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Colloidal and chemical stabilities of iron oxide nanoparticles in aqueous solutions: the interplay of structural, chemical and environmental drivers

Edwige Demangeat, Mathieu Pédrot, Aline Dia, Martine Bouhnik-Le Coz, Fabien Grasset, Khalil Hanna, M. Kamagaté, Francisco Cabello-Hurtado

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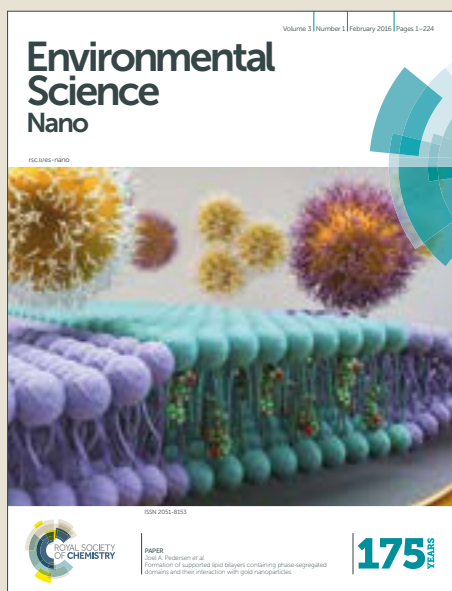
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Environmental significance statement

Amongst engineered nanoparticles, iron oxide nanoparticles (IONPs) appear particularly relevant toward the environment. Indeed, considering their potential uses in environmental fields (water and soil depollution, agrochemistry, etc.), it becomes critical to determine their behavior and fate in the environment. Their stability and reactivity are dependent upon the environmental parameters, and both intrinsic and surficial properties of IONPs. This work focused on the aggregation behavior of IONPs (especially magnetite, maghemite, hematite), their chemical transformation (oxidation of magnetite) and the impact of a surface coating that mimic natural interactions possibly occurring in the environment. Understanding these interactions and transformations will thus bring key insights regarding the mobility, bioavailability and chemical reactivity of IONPs in prevailing environmental conditions.

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ARTICLE

Colloidal and chemical stabilities of iron oxide nanoparticles in aqueous solutions: the interplay of structural, chemical and environmental drivers

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E. Demangeat,^a M. Pédrot,^a A. Dia,^a M. Bouhnik-le-Coz,^a F. Grasset,^b K. Hanna,^c M. Kamagate^c and F. Cabello-Hurtado^d

Nanoparticle (NP) stability in aqueous environments is dependent upon many parameters including environmental conditions, NP concentrations as well as NP intrinsic characteristics. In this study, the effects of pH and surface modifications on the colloidal and chemical stabilities of nanosized magnetite (Fe₃O₄), maghemite (γ-Fe₂O₃) and hematite (α-Fe₂O₃) are investigated. Because changes in surface charge affect the size distribution of NP, pH plays a key role in driving the colloidal stability. More NP aggregation is observed at pH values close to the pH of zero point of charge (pHzpc). Coating of magnetite with humic acid (HA) and phosphatidylcholine (PC) affects the electrostatic interactions and then the colloidal behavior of NP. The rapid transformation of magnetite into maghemite through air oxidation results in significant modification of both surface charge and specific surface area of NP. Because the maghemite almost exclusively formed μm-scale aggregates, the colloidal stability of magnetite is expected to be hindered in oxic environments. For hematite, the particle size distribution data emphasize the influence of both pH and intrinsic surface properties in colloidal stability. These findings may have strong implications for an accurate prediction of the transformation and mobility of Fe-nanoparticles under environmentally relevant conditions and thus their fate in nature.

1 Introduction

2 Understanding the prevailing processes controlling chemical
3 exchanges at soil/water interfaces is an environmental priority with
4 regards to their impacts on both ecosystems and soil services, as
5 well as water resources. Iron (Fe) oxides are ubiquitous minerals
6 constituent of soils, sediments, aquifers and geological materials^{1,2}.
7 Their origin is also anthropogenic as they are increasingly used in
8 various fields such as for industrial, medical and environmental
9 purposes³⁻⁶. Iron oxides nanoparticles (NP) respective stability,
10 specific surface area, porosity, dissolution rate as well as
11 transformation kinetics are controlled by their mineral structure⁷.
12 and determine their fate and behaviour in the environment⁷.
13 Amongst them, iron oxide nanoparticles, which also occur as
14 ubiquitous phases in both soils and waters, play a critical role in the
15 chemical dynamics resulting from environmental condition changes
16 since nano minerals are highly reactive^{8,9}. In the natural conditions,
17 only a small fraction of engineered iron oxide NP persists in its
18 original form¹⁰. Biotransformation, oxidation/reduction, dissolution,
19 precipitation, sorption and photochemical transformation may
20 occur amongst other biogeochemical driven processes^{11,12}. In turn,
21 this transformation can affect the aggregation, mobility,

25 biointeractions, uptake and fate of iron oxide NP in the
26 environment as well as their impacts on the living environment¹³.

27 Engineered iron oxide NP will become new tools for the treatment
28 of contaminated waters and soils^{14,15}. As compared to conventional
29 macroscale materials, nanomaterials exhibit a high surface-to-
30 volume ratio and high reactivity. Thus, their colloidal size may give
31 them high mobility in porous media and their properties allow them
32 to be particularly suitable for the treatment of contaminated soils
33 or aquifers. Iron oxide NP are involved in (i) the dechlorination of
34 organic solvents (CCl₄, C₂Cl₄), (ii) the detoxification of pesticides
35 (such as Lindane, DDT), (iii) the transformation of fertilizers (NO₃),
36 and (iv) the immobilization of metals and metalloids (As, Pb, Cr,
37 etc.)¹⁶⁻¹⁸. If remediation projects using iron oxide NP are currently
38 focused on local-scale pollution, a scale change is initiated to act
39 against diffuse pollution. Moreover, their use in nano-
40 agrochemistry could be developed in the years ahead and would
41 represent an intentional diffuse source of iron oxide NP within the
42 environment¹⁹. A widespread use of iron oxide NP for *in situ*
43 remediation or in agriculture also raises the question of their
44 environmental compatibility.

