A COMPREHENSIVE EVALUATION OF USING MAGNETIC PARTICLES FOR LAKE RESTORATION

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TESIS DOCTORAL

UNIVERSIDAD DE GRANADA

UNIVERSIDAD DE GRANADA

FACULTAD DE CIENCIAS

Departamento de Ecología

Departamento de Física Aplicada

Instituto del Agua

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Granada, Abril 2014

Editor: Editorial de la Universidad de Granada
Autor: Azahara Merino Martos
D.L.: GR 2020-2014
ISBN: 978-84-9083-211-0

Visado en Granada

Abril de 2014

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Parte de los resultados incluidos en esta Memoria han sido presentados en los siguientes Congresos:

Autores: Merino-Martos, A., J. de Vicente, L. Cruz-Pizarro & I. de Vicente.
Título: High gradient magnetic separation for combating eutrophication of inland waters
Tipo de participación: Poster
Congreso: ***International Soft Matter Conference***
Lugar celebración: Granada (España)
Fecha: Julio 2010.

Autores: de Vicente, I., A. Merino-Martos, F. Guerrero, L. Cruz-Pizarro and J. de Vicente.
Título: Chemical interferences when using High Gradient Magnetic Separation for phosphate removal: consequences for lake restoration
Tipo de participación: Poster
Congreso: ***2nd Symposium of International Water Association***
Lugar celebración: Granada (España)
Fecha: Junio 2011

Autores: Merino-Martos, A., J. de Vicente, L. Cruz-Pizarro & I. de Vicente.
Título: A comprehensive evaluation of using magnetic particles for lake restoration
Tipo de participación: Poster
Congreso: ***3th Workshop on Advances in Colloidal Materials WACM***^{3}
Lugar celebración: Granada (España)
Fecha: Octubre 2013

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AGRADECIMIENTOS

Cuando decidí afrontar el reto de realizar este trabajo sabía que podía contar con todos vosotros. Sin vuestra ayuda todo habría sido mucho más complicado.

Estos apoyos tan decisivos me han llegado por distintos caminos, esos que he andado con vosotros y donde no me ha faltado nunca el aliento desinteresado de mi familia, principal baluarte a la hora de afrontar los trayectos de desánimo, por ello le doy un abrazo a todos.

Cuando esta ruta imaginaria se volvía empinada y aparecían sombras que podían hacer que abandonase, siempre había guías que me daban seguridad y presteza. Entre ellos quiero expresar mi más sincero agradecimiento a la Dra. Inmaculada de Vicente Álvarez de Manzaneda que con su tutela y seguimiento de este trabajo, con su plena disposición en todo momento he podido aprender los pasos necesarios para desarrollar su trabajo de investigación. Igualmente sin la ayuda del Dr. Juan de Vicente Álvarez de Manzaneda este trabajo tampoco podría haberse desempeñado.

Me gustaría también agradecer al Dr. Luis Cruz Pizarro por haberme facilitado la oportunidad de realizar esta investigación.

Gracias a la Dr. Victoria Amores Antequera, Francisco José Guerrero Ruiz y Ana I. Funes Cabrerizo por su estrecha colaboración.

Gracias al Instituto del Agua de la Universidad de Granada, al Departamento de Ecología de la Universidad de Granada, Departamento de Física Aplicada de la Universidad de Granada, Grupo de Física de Fluidos y Biocoloides y el Departamento de Biología Animal, Biología Vegetal y Ecología de la Universidad de Jaén por permitirme trabajar en sus instalaciones.

Por último dar las gracias a los proyectos de investigación P10-RNM-6630, P11-FQM-7074 y MINECO MAT 2010-15101, sin los cuales esta tesis no hubiera sido posible.

Ahora, cuando he llegado junto a todos estos compañeros de camino al destino fijado que no es otro que la conclusión de este trabajo, no me resta más que agradecerles que me transmitieran sus conocimientos y su experiencia, por todo ello, gracias.

