



Contents lists available at ScienceDirect

## Journal of Hazardous Materials

journal homepage: [www.elsevier.com/locate/jhazmat](http://www.elsevier.com/locate/jhazmat)



# Chemical interferences when using high gradient magnetic separation for phosphate removal: Consequences for lake restoration

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### ARTICLE INFO

#### Article history:

Received 24 October 2010

Received in revised form 6 May 2011

Accepted 29 May 2011

Available online xxx

#### Keywords:

High gradient magnetic separation

Phosphorus

Eutrophication

Magnetic particles

Chemical interferences

### ABSTRACT

A promising method for lake restoration is the treatment of lake inlets through the specific adsorption of phosphate (P) on strongly magnetizable particles (Fe) and their subsequent removal using in-flow high gradient magnetic separation (HGMS) techniques. In this work, we report an extensive investigation on the chemical interferences affecting P removal efficiencies in natural waters from 20 Mediterranean ponds and reservoirs. A set of three treatments were considered based on different Fe particles/P concentration ratios. High P removal efficiencies (>80%) were found in freshwater lakes (conductivities < 600  $\mu\text{S cm}^{-1}$ ). However, a significant reduction in P removal was observed for extremely high mineralized waters. Correlation analysis showed that major cations ( $\text{Mg}^{2+}$ ,  $\text{Na}^+$  and  $\text{K}^+$ ) and anions ( $\text{SO}_4^{2-}$  and  $\text{Cl}^-$ ) played an essential role in P removal efficiency. Comparison between different treatments have shown that when increasing P and Fe concentrations at the same rate or when increasing Fe concentrations for a fixed P concentration, there exist systematic reductions in the slope of the regression lines relating P removal efficiency and the concentration of different chemical variables. These results evidence a general reduction in the chemical competition between P and other ions for adsorption sites on Fe particles. Additional analyses also revealed a reduction in water color, dissolved organic carbon (DOC) and reactive silicate (Si) concentrations with the addition of Fe microparticles.

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## 1. Introduction

Inland waters are exposed to numerous natural and anthropogenic stress factors. Major problems of inland waters are eutrophication, atmospheric acidification, salinization and contamination by a large number of xenobiotics. In particular, about 30–40% of lakes and reservoirs worldwide are affected by unnaturally high nutrients concentrations (i.e. eutrophication) [1].

A high phosphorus (P) external loading is usually responsible for most cases of eutrophication [1]. As a consequence, mitigation and even the prevention of eutrophication of inland waters are firstly focused on the reduction of P external load before any other action is considered [2]. Among the most promising methods for lake restoration Merino-Martos et al. [3] suggested the P reduction in P enriched inlet waters by using magnetic (carbonyl Fe) particles as seeding agents in combination with high gradient magnetic separation (HGMS) because both the very large volumes of water that can be easily handled and the potential recovery and reutilization

of magnetic particles which drastically reduce economic costs. The HGMS technique is based on the attraction of magnetic particles by a magnetic field gradient created in the neighbourhood of magnetizable wires along which the suspension of particles flows. The field gradient exerts a force on the magnetic particles which causes them to be trapped by the wires [3–6].

Despite of the novelty of using magnetic particles to restore eutrophic inland waters, the application of magnetic particle technology to solve environmental problems is not new (i.e. [7,8]). Indeed, magnetic particles and other emerging techniques such as the application of ionizing radiation sources are among the most innovative methods for water purification [9,10].

Magnetic iron oxides have been previously used for removing color, turbidity and metals for water clarification [7,11,12], supporting the idea that chemical interferences in P removal by magnetic seeding need to be considered. It has also been documented in the literature that the presence of coexisting ions in natural waters such as sodium, calcium, magnesium, silicate, sulfate and dissolved organic carbon (DOC), among others, compete for available adsorption sites.

Little is known yet about the quantitative importance of the ion interactions that may affect the adsorption of P on Fe oxides in natural lake water (e.g. [13]) despite the fact that studies in soil

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chemistry and water treatment have shown a clear effect of inorganic and organic ions [7,14,15]. In lake restoration, Al addition is a very frequently used method for decreasing P concentrations in lake waters [16–19]. As Fe and Al oxides may behave in a rather similar way, next we will present some indirect evidences about the complex interactions between Al oxides and other ions. First, there is a well-documented suppression of toxic effects of Al on fish and freshwater plants due to the presence of Si or DOC (e.g. humic substances) [20–22]. Second, it has been reported a notable reduction in Si [23] and in DOC concentrations [24] in natural waters following Al addition. As a way of example, Berkowitz et al. [23] measured a significant decline of 74% in dissolved Si concentration in lake water 1 h after addition of Al. More direct effects are reported by Cornell and Schwertmann [25] who compiled adsorption studies of different inorganic anions (silicate, chromate, arsenate, borate, selenite and selenate) and cations (mostly heavy metals) on Fe oxides. Adsorption of cations on Fe oxides may be specific (alkaline earth cations) involving interaction with deprotonated surface hydroxyl groups to form mono- and binuclear inner sphere complexes or nonspecific (alkali cations) involving ion pair formation [25].