45 Amongst engineered iron oxide NP of environmental concern,
46 magnetite (Fe₃O₄), maghemite (γ-Fe₂O₃) and hematite (α-Fe₂O₃) are
47 popular engineered iron oxide NP because of their biocompatibility
48 and safety towards living organisms under certain conditions²⁰⁻²². In
49 particular, magnetite has shown an outstanding applicability in
50 many research areas (e.g., semiconductor, magnetic resonance
51 imaging, pigment, biomedicine, drug delivery, heterogeneous

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

^b Univ. Rennes, CNRS-Saint-Gobain-NIMS-UMI LINK 362-J-305-044, Tsukuba, Japan

^c Univ. Rennes, ENSCR- CNRS, ISCR (Institut des Sciences Chimiques de Rennes) - UMR
6226 F-35000 Rennes, France

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

52 catalysis, and environmental remediation)^{23, 24, 25} due to its unique¹⁰⁵ In the environment, soils and soil solutions are prior interfaces
53 magnetic properties and easy manipulation for control of¹⁰⁶ for iron oxide NP interactions⁴⁶ occurring at mineral surfaces and in
54 morphologies, particle size, and Fe^{II}/Fe^{III} stoichiometry^{26, 27}.¹⁰⁷ water. In addition to particle interactions, NP are prone to various
55 However, determination of magnetite compositions which is highly¹⁰⁸ chemical and physical modifications which foster the complexity of
56 sensitive to the preparation conditions is not a trivial task,¹⁰⁹ the reactions and likely affect both NP stability and reactivity.
57 particularly for nanoscale particles with a higher surface-to-volume¹¹⁰ Electrostatic, steric or combined electrosteric forces can result from
58 ratio. Magnetite compositions range, without modification of the¹¹¹ these interactions and promote repulsive forces whereas Van der
59 crystal structure, from that of stoichiometric Fe₃O₄, with 8 Fe³⁺ ions¹¹² Waals and magnetic dipolar interactions foster attraction between
60 in tetrahedral and 8 Fe²⁺ + 8 Fe³⁺ ions in octahedral sites, to that of¹¹³ particles that likely aggregate. The intrinsic physicochemical
61 maghemite γ-Fe^{III}2O₃ (considered as an extreme example of a non-¹¹⁴ properties of iron oxide NP (size, shape, surface area, chemistry,
62 stoichiometric magnetite) with only Fe³⁺ ions in both tetrahedral¹¹⁵ superparamagnetism, etc.), their ensuing high reactivity, together
63 and octahedral sites. As compared to these iron oxides, hematite¹¹⁶ with the surrounding solution composition (dissolved species, pH,
64 has only one type of cation, Fe³⁺ in its structure^{28, 29}.¹¹⁷ ionic strength, nanoparticle concentration), are the main drivers of

65 In aqueous solution, iron oxides (IO) are amphoteric solids that¹¹⁸ iron oxide NP chemical and colloidal stability in aqueous media^{47, 48}.
66 acquire a surface charge in the protonation and deprotonation¹¹⁹ Considering the geochemical, biological and technological
67 reactions of Fe-OH surface sites. The ensuing electrostatic, steric or¹²⁰ significance of iron oxide NP⁴⁹, understanding the mechanisms of
68 combined stabilization layers that develop at the surface of the¹²¹ their stability may turn out to be relevant to unravel the fate and
69 particles are significant in driving iron oxide NP colloidal stability³⁰.¹²² behaviour of iron oxide NP in the environment as well as their
70 The interfacial equilibrium at the surface of iron oxide NP is thus¹²³ impacts on living organisms. Therefore, the aim of this work is to
71 affected by the adsorption and desorption of the various¹²⁴ investigate the dual colloidal and chemical stability of magnetite NP
72 constituents of the soil and soil solution in addition to the solution¹²⁵ in order to (i) understand the effects of their intrinsic properties
73 pH^{31, 32}. The surface charge of iron oxide NP is also dependent upon¹²⁶ (size, morphology, surface chemistry) and those of the
74 their own structural organization such as isomorphous substitutions,¹²⁷ environmental drivers (especially the effect of pH) on their
75 which give iron oxide NP permanent charges.¹²⁸ aggregation state, (ii) assess the oxidation kinetics of magnetite, (iii)

76 As part of the Natural Organic Matter (NOM) occurring within¹²⁹ investigate the link between colloidal and chemical stability of NP,
77 soils and waters, macromolecular polyfunctional humic acid (HA),¹³⁰ as well as (iv) identify the resulting environmental impacts.
78 which displays a particular affinity for metal ions and their various¹³¹ Hematite has also been studied to better understand the impact of
79 acidic functional groups (carboxylic, phenolic, carbonyl), favours the¹³² intrinsic structural properties on iron oxide NP colloidal stability as
80 formation of surface complexes on the Fe-OH sites of iron oxides¹³³ the structure of hematite differs from both magnetite and
81 via chemisorption³³. As a consequence, interactions between iron¹³⁴ maghemite. Indeed hematite NP size and morphology as well as
82 oxide NP and HA should be further investigated. Several studies¹³⁵ internal crystal structure, generally confer a higher stability and
83 have shown that, in aqueous solution, the HA coating on iron oxide¹³⁶ crystallinity to hematite. Last, the method we chose to study the
84 NP likely imparts a negative charge to the nanoparticle surfaces,¹³⁷ iron oxide NP aggregation state allowed us to study their size
85 increasing their surface potential and the ensuing propensity to¹³⁸ distribution over a wide range of sizes (that spread from one tenth
86 stabilize iron oxide NP against aggregation³⁴⁻³⁶. Nevertheless, Hadju¹³⁹ of a nm to μm-scale aggregates) which allowed us to determine NP
87 et al.³⁷ demonstrated that coating magnetite with HA could either¹⁴⁰ behavior in a context comparable to those observed in natural
88 foster or hinder Fe₃O₄-NP colloidal stability depending on the¹⁴¹ waters.

