## **Supporting Information**

## A. Protocol details of the IONP syntheses and the analyses performed within the characterization step.

**Magnetite NP** were synthesized following the method of Khalafalla and Reimers (1980) and Massart (1981) using FeCl<sub>2</sub>.4H<sub>2</sub>O and FeCl<sub>3</sub>.6H<sub>2</sub>O salts. The iron salt solutions were added drop-by-drop into a NaOH-NaNO<sub>3</sub> base solution which triggered magnetite NP precipitation. The magnNP were separated from the supernatant and several washings were made using deionised water and NaCl  $5.10^{-3}$  M solution in between each centrifugation cycle.

**Maghemite NP** were prepared based on the method of Zasonska et al. (2015), by oxidizing the magnetite nanoparticles. NaOCl aqueous solution was added to the magnetite NP solution which was sonicated for 2 hours. MaghNP were then magnetically separated and washed several times with deionised water and NaCl 5.10<sup>-3</sup> M solution in between each centrifugation cycle.

**Coatings of magnetite NP** were performed using HA (Elliott Soil Humic Acid Standard IV - IHSS) and PC (1, 2-bis (10, 12-tricosadiynoyl)-sn-glycero-3-phosphocholine – Avanti Polar Lipid, CAS Registry Number: 76078-28-9). The coating was achieved by mixing the stock solution of the dissolved organic species (HA or PC) with magnNP solution (6.0 g  $L^{-1}$ ), for 48 hours on an oscillating table. Five washings were last carried out to remove the uncoated material in the supernatant after performing centrifugation cycles.

## 2.1.2. Characterization

**High Resolution Transmission Electron Microscopy** (HR-TEM) was conducted with a JEOL2100F electron microscope (voltage 200 kV). MagnNP, maghNP, HA-magnNP and PC-magnNP were suspended in 0.005 mM NaCl (pH=6) and the suspensions were diluted to concentrations of 1  $10^{-3}$  mg L<sup>-1</sup> before they were carefully deposited on 300 mesh Au-grids supported with carbon film.

Multipoint  $N_2$ -Brunauer Emmett Teller (BET) technique was carried out on magnNP and maghNP using a Coulter (SA 3100) analyzer to measure the surface area of the IONP. BET

analyses were not performed on HA- and PC- magnNP because the coated molecules were shown to contain highly narrow microporosity, which adsorbs no  $N_2$  at 77K (Liu et al., 2008, Fu et al., 2015). Prior to the measurements, tubes containing 35 mL - solutions (18 g L<sup>-1</sup>, NaCl 0.005 mM and pH=6) of magnNP and maghNP were centrifuged at 4110 RCF for 30 min. Then, the supernatant was removed and the wet mineral pastes (concentrated at the bottom of the tubes) were placed in an oven where they were gently dried at 49 °C for 2 days. Once completely dry, the solid piece were put in a mortar and crunched with a pestle until a fine powder was obtained.

The acquisition of Attenuated Total Reflectance-Fourier Transform InfraRed (ATR-FTIR) spectra was performed in the 650 - 3700 cm<sup>-1</sup> region using an IS50 Nicolet spectrometer with a resolution of 4 cm<sup>-1</sup>. The spectrophotometer was equipped with a KBr beam splitter, a liquid Nitrogen cooled MCT (Mercury Cadmium Telluride) detector and a nine-reflection diamond ATR (DuraSamplIR<sup>TM</sup>, SensIR Technologies) which allowed recording the spectra of wet samples. Prior to performing ATR-FTIR analyzes, tubes containing 35 mL-solutions (15 g L<sup>-1</sup>, NaCl 0.005 mM and pH = 6) of magnNP, maghNP, HA-magnNP and PC-magnNP were centrifuged at 4110 RCF for 30 min. Wet mineral pastes were immediately and uniformly applied to the diamond ATR crystal and covered with a lid of a flow-through cell to prevent water evaporation. Then, ATR-FTIR spectra were recorded straightaway.

**Fe(II)/Fe(III) ratio** was determined on a 2.5 g  $L^{-1}$  magnNP suspension (NaCl 0.005 mM, pH = 6). In the glovebox, where the suspension was stored, magnNP were dissolved during 12 h using 0.6N HCl. Then, dissolved Fe(II) and Fe(III) concentrations were measured using the 1.10 phenanthroline colorimetric method, AFNOR NF T90-017 using a UV–visible spectrophotometer (Komadel and Stucki, 1988).

