

# Single-ion interferences when using magnetic microparticles for phosphorus removal in aquatic ecosystems

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## ABSTRACT

### Single-ion interferences when using magnetic microparticles for phosphorus removal in aquatic ecosystems

The specific adsorption of phosphate (P) on strongly magnetisable carbonyl iron (Fe) particles and their subsequent removal by in-flow High Gradient Magnetic Separation (HGMS) is considered a promising tool for restoring eutrophied waters. A previous study showed the existence of chemical interferences in natural waters without considering the influence of specific major ions on the P removal efficiency (de Vicente *et al.*, 2011). Therefore, in this manuscript, we assess the single-effect of some of the major ions present in natural waters, including sulphate ( $\text{SO}_4^{2-}$ ), calcium ( $\text{Ca}^{2+}$ ), humic acid (HA, as an indicator of Dissolved Organic Carbon, DOC), and reactive silicate (Si), on P adsorption to magnetic Fe particles in artificial lake water. The results showed that HA and Si significantly decreased the effectiveness of P adsorption by magnetic Fe particles. In particular, P removal efficiency decreased to 12% and 22% when HA and Si concentrations were 35.5 mg HA L<sup>-1</sup> and 10 mg Si L<sup>-1</sup>, respectively. By contrast,  $\text{SO}_4^{2-}$  and  $\text{Ca}^{2+}$  did not significantly reduce P removal. We recommend chemically analysing the lake water and determining the Fe dosage that obtains the highest P removal before using magnetic particles for the restoration of aquatic ecosystems in a whole-lake application.

**Key words:** Phosphate removal, magnetic particles, High Gradient Magnetic Separation, chemical interferences.

## RESUMEN

### Interferencias químicas asociadas a la presencia de un único ión cuando se utilizan micropartículas magnéticas para la eliminación de fósforo en ecosistemas acuáticos

La adsorción específica del fosfato (P) sobre partículas, fuertemente magnetizables, de hierro carbonilo (Fe), y su posterior retirada del medio usando técnicas de Separación Magnética de Alto Gradiente (HGMS), bajo condiciones de flujo continuo, está siendo considerada como una herramienta prometedora para restaurar ecosistemas acuáticos eutrofizados. Un estudio previo puso de manifiesto la existencia de interferencias químicas en aguas naturales, reduciendo, así, la eficiencia en la retirada del P pero ese estudio no pudo explicar el efecto directo que tenía cada ión en la eficiencia en la retirada del P (de Vicente *et al.*, 2011). En base a esto, en este trabajo hemos evaluado el efecto individual de algunos de los iones mayoritarios presentes en las aguas naturales tales como el sulfato ( $\text{SO}_4^{2-}$ ) y el calcio ( $\text{Ca}^{2+}$ ) así como los ácidos húmicos (HA) y la sílice (Si), en la adsorción del P sobre las partículas magnéticas de Fe. Los resultados han mostrado que los HA (usado como un indicador del DOC) y el Si decrecen significativamente la adsorción del P por las partículas magnéticas de Fe. En particular, la eficiencia en la retirada del P decreció a un 12% y un 22% cuando las concentraciones de HA y Si eran de 35.5 mg HA L<sup>-1</sup> y 10 mg Si L<sup>-1</sup>, respectivamente. Por el contrario, los iones  $\text{SO}_4^{2-}$  y  $\text{Ca}^{2+}$  no reducen significativamente la retirada del P por la adsorción sobre las partículas magnéticas de Fe. Por todo ello, se recomienda que antes de usar las partículas magnéticas para restaurar ecosistemas acuáticos eutrofizados es esencial hacer un análisis químico del agua del lago para poder determinar la dosis más adecuada de Fe y conseguir, así, la mayor eficiencia en la retirada del P.

**Palabras clave:** Eliminación de fósforo, partículas magnéticas, Separación Magnética de Alto Gradiente, interferencias químicas.

## INTRODUCTION

Eutrophication is one of the most important and long lasting water quality problems in the European Union. For at least two decades now, several policies have been adopted to tackle nutrient pollution and its consequences. The Water Framework Directive (WFD, 2000/60/EC) established an integrated and coordinated framework for the sustainable management of water, including the prevention of the deterioration of water bodies (lakes, rivers, coastal and transitional, groundwater), the promotion of sustainable water use, and ensuring the “enhanced protection and improvement of the aquatic environment.” This last point requires that rivers, lakes, estuaries, coastal waters and groundwater achieve and/or maintain at least a ‘good status’ by 2015.