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SUMMARY

Humans, after several decades interacting with their environment, looking for a higher field productivity, have drastically transformed the pristine natural ecosystems. These transformations has triggered artificial inputs of inorganic nutrients (mainly phosphorus and nitrogen) to water bodies, and hence, lastly causing an increase in primary production. The increase in primary production sets off a series of negative environmental effects which results in a deterioration of waters´ quality. One of the most evident sign is the increase in biological turbidity due to an intensive proliferation of algal biomass. On the other hand, its subsequent death and organic matter decomposition usually leads to a noticeable dissolved oxygen concentration decrease which lastly caused fish mortality, metals mobilization and an increase in phosphorus internal loading. As a result, water quality decreases, greatly interfering in the use that humans have of it.

The Organisation for Economic Co-operation and Development (OECD, 1982) defined "Eutrophication" as an increase of nutrients´ concentration and its effects coming from aquatic systems. Eutrophication has become one of the most widespread environmental problems in water bodies. It is estimated that around 30-40% of lakes and reservoirs all around the world are affected by eutrophication. This problem has become even bigger in shallow lakes typical from Mediterranean regions where there is a close and mutual connection between the sediment and water body. So, apart from the external load of nutrients received, it is added its predisposition to receive a high internal load. There is, in this case, an urgent necessity to take measures in order to restore water eutrophicated systems.

Then, in order to restore water eutrophicated systems, it has been essential to identify the limiting nutrient of primary productivity and, so, to reduce external and internal inputs of the identified limiting nutrient to water ecosystems. Although there was considerable controversy regarding this point, currently it is worldwide accepted that phosphorus is the most important limiting nutrient of primary production in inland waters. However, it is important to remark that there exist other environmental factors and different feedbacks that can also affect the primary production. So, the measures for mitigating freshwaters eutrophication would consider strategies which take into account these factors, apart from measures for reducing in-lake phosphorus concentration.

Despite all these last considerations, in this PhD dissertation we focus on developing a method for decreasing phosphorus availability in lake water. Basically, there exist three different types of management tools for reducing phosphorus concentration in lake water bodies: (i) reducing external phosphorus loading; (ii) increasing phosphorus retention in the sediment and (iii) increasing phosphorus export from the lake. Nevertheless, a combination of several measures is, in some cases, recommended for eutrophication to be successful. An illustrative example related to the control of external phosphorus loading is a better sewage treatment. In addition, it has been proposed the use of artificial wetlands for increasing phosphorus retention or pre-dams to purify water inlets before coming into the lake. In relation to the reduction of internal phosphorus loading, aluminum, calcium or iron salts have been used for phosphorus precipitation and, so, increasing its retention in lake sediments. Other methods for the reduction of internal loading are hypolimnetic aeration or nitrate addition. On the other hand, it is possible to increase the phosphorus export by the selective hypolimnetic withdrawal (with high phosphorus concentrations). Physical and biological manipulations have been also developed. In the first case, the air is introduced provoking a destratification and, so, improving oxygenation conditions. Biological manipulation

(“biomanipulation”) is based on manipulating the fish populations for controlling algal biomass. Finally, new measures, called “ecotechnology”, have been recently proposed, such as the use of bivalve (for example, the bivalve mussels) as grazer to control algal populations.

Despite of the wide variety of traditional and novel restoration methods, up to date, there exist an increasing affection of freshwater and coastal waters by eutrophication which has worries to scientists and politicians and requires new and innovative methods for dealing with it. The application of magnetic particle technology is one of these methods that have received considerable attention in recent years. The singularity of these particles is that, after they adsorb contaminants from aqueous effluents, they can be separated from the medium by a simple high gradient magnetic separation process.

In this context, the main purpose of this PhD dissertation was to evaluate the feasibility of using magnetic particles to phosphorus removal from natural and artificial aqueous solutions.

To do so, firstly, we quantified the maximum phosphorus adsorption capacity onto two types of magnetic particles, commercial iron and synthesized magnetite particles. It is important to highlight that particle size, apart from morphology, magnetic and electrokinetic characteristics, plays a very important role in adsorption capacity and in its subsequent removal from the medium under a magnetic field. In this way, small particles have a larger specific surface and so greater adsorption capacity. However, larger magnetic fields would be required for magnetic particle removal from solution. Contrarily, magnetic separation of large particles is easier but their adsorption capacity is smaller. Other important drawback comes from the fact that these particles are expected to quickly sediment under gravity. All in all, we took special care by choosing the particles. Carbonyl iron particles were supplied by BASF company (Germany) whereas magnetite particles were synthesized following a sol-gel precipitation and re-crystallization method. With this synthesis method, it could be obtained nanosized magnetite particles having a mean diameter of 90.0 ± 1.2 nm, one order of magnitude smaller than micronsized carbonyl iron particles (805 ± 10 nm). As a consequence, after applying Langmuir model to quantify the maximum adsorption capacity, laboratory results showed that it was 1.4 times higher for the magnetite than for carbonyl iron (empirical saturation constant was 27.15 and 18.83 mg g^{-1} for magnetite and carbonyl iron particles, respectively).