89 amount of HA present at the mineral surfaces. Other natural
90 constituents such as amphiphilic phospholipids (integral major

91 component of cell membranes) likely affect iron oxide NP stability.¹⁴² **Experimental**

92 Using phospholipids as a coating on pyrite surfaces, Hao et al.³⁸ **Iron oxide nanoparticles and coated magnetite NP**

93 demonstrated that surface-bound lipids inhibit the iron core from¹⁴⁴ **Synthesis of bare iron oxide NP.** Magnetite (Fe₃O₄) was
94 oxidizing, even in the presence of bacteria, by forming a¹⁴⁵ prepared by the co-precipitation of iron salts according to the
95 hydrophobic pocket^{38, 39}. In addition, several authors have shown¹⁴⁶ modified literature procedure^{50, 51}. In brief, FeCl₂·4H₂O (1.988 g)
96 that a phospholipid coating likely decreases nanoparticle size¹⁴⁷ and FeCl₃·6H₂O (5.406 g) were dissolved in 5 mL HCl (2 M) and 20
97 dispersion and favours narrow-sized nanoparticles^{40, 41}.¹⁴⁸ mL H₂O, respectively, and then mixed with magnetic stirring to
98 Furthermore, the instability of magnetite in air causes NP to¹⁴⁹ obtain an iron solution with a molar ratio of Fe(II)/Fe(III) = 0.5.
99 undergo a partial oxidation to maghemite (γ-Fe₂O₃), ending up with¹⁵⁰ Magnetite NP were then precipitated by the dropwise addition of
100 a core-shell structure in which the thickness of the oxidized layer is¹⁵¹ the iron salt solution into a 0.7 M NaOH-NaNO₃ base solution (250
101 a function of the particle size^{42, 43}. This phase transformation¹⁵² mL). The black precipitate was left to settle in anaerobic conditions
102 directly affects the surficial properties and internal characteristics¹⁵³ for a few hours to get rid of the supernatant. Three washings were
103 of NP, which are deeply involved in driving iron oxide chemical¹⁵⁴ then conducted in anaerobic conditions with deoxygenated
104 stability and reactivity^{44, 45}.¹⁵⁵ deionized water and 5 10⁻³ M NaCl solution.

156 Maghemite (γ - Fe_2O_3) was synthesized following the method of 209 re-solubilized in 0.37 M HNO_3 after complete evaporation before
157 Anna et al.⁵², through the oxidation of the previously synthesized 210 measurement. Major- and trace-element concentrations were
158 magnetite by adding 5 wt% NaOCl aqueous solution (16 mL) and 211 determined by ICP-MS (Agilent 7700x), using rhenium and rhodium
159 sonicating for 2 hours. The solid product was magnetically 212 as the internal standard. The international geostandard SLRS-5 was
160 separated and washed with water. 213 used to check the validity and reproducibility of the results⁵³.

161 Hematite (α - Fe_2O_3) was synthesized by the forced hydrolysis of acid 214

162 Fe(III) salt solutions at 98°C from 0.02 M $\text{Fe}(\text{NO}_3)_3$ following the 215 **Characterization**

163 protocol described in Schwertmann & Cornell (2003)¹. 216

Size, morphology and surface properties. The morphology and

164 **Coatings with humic acid and phosphatidylcholines.** Fe_3O_4 -NP 217 individual particle size of Fe_3O_4 , HA- Fe_3O_4 , PC- Fe_3O_4 , γ - Fe_2O_3 and α -
165 were coated with HA (Elliott Soil Humic Acid Standard IV) and PC (1, 218 Fe_2O_3 were determined using High Resolution Transmission
166 2-bis (10, 12-tricosadiynoyl)-sn-glycero-3-phosphocholine - CAS 219 Electron Microscopy (HR-TEM) with a JEOL2100F (voltage 200 kV).
167 Registry Number: 76078-28-9) to model a natural surface 220 Specimens were prepared by drop-casting diluted Fe-NP
168 modification. The coating was carried out by physical interactions 221 suspensions on 300 mesh Au-grids supported with carbon film.

169 between the dissolved organic species (HA and PC) and a 222 The specific surface area of the iron oxides was determined by
170 concentrated fraction of the Fe_3O_4 -solution. Humic acid (0.2 g) was 223 multipoint N_2 -BET (Brunauer Emmett Teller) analysis using a
171 dissolved in 10 mL NaOH (1 M) and the obtained HA-solution was 224 Coulter (SA 3100) surface area analyzer.

172 completed to 56 mL with deionized water. A similar PC-solution was 225 The pH of zero point of charge was determined by potentiometric
173 obtained by dissolution in deionized water and ultrasonication. 226 titrations, which were conducted with 1 and 2 g L^{-1} of solid at three
174 Forty-four mL of a 6.0 g L^{-1} Fe_3O_4 -NP solution was then added to 227 ionic strengths (10^{-2} , $5 \cdot 10^{-2}$, and 10^{-1} M of NaCl). The suspension
175 each organic stock solution and each 100 mL of solution was shaken 228 was purged with nitrogen gas to remove CO_2 in a double-walled
176 for 48 hours. At the end of the interaction, five washings were 229 Pyrex cell, which was kept at constant temperature by circulating
177 performed to remove the uncoated materials present in the 230 water from thermostat. Titrations were conducted from 4 to 10 by
178 supernatant after centrifugation. 231 addition of titrant solutions (HCl or NaOH).

179 **Nanoparticle mass concentration measurement.** The 232 Synthesized NP were characterized using X-ray powder diffraction
180 concentration of the iron oxide NP solution was inferred from the 233 (XRD). XRD data were collected with a Johanson monochromator
181 ICP-MS measurements of iron on triplicate samples for the iron 234 using CuK_α radiation ($\lambda = 1.5406 \text{ \AA}$). The X-ray diffractograms were
182 oxide NP solutions and then recalculated regarding the total 235 found to be identical with the expected oxides.