Eutrophication is mainly caused by excessive inorganic nutrient loading (e.g., Hupfer & Hilt, 2008). In particular, phosphorus (P) has been identified as the main nutrient responsible for eutrophication (Hupfer & Hilt, 2008; Jeppesen *et al.*, 2009; Smith, 2009). Concurrently, the demand for good quality freshwater is increasing and this makes the development of new and efficient technologies for removing P from aqueous solutions an important challenge for limnologists and for water resource managers (Jeppesen *et al.*, 2009). Hence, new adsorbents were developed in the last decade for the treatment of polluted water (Hsu *et al.*, 2008; Panther *et al.*, 2011; Zhang *et al.*, 2011). Of these adsorbents, aluminium (Al) compounds are increasingly being used for trapping P in lake sediments (e.g., Smeltzer *et al.*, 1999; Welch & Cooke, 1999; Reitzel *et al.*, 2005; Egemose *et al.*, 2011; Reitzel *et al.*, 2013a). They adsorb and precipitate both phosphate ( $\text{PO}_4^{3-}$ ) and dissolved organic P-compounds (Reitzel *et al.*, 2009), but the resulting Al phases and floc quality are pH dependent, showing the highest efficiency when pH is in the range 6 to 8 (e.g., Kennedy & Cooke, 1982). Phoslock is another promising P adsorbent (Robb *et al.*, 2003; Reitzel *et al.*, 2013b, 2013c). It is made from modified bentonite clay containing an active P-adsorbing rare earth ingredient Lanthanum (La) within its chemical structure. Phoslock is most effective

at pH values between 5 and 7, and the adsorption capacity decreases above pH 9 (Ross *et al.*, 2008). Additionally, natural and modified zeolites, consisting of a three-dimensional framework structure bearing  $\text{SiO}_4$  and  $\text{AlO}_4$  tetrahedral, have recently been used for P removal from an aqueous solution (e.g., Karapinar, 2009; Gibbs & Özkundakci, 2011). They were demonstrated to be highly effective P-inactivation agents under both aerobic and anaerobic conditions.

In addition to these novel effective adsorbents, an alternative technology based on the use of magnetic particles could be considered for lake restoration (de Vicente *et al.*, 2010; de Vicente *et al.*, 2011; Merino-Martos *et al.*, 2011). Two outstanding advantages of using these particles for lake restoration, as previously suggested, are (i) the recovery of magnetic particles from the solution, reducing any effects on the aquatic biota and (ii) the reusability of the particles, thus reducing economic costs. In this context, the high P adsorption capacity of micron-sized carbonyl iron particles was tested under batch conditions, and the most favourable working conditions were identified by de Vicente *et al.* (2010). Later on, Merino-Martos *et al.* (2011) set up a laboratory-scale device for separating P from water under continuous flow conditions by using High Gradient Magnetic Separation (HGMS), which allows the handling large volumes of water because of decreasing retention times. In brief, this method is based on the use of highly magnetisable particles as the seeding adsorbent material and their later removal from solution by HGMS. Finally, and considering that Fe oxides have been previously used for removing colour, turbidity and metals for water clarification (Chang *et al.*, 2004; Dixon, 1984; Girginova *et al.*, 2010) and chemical interferences in P removal by magnetic seeding in natural waters were studied by de Vicente *et al.* (2011). In particular, these authors reported chemical interferences affecting P removal efficiencies in natural waters from 20 Mediterranean ponds and reservoirs. Their results showed that high P removal efficiencies (>80%) were found in freshwater lakes (conductivities < 600  $\mu\text{S cm}^{-1}$ ), while P

removal was very small (20%) in extremely high mineralised waters. Although a correlation analysis showed that major cations ( $\text{Mg}^{2+}$ ,  $\text{Na}^+$  and  $\text{K}^+$ ) and anions ( $\text{SO}_4^{2-}$  and  $\text{Cl}^-$ ) were the driving factors controlling the effectiveness of P removal, these experiments could not determine whether anions or cations by themselves were able to reduce P removal efficiency or, if by contrast, the observed inefficiency was just an indirect consequence of the significant correlation between cation and anion concentrations. As a result, further experimental research using specific anions in artificial lake water is needed.

The main aim of the present study was to improve our knowledge about the effectiveness of P adsorption on carbonyl iron particles in the presence of relevant specific ions. To achieve this goal, we ran a set of laboratory single-ion experiments in artificial lake water and increased the specific ion concentration. In particular, we studied the effect of humic acid, sulphate, silicate and calcium on P removal efficiency by magnetic particles using the in-flow HGMS technique. In order to quantify single-ion interferences when adding magnetic particles, it was a preliminary task to determine the appropriate Fe dose to achieve the highest P removal efficiency.