The pH-dependent **surface charge** ( $pH_{zpc}$ ) of magnetite was determined by potentiometric acidbase titration using a self-developed titration system with two titrators (794 Basic Titrino -Metrohm). MagnNP suspensions (18.8 g L<sup>-1</sup>) were initially equilibrated, by adding a small volume of 1 M NaOH solution, in an electrolyte solution (NaCl) at three ionic strengths (0.005 M, 0.05 M and 0.5 M NaCl), with a starting pH = 8. For each suspension (i.e. ionic strength), two aliquots were set before adding either the base (0.1M NaOH) or the acid (0.1M HCl). Acquisition of the titrant volumes and precise pH were monitored until the expected pH was reached. Last, calculations of the net proton surface excess amounts were made based on the material balance for OH<sup>-</sup>/H<sup>+</sup>. All potentiometric titrations were performed in a thermostated vessel at ( $21 \pm 0.2^{\circ}$ C) and under N<sub>2</sub> atmosphere.

## B. TEM pictures of (a.) MagnNP, (b.) MaghNP, (c.) PC-magnNP and (d.) HA-magnNP.



C. ATR-FTIR spectra of bare magnNP, HA-magnNP and PC-magnNP in the range 650 - 3700 cm<sup>-1</sup> obtained from 0.5 g L<sup>-1</sup> NP suspensions at pH= 6 and ionic strength (IS) = 0.005M NaCl.



Wavelenght number (cm<sup>-1</sup>)

D. ATR-FTIR spectra of Cu, magnNP (pH 6) and magnNP after interaction with Cu = 0.5 mM at pH 3.5, pH 5, pH 6, pH 7 and pH 8 in the range 650 - 3700 cm<sup>-1</sup> obtained using 0.5 g L<sup>-1</sup> NP and ionic strength (IS) = 0.005 M NaCl.



E. Freundlich and Langmuir parameters calculated from Cu(II) adsorption isotherms of the IONP.

	Freundlich constants			Langmuir constants		
	<b>R</b> <sup>2</sup>	n	K <sub>F</sub>	<b>R</b> <sup>2</sup>	Q°	b
MagnNP	0.975	1.72	12.6	0.788	52.4	0.59
MaghNP	0.982	1.80	13.4	0.967	71.4	0.47
PC-magnNP	0.980	1.44	12.6	0.962	43.3	1.03
HA-magnNP	0.972	2.01	130.3	0.856	66.7	10.7

F. Freundlich isotherms of Cu adsorption onto the IONP. The isotherms were carried out at constant pH = 6, with an adsorbent concentration of 0.5 g L<sup>-1</sup> IONP.



G. Adsorption isotherms for magnNP, maghNP, PC-magnNP and HA-magnNP. The experimental data (n = 5) are represented by geometric symbols (the error bars are within the markers), whereas the solid lines indicate calculated data (incrementation step = 0.04 mg  $L^{-1}$  resulting in 181 points). The calculated isotherms were plotted using the Freundlich equation (3) with the calculated parameters (K<sub>F</sub>, n) obtained after linearization.



H. Speciation of Cu with 0.5 g L<sup>-1</sup> IONP at a temperature = 21°C and ionic strength = 0.005 mM NaCl. The concentrations of Cu species were calculated using Visual Minteq3.1 (solid lines) and determined from our experimental data for (a) 0.05 mM Cu and 0.5 g L<sup>-1</sup> magnNP, (b) 0.05mM Cu and 0.5 g L<sup>-1</sup> maghNP, (c) 0.1 mM Cu and 0.5 g L<sup>-1</sup> magnNP and (d) 0.5 mM Cu and 0.5 g L<sup>-1</sup> magnNP. The black lines, referred to as "Cu bound", denote the Cu adsorbed onto magnNP and the red dots, called "exp data", refer to the amounts of Cu adsorbed onto magnNP from our experimental data (Cu > 2 kDa = adsorbed and/or precipitated Cu species). In SI - H (a) and (b), CuOH<sup>+</sup> and Cu(OH)<sub>2</sub>(s) curves are mixed up with the horizontal axis as the concentration of these species in the solutions is null.