Investigations of the adsorption of organic compounds on Fe oxides have been prompted by the role of chelating agents [25]. DOC, which includes a broad classification of organic molecules of varied origin and composition within aquatic systems, represents the most important pool of organic carbon in inland waters affecting to the global carbon cycle [26,27]. Organic acids typically account for much more of the DOC than organic bases and neutrals, and acidic functional groups are very likely to act as ligands in ligand exchange reactions at the oxide surface [28]. Hence, the well-known ability of DOC to bind metals [29] reveals the need for considering DOC interference when adding Fe particles for P removal.

Most of the Mediterranean ponds present high mineralized waters due to their frequent endorheic character (a close drainage basin) and the extreme seasonal variability in rainfall patterns. Accordingly, we hypothesized that studying the interference of the typical ions dissolved in lake waters on P removal by magnetic seeding represents a crucial and necessary task especially when dosing the Fe particles/P ratio as the existence of chemical interferences would cause an increase in the optimal Fe particles/P ratio [3]. The need for this study is also supported by the contradictory results existing in the literature about the effect of anion and cation concentrations on P removal by metal oxides [11,25,29,30]. In this study, we conducted a set of laboratory experiments to examine the complex interactions occurring in natural water bodies affecting the P removal efficiency by using magnetic seeding and HGMS techniques. This objective was accomplished by collecting water from 20 Mediterranean shallow lakes, widely differing in their water chemistry. Statistical analysis (correlation coefficients and multiple regression analysis) was used as a tool for recognizing the main factor controlling P removal from lake water.

## 2. Materials and methods

### 2.1. Samples collection

In November 2009, an extensive sampling was carried out in a total of 20 inland aquatic ecosystems widely differing in their chemical composition and especially in their trophic state as reflected by their nutrient concentrations (Table 1). 3 L of surface water were collected and stored in plastic bottles. pH and conductivity were determined in the unfiltered samples using a WTW microprocessor pH meter (pH 196) and a WTW TetraCon 325 (inoLab Cond Level

**Table 1**  
Chemical composition of the studied lakes. TA is total alkalinity. nd = non detectable.

Lake	Conductivity ( $\mu\text{S cm}^{-1}$ )	pH	$\text{PO}_4^{3-}$ ( $\mu\text{g l}^{-1}$ )	$\text{Na}^+$ ( $\text{mg l}^{-1}$ )	$\text{K}^+$ ( $\text{mg l}^{-1}$ )	$\text{Mg}^{2+}$ ( $\text{mg l}^{-1}$ )	$\text{Ca}^{2+}$ ( $\text{mg l}^{-1}$ )	$\text{Cl}^-$ ( $\text{mg l}^{-1}$ )	$\text{SO}_4^{2-}$ ( $\text{mg l}^{-1}$ )	DOC ( $\text{mg l}^{-1}$ )	$\text{NO}_3^-$ ( $\text{mg l}^{-1}$ )	$\text{NH}_4^+$ ( $\text{mg l}^{-1}$ )	Si ( $\text{mg l}^{-1}$ )	TA ( $\text{mg l}^{-1}$ )	Mn ( $\text{mg l}^{-1}$ )
Agia	5440	7.96	51.1	17.05	2.44	213.28	449.20	63.50	2921.66	22.20	0.65	0.25	2.52	804.00	0.53
Alhama	385	8.01	2.9	2.37	1.10	16.57	32.40	2.41	6.20	1.29	0.35	0.03	1.08	218.87	0.03
Bermejales	534	8.19	0.8	3.37	2.28	23.28	46.98	5.12	165.42	1.92	0.32	nd	0.25	162.75	0.04
Beznar	414	8.47	nd	10.52	2.30	24.28	27.16	16.61	73.72	1.490	0.45	0.02	2.96	267.70	0.04
Canales	141	8.56	4.3	4.21	0.77	12.54	18.87	24.88	25.20	1.28	0.05	0.00	nd	106.02	0.09
Colomera	727	8.03	1.4	26.88	3.90	15.21	76.86	42.54	296.86	3.28	3.46	0.11	0.62	41.97	0.05
Cubillas	765	8.14	1.4	17.91	4.20	19.17	81.34	29.88	357.23	2.80	1.14	0.07	0.31	52.83	0.07
Chica	43,000	8.7	nd	4119.55	41.12	1978.46	576.56	8396.97	12,236.98	41.71	1.67	0.12	5.1	684.40	0.56
Doñana	22,500	9.38	10.2	2828.69	93.49	131.97	104.50	6028.87	517.77	274.50	11.65	0.03	1.42	823.50	0.32
Francisco	657	8.21	0.9	12.42	2.91	31.40	50.60	20.05	217.48	2.32	0.22	0.01	nd	290.73	0.08
Abellán															
Grande	5700	7.25	0.3	210.50	7.71	198.68	502.40	327.59	2621.00	11.23	0.08	0.84	10.19	335.50	0.56
Güejar	1182	7.76	131.1	31.05	23.64	59.53	102.70	62.15	410.29	53.05	0.63	0.40	4.22	458.70	0.50
Sierra															
Honda	364,000	8.33	nd	23,601.19	703.64	15,050.16	346.90	60,138.22	70,265.78	136.00	8.02	1.02	0.65	1201.70	5.88
Quentar	392	8.29	0.3	1.68	0.68	27.99	29.52	2.05	38.18	1.37	0.33	0.05	0.78	280.36	0.04
La Laguna	1364	7.9	1634.2	56.36	14.79	57.00	71.18	88.54	298.60	14.77	0.07	11.58	3.48	897.90	0.51
Loja	415	7.72	48.4	3.14	14.72	3.27	52.13	5.03	5.48	22.84	0.31	0.32	3.05	380.60	0.27
Rico	455	9.04	475.8	6.72	30.58	10.75	32.43	19.15	7.91	16.00	0.53	0.16	1.24	256.20	0.37
Ruidera	686	8.10	nd	14.59	2.46	13.98	57.63	7.37	58.37	3.70	10.55	0.05	1.85	210.33	0.07
Torrente	548	8.50	112.2	14.00	3.69	27.72	45.18	20.26	95.23	1.32	0.83	0.02	6.22	348.30	0.04
Zafarraya	577	7.76	734.2	18.76	10.12	11.99	27.80	46.18	12.29	16.92	0.23	3.61	3.21	323.30	0.37