## MATERIAL AND METHODS

### Preparation of magnetic particles, phosphate and specific-ion solutions

Fe suspensions were prepared by dispersing 5 g Fe of carbonyl iron powder (BASF, Germany) particles in 100 mL distilled  $\text{H}_2\text{O}$ . The physico-chemical properties and elemental compositions of these particles were described by de Vicente *et al.* (2010).

A stock 1 mM P solution was prepared by adding 136 mg  $\text{KH}_2\text{PO}_4$  (Panreac, Spain) to 1 L of distilled water.

Humic acid (HA), from Sigma-Aldrich, was used as a simulator of lake dissolved organic carbon (DOC). The content of carboxylic groups of this particular humic acid is approximately 3.1 mmol/g (de Vicente *et al.*, 2008). The HA stock solution

was prepared by the addition of 1.4 g humic acid to 1 L 3 mM  $\text{NaHCO}_3$  solution and the pH was adjusted to 8.5 (de Vicente *et al.*, 2008). The stock solution was stirred for 12 hours and filtered through fibre filters (Whatman GF/C) to remove residual non-dissolved humic acid powder. The amount of DOC in the filtered solution was measured by High-Temperature Catalytic Oxidation on a Shimadzu TOC-V CSH. The final DOC concentration in the HA stock solution was 35.5 mg/L.

A stock sulphate solution was prepared by adding 18.14 g  $\text{K}_2\text{SO}_4$  (Panreac, Spain) to 1 L distilled water. The final  $\text{SO}_4^{2-}$  concentration was 10000 mg/L. Commercially available standard solutions of silicate and calcium (Merck, Spain) with concentrations of 1000 mg/L were used.

### Laboratory experiments

A set of laboratory single-ion experiments was conducted to study the interference of specific ions on  $\text{PO}_4^{3-}$  adsorption by carbonyl Fe particles. Each test consisted of adding 2 mL of the stock Fe solution (50 g/L) and 2 mL of the P solution (1 mM) to 100 mL volumetric flasks. Afterwards, different aliquots of the specific-ion solutions were added to give a desired final concentration. The pH of the samples was adjusted to pH = 7 with the addition of HCl 1 M or NaOH 1 M and left shaking overnight. After 24 h, the pH was again re-adjusted to pH = 7, and suspensions were finally transferred to 100 mL volumetric flasks, making the total volume 3 mM  $\text{NaHCO}_3$ . The Fe/P concentrations ratios used in all of the treatments were those identified by Merino-Martos *et al.* (2011) as necessary for achieving the highest P removal efficiency.

- *Testing the interference with humic acid:* For testing the effect of HA on P removal efficiency, two suspensions with different concentrations of HA (17 and 35.5 mg C  $\text{L}^{-1}$ ) were prepared. The first suspension was obtained by adding 2 mL of the stock Fe solution (50 g/L) and 2 mL of P solution (1 mM) to 100 mL of the HA stock solution, for a final HA concentration of 35.5 mg C  $\text{L}^{-1}$ . The second

suspension was obtained by using 50 mL of the HA stock solution and adding NaHCO<sub>3</sub> up to 100 mL, for a final HA concentration of 17 mg C L<sup>-1</sup>. The suspensions were then passed through the HGMS as described below, and PO<sub>4</sub><sup>3-</sup> was quantified in the filtered samples.

- *Testing the interference with sulphate:* Different aliquots (1, 2.5, 5, 10 and 50 mL) of the stock SO<sub>4</sub><sup>2-</sup> solution were added to different magnetic suspensions (containing 2 mL of the 50 g Fe L<sup>-1</sup> and 2 mL of 1 mM P solution in 100 mL NaHCO<sub>3</sub>) to yield final SO<sub>4</sub><sup>2-</sup> concentrations of 100, 250, 500, 1000 and 5000 mg/L, respectively. The suspensions were treated as described below, and the filtered samples were analysed for PO<sub>4</sub><sup>3-</sup> and SO<sub>4</sub><sup>2-</sup>.
- *Testing the interference with silicate:* Different aliquots (0.5, 1, 2.5 and 5 mL) of the stock silicate solution were added to each magnetic suspension and prepared as previously described. The final silicate concentrations were 5, 10, 25 and 50 mg/L. The suspensions were treated as described below, and the filtered samples were analysed for PO<sub>4</sub><sup>3-</sup> and dissolved reactive silicate (Si).
- *Testing the interference with calcium:* Different aliquots (1, 5, 10 and 50 mL) of the stock Ca<sup>2+</sup> solution were added to each magnetic suspension and prepared as previously described. The final Ca<sup>2+</sup> concentrations were 10, 50, 100 and 500 mg/L. Each sample was subjected to HGMS treatment described below, and the filtered samples were analysed for PO<sub>4</sub><sup>3-</sup> and Ca<sup>2+</sup>.