183 theoretical iron content of the minerals. Each NP sample was 236 Laser particle size analyses allowed the characterization of the size
184 digested with sub-boiled nitric acid (14.6 M HNO_3) at 85°C, and then 237 distribution of magnetite, maghemite, hematite and HA- and PC-

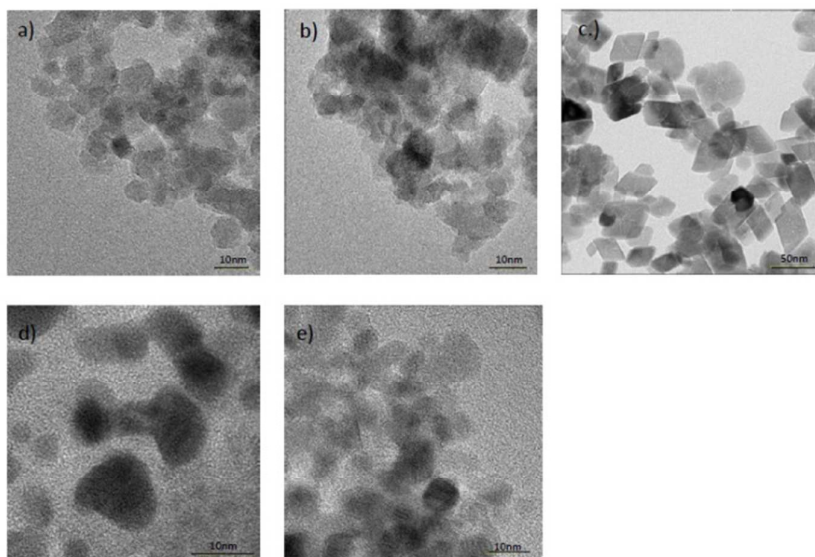


Fig. 1: High Resolution TEM (HRTEM) images of a) Fe_3O_4 , b) γ - Fe_2O_3 , c) α - Fe_2O_3 , d) HA- Fe_3O_4 and e) PC- Fe_3O_4

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Journal Name

NP	TEM (nm)	BET (m ² g ⁻¹)	pHzpc
Magnetite	7 ± 2	115	5.8
Maghemite	6 ± 2	131	7 - 8.4
Hematite	28 ± 5 39 ± 5	49	8.2

Table 1: Physicochemical properties of a) Fe₃O₄, b) γ-Fe₂O₃ and c) α-Fe₂O₃ obtained from TEM, BET analyses and potentiometric titration.

coated magnetite to study the colloidal stability and, conversely, their aggregation behaviour. Assuming measurements on spherical particles, the technique provided sizes amongst the 100 size classes detected, which spread from 0.04 μm to 2500 μm. Analyses were performed by the laser diffraction technique on a Cilas1180 analyzer. Measurements were taken on each bare iron oxide (Fe₃O₄, γ-Fe₂O₃ and α-Fe₂O₃) and coated magnetite (HA-Fe₃O₄ and PC-Fe₃O₄) at five different pH values (pH = 3, 4, 5, 6, 7.5). Particle size measurements were performed by adjusting obscuration values allowing for an optimal analysis. Then, the pH was equilibrated with HCl and NaOH solutions (0.1 M and 0.1 M to 1.0 M, respectively) until the target pH was reached.

ATR-FTIR. Attenuated total reflectance-Fourier transform infrared (ATR-FTIR) spectra were recorded in the 780 - 1800 cm⁻¹ region on an IS50 Nicolet spectrometer equipped with a KBr beam splitter and a liquid Nitrogen cooled MCT (Mercury Cadmium Telluride) detector. A nine-reflection diamond ATR accessory (Durasampler™, SensIR Technologies) was used for acquiring spectra of wet samples. The resolution of the single beam spectra was 4 cm⁻¹. Prior to ATR-FTIR analyzes, tubes containing coated NP were centrifuged at 4110 RCF for 30 min. Wet mineral pastes were directly and uniformly applied to the diamond ATR crystal then covered with a lid of a flow-through cell to prevent the evaporation of water. ATR-FTIR spectra were then recorded immediately.

To monitor potential dissolution of NP, aliquots were collected at each pH value, centrifuged and the supernatants were filtered using 5 KDa ultrafiltration cells (from Sartorius) in order to stop NP on the filter. ICP-MS was then performed to measure total iron concentration.

Oxidation kinetics. A NP suspension (2.5 g L⁻¹), prepared in anoxic conditions, was placed outside the glove box under ambient environment to monitor the oxidation. The total Fe(II)/Fe(III) ratio in suspension was then analyzed versus time over nine days. For each sampling, two aliquots were placed in an anaerobic chamber: the first aliquot contained bulk solution and the second was filtered (0.2 μm, Whatman). NP suspension was dissolved during 12h using 0.6 N HCl while filtered NP were directly dissolved. Dissolved Fe(II) and Fe(III) concentrations were then determined using the phenanthroline method^{54, 55} and the bulk Fe(II) content turned out to be very close to that determined by acid digestion on the filtered solid. The amount of magnetite bound-Fe(II) ([Fe(II)]_{bound} = [Fe(II)]_{tot} - [Fe(II)]_{aq}) was used to calculate the effective Fe(II)/Fe(III) ratio (denoted as (Fe(II)/Fe(III))_{bound}) in magnetite which was shown to vary with pH, as reported

in Cheng et al.⁵⁶. [Fe(II)]_{tot} is the total concentration of Fe(II) in the suspension (solid + solution) and [Fe(II)]_{aq} is the dissolved concentration of Fe(II), measured after filtration (0.2 μm, Whatman) of the magnetite suspension.

Results and discussion

Iron oxide NP physicochemical properties.

