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

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## 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 Cu<sup>2+</sup> 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 Cu<sup>2+</sup> can be explained by both the diversity of the binding sites HA procured and the formation of multidendate complexes between Cu<sup>2+</sup> 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*

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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  $\text{Cu}^{2+}$  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** ( $\text{Fe}_3\text{O}_4$ ) 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 N<sub>2</sub>-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 N<sub>2</sub> 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<sup>-1</sup> 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<sub>zpc</sub>)** 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  $0.05 \text{ g L}^{-1}$  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  $0.05 \text{ mM}$  by diluting a  $250 \text{ mg L}^{-1}$  Cu stock solution in tubes containing  
189  $20 \text{ mL}$  of  $0.5 \text{ g L}^{-1}$  IONP suspension. The pH was adjusted using  $0.1 \text{ M NaOH}$  or  $\text{HCl}$  to reach  
190 the targeted pH (pH 3, 4, 5, 6 and 7). In the last experiment, Cu was added to  $20 \text{ mL}$  of  $0.5 \text{ g L}^{-1}$   
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  $0.1 \text{ M NaOH}$ . 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  $C_0$  ( $\text{mg L}^{-1}$ ) and  $C_e$  ( $\text{mg L}^{-1}$ ) are the initial dissolved Cu concentrations and dissolved  
201 concentrations of metal ions after adsorption, respectively. The equilibrium adsorption capacity,  
202  $Q_e$  ( $\text{mg g}^{-1}$ ) 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  $\text{Cu}^{2+}$  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 ( $\text{mg L}^{-1}$ ),  $Q_e$  is the mass of the  
217 contaminant adsorbed per unit weight of the adsorbent ( $\text{mg g}^{-1}$ ),  $Q^\circ$  ( $\text{mg g}^{-1}$ ) and  $b$  ( $\text{L mg}^{-1}$ ) 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 ( $\text{mg L}^{-1}$ ),  $Q_e$  is the mass of the  
227 contaminant adsorbed per unit weight of the adsorbent ( $\text{mg g}^{-1}$ ),  $K_F$  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  $0.5 \text{ g L}^{-1}$  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 ( $21 \text{ }^\circ\text{C}$ ,  $0.005 \text{ M NaCl}$ ). The model considered the presence of IONP  
240 ( $0.5 \text{ g L}^{-1}$ ) including the properties of IONP determined from the BET analyses and  
241 potentiometric titration (i.e. number of adsorption sites,  $\text{pK}_{\text{a}1}$  and  $\text{pK}_{\text{a}2}$ ). From the potentiometric  
242 titration experiment conducted at  $\text{NaCl} = 0.005 \text{ M}$ , we calculated  $\text{pK}_{\text{a}1}=4.6$  and  $\text{pK}_{\text{a}2}=7.8$  for  
243 magnNP. For maghNP,  $\text{pK}_{\text{a}1}=5.4$  and  $\text{pK}_{\text{a}2}=9.3$  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  $\text{nm}^2$  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 ( $\text{Cu}^{2+}$ ,  $\text{CuOH}^+$ ,  $\text{Cu}(\text{OH})_2(\text{aq})$ ,  $\text{Cu}(\text{OH})_3^{3-}$ ,  $\text{Cu}_3(\text{OH})_4^{2+}$ ,  $\text{Cu}(\text{OH})_2(\text{s})$ ) 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  $7 \pm 2$  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  $115 \pm 4$  m<sup>2</sup> g<sup>-1</sup> before oxidation (magnNP) to  $130 \pm 4$  m<sup>2</sup> g<sup>-1</sup> 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  $0.38 \pm 0.02$  at the beginning of the experiment to  $0.34 \pm 0.02$  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  $0.05 \pm 0.02$ . 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 Fe<sub>3</sub>O<sub>4</sub>-PC, as observed in pure PC sample, the absorption bands at 2849 cm<sup>-1</sup> and  
283 2940 cm<sup>-1</sup> were assigned to symmetric and asymmetric methylene (CH<sub>2</sub>) and methyl (CH<sub>3</sub>)  
284 vibrations, respectively (Debnath et al., 2010). The bands at 1272 cm<sup>-1</sup>, 1088 cm<sup>-1</sup>, 970 cm<sup>-1</sup> and  
285 820 cm<sup>-1</sup> were attributed to the presence of PO<sub>4</sub><sup>3-</sup> group onto magnetite surface (Debnath et al.,  
286 2010), and those at 1470 cm<sup>-1</sup> and 1412 cm<sup>-1</sup> were ascribed to CH<sub>2</sub> scissoring. The anchoring of  
287 PO<sub>4</sub><sup>3-</sup> 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<sup>-1</sup> 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<sup>-1</sup> vibration band (C=O stretch of free