The experimental set-up was similar for all of the competitive adsorption tests. An axial HGMS filter was used through which Fe + P + single-ion suspensions were passed by using a peristaltic pump (Watson Marlow 205S). More details on the theoretical background of the axial HGMS filter design and the standard protocol can be found in Merino-Martos *et al.* (2011). Briefly, Fe + P + ion suspensions were first sonicated and then passed through the axial HGMS filter. The experiments were performed

**Table 1.** Effect of HA on P removal efficiency, including standard deviations (SD). The values reported are the average of the three replicates. *Efecto de los ácidos húmicos (HA) sobre la eficiencia en la retirada de P, incluye la desviación estándar (SD). Los valores mostrados son la media aritmética de las tres réplicas.*

HA(mg C L <sup>-1</sup> )	P removal (%)	SD
0	97.0	1.3
17	94	9
35.5	12	7

under optimal conditions with a sonication time = 5 min, flow rate = 0.36 mL/s, and the Fe/P concentration ratio = 3.22. The magnetic field strength in the filter was fixed at 450 kA/m. The treated samples coming from the HGMS device were filtered through a fibre filter (Whatman GFF) and P, Si, SO<sub>4</sub><sup>2-</sup> and Ca<sup>2+</sup> concentrations were determined in the filtered samples. In particular, equilibrium P concentrations were determined using the spectrophotometric method described by Murphy & Riley (1962). The dissolved reactive silicate (Si) was determined by using a spectrophotometric method described by Koroleff (1983). The determination of calcium (Ca<sup>2+</sup>) and sulphates (SO<sub>4</sub><sup>2-</sup>) was performed by ionic chromatography (DIONEX DX300) after filtering the samples (Millipore, 0.22 µm). Samples for dissolved organic carbon (DOC) analyses were collected after filtration through pre-combusted Whatman GF/F filters into pre-combusted 30 mL glass ampoules, acidified with hydrochloric acid (final pH = 2), sealed and stored at 4 °C until the analysis. The DOC was analysed by high-temperature catalytic oxidation on a Shimadzu TOC-V CSH.

Finally, to examine the effect of HA, SO<sub>4</sub><sup>2-</sup>, Si and Ca<sup>2+</sup> on carbonyl Fe particles, an adsorption experiment similar to the experiment described above was conducted without adding PO<sub>4</sub><sup>3-</sup>.

### Statistical analysis

All of the experiments were carried out in triplicates. The mean values were compared using Student's t-test and, unless otherwise stated,  $p < 0.05$  was considered statistically significant. The statistical analyses were performed using Statistica 6.0 Software.

## RESULTS AND DISCUSSION

### Effect of humic acid on P adsorption by carbonyl Fe particles

To study the interferences of HA on P adsorption by magnetic Fe particles, we analysed changes in the P removal efficiency in the presence of different HA concentrations (17 and 35.5 mg/L). Single-ion experiments showed a significant reduction in P adsorption by Fe particles in the presence of the highest HA concentrations (35.5 mg/L). In fact, the P removal efficiency decreased from 94% to 12% when HA concentrations increased from 17 to 35.5 mg/L (Table 1).

From these results, we concluded that the organic molecules of HA were more likely to have a greater preference for adsorption sites of Fe particles rather than P particles at higher concentrations of HA. This conclusion emerges from the fact that acidic functional groups of HA are able to act as ligands in a ligand exchange reaction on the oxide surface that is consistent with the specific adsorption mechanism in P adsorption on Fe particles. Consequently, there is strong competition between P and HA for adsorption sites on Fe particles (de Vicente *et al.*, 2011).

The adsorption of HA on Fe oxides has been widely reported in literature and it is known that HA can bind metals over the entire pH range (Zhang *et al.*, 2009a). Cornell & Schwertmann (1996) and Schindler (1990) reported that the adsorption of organic ligands predominated in

pH's below the point of zero charge (pzc) of the oxide dominating the electrostatic effects. However, ligand exchange and hydrophobic bonding may also be involved at pH's above the pzc. More recently, Illés & Tombác (2004, 2006) investigated the pH-dependent adsorption of HA on magnetite and revealed that the adsorption capacity was severely influenced by pH and ionic strength. Their experiments demonstrated that the amount of adsorbed HA was greater under acidic conditions, although at basic pH's, notable amounts of HA were also adsorbed in accordance with previous literature.

