-free).

402 **HA-magnNP.** Copper adsorption onto magnNP coated with HA rapidly increased with
403 the increasing pH. The rapid removal capacity of Cu^{2+} by HA-magnNP shows that HA provided
404 readily accessible sorption sites to Cu^{2+} . It is believed that HA improve metal adsorption in HA-
405 coated NP by providing numerous phenolic and carboxylic groups to HA-coated NP (Illès and
406 Tombacz, 2004, Gomes de Melo et al., 2016). Besides, the surface chemical modifications
407 induced by HA coating likely lowered the pH_{zpc} of bare magnNP because of the acidic oxygen-
408 containing functional groups content (Liu et al., 2008, Gomes de Melo et al., 2016, Peng et al.,
409 2012, Chekli et al., 2013). HA pH_{zpc} is close to pH = 2.3 (Liu et al., 2008). Hence, Cu^{2+}
410 adsorption onto HA-magnNP was favored when the pH increased. Decreased pH_{zpc} resulting
411 from HA coating was shown to favor the adsorption of several metals (such as Cu(II), Cd(II),
412 Hg(II), Pb(II), Zn(II)) since HA imparted negative surface charge to IONP which increased the
413 affinity of mineral surfaces for cations over a wide pH range (Liu et al., 2008, Illès and Tombacz,
414 2004, Lin et al., 2011). On the other hand, HA likely formed a network around coated magnNP

415 which could influence the aggregation of the IONP, especially with increased time exposure, and
416 favors metal trapping and adsorption (Zhang et al., 2009, Liu et al., 2008). Hence, the adsorption
417 capacity of HA-coated magnetite is generally higher than that of magnNP and HA alone. The
418 effects of pH on HA own conformation also do play an important role in driving HA / metals
419 interactions. In fact, HA exists in a rather linear or stretched structure at high pH, which favors
420 multiple sites binding with inorganic species including Cu cations (Liu et al., 2008; Grillo et al.,
421 2015). Furthermore, results show that adsorbed Cu% to HA-magnNP was high even at acidic pH
422 (Figure 1). Hence, HA likely promoted the adsorption of Cu^{2+} to HA-magnNP through the
423 formation of strong complexes, with a covalent character, and resistant against proton exchange
424 (Kostic et al., 2011; Senesi et al., 1986). In fact, it was shown that most Cu species bind to HA by
425 forming inner-sphere complexes with the acidic functional groups in HA, although binding
426 through hydrated outer-sphere surface complexes is also expected under favorable conditions (Li
427 et al., 2015; Komy et al., 2014; Otero-Farina et al., 2015).

428

429 3.2.2. Adsorption isotherms

430 The adsorption data were fitted with the Langmuir and Freundlich adsorption equations to
431 determine the adsorption parameters and the consistency with the models. The Freundlich
432 adsorption model provided the best fit regarding the experimental results (SI-E) with higher R^2
433 obtained for the four IONP investigated. The calculated linear regression coefficients (R^2)
434 calculated from Freundlich linearized plots were higher than 0.95 suggesting a strong linear
435 relationship between $\log Q_e$ and $\log C_e$ (SI-F). The obtained K_F and n values are comparable to
436 the Freundlich parameters reported in previous studies (Kakavandi et al., 2015; Karami, 2013).
437 The K_F data highlight the highest affinity of Cu to HA-magnNP (in the following order of
438 affinity: HA-magnNP >> maghNP > PC-magnNP = magnNP). The values decreased in the range
439 usually reported for the adsorption of trace metals onto nanomaterials in aqueous solution (Vatta
440 et al., 2006). For the n parameter, the values lie between 1 and 10, indicating a favorable and
441 specific adsorption (chemisorption) of Cu to the IONP over the entire range of Cu concentration
442 investigated. In particular, the adsorption isotherm of HA-magnNP was implemented based on
443 the obtained high n value (SI-G), highlighting a high heterogeneity in the process of Cu sorption
444 to HA-magnNP (Xu et al. 2012; Li et al., 2015). Metals, including Fe and Cu, can be held to very
445 strong binding sites onto humic substances. It was already reported (Tipping, 2002) that the

446 sorption between HA and metals formed complexes with either the carboxylic and phenolic
447 groups of HA or through specific binding between metals and the N and S groups of HA.
448 Therefore, the heterogeneous adsorption between HA-magnNP and Cu can be explained by both
449 the diversity of the binding sites provided by HA and the formation of multidendate complexes
450 between Cu and some HA functional groups.