**Table 2**

Experimental set-up for studying the chemical interferences of coexisting ions on P adsorption on Fe particles.

	Fe/P (g mg <sup>-1</sup> )	P (μM)	Fe (g l <sup>-1</sup> )
T1	6.45	5	0.25
T2	6.45	10	0.50
T3	25.81	5	1.00

1). Once in the laboratory, waters were filtered through fiber filters (Whatman GF/C) for the subsequent chemical analysis.

## 2.2. Chemical analysis

The filtered water was analyzed for P [31], nitrate (NO<sub>3</sub><sup>-</sup>) and ammonium (NH<sub>4</sub><sup>+</sup>) concentrations [32]. Dissolved reactive silicate (Si) was determined by using a spectrophotometric method described by Koroleff [33], after a reaction with ascorbic acid and molybdate. Total alkalinity (TA) was determined by using the titrimetric method (METROHM 716 DMS). Manganese (Mn<sup>2+</sup>) was analyzed following APHA [34]. The determination of sodium (Na<sup>+</sup>), potassium (K<sup>+</sup>), calcium (Ca<sup>2+</sup>), magnesium (Mg<sup>2+</sup>), sulfates (SO<sub>4</sub><sup>2-</sup>) and chlorides (Cl<sup>-</sup>) was performed by ionic chromatography (DIONEX DX300) after filtering the samples (Millipore, 0.22 μm). This technology is based on injecting a water sample into a current of carbonate–bicarbonate that makes pass across a series of columns of adsorption. Ions of interest are separated, at different times of retention, according to its relative affinity for the active sites of the filler material found in the cationic or anionic column, and later they are quantified in a conductivity detector. 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 analysis. DOC was analyzed by high-temperature catalytic oxidation on a Shimadzu TOC-V CSH.

## 2.3. Preparation of Fe and P solutions

Carbonyl Fe powder was supplied by BASF (Germany) and used as received. The manufacturer indicates the following chemical composition (wt%): minimum 97.5% Fe; 0.7–1.0% C; 0.7–1.0% N; 0.3–0.5% O. Scanning electron microscopy pictures show that the particles are spherical and polydisperse, with an average diameter of ~800 nm [24]. A stock of Fe suspension was prepared by dispersing 5 g Fe particles in 100 mL distilled H<sub>2</sub>O. A stock 1 mM P solution was prepared by adding 136 mg KH<sub>2</sub>PO<sub>4</sub> (Panreac) to 1 L of distilled water.

## 2.4. Laboratory experiments

Three different treatments were tested (see Table 2). Each one consisted in adding 0.5 mL (T1), 1 mL (T2) and 2 mL (T3) of the stock Fe solution (50 g L<sup>-1</sup>) in 100 mL of lake water. Depending on the initial P concentration of lake water, different aliquots of a standard P solution (1 mM) were added to give a final concentration of 5 μM (T1 and T3) and 10 μM (T2). Accordingly, Fe/P concentrations ratios were 6.45 g mg<sup>-1</sup> in T1 and T2, and 25.81 g mg<sup>-1</sup> in T3. The final aim of distinguishing three different treatments was to test the effect on P removal efficiency of increasing P and Fe concentrations at the same rate (T1 vs T2) and of increasing Fe concentrations for a fixed P concentration (T1 vs T3). Fe/P ratios were in all treatments higher than those recognized as necessary for getting the highest P removal efficiency [2].