Similar findings have been observed for other oxides and hydroxides. Sibanda & Young (1986) observed that organic matter in solution strongly decreased P adsorption by aluminium and iron oxides, and particularly of low pH soils. For instance, using single-ion experiments, de Vicente *et al.* (2008) found a noteworthy reduction in P adsorption to Al(OH)<sub>3</sub> by the presence of HA. More recently, Zhang *et al.* (2009b) indicated the reduction in the P removal efficiency through the addition of natural organic matter (NOM) in a suspension with iron oxide nanoparticles. They justified this conclusion by the fact that NOM adsorption can impart a negative charge to nanoparticle surfaces and increase their surface electrostatic potentials.

However, there are also publications that demonstrated negligible interactions between HA and P adsorption. For example, Borggaard *et al.* (1990, 2005) studied the effects of HA and

**Table 2.** Results of P removal and SO<sub>4</sub><sup>2-</sup> removal by magnetic Fe particles, at different initial concentrations of SO<sub>4</sub><sup>2-</sup>, in the presence and absence of P. The values reported are the averages of the three replicates. *Resultados de la retirada de P y de SO<sub>4</sub><sup>2-</sup> mediante las partículas de Fe a diferentes concentraciones iniciales de SO<sub>4</sub><sup>2-</sup>, en presencia y en ausencia de P. Los valores mostrados son la media aritmética de las tres réplicas.*

SO <sub>4</sub> <sup>2-</sup> (mg/L)	P + Fe + SO <sub>4</sub> <sup>2-</sup>				Fe + SO <sub>4</sub> <sup>2-</sup>	
	PO <sub>4</sub> <sup>3-</sup> removal (%)	PO <sub>4</sub> <sup>3-</sup> removal (mg P/g Fe)	SO <sub>4</sub> <sup>2-</sup> removal (%)	SO <sub>4</sub> <sup>2-</sup> removal (mg SO <sub>4</sub> <sup>2-</sup> /g Fe)	SO <sub>4</sub> <sup>2-</sup> removal (%)	SO <sub>4</sub> <sup>2-</sup> removal (mg SO <sub>4</sub> <sup>2-</sup> /g Fe)
100	100.0 ± 0.3	15.06 ± 0.05	0 ± 30	0 ± 30	44 ± 10	37 ± 8
250	98.4 ± 1.9	14.8 ± 0.3	6.6 ± 1.2	18 ± 3	3.8 ± 1.7	10 ± 5
500	96 ± 6	14.4 ± 0.9	6.8 ± 0.9	37 ± 5	5.54 ± 0.18	30 ± 1
1000	94 ± 3	14.1 ± 0.5	4.4 ± 0.9	45 ± 9	9.1 ± 4	69 ± 8
5000	92 ± 4	13.8 ± 0.6	3.8 ± 1.5	210 ± 80	8 ± 5	600 ± 40

fulvic acids on P adsorption by aluminium and iron oxides in soil samples and found that organic matter did not compete with P for adsorption sites of oxides. This observation is similar to that previously described by Gerke & Hermann (1992) that reported P bonding onto humic-Fe complexes via ligand exchange by the substitution of H<sub>2</sub>O and OH<sup>-</sup>. This reaction was found to be dependent upon pH, as well as the presence of Ca<sup>2+</sup> ions. Ca<sup>2+</sup> adsorbed on negative charged groups reduces electrostatic repulsion of the P anions and, therefore, P adsorption is increased at a pH above 5.2.

### Effect of sulphate ions on P adsorption by carbonyl Fe particles

Using a combination of solutions (Fe+P+SO<sub>4</sub><sup>2-</sup> and Fe+SO<sub>4</sub><sup>2-</sup>), we observed that there was not a significant ( $p > 0.05$ ) effect of SO<sub>4</sub><sup>2-</sup> anions on P adsorption by magnetic Fe particles (Table 2). In fact, an increase in SO<sub>4</sub><sup>2-</sup> concentrations from 100 to 5000 mg/L caused a slight, but not significant, reduction in the P removal efficiency (from 100% to 92%). These results were consistent with other data reported in the literature on iron oxides (Zhang *et al.*, 2009a; Geelhoed *et al.*, 1997). Geelhoed *et al.* (1997) found that the presence of SO<sub>4</sub><sup>2-</sup> caused only a small reduction in P adsorption per surface area unit of goethite. Zhang *et al.* (2009a) found that the presence of SO<sub>4</sub><sup>2-</sup> had no significant effect on P removal by a Fe-Mn binary oxide adsorbent. Notable differences existed, however, between our experimental design and that by Zhang *et al.* (2009a). For example, we used a much lower initial P concentration (0.62 mg/L instead of 5 mg/L) and much higher SO<sub>4</sub><sup>2-</sup> concentrations (from 100 to 5000 mg/L instead of from 96 to 960 mg/L) than Zhang *et al.* (2009a). This means that even in our scenario with low P and high SO<sub>4</sub><sup>2-</sup> concentrations, which was more likely to determine the existence of chemical interference, no significant interactions occurred.