HR-TEM analyses provided images to assess the individual sizes and shapes of the nanoparticles (Fig. 1). Magnetite and maghemite oxides both displayed rounded shapes and similar sizes with average diameters of 7 ± 2 nm and 6 ± 2 nm (Table 1), suggesting that the oxidation of magnetite to maghemite did not impact the particle size. Accordingly, BET surface area for maghemite (131 m²g⁻¹) is relatively close to that of magnetite (115 m²g⁻¹) (Table 1). Hematite displayed different morphologies with rhombohedral shapes measuring 28 nm-wide and 39 nm-long on average, with a surface area of 49 m²g⁻¹ (Table 1). No significant changes were reported for neither HA- nor PC-coated magnetite from TEM images, suggesting that the coating process did not modify the morphology of magnetite. Although the surface area was not determined for coated materials, no significant modification is expected, according to previous findings⁵⁷.

ATR-FTIR spectroscopy

The IR spectrum recorded for of Fe₃O₄, HA-Fe₃O₄ and PC-Fe₃O₄ showed successful coating of HA and PC on magnetite surfaces (Fig. 2). In the spectra of HA-Fe₃O₄, the presence of an acid carboxylic group was proven by the vibrational bands at 1410 cm⁻¹ and 1614 cm⁻¹. In the spectra of PC-Fe₃O₄, the absorption bands at 1239 cm⁻¹, 1088 cm⁻¹ and 970 cm⁻¹ were assigned to the presence of the PO₄³⁻ group, suggesting that PC was coated on the magnetite surface^{61, 62}.

Oxidation kinetics

The variation of total Fe(II)/Fe(III) ratio versus time for magnetite suspension exposed to air is characterized by a two-steps' behavior. Over the four first days (0-96 h), a sharp decrease in total

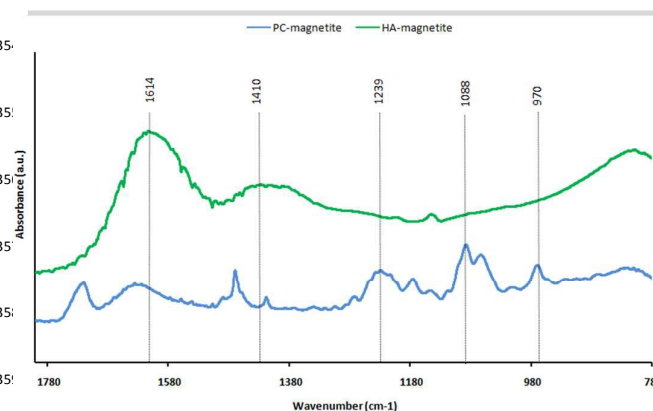


Fig 2: ATR-FTIR spectra of HA-magnetite and PC-magnetite in the range 780-1800 cm⁻¹ obtained from 0.5 g L⁻¹ NP suspensions at pH = 6.

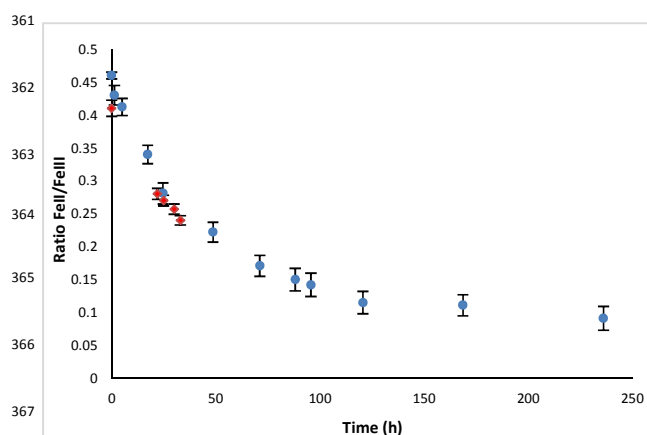


Fig 3: Evolution of the total Fe(II)/Fe(III) ratio (blue circles) and bound Fe(II)/Fe(III) ratio (red diamond) as a function of time. The reaction was performed with 2.5 g L^{-1} magnetite NP at pH = 7.5 in oxic conditions.

Fe(II)/Fe(III) ratio was observed (from 0.46 to 0.09). During this first stage, the bound Fe(II)/Fe(III) ratio was also decreased for magnetite as represented by red symbols in Figure 3. Then, the total Fe(II)/Fe(III) ratio slightly decreased beyond 5 days to reach 0.09 at the end of the experiment (236 h). As expected from the magnetite solubility at pH = 7.5¹, very little difference was observed between the total and bound Fe(II)/Fe(III) ratios.

Aggregation state

To assess the effect of pH and the effects of coating, laser diffraction analyses were performed on each iron oxide (Fe_3O_4 , HA- Fe_3O_4 , PC- Fe_3O_4 , $\gamma\text{-Fe}_2\text{O}_3$ and $\alpha\text{-Fe}_2\text{O}_3$) at five different pH values. For all experiments, the aggregation state was associated with the size distribution of the NP, which was described by considering the evolution of the sizes (based on number analyses) with the pH, occurrence rate and the polydispersity of the sizes (PDI, size range, mode and mean) of each iron oxide NP.

Effects of pH. The impact of pH on particle size distribution provides valuable information that could be used to distinguish the colloidal stability from the aggregation state of the various NP (Table 2). The different pH-dependent configurations highlighted the role of pHzpc in controlling NP aggregation through electrostatic interactions (Fig. 4). The effect of pH was studied by considering the evolution of the size distributions into four size classes (Fig. 4). The fractions were defined with regards to the most common sizes (representability) and depending on the way they vary with pH. However, it should be noted that fractions are not fully comparable to one another, as they were not spread out equally (i.e. fraction $>0.4 \mu\text{m}$ (μm -scaled size class) as compared to 40-100 nm fraction (nm-scaled sizes)). The full-size distribution diagrams obtained from laser particle analyses as well as the precise occurrence rates (detectors) are provided in the Electronic Supporting Information (ESI).