451

452 **3.2.3. Cu speciation**

453 Copper speciation was studied relative to the pH, at three Cu concentrations (Cu = 0.05
454 mM, Cu = 0.1 mM and Cu = 0.5 mM) and taking into account the leaching of Fe (**SI-H**). At the
455 lowest Cu concentration (Cu = 0.05 mM), Cu speciation displayed the same pattern with magnNP
456 and maghNP. Dissolved Cu²⁺ was the predominant species up to pH = 5. Beyond this pH, most of
457 the Cu was bound to the surface of the IONP and most of the dissolved Cu species occurred in
458 minor amounts ($< 1.10^{-5}$ mM). When the initial Cu concentration increased up to Cu = 0.5 mM,
459 Cu²⁺ was the dominant species until pH = 6.5. Copper adsorption occurred from pH 4 to 6.5. Cu
460 precipitation was expected as the pH reached 6.5, as observed in previous studies ([Hidmi and](#)
461 [Edwards, 1999](#); [Boukhalfa et al., 2007](#), [Balintova and Petrilakova, 2011](#)).

462 Several conclusions can be drawn from the speciation calculation and the present results:

- 463 • the pH edges obtained for magnetite and maghemite at Cu = 0.05 mM turned out to be
464 consistent with our results showing an increasing adsorbed Cu% with the increasing
465 pH (pH > 4);
- 466 • the decreasing adsorbed Cu%, observed with the increasing Cu concentrations, was
467 both related to the precipitation of Cu and, mostly, to the surface site saturation of
468 magnNP;
- no Cu precipitation was expected for Cu = 0.05 mM, whereas the increasing Cu
concentration up to Cu = 0.5 mM induced saturation and precipitation at pH values
above 6.5;
- modeled data displayed a good consistency with our experimental results and therefore
the use of the diffuse layer surface complexation model, along with the characteristics
of the IONP, could be used to predict Cu dynamics in the presence of IONP.

469 **3.3. Environmental implications**

470 **3.3.1. Impacts of IONP dissolution on the IONP stability and solution chemistry**

471 IONP dissolution is relevant regards to several environmental issues (Goswani et al.,
472 2017). From the nanoparticle perspective, IONP dissolution is expected to favor the formation of
473 smaller-sized IONP with new intrinsic properties as compared with pristine particles
474 (Mudunkotuwa and Grassian, 2011). Increase in the surface free energy (Guzman et al., 2006),
475 resulting from IONP size decrease, could favor the aggregation of IONP. Nevertheless, the last
476 hypothesis was not verified in our study since magnNP dissolution occurred at pH=3 and pH=4,
477 which refers to pH where magnNP are less aggregated (Figure 1). On another hand, aggregation
478 of IONP could limit their dissolution by forming larger bulk particles (thereby decreasing the
479 surface contact in between the IONP) (Mudunkotuwa and Grassian, 2011). Dissolution of IONP
480 resulting from pH decrease (proton-promoted dissolution) also induced Fe release in the solution.
481 The presence of dissolved Fe could modify the solution chemistry and influence the
482 stoichiometry, reactivity and recrystallization of magnNP in aqueous environments (Gorski et al.,
483 2010). Doing so, the release of Fe(II) induced by IONP dissolution plays a key role in a wide
484 range of biogeochemical processes (Byrne et al., 2015, Peng et al., 2018, Peng et al., 2019).
485 Fe(II) interactions with IONP are also of great concern in several environmental applications
486 such as remediation, by influencing the mobility and the redox state of heavy metals (Gorski et
487 al., 2012). Besides, IONP dissolution can also directly control TE release in the environment and
488 lead to some more interactions with aqueous Fe or other dissolved species (complexation,
489 precipitation, etc.) upon certain environmental conditions (Bhatt and Tripathi, 2011). And these
490 interactions may become more complex in the presence of other ligands such as HA (Aiken et al.,
491 2011, Pédrot et al., 2011) since HA can prevent mineral precipitation, even at high cation
492 concentration and high pH, by increasing cations adsorption (which decreased the saturation
493 index of metal).