Our results also showed that adsorption of SO<sub>4</sub><sup>2-</sup> by magnetic Fe particles was strongly controlled by the presence or absence of P in the solution (Table 2). Hence, for the highest SO<sub>4</sub><sup>2-</sup>

concentration, a three-fold significant increase in SO<sub>4</sub><sup>2-</sup> removal (in mg SO<sub>4</sub><sup>2-</sup> g<sup>-1</sup> Fe) was measured when no P was in the solution compared to when the P concentration was higher than 100 mg/L. Our results were consistent with those reported by Geelhoed *et al.* (1997), who observed that P experienced a higher affinity for adsorption sites on goethite than SO<sub>4</sub><sup>2-</sup> over a wide range of pH (2.5, 4.0, 5.5, 7.0 and 8.5) and, therefore, is a stronger competitor. It is important to note that adsorption of SO<sub>4</sub><sup>2-</sup> by Fe oxides may be nonspecific involving ion pair formation and dominated by electrostatic interaction (Cornell & Schwertmann, 1996). In fact, SO<sub>4</sub><sup>2-</sup> adsorption strongly depends on the pH, with adsorption being the highest at a low pH and decreasing when the pH rises, up to a negligible adsorption above the pzc (Cornell & Schwertmann, 1996). In this sense, it is important to emphasise that all of our experiments were run at pH 7 and that de Vicente *et al.* (2010) measured an isoelectric point (i.e.p) of the carbonyl Fe particles of approximately 6.5, so at pH 7 only minor adsorption of SO<sub>4</sub><sup>2-</sup> ions by Fe particles can be expected. Also in agreement with our results, Boukhalfa (2010) found that SO<sub>4</sub><sup>2-</sup> removal from aqueous solutions by hydrous Fe oxide was very dependent on the presence of P. Nevertheless, it is important to note that Boukhalfa used extremely high P concentrations (500 times higher than ours: 10 mM instead of 20 µM). This author found a noteworthy reduction in SO<sub>4</sub><sup>2-</sup> adsorption when the concentration of P increased from 2.5 mM to 10 mM (pH = 3-8). Even more, at pH above 6, no adsorption of SO<sub>4</sub><sup>2-</sup> was observed for 10 mM concentration as a result of the strong interaction of P with the surface of the hydroxide relatively to SO<sub>4</sub><sup>2-</sup>. In summary, these results were explained by the fact that both of the ions competed for the same sorption sites.

### Effect of silicate on P adsorption by carbonyl Fe particles

Single-ion experiments using Fe+P+Si and Fe+Si suspensions were conducted to test the effectiveness of P adsorption by magnetic Fe particles in the presence of Si. Our results

showed that a significant reduction in P adsorption by Fe particles occurred when the Si concentration increases (Table 3). In fact, the P removal efficiency was reduced from 81% to 35% when the Si concentration increased from 5 to 50 mg/L. These findings were consistent with previous studies which noted that Si and P had the same specific adsorption behaviour, and competition for adsorption sites should occur (Sigg & Stumm, 1981; Cornell & Schwertmann, 1996; Hartikainen *et al.*, 1996). A similar behaviour was observed by de Vicente *et al.* (2008) when using Al(OH)<sub>3</sub> as the P adsorbent. These authors concluded that Si (at similar concentrations used in the present study) significantly decreased the effectiveness of P adsorption by Al(OH)<sub>3</sub> in single-ion experiments. More recently, Egemose *et al.* (2011) observed that after Al treatment to a eutrophic lake (Lake Nordborg, Denmark), silicate regeneration from the sediment was reduced by 69%-76% and consequently, lake water silicate concentration decreased by 87%. Our results were also consistent with those obtained by Hartikainen *et al.* (1996), who analysed sediment samples from Lake Vesijärvi (southern Finland). These authors observed that P oxyanions competed directly with Si compounds for sorption sites, but their results indicated that Si retention on the oxide surface was less effective than that of P. They justified it as a result of the high pK<sub>a</sub> value of silicic acid (9.7), which implied that Si sorption is at a maximum at a pH above 9. Again, it is important to note that our experiments were performed at pH 7, therefore, Si ions were expected to be less adsorbed by Fe particles

than P (Hartikainen, 1996). Sigg & Stumm (1981) reported the dependence of pK values on the surface charge of  $\alpha$ -FeOOH (goethite). They investigated the adsorption of several ions, including Si, on the surface of goethite and observed that Si is adsorbed over a wide pH range with a maximum near pH 9. Furthermore, Meng *et al.* (2000) observed that Si significantly decreased Arsenite removal, an anion with a similar chemical behaviour as P, when the Si concentration was higher than 1 mg/L and the pH was greater than 5. For example, they found that in the presence of 10 mg/L Si and a pH of approximately 6.8, the adsorption capacity of ferric hydroxide for Arsenite was reduced from 116  $\mu$ g/mg to 23  $\mu$ g/mg Fe.