It is worth noting that the total dissolved iron content was only detected in the magnetite suspension at pH = 3 and pH = 4 (90 and 23 $\mu\text{mol L}^{-1}$ respectively). These values correspond to 1.4 % and 0.4 %, respectively, of the total iron amount in NP suspension. For HA- and PC-magnetite samples, no dissolved iron was detected regardless of the investigated pH.

Magnetite. The NP size distribution displayed two configurations: at pH = 5, 4 and 3, magnetite NP showed colloidal stability as compared to their size distribution at pH = 6 and 7.5. Magnetite size distribution at acidic pH was characterized by a high proportion of small NP ($\leq 0.04 \mu\text{m}$), and the occurrence of few dispersed μm -scaled aggregates (with sizes ranging between 1.6 μm and 32 μm). Such distribution allowed a large amount of NP not to sediment, as defined by Buffle et al.⁶³. When the pH increased to 6 and 7.5, the number of coarser 100-400 nm and 40-100 nm-sized aggregates increased as the proportion of small aggregates decreased. This is consistent with the measured pHzpc = 5.8 (in accordance with previously published values⁴), since aggregation is commonly favoured at pH close to the pHzpc. Therefore, particles exhibiting negative charges likely formed coarser aggregates when the pH approached the pHzpc because of favorable electrostatic interactions⁶⁴.

pH	Magnetite		HA-Magnetite		PC-Magnetite			Maghemite			Hematite	
	6	5	4	3	7.5	5	4	7.5	6	5	7.5	5
Range (μm)	0.04 - 0.4; 1.6 - 32	0.04 - 0.4; 1.6 - 32	0.04 - 18	0.04 - 0.4; 1.1 - 19	0.04 - 0.4; 1.2 - 45	0.04 - 0.4; 1.1 - 40	0.04 - 0.4; 1.6 - 56	0.04 - 0.4; 1.6 - 28	0.04 - 0.4; 1.6 - 28	0.5 - 0.7; 1.1 - 28	0.04 - 6	0.04 - 0.4; 1.1 - 12
Mode (μm)	0.04	0.04	0.04	0.04	0.04	0.04	0.04	0.04	0.04	8	1.4	0.04
Mean (μm)	1.3	0.9	0.4	0.6	1.1	0.8	1.3	4.1	1.1	6.8	1.3	0.5
Median (μm)	0.07	0.04	0.04	0.07	0.07	0.04	0.07	0.2	0.04	7	1.2	0.04
PDI	1.38	2.74	13	5	1.9	3.4	1.3	0.56	2.06	0.72	4.8	7.6

Table 2: Size distribution characteristics of each NP at some typical pH (aggregation state versus colloidal stability). The table shows the size-range, mode, mean size, median value and the PDI (polydispersity index) of magnetite, HA-coated magnetite, PC-coated magnetite, maghemite and hematite. High PDI have values up to 1.0 and very high PDI are up to 2.0.

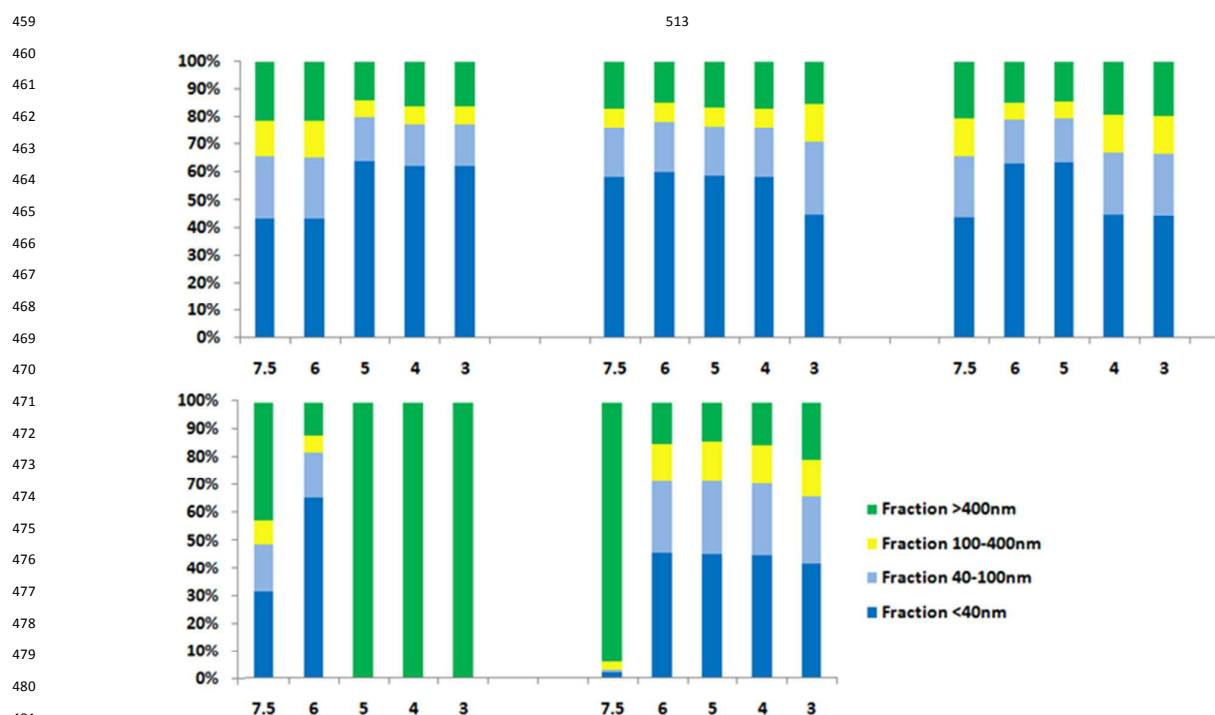


Fig 4: Evolution of four typical size-class (proportion in %) with pH for a) magnetite, b) HA-magnetite, c) PC-magnetite, d) maghemite and e) hematite. Below the histograms, the table displayed the percentages of each fraction for typical pH (3, 4, 5, 6 and 7.5).