494 **3.3.3. Is there any link in between IONP aggregation and Cu adsorption?**

495 In a previous study, we inferred that, in addition to pH, the surface area and surface
496 chemistry (HA and PC coatings) turned out to be key drivers in controlling the aggregation of
497 IONP (Demangeat et al., 2018), resulting mainly from electrostatic and combined electrosteric
498 interactions. In the present study, the observations of Cu adsorption onto IONP showed that
499 adsorption was likely dependent upon the available active sites for Cu. Nevertheless, the

500 distribution, density and surface binding geometries may vary with the morphology of the
501 aggregates (Gilbert et al., 2009). Therefore, the aggregation of IONP was expected to influence
502 Cu adsorption. By correlating aggregates' sizes, Cu adsorption and pH, no clear relationship can
503 be established between IONP aggregation and Cu adsorption capacities (Figure 1). For magnNP,
504 in particular, although adsorption experiments showed that increasing pH lead to increasing Cu
505 adsorption, the aggregation study highlighted that larger magnNP aggregates were formed at pH
506 > 5. In a previous study (Demangeat et al., 2018), the same size-distribution were observed at pH
507 3, 4 and 5 (with about 80% of magnNP being particles with diameter ≤ 100 nm) whereas, in the
508 present study, the proportion of adsorbed Cu increased when pH increased from pH 4 to pH 5.
509 Thus, the proportion of Cu is modified regardless of magnNP colloidal state. Furthermore, the
510 proportion of these small size particles (with diameter ≤ 100 nm) diminished to 65% at pH 6 and
511 7.5, the optimum pH for Cu adsorption in the present work. Hence, instead of diminishing the
512 available reactive surface, aggregation did not prevent Cu from being adsorbed onto those bigger
513 particles. We therefore hypothesized that the aggregation of IONP would rest on weak attraction
514 forces and result in the formation of loosely packed aggregates, without any loss of reactive
515 surface area.

516 Although no clear link is concluded regarding the impact of IONP colloidal behavior on
517 Cu adsorption capacity, IONP colloidal stability may still have an impact on Cu dynamics. It was
518 shown that less aggregation between IONP yielded lower rates of sedimentation and increased
519 the mobility of adsorbed cations (Ju-Nam and Lead, 2008). Consequently, rather than being
520 involved directly within the adsorption step, IONP colloidal stability could play a key role in Cu
521 transport, mobility, bioavailability and toxicity once the metal is bound to the IONP (Baumann et
522 al., 2014, Bottero et al., 2011).

523 4. Conclusion

524 IONP can undergo many changes in natural waters and soils. In this study, oxidation of
525 magnetite and HA and PC natural organic coatings induced surface changes that affected both the
526 behavior of the IONP in aqueous solution and the interactions occurring at oxide/water interface.
527 In term of Cu adsorption capacity, the structural and chemical diversity of HA decreased the
528 pH_{zpc} of HA-magnNP and provided a large amount of hydrophobic and heteroaliphatic functional
529 groups, which also favored the formation of strong surface complexes onto HA-magnNP over a

530 wide pH-range. Contrary to HA-magnNP, PC-magnNP and maghNP displayed similar behavior
531 than pristine magnNP showing that neither PC coating nor magnNP oxidation affected Cu
532 adsorption capacity. On another hand, both HA and PC surface coatings prevented Fe release
533 from the IONP at low pH. Oxidation of mixed-oxidation state magnNP to maghNP also
534 considerably reduced its dissolution rate, suggesting that Fe^{2+} in magnNP is more soluble than
535 Fe^{3+} in maghNP. Last, if aggregation did not affect the adsorption of Cu, it could be secondarily
536 involved in driving the metal fate by impacting its speciation and thus its mobility and solubility.
537 Deciphering the interactions between IONP, cations and organic molecules as well as
538 investigating the behavior and fate of IONP in the environment (aggregation, transport, toxicity)
539 could have strong implications towards diverse scientific issues including water quality,
540 agronomics, and environmental remediation.