For completeness, we also investigated the adsorption behaviour of Si by magnetic Fe particles in the presence and absence of P (Table 3). We found that Si removal was at all Si concentrations significantly lower in the presence (P+Fe+Si) than in the absence (Fe+Si) of P. These results, together with the drastic reduction in P removal in the presence of Si, again confirm the existence of a strong competition for adsorption sites on Fe particles. We have also fit our experimental data, from experiments Si+Fe and Si+Fe+P, to a linear regression line reaching values for  $r^2$  higher than 0.8. Our results showed that for an initial Si concentration of 10 mg L<sup>-1</sup>, Si removal decreased from 12.2% to 8.2% in the presence of 10  $\mu$  M P. However, if we compare P and Si removal, we could conclude that despite the competition among both anions, P is clearly preferentially adsorbed by Fe particles (Table 3). For ex-

**Table 3.** Results of P removal and Si removal by magnetic Fe particles, at different initial concentrations of Si, in the presence and in the absence of P. The values reported are the averages of the three replicates. *Resultados de la retirada de P y de Si mediante las partículas de Fe a diferentes concentraciones iniciales de Si, en presencia y en ausencia de P. Los valores mostrados son la media aritmética de las tres réplicas.*

Si (mg/L)	P + Fe + Si				Fe + Si	
	PO <sub>4</sub> <sup>3-</sup> removal (%)	PO <sub>4</sub> <sup>3-</sup> removal (mg P/g Fe)	Si removal (%)	Si removal (mg Si/g Fe)	Si removal (%)	Si removal (mg Si/g Fe)
5	81 ± 9	22 ± 2	12 ± 9	0.6 ± 0.5	14 ± 5	0.7 ± 0.3
10	22 ± 4	6.1 ± 1.2	6.3 ± 1.8	0.65 ± 0.19	12 ± 4	1.3 ± 0.4
25	24 ± 4	4.2 ± 0.8	3.3 ± 1.6	0.8 ± 0.4	7 ± 6	1.6 ± 1.4
50	35 ± 12	6 ± 2	0.3 ± 0.5	0.2 ± 0.2	4.2 ± 1.0	2.0 ± 0.5

ample, at an initial Si concentration of 10 mg/L, P removal was significantly higher (22%, 6.1 mg P g<sup>-1</sup> Fe) than Si removal (6.3%, 0.6 mg Si g<sup>-1</sup> Fe).

In general, it is important to note that in most natural waters the Si concentration is below 10 mg/L. In fact, an extensive survey performed by de Vicente *et al.* (2011) in 20 inland aquatic ecosystems with widely differing chemical composition revealed that 19 of 20 Si concentrations were below 10 mg/L and that 17 of 20 presented Si concentrations lower than 5 mg/L. Therefore, according to Table 3, for such a low Si concentration, only minor competition is likely to occur between P and Si. For those cases where Si concentration is higher, it is essential to consider Si competition in order to dose the right amount of Fe particles for the adsorption of P.

#### Effect of calcium ions on P adsorption by carbonyl Fe particles

To assess the role of Ca<sup>2+</sup> ions in controlling the effectiveness of P removal by Fe particles, single-ion experiments were performed using Fe+P+Ca<sup>2+</sup> suspensions. The results showed that Ca<sup>2+</sup> did not significantly affect the P removal efficiency by Fe particles, denoting no competition for adsorption sites (Table 4). In fact, in a wide Ca<sup>2+</sup> concentration range (10-500 mg/L) resembling the Ca<sup>2+</sup> concentration in inland waters typical of Southeastern Spain (i.e., de Vicente *et al.*, 2011), the P removal efficiency was always higher than 93%.

Stachowicz *et al.* (2008) studied the interaction between Ca<sup>2+</sup>-PO<sub>4</sub><sup>3-</sup> and Mg<sup>2+</sup>-PO<sub>4</sub><sup>3-</sup> on goethite. Specifically, in the Ca<sup>2+</sup>-PO<sub>4</sub><sup>3-</sup>, they

found that P adsorption existed, as well as Ca<sup>2+</sup> adsorption in a pH range 3-11, in spite of the fact that Ca<sup>2+</sup> had a much lower affinity for goethite than PO<sub>4</sub><sup>3-</sup>. This result was explained by the electrostatic interactions, as the negative charges of the adsorbed PO<sub>4</sub><sup>3-</sup> ions on goethite stimulated the binding of the positively charged Ca<sup>2+</sup> ion. However, contrary to these observations, we have not found any Ca<sup>2+</sup> removal by Fe particles in the presence of P (Table 4).