Fe + P suspensions were first sonicated for 5 min and then passed through a home-built HGMS device by using a peristaltic pump (Watson Marlow 205S). The HGMS filter was specially designed to get the highest efficiency in P removal [3]. This consisted in an axial filter containing a 0.5 mm diameter Aluchrom wire (Fe 70%, Cr 25% and Al 5%) with a filling factor of 0.16. The magnetic field strength in the filter was fixed at 450 kA m<sup>-1</sup>. The flow rate (0.36 mL s<sup>-1</sup>) was small enough for the particles to be captured in the filter but large enough to handle sufficiently large volumes of water (for more details on the HGMS assembly we refer to [3]). The treated water coming from the HGMS device was filtered through a fiber filter (Whatman GFF). Later, filtered samples were again analyzed for P using the spectrophotometric method described by Murphy and Riley [31].

An additional experiment was also carried out to check the adsorption of other species on Fe particles. For that purpose, filtered waters from some of the more P-enriched lakes (Güejar Sierra, La Laguna, Loja, Rico and Zafarraya) were firstly treated to get a final Fe/P ratio of 1.61 g mg<sup>-1</sup> as recommended by Merino-Martos et al. [3] for achieving the highest efficiency in P removal. Later, treated waters at the outlet of the HGMS device were again filtered and analyzed for DOC, Si and conductivity following the methods described in Section 2.2.

For completeness, wavelength scans from 250 to 800 nm (as an indicator of lake color) were run for each sample before adding Fe particles (initial) and after Fe addition and once passed the HGMS device (treatment). Water absorptivities were calculated:

$$a_{\lambda} = \frac{2.303A_{\lambda}}{l} \quad (1)$$

where  $A_{\lambda}$  is the absorbance at different wavelengths,  $l$  is the optical path length in meters and 2.303 is the conversion from natural logarithms.

## 2.5. Electrokinetic characterization

The electrophoretic mobility of Fe particles suspended in different lake waters was ascertained using a MALVERN Instruments. For this purpose, a dilute suspension was prepared by adding 2 mL of the concentrated Fe solution (50 g L<sup>-1</sup>) to 100 mL of lake water. Every mobility data point is the average of 10 measurements taken for the same sample in the course of a 'run'. Because of the high density of the particles and therefore their tendency to sediment under gravity, the samples were sonicated for 5 min and the measuring cell was turned over a couple of times before every run.

## 2.6. Statistical analysis

All experiments were run in triplicates. Statistical analyses were performed using Statistica 7.0 Software [35] and Excel. For Student's *t* tests the significance level was set at  $p < 0.05$ . Regression analyses were performed to assess the potential chemical drivers of P removal by magnetic seeding. Data were log transformed to comply with the assumptions of regression analyses.

## 3. Results and discussion

### 3.1. Drivers of P removal by magnetic seeding

P removal by magnetic seeding is mainly achieved by the replacement of surface hydroxyl groups by the P species and formation of inner-sphere surface complexes at the water/oxide interface [36–38]. As a consequence, the specific adsorption of P makes the surface more negatively charged, which results in a shift of the isoelectric point of the magnetic particles (typically around pH = 6.5) to a lower pH value [38].

**Table 3**  
pH, electrophoretic mobility ( $\mu_e$ ), zeta potential and conductivity of Fe particles suspended in different lake waters.

	pH	Electrophoretic mobility ( $\times 10^{-8} \text{ m}^2 \text{ V}^{-1} \text{ s}^{-1}$ )	Zeta potential (mV)	Conductivity ( $\text{mS cm}^{-1}$ )
Agia	8.09	$-1.08 \pm 0.07$	$-13.8 \pm 0.9$	4.11
Alhama	8.10	$-1.37 \pm 0.06$	$-17.5 \pm 0.7$	0.34
Bermejales	8.12	$-1.32 \pm 0.09$	$-16.9 \pm 1.1$	0.61
Beznar	8.45	$-1.29 \pm 0.03$	$-16.5 \pm 0.3$	0.51
Canales	8.38	$-1.61 \pm 0.05$	$-20.5 \pm 0.6$	0.18
Colomera	8.01	$-1.31 \pm 0.05$	$-16.7 \pm 0.7$	0.74
Cubillas	8.22	$-1.37 \pm 0.02$	$-17.5 \pm 0.3$	0.68
Chica	8.72	$-0.64 \pm 0.07$	$-8.2 \pm 1.0$	30.90
Doñana	9.21	$-1.19 \pm 0.16$	$-15.2 \pm 2.1$	20.40
Francisco Abellán	8.54	$-1.41 \pm 0.05$	$-18.0 \pm 0.7$	0.81
Grande	7.57	$-1.08 \pm 0.11$	$-13.8 \pm 1.5$	5.48
G. Sierra	8.24	$-1.33 \pm 0.07$	$-16.9 \pm 0.9$	1.47
Honda	8.05	$-0.21 \pm 0.03$	$-2.7 \pm 0.4$	132.00
La Laguna	7.71	$-1.01 \pm 0.04$	$-12.9 \pm 0.5$	1.54
Loja	7.71	$-1.42 \pm 0.03$	$-18.1 \pm 0.3$	0.43
Quentar	8.10	$-1.46 \pm 0.04$	$-18.7 \pm 0.5$	0.52
Rico	8.05	$-1.27 \pm 0.02$	$-16.1 \pm 0.3$	0.48
Torrente	8.19	$-1.19 \pm 0.01$	$-15.2 \pm 0.1$	0.66
Zafarraya	7.90	$-1.22 \pm 0.02$	$-15.5 \pm 0.3$	0.68