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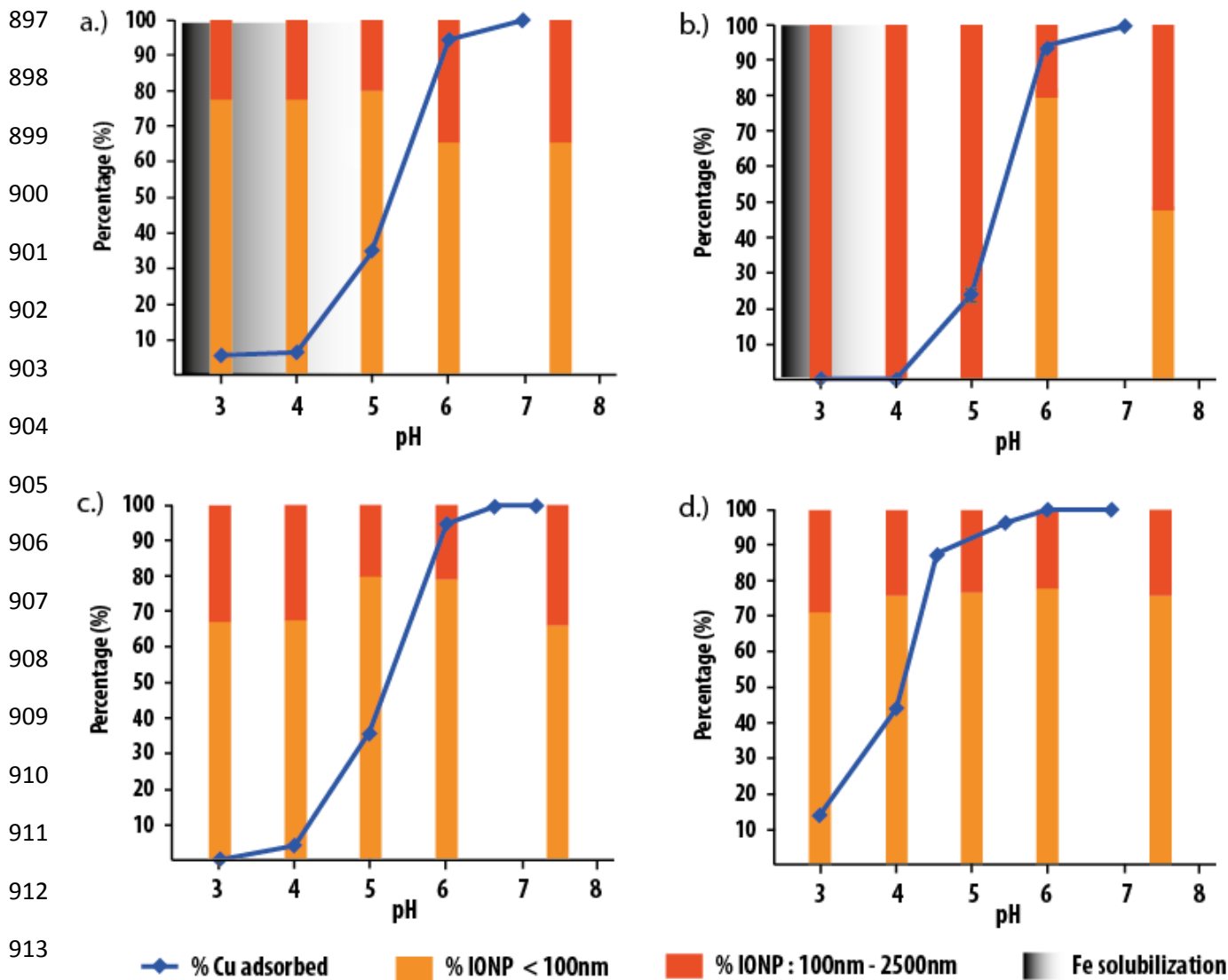
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914 **Figure 1:** Adsorbed Cu%, aggregates sizes and Fe dissolution versus pH on the four IONP: (a) magnNP, (b)
 915 maghNP, (c) PC-magnNP and (d) HA-magnNP. The data were obtained at the same initial NP
 916 concentration (NP= 0.5 g L⁻¹), ionic strength = 5 10⁻³ M NaCl, and starting Cu = 0.05 mM. The error bars,
 917 resulting from triplicates, are within the markers. The intensity of IONP dissolution is represented by
 918 dark areas (black to light grey refer to high to decreased dissolution rate).

919

920 **Table 1:** Fe concentrations (mg L^{-1}) released from the IONP relative to the pH (from triplicates). The
 921 experiments were conducted at 0.5 g L^{-1} IONP suspensions with a constant ionic strength of 5.10^{-3} M
 922 NaCl. LQ refers to the Fe limit of quantification ($0.12 \mu\text{g L}^{-1}$).

923

	pH 3	pH 4	pH 5	pH 6	pH 7
MagnNP	5.23 ± 0.08	1.34 ± 0.07	0.005 ± 0.001	<LQ	<LQ
MaghNP	1.63 ± 0.07	0.33 ± 0.05	<LQ	<LQ	<LQ
PC-magnNP	0.009 ± 0.001	0.001 ± 0.001	<LQ	<LQ	<LQ
HA-magnNP	0.006 ± 0.001	0.0007 ± 0.001	<LQ	<LQ	<LQ

924