The effect of pH on phosphorus adsorption by particles was investigated. The experiments carried out, under batch conditions, show a strong dependence on pH. Adsorption capacity was larger at low pH values, however, whatever the pH, the efficiency was larger than 80% (in the studied range 5-9). Therefore, we worked at pH 7 due to natural waters are, commonly, from neutral to basic. Phosphorus removal efficiency was always larger than 85% at pH 7.

Magnetic particles were surface treated with amino silane groups (APTS). These $-NH_2$ groups provide the particles with a positive charge hence increasing adsorption capacity. As expect, APTS-coated iron particles experienced a notable increase in phosphorus maximum adsorption capacity. But, the effect of APTS-coating on phosphorus maximum adsorption capacity was less pronounced for the case of magnetite particles.

Finally, adsorption capacity of reused magnetic particles was assessed and we observed that phosphorus adsorption was reduced 20% for reusable carbonyl iron and 18% for reusable magnetite.

We set up a laboratory-scale for separating phosphorus from water under continuous flow conditions by using High Gradient Magnetic Separation (HGMS). This method hands large volumes of water because of the decreasing retention times.

Next, the investigation was focused on the identification of the best working conditions for removing phosphorus from solution. The results, from different tests showed that while flow rate does not significantly affect phosphorus removal efficiency, sonication time, magnetic field strength and the iron particles/phosphorus concentration ratio are the main factors controlling magnetic separation process.

Later, we used this prototype for assessing chemical interferences that other dissolved ions in lake waters could caused on phosphorus removal by magnetic particles. It was realized a study with natural waters collected from 20 Mediterranean lakes, widely differing in their water chemistry, some of them characterized by highly mineralized waters due to their endorheic character. The results showed a strong ionic strength dependence; phosphorus removal efficiencies decreased when ion concentrations increased. Thus, major cations such as Ca^{2+}, Mg^{2+}, Na^+ and K^+, anions such as SO_4^{2-} and Cl^- as well as dissolved organic carbon (DOC) were the driving factors controlling the effectiveness of phosphorus removal. In these experiments using natural lake waters we also considered important to analyze if magnetic particles adsorbed, apart from phosphorus, others dissolved ions present in lake waters. Therefore, experiments were carried out to test the effect of magnetic particles on other coexisting ions such as dissolved organic carbon (DOC) and reactive silicate concentrations, as well as conductivity and dissolved total solids. The results showed a notable reduction in these ions and confirm that phosphorus removal efficiency decreases when increasing salt concentrations, as was mentioned above.

Finally, and in order to identify the single-effect of each ion on phosphorus removal efficiency, we ran a set of laboratory single-ion experiments. The ions evaluated were SO_4^{2-}, Ca^{2+}, humic acid (HA) used as an indicator of DOC and reactive silicate. The results showed that HA and reactive silicate significantly decreased the effectiveness of phosphorus adsorption by iron particles due to the fact that they are competing for adsorption sites. Contrarily, the ions $SO_4^{2-}$and Ca^{2+} did not affect the phosphorus removal.

SPANISH SUMMARY

El ser humano, durante siglos de interacción con su entorno, buscando una mayor productividad de la tierra, ha transformado los primigenios ecosistemas naturales. Este proceso de transformación ha ido provocando un aporte excesivo de nutrientes inorgánicos (principalmente fósforo y nitrógeno) a las masas de agua causando un incremento de la producción primaria. El aumento de la producción primaria desencadena una serie de procesos ecológicos negativos que redunda en un empeoramiento de la calidad del agua. Una de las manifestaciones más evidente de este proceso es la elevada turbidez biológica debido a la intensa proliferación de la biomasa algal. Por otro lado, su posterior muerte y descomposición suele conducir a una marcada disminución de la concentración de oxígeno disuelto en el sistema que conlleva, generalmente, a una elevada mortalidad de la ictiofauna, disolución de metales pesados e incremento de la carga interna de fósforo al sistema. Por todo lo dicho, la calidad del agua se ve disminuida, interfiriendo, de esta manera, en el uso que el hombre pueda hacer de ella.