The pH of natural lake waters ranged from 7.57 to 9.21 (see Table 3). At these pH values Fe particles are expected to be negatively charged [36] as confirmed by electrophoretic mobility measurements in Table 3. In spite of their negative charge, Fe particles do still adsorb a very significant amount of P because of the prevailing specific adsorption mechanism discussed above. Experimental data reported in the literature suggest that P specifically adsorbs for a very wide pH range (from 3 to 9.5). However, adsorption is still dependent on pH with the greatest adsorption occurring under acidic conditions and decreasing with increasing in solution pH [38].

Another important parameter to be considered is the ionic strength, and in particular, the effect of ionic strength on electrophoretic mobility of Fe particles. Our results evidenced that the electrophoretic mobility dramatically decreased when increasing the conductivity (Table 3). Indeed, lower negative mobilities were observed in lake waters characterized by the highest conductivity values (Honda and Chica lakes). By contrast, the highest negative

charge ( $-1.61 \times 10^{-8} \text{ m}^2 \text{ V}^{-1} \text{ s}^{-1}$ ) was measured when Fe particles were dissolved in the lowest mineralized lake water (Canales,  $0.18 \text{ mS cm}^{-1}$ ). Similarly to our results, Dixon [11] found that the addition of ions did not alter the isoelectric point of the particles but it reduced their surface charge and/or potential by a Coulomb screening mechanism. These results are in agreement with predictions from the DLVO theory of colloidal stability [39].

To assess potential drivers of P removal efficiency by using magnetic seeding, we analyzed the relationships between P removal efficiency and the concentration of different chemical variables using linear regression (Tables 4–6). Fitting equations to experimental data and correlation coefficients ( $r^2$ ) are shown in Tables 4–6. In all cases investigated, P removal efficiency decreased with increasing the concentration of other coexisting species as confirmed by a negative slope in the fitting equations. This is a clear manifestation of the interferences occurring under P adsorption.

In all treatments, P removal was significant ( $p < 0.05$ ) and inversely related to  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Mg}^{2+}$ ,  $\text{Cl}^-$ ,  $\text{SO}_4^{2-}$ ,  $\text{Mn}^{2+}$  and

**Table 4**  
Results of the regression analyses performed between P removal (%) and different significantly ( $p < 0.05$ ) related variables. All variables were  $\log_{10}$  transformed,  $n = 16$ .

Independent variable	Fe/P ratio ( $\text{g mg}^{-1}$ )	Fitting equations	$r^2$	p Level
Cond	6.45 (T1)	$y = 2.23 - 0.19x$	0.50	<0.005
	6.45 (T2)	$y = 1.94 - 0.09x$	0.26	<0.05
	25.81 (T3)	$y = 2.08 - 0.13x$	0.40	<0.01
$\text{Na}^+$	6.45 (T1)	$y = 1.84 - 0.15x$	0.54	<0.01
	6.45 (T2)	$y = 1.79 - 0.08x$	0.41	<0.01
	25.81 (T3)	$y = 1.81 - 0.11x$	0.51	<0.005
$\text{K}^+$	6.45 (T1)	$y = 1.74 - 0.17x$	0.29	<0.05
	6.45 (T2)	$y = 1.75 - 0.11x$	0.32	<0.05
	25.81 (T3)	$y = 1.79 - 0.19x$	0.59	<0.005
$\text{Mg}^{2+}$	6.45 (T1)	$y = 1.97 - 0.20x$	0.52	<0.005
	6.45 (T2)	$y = 1.84 - 0.10x$	0.33	<0.05
	25.81 (T3)	$y = 1.88 - 0.14x$	0.39	<0.05
$\text{Cl}^-$	6.45 (T1)	$y = 1.88 - 0.15x$	0.61	<0.005
	6.45 (T2)	$y = 1.80 - 0.08x$	0.42	<0.01
	25.81 (T3)	$y = 1.83 - 0.10x$	0.47	<0.05
$\text{SO}_4^{2-}$	6.45 (T1)	$y = 2.01 - 0.17x$	0.58	<0.005
	6.45 (T2)	$y = 1.85 - 0.08x$	0.32	<0.05
	25.81 (T3)	$y = 1.87 - 0.09x$	0.30	<0.05
$\text{Mn}^{2+}$	6.45 (T1)	$y = 1.38 - 0.27x$	0.48	<0.005
	6.45 (T2)	$y = 1.56 - 0.13x$	0.28	<0.05
	25.81 (T3)	$y = 1.47 - 0.19x$	0.39	<0.01

