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

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

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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 (pH_{zpc}). 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

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

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

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

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

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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 isomorphic 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.³⁸¹⁴³ **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.

Maghemite ($\gamma\text{-Fe}_2\text{O}_3$) was synthesized following the method of re-solubilized in 0.37 M HNO_3 after complete evaporation before Anna et al.⁵², through the oxidation of the previously synthesized measurement. Major- and trace-element concentrations were magnetite by adding 5 wt% NaOCl aqueous solution (16 mL) and determined by ICP-MS (Agilent 7700x), using rhenium and rhodium sonicating for 2 hours. The solid product was magnetically as the internal standard. The international geostandard SLRS-5 was separated and washed with water. used to check the validity and reproducibility of the results⁵³.

Hematite ($\alpha\text{-Fe}_2\text{O}_3$) was synthesized by the forced hydrolysis of acid²¹⁴

Fe(III) salt solutions at 98°C from 0.02 M $\text{Fe}(\text{NO}_3)_3$ following the²¹⁵ **Characterization**

protocol described in Schwertmann & Cornell (2003)¹.

Size, morphology and surface properties. The morphology and

Coatings with humic acid and phosphatidylcholines. Fe_3O_4 -NP individual particle size of Fe_3O_4 , HA- Fe_3O_4 , PC- Fe_3O_4 , $\gamma\text{-Fe}_2\text{O}_3$ and $\alpha\text{-Fe}_2\text{O}_3$ were coated with HA (Elliott Soil Humic Acid Standard IV) and PC (1,2-bis (10, 12-tricosadiynoyl)-sn-glycero-3-phosphocholine - CAS Registry Number: 76078-28-9) to model a natural surface. Specimens were prepared by drop-casting diluted Fe-NP modification. The coating was carried out by physical interactions suspensions on 300 mesh Au-grids supported with carbon film.

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

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

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

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

Fig. 1: High Resolution TEM (HRTEM) images of a) Fe_3O_4 , b) $\gamma\text{-Fe}_2\text{O}_3$, c) $\alpha\text{-Fe}_2\text{O}_3$, d) HA- Fe_3O_4 and e) PC- Fe_3O_4

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 (Durasampl/IR™, 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 air 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 pH_{zpc} 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 μm (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 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 pH_{zpc} = 5.8 (in accordance with previously published values⁴), since aggregation is commonly favoured at pH close to the pH_{zpc}. Therefore, particles exhibiting negative charges likely formed coarser aggregates when the pH approached the pH_{zpc} because of favorable electrostatic interactions⁶⁴.

	Magnetite		HA-Magnetite		PC-Magnetite			Maghemite			Hematite	
pH	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.

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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).

HA-Magnetite. HA-magnetite nanoparticles displayed both a continuous size distribution (pH = 4 to pH = 7.5) and a dual size distinct fractions whose proportions were strongly controlled by the distribution (pH = 3). In both cases, fraction below 0.04 μm was more important but their proportion decreased as the pH decreased and made up of coarse aggregates ($>0.4 \mu\text{m}$), which decreased from pH = 4 to 3. This decrease was accompanied by a spread over a large size range. Maghemite NP displayed colloidal slight increase in 40–100 nm-sized fraction and an increase in the stability at pH = 6 with a size distribution similar to that of proportion of coarser intermediate 100–400 nm NP size-class, which appeared to be more dependent upon pH than other fractions. The small-sized NP and NP aggregates disappeared to occurrence rate of the coarse aggregate fraction ($>0.4 \mu\text{m}$ and $>1.1 \mu\text{m}$) remained constant regardless of the pH, hence a lower pH sizes ($>1 \mu\text{m}$). Thus, the maghemite size distribution would be in implied a moderated aggregation with small ($\leq 0.04 \mu\text{m}$) particles good agreement with a high pHzpc close to 7.5^{67, 68}, as it became aggregating in only slightly coarser (0.05–0.4 μm) aggregates. Thus coarser than at pH = 6, but the high aggregation observed from pH 7 in HA-coated iron oxide NP, HA appeared to be an effective organic stabilizer towards iron oxide NP as previously demonstrated^{65, 66}.
PC-Magnetite. PC-magnetite nanoparticles highlighted two size distribution depending on the pH. At pH = 6 and 5, the size distribution was similar to that of bare magnetite at acidic pH (pH = 3 and pH = 4) where the colloidal stability displayed its maximum. At pH = 7.5, the sizes were 3 and pH = 4) where the colloidal stability displayed its maximum. continuously distributed with a unique narrow size range composed of coarse homogeneous sizes displaying high polydispersity bare magnetite at pH >6 , when it aggregated. When the pH decreased to pH = 4 and pH = 3, small aggregates ($\leq 0.04 \mu\text{m}$) were still the most common but in a lower proportion which was compensated by a higher amount of the three other coarser fractions (in order: 40–100 nm; $>1.6 \mu\text{m}$ and 100–400 nm). Although abundance of finer particles ($<0.4 \mu\text{m}$). In accordance with the 100–400nm-sized aggregates were still the least common, this fraction was the most sensitive to pH as its proportion more than doubled from pH 6 and 5 to pH 4 and 3.

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

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

Conclusions

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

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