La Organización para la Cooperación y el Desarrollo Económico (OCDE, 1982) propuso el término “eutrofización” para aludir a este incremento de la concentración de nutrientes y sus efectos derivados en los sistemas acuáticos. La eutrofización se ha convertido en uno de los problemas medioambientales más extendidos en las masas de agua. Se estima que alrededor de un 30-40% de lagos y embalses del mundo están afectados por la eutrofización. Este problema se ha agudizado aun más en sistemas someros típicos de las regiones Mediterráneas donde hay una estrecha y recíproca conexión entre el sedimento y la columna de agua. Así pues, además de la carga externa de nutrientes que reciben, se suma su predisposición a recibir una elevada carga interna. Existe, por lo tanto, una necesidad urgente de adoptar medidas para la restauración de los ecosistemas acuáticos eutrofizados.

Ahora bien, para poder restaurar los sistemas acuáticos eutrofizados ha sido una labor primordial identificar el nutriente limitante de la producción primaria y por tanto actuar sobre él. A pesar de las controversias generadas en este tema, actualmente es bien reconocido el papel del fósforo como el principal nutriente limitante para el crecimiento de los productores primarios en los ecosistemas acuáticos continentales. No obstante, es preciso tener en cuenta que no sólo el fósforo afecta a la producción primaria pues existen diferentes factores ambientales y una gran diversidad de reacciones y transformaciones, que en última instancia conducen a un aumento en dicha producción. Así pues, las técnicas de recuperación de sistemas eutrofizados, para ser eficaces, no deberían estar basadas sólo en la reducción de la carga externa sino que deberían abarcar otras medidas que tuvieran en cuenta estos factores.

En este trabajo nos centramos en desarrollar una técnica para disminuir la concentración de fósforo en efluentes acuosos. Para la reducción de la concentración de fósforo en la masa de agua existen tres aproximaciones, si bien en algunos casos es recomendable una combinación de ellas para que la restauración sea exitosa: (i) reducir la carga externa de fósforo, (ii) incrementar la retención de fósforo en el sistema e (iii) incrementar la salida o exportación de fósforo desde el sistema. A modo ilustrativo, la entrada de fósforo al sistema se puede reducir en plantas de tratamiento. También, construyendo zonas húmedas artificiales para incrementar la capacidad de retención de fósforo o preembalses para purificar el agua de entrada inmediatamente antes de que entre al lago. Para reducir la concentración de fósforo dentro de un lago, se pueden aplicar sales de aluminio, calcio o hierro para precipitarlo y dejarlo inactivo en el sedimento. La oxigenación del hipolimnion con oxígeno puro o la adición de nitratos crean las condiciones redox deseables, en la capa superficial del sedimento, para evitar la liberación del fósforo, reduciendo, de ese modo, la carga interna. Por otro lado, también es posible aumentar la salida del fósforo por ejemplo mediante la eliminación selectiva de aguas hipolimnéticas (ricas en fósforo). También se puede hacer una manipulación física o biológica de la estructura del sistema. En la primera, el aire es artificialmente introducido y se hace circular a través de la columna de agua rompiendo de esa manera la estratificación térmica y, por tanto, mejorando las condiciones de oxigenación en el sistema. La manipulación biológica (“biomanipulación”) consiste básicamente en la retirada de peces planctívoros o en la introducción de peces piscívoros para controlar el crecimiento de algas y/o otros componentes de la cadena trófica. Finalmente, más recientemente, ha surgido una línea de nuevas medidas llamadas “eco-tecnológicas”. Una de ellas incluye el uso de bivalvos (por ejemplo, el mejillón cebra) como animal de pasto para controlar, de esta manera, las poblaciones de algas.