**Table 5**

Results of the regression analyses performed between P removal (%) and different no significantly related ( $p > 0.05$ ) variables. All variables were  $\log_{10}$  transformed,  $n = 16$ .

Independent variable	Fe/P ratio ( $\text{g mg}^{-1}$ )	Fitting equations	$r^2$
pH	6.45 (T1)	$y = 2.02 - 0.05x$	0.01
	6.45 (T2)	$y = 2.14 - 0.06x$	0.03
	25.81 (T3)	$y = 1.93 - 0.03x$	0.00
$\text{NO}_3^-$	6.45 (T1)	$y = 1.58 - 0.12x$	0.10
	6.45 (T2)	$y = 1.65 - 0.06x$	0.06
	25.81 (T3)	$y = 1.60 - 0.15x$	0.23
$\text{NH}_4^+$	6.45 (T1)	$y = 1.47 - 0.95x$	0.10
	6.45 (T2)	$y = 1.60 - 0.03x$	0.03
	25.81 (T3)	$y = 1.49 - 0.10x$	0.21
Si	6.45 (T1)	$y = 1.62 - 0.09x$	0.03
	6.45 (T2)	$y = 1.70 - 0.13x$	0.15
	25.81 (T3)	$y = 1.65 - 0.11x$	0.07
TA	6.45 (T1)	$y = 1.97 - 0.15x$	0.06
	6.45 (T2)	$y = 1.92 - 0.11x$	0.08
	25.81 (T3)	$y = 2.16 - 0.21x$	0.19

conductivity (Table 4). On the contrary, the correlation was not significant for pH,  $\text{NH}_4^+$ ,  $\text{NO}_3^-$ , Si and TA as  $p > 0.05$  (Table 5), and a complex scenario appears for DOC and  $\text{Ca}^{2+}$  where their effect on P removal efficiency was found to strongly depend on the treatments (Table 6). In particular, DOC was significant and inversely related ( $p < 0.05$ ) to P removal in all treatments except for treatment T2. It is also important to note that  $\text{Ca}^{2+}$  concentration was significant and inversely related to P removal only for the lower Fe particles/P ratio (T1), while when increasing Fe addition, no significant effect of  $\text{Ca}^{2+}$  on P removal efficiency was observed (T3).

Comparison between treatments T1 and T2 reveals that when increasing P and Fe concentrations at the same rate there exists a systematic decrease ( $50 \pm 9\%$ , only for the significant relationships) in the slope of the regression lines evidencing a reduction in the chemical competition between P and other ions for adsorption sites on Fe particles. Similarly, and as expected, when increasing Fe concentrations for a fixed P concentration (T1 vs T3), we have found a general reduction in the slope of the regression lines ( $38 \pm 12\%$ , only for the significant relationships except for  $\text{K}^+$ ) denoting again a reduction in the competition for adsorption sites.

The negative relationships observed between P removal efficiency and cation concentrations are in agreement with Dixon [11] who already found that the addition of multivalent cations to an oxide suspension significantly changes the surface properties of the oxide. In particular, he observed that  $\text{Mg}^{2+}$  and  $\text{Ca}^{2+}$  adsorb on the magnetite surface but the extent of adsorption depended on pH. Dixon [11] suggested that cations are likely to be bound not only by electrostatic forces but also by specific adsorption since there is evidence of adsorption of unhydrolysed cations at pH equal or lower than the isoelectric point. Contrarily to these observations, Stachowicz et al. [40] did not find any effect of  $\text{Mg}^{2+}$  and  $\text{Ca}^{2+}$  on arsenite adsorption on goethite in the pH range relevant for natural waters (pH 5–9).

**Table 6**

Results of the regression analyses performed between P removal (%) and different variables which showed significant ( $p < 0.05$ ) or no significant ( $p > 0.05$ , ns) relationship depending on the treatment. All variables were  $\log_{10}$  transformed.