484
485 **HA-Magnetite.** HA-magnetite nanoparticles displayed both a ⁵³⁹Maghemite. The size distribution displayed three configurations as
486 continuous size distribution (pH = 4 to pH = 7.5) and a dual size ⁵⁴⁰distinct fractions whose proportions were strongly controlled by the
487 distribution (pH = 3). In both cases, fraction below 0.04 μm was ⁵⁴¹pH. At a weak basic pH (pH = 7.5), the distribution was highly
488 more important but their proportion decreased as the pH ⁵⁴²polydispersed and made up of coarse aggregates (>0.4 μm), which
489 decreased from pH = 4 to 3. This decrease was accompanied by a ⁵⁴³spread over a large size range. Maghemite NP displayed colloidal
490 slight increase in 40–100 nm-sized fraction and an increase in the ⁵⁴⁴stability at pH = 6 with a size distribution similar to that of
491 proportion of coarser intermediate 100–400 nm NP size-class, which ⁵⁴⁵magnetite. However, when the pH decreased to a more acidic pH
492 appeared to be more dependent upon pH than other fractions. The ⁵⁴⁶(pH = 5, 4 and 3), small-sized NP and NP aggregates disappeared to
493 occurrence rate of the coarse aggregate fraction (>0.4 μm and >1.1 ⁵⁴⁷form much coarser aggregates with almost exclusively μm -scale
494 μm) remained constant regardless of the pH, hence a lower pH ⁵⁴⁸sizes (>1 μm). Thus, the maghemite size distribution would be in
495 implied a moderated aggregation with small (≤ 0.04 μm) particles ⁵⁴⁹good agreement with a high pH pH_{zpc} close to 7.5^{67,68}, as it became
496 aggregating in only slightly coarser (0.05–0.4 μm) aggregates. Thus ⁵⁵⁰coarser than at pH = 6, but the high aggregation observed from pH
497 in HA-coated iron oxide NP, HA appeared to be an effective organic ⁵⁵¹= 3 to 5 suggested the possible implication of parameters other
498 stabilizer towards iron oxide NP as previously demonstrated^{65,66}. ⁵⁵²than electrostatic interactions to drive maghemite colloidal
499 **PC-Magnetite.** PC-magnetite nanoparticles highlighted two size ⁵⁵³stability.
500 distribution depending on the pH. At pH = 6 and 5, the size ⁵⁵⁴Hematite. The hematite size distribution showed two pH-
501 distribution was similar to that of bare magnetite at acidic pH (pH = ⁵⁵⁵dependent size distribution patterns. At pH = 7.5, the sizes were
502 3 and pH = 4) where the colloidal stability displayed its maximum. ⁵⁵⁶continuously distributed with a unique narrow size range composed
503 At pH = 7.5, 4 and 3, Fe_3O_4 -PC showed a similar size distribution to ⁵⁵⁷of coarse homogeneous sizes displaying high polydispersity
504 bare magnetite at pH >6, when it aggregated. When the pH ⁵⁵⁸(multimodal distribution centered on 1.4 μm). When the pH
505 decreased to pH = 4 and pH = 3, small aggregates (≤ 0.04 μm) were ⁵⁵⁹decreased to pH = 6 and lower, the pH drastically modified the
506 still the most common but in a lower proportion which was ⁵⁶⁰hematite size distribution to a more stable aggregation state⁶⁹
507 compensated by a higher amount of the three other coarser size ⁵⁶¹characterized by a monomodal distribution (0.04 μm) and higher
508 fractions (in order: 40–100 nm; >1.6 μm and 100–400 nm). Although ⁵⁶²abundance of finer particles (<0.4 μm). In accordance with the
509 100–400nm-sized aggregates were still the least common, this ⁵⁶³hematite pH_{zpc} at pH = 8.2, hematite NP tended to aggregate when
510 fraction was the most sensitive to pH as its proportion more than ⁵⁶⁴the pH reached pH = 7.5.

511 doubled from pH 6 and 5 to pH 4 and 3.

512
565 Effects of coating. The physico-chemical characteristics
566 obtained from the combination of HR-TEM and ATR-FTIR showed