Sin embargo, la resolución del problema de eutrofización, cada vez más preocupante para las entidades públicas, requiere del desarrollo y aplicación de nuevos e innovadores métodos. La aplicación de tecnologías basadas en el uso de partículas magnéticas es uno de los métodos que recientemente ha centrado la atención de numerosos investigadores. La singularidad de estas partículas viene dada por el hecho de que pueden ser separadas del medio mediante un proceso sencillo de separación magnética con alto gradiente. Así, al poderse recuperar las partículas, es posible su posterior reutilización, y como consecuencia los costes económicos se ven reducidos fuertemente. Este método se puede aplicar en múltiples campos, pero debido a su eficiencia para adsorber partículas sólidas, se ha fomentado su uso, principalmente, en tratamientos de aguas residuales.

Con estas premisas, el objetivo general de la presente tesis doctoral es evaluar la viabilidad de usar partículas magnéticas para retirar el fósforo presente en medios acuosos naturales y artificiales.

Para ello, en primer lugar, se cuantificó, la capacidad máxima de adsorción de fósforo sobre dos tipos de partículas magnéticas, por un lado, partículas de hierro comercial puro, y por otro lado, partículas de magnetita sintetizadas en el laboratorio. Es importante destacar que el tamaño de las partículas así como sus características morfológicas, magnéticas y electrocinéticas juega un papel muy importante en la capacidad de adsorción y en su retirada en presencia del campo magnético. Así, partículas muy pequeñas tendrán una superficie específica mayor y por tanto una capacidad de adsorción también mayor, sin embargo se necesitará aumentar la intensidad del campo magnético para que la separación sea posible. Por el contrario, en partículas más grandes, su separación magnética será más fácil pero disminuirá su capacidad de adsorción, además de presentar el problema de sedimentación. Por todo ello, se tuvo especial cuidado a la hora de elegir las partículas. El hierro (carbonilo) puro nos fue proporcionado por la empresa BASF (Alemania) mientras que las partículas de magnetita fueron sintetizadas utilizando el método de precipitación sol-gel y re-cristalización. Mediante esta síntesis se pudo obtener nano-partículas de magnetita con un diámetro medio de 90 ± 1.2 nm, un orden de magnitud inferior al de las macro-partículas de hierro carbonilo (805 ± 10 nm). Es por ello, por lo que los resultados obtenidos de los experimentos realizados para cuantificar la capacidad máxima de adsorción (aplicando el modelo de Langmuir) mostraron que la magnetita adsorbe 1.4 veces más que las macro-partículas de hierro carbonilo (la capacidad de adsorción de fósforo para la magnetita presentó un valor de 27.15 mg g^{-1}, mientras que para el hierro carbonilo fue de 18.83 mg g^{-1}).

Se estudió el efecto que tenía el pH de la solución en la adsorción de fósforo sobre las partículas. Los experimentos, realizados en condiciones "batch", demostraron una fuerte dependencia con el pH. La mayor adsorción fue encontrada a pH bajos, sin embargo, la eficiencia en la retirada de fósforo fue siempre superior al 80% en todo el intervalo de pH estudiado (5-9). Así, en lo sucesivo se decidió trabajar a pH 7 ya que es el pH más frecuente en los sistemas acuáticos naturales. La eficiencia en la retirada de fósforo fue mayor del 85% para dicho pH.

Las partículas magnéticas fueron funcionalizadas con aminopropiltrietoxisilano (APTS). Esta molécula contiene un grupo amino ($-NH_2$) que dota de carga positiva a las partículas, evitando, de esta manera la agregación e incrementando su capacidad de adsorción. Como era de esperar, haciendo un estudio comparativo de la eficiencia en la adsorción de fósforo sobre partículas del hierro carbonilo con y sin recubrimiento de APTS, se observó que las partículas de hierro recubiertas adsorbían más que las partículas sin recubrir. De manera similar, el comportamiento de magnetita sin recubrir se comparó con magnetita recubierta de APTS. Sin embargo, a diferencia de lo encontrado para las partículas de hierro, mediante el recubrimiento de las partículas de magnetita no se consiguió mejorar significativamente la adsorción de fósforo.

Finalmente, se evaluó también la capacidad de adsorción de las partículas magnéticas reutilizadas y se observó una reducción del 20% para el caso del hierro carbonilo y de un 18% para la magnetita.