Independent variable	Fe/P ratio ( $\text{g mg}^{-1}$ )	Fitting equations	$r^2$	p Level
$\text{Ca}^{2+}$	6.45 (T1)	$y = 2.34 - 0.38x$	0.52	<0.005
	6.45 (T2)	$y = 1.92 - 0.13x$	0.17	ns
	25.81 (T3)	$y = 1.96 - 0.16x$	0.16	ns
DOC	6.45 (T1)	$y = 1.74 - 0.16x$	0.25	<0.05
	6.45 (T2)	$y = 1.73 - 0.07x$	0.15	ns
	25.81 (T3)	$y = 1.75 - 0.13x$	0.25	<0.05

Contradictory results appear when analyzing the effect of anions on P removal by Fe oxides. Contrarily to our results, Dixon [11] observed that the presence of other anionic species did not affect the ability of magnetite to remove P from solution. Similarly, Zhang et al. [38] concluded that the presence of anions such as  $\text{Cl}^-$ ,  $\text{SO}_4^{2-}$  and  $\text{CO}_3^{2-}$  had no significant effect on P removal. A likely explanation for the difference between our results and those reported in the literature is that those authors used anion concentrations much lower than the concentrations used in the present study. Likewise, Tanada et al. [30] found that the hydroxyl groups on Al oxide hydroxide have selective adsorptivity for P and other anions such as  $\text{Cl}^-$  did not interfere. Unexpectedly, we have not found any significant effect of Si on P adsorption by magnetite although some previous studies have detected Si adsorption on goethite [41,42]. Similarly, single-ion experiments evidenced that Si ( $>200 \mu\text{M}$ ) significantly decreased the effectiveness of P adsorption to  $\text{Al}(\text{OH})_3$  by 10–13% at  $450 \mu\text{M}$  Si [19]. Again, a reasonable explanation for the lack of consistency between our results and those reported in the literature could be the different Si concentrations as only 2 of our 20 study sites showed Si concentrations higher than the threshold ( $>200 \mu\text{M}$ ) identified by de Vicente et al. [19].

From these experiments we cannot conclude that anions or cations by themselves are able to reduce P removal efficiency by magnetic seeding or if by contrast, the negative relationship observed between anion or cation concentration and P removal is just an indirect consequence of the positive relationship between cation and anion concentrations. Actually, ternary adsorption may occur as the presence of anions in solution may enhance cation adsorption by formation of mixed metal/ligand surface complexes [25,43]. Accordingly, and in order to determine the single-effect of each anion on P removal efficiency, further research must be focused on experiments in artificial lake water where adding specific anions.

In relation to the role of DOC in controlling the effectiveness of P removal, our results generally confirmed those obtained by Mcknight et al. [28] who already noticed that 40% of the DOC present in a pristine stream was removed from solution by sorption onto Fe and Al oxides. These authors also observed that molecules with greater contents of aromatic moieties, carboxylic acid groups and aminoacid residues were preferentially sorbed which is consistent with the ligand-exchange surface complexation model. Similarly, de Vicente et al. [19] by using single-ion experiments, found a noteworthy reduction in P adsorption to  $\text{Al}(\text{OH})_3$  by the presence of humic acids. In relation to humic acid adsorption on magnetite, Illés and Tombác [44] observed that humic acid has high affinity to magnetite surface especially at lower pH, where interacting

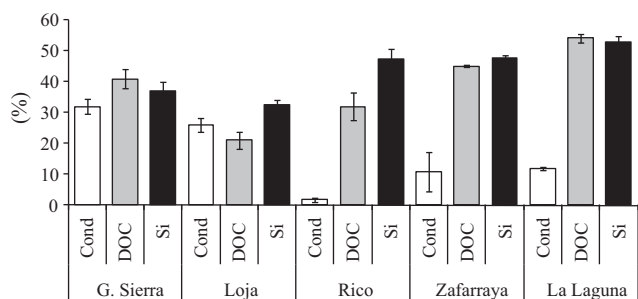


Fig. 1. Reduction (%) of conductivity, dissolved organic carbon (DOC) and total dissolved silicate (Si) by magnetic seeding (Fe/P ratio 1.61 mg mg<sup>-1</sup>).