292 carboxylic acid) observed in pure HA spectra. The band at  $1410\text{ cm}^{-1}$  could be related to  $\text{COO}^-$   
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 ( $\text{Fe}_3\text{O}_4$ ) 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  $\text{pH}_{\text{zpc}}$ , the IONP surfaces became negatively charged resulting from deprotonation reactions. The  
356 decreasing protons concentration at magnetite surface favors cation attraction and allows  $\text{Cu}^{2+}$  to  
357 complex onto the  $\text{FeO}^-$  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  $1350 \text{ cm}^{-1}$ . 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  $1350 \text{ cm}^{-1}$  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  $\text{cm}^{-1}$  suggesting that no Cu was adsorbed on magnNP surface at pH 3.5. The broad band at  $3150 -$   
365  $3400 \text{ cm}^{-1}$  and the band at circa  $1630 \text{ cm}^{-1}$  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  $\text{Cu}^{2+}$  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  $\text{pH}_{\text{zpc}}$  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  $\text{Zn}^{2+}$  (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  $\text{Ca}^{2+}$  was found to  
395 coordinate and bind electrostatically with oxygen molecules on four adjacent lipid molecules,  
396 whereas  $\text{Mg}^{2+}$  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  $\text{Cu}^{2+}$  by HA-magnNP shows that HA provided  
404 readily accessible sorption sites to  $\text{Cu}^{2+}$ . 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  $\text{pH}_{\text{zpc}}$  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  $\text{pH}_{\text{zpc}}$  is close to pH = 2.3 (Liu et al., 2008). Hence,  $\text{Cu}^{2+}$   