The formation of mixed metal/ligand surface complexes may occur and promote the adsorption of ions (Balistrieri & Murray, 1982; Cornell & Schwertmann, 1996; Gao & Mucci, 2003; de Vicente *et al.*, 2011). Nevertheless, adsorption behaviour can be affected by factors such as pH, concentrations and ionic strength (Kim & Walker, 2001). It was reported in the literature that the extent of adsorption of cations on Fe oxides depended on pH (Dixon, 1984). Indeed, there was a narrow pH range where the adsorption of cations went from near zero adsorption to 100% adsorption, and this is commonly called the adsorption edge (Balistrieri & Murray, 1982). For example, Gao & Mucci (2003) observed that the addition of Ca<sup>2+</sup> increased P adsorption on goethite slightly at pH <8.5 and extensively at pH >9. Ca<sup>2+</sup> cations adsorb on goethite and render the Fe oxides surface more positively charged, promoting P adsorption. Again, we have to note that all of the experiments were run at pH = 7, so a secondary effect of Ca<sup>2+</sup> on P removal occurred in our experiments.

Next, we aimed to study the Ca<sup>2+</sup> adsorption by the Fe particles both in the presence and in the absence of P (Table 4). Although we have

**Table 4.** Results of P removal and Ca removal by magnetic Fe particles, at different initial concentrations of Ca, in the presence and in the absence of P. The values reported are the averages of the three replicates. *Resultados de la retirada de P y de Ca mediante las partículas de Fe a diferentes concentraciones iniciales de Ca, en presencia y en ausencia de P. Los valores mostrados son la media aritmética de las tres réplicas.*

Ca <sup>2+</sup> (mg/L)	PO <sub>4</sub> <sup>3-</sup> removal (%)	Fe + P + Ca <sup>2+</sup>			Fe + Ca <sup>2+</sup>	
		PO <sub>4</sub> <sup>3-</sup> removal (mg P/g Fe)	Ca <sup>2+</sup> removal (%)	Ca <sup>2+</sup> removal (mg Ca <sup>2+</sup> /g Fe)	Ca <sup>2+</sup> removal (%)	Ca <sup>2+</sup> removal (mg Ca <sup>2+</sup> /g Fe)
10	96 ± 4	16.8 ± 0.7	0 ± 4	0.0 ± 0.2	59.6 ± 1.1	3.11 ± 0.06
50	100.0 ± 0.3	17.5 ± 0.1	0.0 ± 1.7	0.0 ± 0.4	0 ± 10	0 ± 2
100	100.0 ± 0.3	17.5 ± 0.1	0 ± 3	0.0 ± 1.6	0.0 ± 1.7	0.0 ± 0.9
500	93 ± 6	16 ± 1	0 ± 3	0 ± 8	17 ± 4	52 ± 14



not found a clear tendency as a function of  $\text{Ca}^{2+}$  concentrations, the  $\text{Ca}^{2+}$  removal was generally higher when P was not present in the solution. In particular, for the highest  $\text{Ca}^{2+}$  concentration (500 mg/L), the mean  $\text{Ca}^{2+}$  removal was 52 mg Ca  $\text{g}^{-1}$  Fe in the absence of P. No  $\text{Ca}^{2+}$  removal was achieved in the presence of P. Gao & Mucci (2003) studied  $\text{Ca}^{2+}$  adsorption on goethite in the absence of P and found that the  $\text{Ca}^{2+}$  adsorption was zero at  $\text{pH}=7.5$ , but it increased to close to 50% at  $\text{pH}=10$ . Again, it is important to note that cation adsorption not only depends on pH but also on ionic strength. For example, Gao & Mucci (2003) compared P adsorption on goethite in a 0.7 M NaCl solution and an artificial seawater solution. They found that P adsorption was slightly lower in the 0.7 M NaCl solution when compared to the artificial seawater.

## CONCLUSIONS

This study showed that the main drivers of P removal by adsorption on magnetic carbonyl iron microparticles were HA and Si, while other ions typically present in lake waters, such as  $\text{SO}_4^{2-}$  and  $\text{Ca}^{2+}$ , did not significantly affect the P removal efficiency. In particular, single-ion experiments showed that P adsorption by Fe particles was significantly reduced at high HA concentrations (35.5 mg/L). On the contrary, Si suppressed P adsorption at several high concentrations tested (10, 25 and 50 mg/L), but showed no significant effect at the lowest concentration (5 mg/L).

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