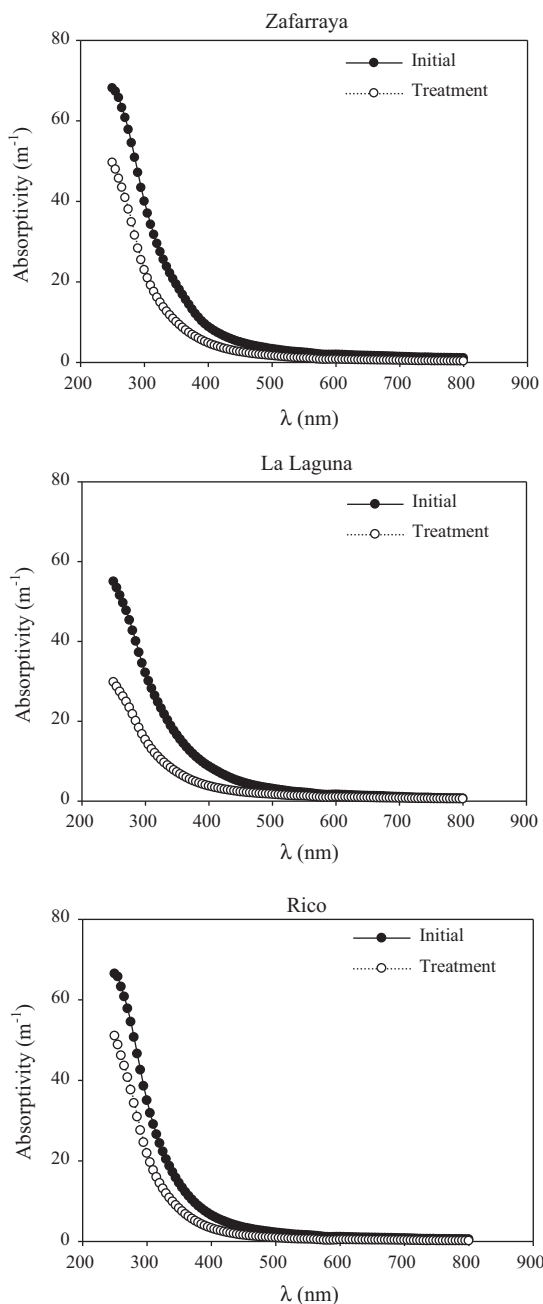


Fig. 2. Absorptivities from 250 to 800 nm of lake waters before adding Fe particles (initial) and after the addition of Fe particles and once passed through the HGMS device (treatment, Fe/P ratio 1.61 mg mg<sup>-1</sup>) in some selected lakes.

partners have opposite charges, although at pH 9 and despite of electrostatic repulsion, notable amounts of humic acid were also adsorbed. The addition of natural organic matter has been reported to further increase the negative charge of water-based iron oxide nanoparticles hence possibly reducing the P removal efficiency [29].

### 3.2. Effect of magnetic seeding on other ions typical of inland waters

An additional experiment was carried out in some of the lakes presenting higher P concentrations (Fig. 1) to test the effect of magnetic seeding on other coexisting ions in natural lake waters. DOC and Si removal efficiencies ranged from 21% (Loja lake) to 54% (La Laguna lake) and from 32% (Loja lake) to 53% (La Laguna lake), respectively (Fig. 1a). As it has been already mentioned above, the reduction in DOC and Si concentrations after adding Fe particles to lake waters are in agreement with results reported in the literature (i.e. [19,28]). In general, lower reductions in conductivity after the addition of Fe particles were observed, showing average values of 16% (Fig. 1b).

Changes in water color when adding Fe particles were also evaluated by measuring absorptivities from 250 to 800 nm (Fig. 2). The fraction of dissolved organic matter (DOM) that absorbs ultraviolet (UV) and visible light is referred to as chromophoric or colored dissolved organic matter (CDOM) [45]. UV-visible absorption spectra for CDOM increase approximately exponentially with decreasing wavelength [46]. Accordingly, UV-visible absorption spectra for our study lakes are directly linked to the presence of CDOM. Upon Fe particles addition, drastic reductions in absorptivity were observed specially at lower wavelengths. Reduction in water absorptivity ranged from 23% (Rico lake) to 46% (La Laguna lake). Our results are similar to those reported by Dixon [11], who found that magnetite addition to water suspensions caused a reduction in color and turbidity.

## 4. Conclusions

Our results evidence the strong ionic strength dependence of P removal efficiency. High P removal efficiencies (>80%) have been found in freshwater lakes (conductivities < 600  $\mu\text{S cm}^{-1}$ ). However, a drastic reduction in P removal was observed for extremely high mineralized waters. Correlation analysis has shown 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. By contrast, no significant effect of pH,  $\text{NO}_3^-$ ,  $\text{NH}_4^+$ , Si and TA was observed. Additionally, interesting results related to the effect of  $\text{Ca}^{2+}$  on P removal efficiencies were observed. Hence,  $\text{Ca}^{2+}$  concentration was significant and inversely related to P removal only for the lower Fe particles/P ratio while when increasing Fe addition, no significant effect of  $\text{Ca}^{2+}$  on P removal efficiency was observed. Additional experiments have shown that after adding Fe particles, a notable reduction in DOC and Si concentrations, as well as a change in water color are observed. All in all, future research might be focused on determining, and if possible quantifying, the single-effect of each ion on P removal efficiency by conducting experiments in artificial lake water where adding specific anions.

## Acknowledgements

This work was supported by Junta de Andalucía project No. RNM-6630 (Proyecto de Excelencia, 2010, Spain), an Integrated Action Project "Acción Integrada (2953/07)" from the University of Granada and MICINN MAT-2010-15101 project (Spain).

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