410 adsorption onto HA-magnNP was favored when the pH increased. Decreased  $\text{pH}_{\text{zpc}}$  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  $\text{Cu}^{2+}$  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 Cu<sup>2+</sup> 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 Cu<sup>2+</sup> 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  $\leq 100$  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  $\leq 100$  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  $\text{pH}_{\text{zpc}}$  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<sup>2+</sup> in magnNP is more soluble than  
535 Fe<sup>3+</sup> 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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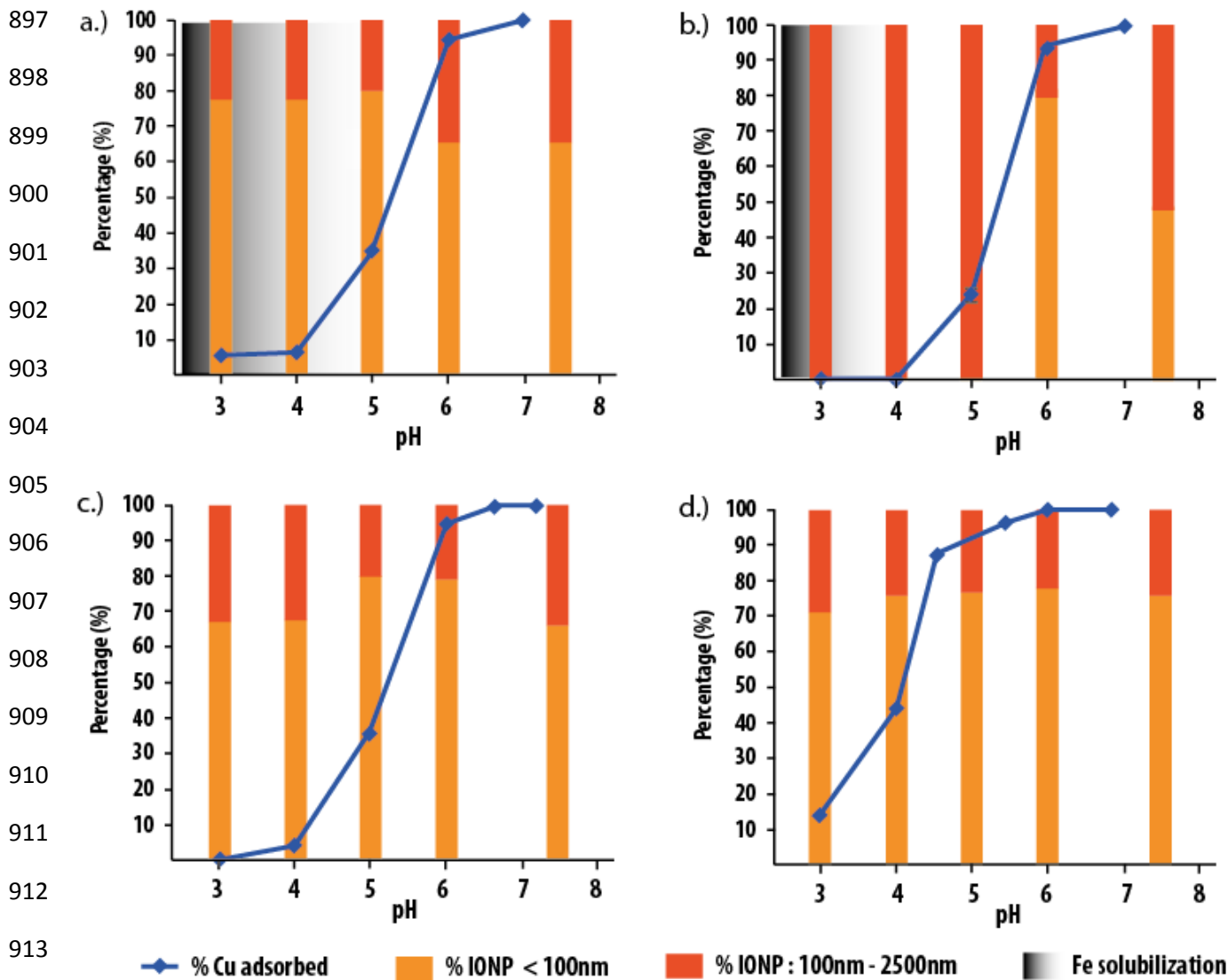
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914 **Figure 1:** Adsorbed Cu%, aggregates sizes and Fe dissolution versus pH on the four IONP: (a) magnNP, (b)  
 915 maghNP, (c) PC-magnNP and (d) HA-magnNP. The data were obtained at the same initial NP  
 916 concentration (NP= 0.5 g L<sup>-1</sup>), ionic strength = 5 10<sup>-3</sup> 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 ( $\text{mg L}^{-1}$ ) released from the IONP relative to the pH (from triplicates). The  
 921 experiments were conducted at  $0.5 \text{ g L}^{-1}$  IONP suspensions with a constant ionic strength of  $5.10^{-3} \text{ M}$   
 922 NaCl. LQ refers to the Fe limit of quantification ( $0.12 \mu\text{g L}^{-1}$ ).

923

	<b>pH 3</b>	<b>pH 4</b>	<b>pH 5</b>	<b>pH 6</b>	<b>pH 7</b>
<b>MagnNP</b>	$5.23 \pm 0.08$	$1.34 \pm 0.07$	$0.005 \pm 0.001$	<LQ	<LQ
<b>MaghNP</b>	$1.63 \pm 0.07$	$0.33 \pm 0.05$	<LQ	<LQ	<LQ
<b>PC-magnNP</b>	$0.009 \pm 0.001$	$0.001 \pm 0.001$	<LQ	<LQ	<LQ
<b>HA-magnNP</b>	$0.006 \pm 0.001$	$0.0007 \pm 0.001$	<LQ	<LQ	<LQ

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