567 that HA have been successfully coated onto magnetite NP, displaying coarse aggregates with homogeneous sizes suggests that
568 According to HR-TEM images, HA coating on magnetite did not other mechanisms are involved at basic pH. Further investigations
569 affect the original morphology and size of the precursor NP. As the are thus needed to fully assess iron oxide NP colloidal stability⁷⁴⁻⁷⁶.
570 surface modification with HA provided primarily acidic functional **Environmental perspectives.** Aggregation and stabilization have
571 groups, the HA-coated magnetite pHzpc likely decreased to a lower significant effects on the mobility, reactivity and environmental fate
572 pH (pHzpc = 2.3). Accordingly, magnetite-HA promoted colloidal of NP. Once released in surface waters, unstable particles tend to
573 stability from pH = 7.5 to pH = 4 because of repulsive electrostatic agglomerate, sediment or flocculate or they preferentially adsorb
574 interactions. The aggregation observed at pH = 3 - close to the new onto bigger particles or surfaces⁷⁷. As a result, aggregated NP that
575 pHzpc - would then be explained by the lack of negative surface form larger colloids with a possible smaller surface area are less
576 sites to compensate for the protonation induced by the H⁺ easy to transport and do not get through the soil as easily as smaller
577 concentration increase in the aqueous solution. Both HA and bare particles⁷⁸. As aggregated NP become less mobile, they may
578 magnetite evidenced that the proportion of their size- fractions was become more ineffective in acting as nutrient carriers⁷⁹. It is also
579 strongly controlled by the pH, which induced either colloidal more difficult for these colloids to be taken up by plants and living
580 stability or aggregation. Nevertheless, HA coating promoted organisms as they are less soluble than their smaller counterparts⁸⁰.
581 smaller-sized aggregates as well as a narrower size distribution and The dissolution of NP induces the mobilization of ions which are
582 more homogeneous stable sizes (especially for coarser particles likely complexed with molecules that foster their absorption by
583 (>0.4 μm)) compared to bare magnetite (Table 2). This enhanced plants and animals. In addition, depending on their concentration
584 stabilization may stem from a HA steric barrier that helped maintain and speciation as well as on the physiology of the organism that
585 a space between the particles to prevent the aggregation of NP^{70,71}. absorbs it, metal atoms or ions can be either positive nutrients or
586 Similar to the HA coating, the PC surface modification did not affect toxic elements. On the other hand, aggregation may directly affect
587 the size and morphology of magnetite. Magnetite coated with PC NP toxicity towards living organisms since smaller NP have been
588 displayed a different colloidal behaviour as compared to bare shown to penetrate the cell walls of certain species more easily^{81, 82}.
589 magnetite. As PC imparted both negative and positive surface Considering the pH effect, the physicochemical properties of the
590 groups on the surfaces of the NP (glycerophosphate group, soil solution have to be considered in order to accurately assess the
591 trimethylethanolammonium group), and because of the complex fate of NP in the environment. NP intrinsic properties, such as their
592 and heterogeneous surface structures that are generated by surface chemistry, are also of prime importance since they are
593 adsorbed PC⁷², PC-coated nanoparticles likely displayed variable involved in both electrostatic and steric interactions, which may
594 colloidal behaviours. As compared to magnetite, PC-NP showed impact their dispersion, bioavailability and biocompatibility⁸³. In
595 similar size proportions and repartition although the magnetite-PC natural waters and surficial aerobic environments, NP likely
596 coarse fraction displayed a few large aggregates (hence its wider undergo many surficial modifications and become embedded in
597 size range, see Table 2) regardless of the pH. PC-NP were thus matrixes or functionalized with specific molecules⁸⁴. As a result,
598 probably able to form highly contrasted structures (according to these attached molecules can both passivate and/or confer their
599 their size) suggesting that PC-coated magnetite did not entirely own properties to mineral surfaces; e.g. polyanionic HA coating on
600 depend on electrostatic interactions but also on steric forces⁷². magnetite, resulting in a lower pHzpc and enhanced colloidal
601 **Effects of iron oxide intrinsic physicochemical properties.** The stability. In addition, HA coating - as well as PC covering - might
602 oxidation of magnetite (Fe₃O₄) to maghemite (γ-Fe₂O₃) did not passivate iron oxide NP surfaces to yield a steric barrier that
603 change morphology and particle size. Maghemite still displayed a prevents Fe leakage from mineral surfaces and the ageing of the
604 higher surface area (131 m² g⁻¹) than magnetite (115 m² g⁻¹) and magnetic core by oxidation. HA, which are ubiquitous in most
605 oxidized NP very likely yielded intrinsic compositional differences. aquatic systems, display a specific affinity for iron oxide NP as well
606 These modifications probably resulted in a higher surface potential as trace elements and therefore HA-iron oxide NP complexed
607 thereby explaining the variable size distributions observed as the structures may also enhance ETM adsorption to NP. However,
608 pH changed. Maghemite NP aggregation was favoured at acidic pH although natural coatings demonstrated improved iron oxide NP
609 (equal or below 5), which would be in good agreement with their stability and reactivity, their effects depend upon the amount and
610 high surface potential. Indeed, the tendency to form large chemical composition of the substances⁴.
611 aggregates at these pH values likely resulted from a high energetic The rapid oxidation of magnetite into maghemite is important since
612 barrier that had to be overcome at the mineral surfaces⁷³. Indeed, iron plays an active redox catalytic role in many energy transfer and
613 increasing NP surface to volume ratio leads to a higher surface electron transfer processes⁸⁵⁻⁸⁷. The iron oxide redox state also
614 energy which induces aggregation between particles. As hematite plays a key role in specific anaerobic environments where Fe(II) and
615 displayed a much lower surface area, the higher colloidal stability Fe(III) are used as energetic catalysts for bacteria^{88, 89}. Finally, the
616 observed over a wide pH range may result from a lower energetic transformation of magnetite into maghemite is also relevant
617 barrier at the surface of the particles in accordance with NP having considering its adsorption capacity towards environmental
618 a relatively lower surface potential. Hematite stability would thus compounds⁹⁰. Several questions are raised from these
619 be related, in part, to its smaller surface area and surface potential. environmental considerations, especially, what are the impacts of
620 However, the typical aggregation behaviour of hematite NP these modifications regarding iron oxide NP reactivity?

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675 **Conclusions**

676 The pH appears to be a key driver in controlling iron oxide NP
677 colloidal behaviour as resulting from protonation and
678 deprotonation reactions of surface hydroxyl-groups. Surface
679 modifications also implied considerable effects on iron oxide NP
680 colloidal stability as they promoted electrostatic interactions. In
681 contrast to PC, HA was shown to be particularly efficient in
682 enhancing magnetite colloidal stability. Magnetite seems to be
683 highly unstable in aerobic conditions. The oxidation of magnetite
684 into maghemite modified its surface chemistry and surface area,
685 and these modifications resulted in higher aggregation at most pH
686 values. Compared to maghemite, hematite appeared to be less
687 sensitive to pH and displayed a lower surface area and surface
688 potential. Both hematite and maghemite displayed high
689 aggregation size distributions at different pH values.
690 Considering the widespread use of iron oxide NP and their
691 subsequent release in the environment, their fate and behaviour in
692 soils and natural waters raise many environmental questions not
693 only in terms of their possible impacts on living organisms but also
694 for their mobility and fate in ecosystems. Therefore, more attention
695 should be paid for the understanding of colloidal and chemical
696 stabilities of iron oxide NP as it is likely involved in many major
697 interactions within the environment.

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