A continuación, y con la apuesta decidida hacia la idea de poner a punto una técnica para la restauración de sistemas acuáticos eficiente y económicamente viable, se diseñó un prototipo (a escala de laboratorio), para la retirada del fósforo de soluciones acuosas en flujo continuo mediante separación magnética de alto gradiente (HGMS). Dicha técnica permite tratar volúmenes de agua relativamente elevados al reducirse notablemente el tiempo de retención. Seguidamente, la investigación se enfocó en identificar las mejores condiciones de trabajo que permitieran conseguir mayor eficiencia en la retirada del fósforo. Los diferentes ensayos realizados, reflejaron que los factores que más determinantes en el proceso de separación magnética son el tiempo de sonicación, el gradiente de campo magnético y la razón entre las concentraciones de partículas de hierro y de fósforo.

Más tarde, se utilizó el prototipo en la evaluación de las interferencias químicas que otros iones disueltos en las aguas podrían ocasionar en la retirada de fósforo. Se realizó un estudio con aguas naturales procedentes de 20 lagunas y embalses distribuidos por Andalucía, cada una con una composición química diferente pero con concentraciones elevadas de sales debido a su carácter endorreico. Los resultados mostraron una fuerte dependencia con la fuerza iónica del agua; la eficiencia en la retirada de fósforo disminuye al aumentar la concentración de iones. Así, los cationes Ca^{2+}, Mg^{2+}, Na^+ y K^+, los aniones SO_4^{2-} y Cl^- y el carbono orgánico disuelto (DOC) fueron los factores determinantes.

Se consideró interesante también analizar si las partículas magnéticas adsorbían, además de fósforo, otros iones disueltos. Por tanto, se realizaron experimentos para analizar la reducción en las concentraciones de carbono orgánico disuelto (DOC) y de sílice así como la concentración de sólidos totales disueltos y la conductividad. En general, se observó una reducción notable en la concentración de estos iones lo que confirma los resultados anteriormente expuestos acerca de una reducción en la eficiencia de retirada de fósforo a medida que se incrementa la concentración en sales.

Finalmente, se llevaron a cabo experimentos para determinar el efecto individual que tenía cada ión en la eficiencia de retirada de fósforo por las partículas de hierro carbonilo. Los iones evaluados fueron SO_4^{2-}, Ca^{2+}, ácido húmico (HA) como un indicador del DOC y sílice. Los resultados mostraron que el HA y el sílice decrecen significativamente la eficiencia de la retirada del fósforo por las partículas de hierro pues están compitiendo por los sitios de adsorción. Por el contrario, los iones SO_4^{2-} y Ca^{2+}no afectan significativamente a la retirada del fósforo.

Chapter I. *General Introduction*

Chapter I

GENERAL INTRODUCTION

1. The problem: world-wide affection of inland waters by eutrophication

During several centuries since the industrial revolution, human activities have strongly affected the structure and function of the environment (Smith et al., 1999). Exponential human population growth has caused a continuous increase in aquatic and terrestrial resources demand. In particular, we have dramatically changed the globe by land clearing, agriculture, forestry, animal husbandry and urbanization, and by altering hydrological cycles. It is generally accepted that between one-third to one-half of the land´s surface has been transformed (Vitousek et al., 1997). Therefore, as a result of human activities, phosphorus (P) biogeochemical cycle has been completely modified. In fact, large quantities of P minerals are mined and processed to create P-containing fertilizers, and these fertilizers are heavily applied worldwide even to soils that already contain ample P reserves; hence, causing P accumulation in soils (Smith et al., 1999). This trend is greatly important for aquatic ecosystems functioning as it is responsible for an increase in P export, through runoff, from landscape to surface waters. In this sense, it is important to consider that recent studies have suggested that the rock phosphate reserves, which are necessary for creating P-containing fertilizers that are essential nowadays for the crop fields producers of large-scale food, are a non-renewable resource and could be exhausted in the next 50-100 years (Cordell et al., 2009). This situation has become alarming due to the increasing population density, above all in developing and emerging countries, which demands a high food production. So, it is required new challenges to find solutions where the equilibrium P-cycle is reached. Finally, an additional external P source to natural aquatic systems is the direct P-enriched waste spill. As a result, P loading to inland waters is thus strongly influenced by human population densities, the population densities of livestock and land use (Cole et al., 1993; Caraco, 1995; Smith et al., 1997).

A direct consequence of the above mentioned increase tendency in P export to inland waters is the eutrophication, which is defined as an increased primary productivity (trophy) in a water body due to enhanced availability of nutrients (OECD, 1992; Hupfer and Hilt, 2008; Smith, 2009). Among the major problems reducing water quality (i.e. atmospheric and geogenic acidification, salinization, and contamination by a large number of xenobiotics), eutrophication is one of the most widespread problem as about 30–40% of lakes and reservoirs worldwide are considered to be affected by unnaturally high nutrient concentrations (Hupfer and Hilt, 2008; Jeppesen et al., 2009). The majority of ecological effects in the aquatic environment have often been excessive blooms of harmful cyanobacteria (blue green algae) causing high turbidity, formation of hydrogen sulfide, drastic oxygen depletions as a result of the bacterial decomposition of the organic matter and as a consequence, death of fish and smell nuisance (Ryding and Rast, 1992; Hupfer and Hilt, 2008). Accordingly, a drastic reduction in species diversity and, in general, of water quality is occurring, hence also affecting human water uses such as consumption, irrigation, fishery and recreational activities. As a result of the increasing concern about eutrophication, European Parliament and Council adopted the Water Framework Directive (WFD, 2000/60/EC) as an operational tool for protecting the future of the water resources. One of the key objectives of this WFD is to ensure a minimum of good ecological quality in natural lakes in all member countries by 2015.

The study of small aquatic systems, which dominate Mediterranean landscape, has lagged behind larger-lake limnology over much of the past century. An analysis of publications on “ponds” versus “lakes” in the publications indexed by Web of Science suggests the bias of ecologists and limnologists toward studying larger water bodies as well as the differential rates of growth of publications in these areas (Downing, 2010). However, recent inventories based on modern geographical and mathematical approaches have shown that small lakes and ponds dominate the areal extent of continental waters, correcting a century long misconception that large lakes are most important (Downing, 2010). This is especially important because shallow and deep lakes exhibit significant differences in trophic structure and dynamics as well as in their sensitivity to threats such as that posed by increasing nutrient loading (Søndergaard et al., 2005; Jeppesen et al., 2009). In fact, as the lake response to changes in P loading mainly depends, among others, on the water-retention time as well as the size, structure, and use of the catchment area (Hupfer and Hilt, 2008), the typically high catchment area to lake area ratio characterizing shallow Mediterranean lakes makes these unique ecosystems especially sensible to eutrophication problem. Apart from the typically high P external loading, shallow lakes are also characterized by an important P internal loading (P release from lake sediments) as a result of the traditionally long eutrophication history. In this sense, Golterman (1995) established that P concentrations in the sediment and the overlying water are in a dynamic equilibrium where the position of this equilibrium, that controls whether input or output dominates, is determined by the interaction of multiple factors that may change over different time-scales. As a result of the relevance of the P internal loading, a delay in water quality improvement following reduced external P loading has been commonly observed in shallow lakes (Marsden, 1989; Sas, 1989; Harper, 1992; Ryding and Rast, 1992;; Istvánovics and Somlyódy, 1999; Søndergaard et al., 1999; Schauser et al., 2003; Romo et al., 2005, among others).

However, this “chemical” resistance to the improvement linked to P release from the sediment pool accumulated is not the only reason for the delay in recovery of eutrophic lakes after a reduction in external P loading. Jeppesen et al., 2005 have suggested that there also exists a “biological” resistance especially in shallow eutrophic lakes as a result of high fish predation pressure preventing the appearance of large herbivorous zooplankton that would otherwise clear the water.

Another difficulty for studying the function and structure of shallow lakes is their typically high temporal variability as a consequence, among others, of the close contact between the sediment and the overlying water lastly responsible for the high resuspension rates (i.e. de Vicente et al., 2006; de Vicente et al., 2010a). All in all, before considering any restoration method it is essential to know the exact functioning of the study system which is an especially difficult task for the case of shallow lakes due to their inherent inter and intra-annual variability.

2. Measures for mitigating eutrophication

Because eutrophication constitutes a key problem for water quality (Harper, 1992; Cooke et al., 1993), there was considerable controversy regarding its causes, especially in the 1960s and 1970s, when the problem began to be more fully recognized. Although few would deny that nutrient enrichment was involved, the question was which nutrient was responsible for eutrophication. The economic implications were clear as whichever industry was responsible for adding the critical nutrient, it would also be responsible for addressing the problem (Smol, 2008). Although commercial interests were promoting a view that most lakes were carbon (C) limited (Vallentyne, 1974); a contrasting view supported by observational, comparative studies of multiple lakes (Vollenweider, 1968), whole-lake fertilization experiments in oligotrophic Canadian lakes (Schindler, 1974) and studies of trends within individual lakes (Edmonson, 1970) emerged. That was the worldwide recognized “P limitation paradigm” which considered P as the single most important limiting element in lakes (Schindler, 1977). However, more recently, some authors support an alternative point of view considering P as a limiting nutrient over multi-annual time scales, but over shorter, co-limitation of multiple nutrients is expected to occur (Sterner, 2008). Anyway, the “P limitation paradigm" conducted to effective legislation, being a clear case study where science evolved public policy (Edmonson, 1991).

Once recognized the strong relationship between P and phytoplankton biomass, which also supports the "P limitation paradigm", valuable management tools were proposed for reducing in-lake P concentrations. However, the high variance between one specific P concentration and the resulting chlorophyll a (Chl a) concentration confirms, as it was stated before, that other environmental factors and different feedbacks can also affect the primary production (multiple control) (Hupfer and Hilt, 2008). This variance in regressions between P concentrations and algal biomass implies an alternative strategy, apart from reducing in-lake P concentrations, which is based on controlling the physical, chemical, or biological structure. Therefore, and according to Hupfer and Hilt (2008), restoration measures could be classified into two groups, those aimed on reducing in-lake P concentrations and those based on controlling physical, chemical or biological structure.

Among the management tools for decreasing P availability in lake water we can distinguish three different types: (i) reducing external P loading; (ii) increasing P retention in the sediment and (iii) increasing P export from the lake (Figure 1). Although a combination of several measures are, in some cases (see later), recommended, successful eutrophication management and control is primarily based on the restriction of P external inputs to the waterbody. In this sense, Jeppesen et al. (2009) indicate that the restoration of eutrophicated waterbodies will always require reductions of external nutrient loading and often supplementary in-lake measures to speed up the recovery process.

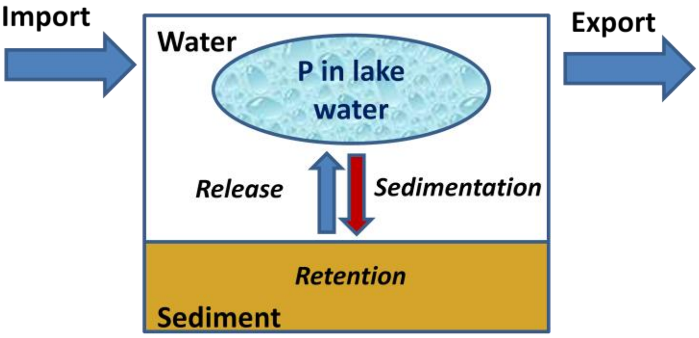


Figure 1. P balance and main P fluxes in a lake (modified from Hupfer and Hilt, 2008).

Next, we present the existing tools for combating eutrophication in inland waters, being focused on their main advantages and disadvantages (Table 1).

Table 1. Methods for mitigating eutrophication of inland waters (modified from Cooke et al., 2005; Hupfer and Hilt, 2008; Jeppesen et al., 2009).

✓ ***Reduction of P concentration***		
Reduction of external P loading	**Decreasing of P emission**	• Sewage treatment • Control of agricultural land use • Recycling P in industrial wastes
	Increasing P retention capacity	• Artificial wetlands
	Purification of inlet water	• Pre-dams • Macrophyte belts • Phosphorus elimination plant (PEP)
Reduction of internal P loading	**P inactivation**	• Aluminum, iron and calcium treatment
	Aeration and oxygenation	• Deep water aeration with deep-water aerator or full-lift reactor. • Shallow water aeration with hydropneumatic pumps, turbines, rollers or fountains
	Nitrate addition	• Calcium nitrate treatment
	Sediment capping	• Artificial barrier (fly ash, sand, clay minerals and autochthonous calcite).
Increasing of P export	**Hypolimnetic withdrawal**	• Use of withdrawal pipe
	External P elimination	• Precipitation, flocculation, flotation, adsorption or filtration treatment in stationary or transportable devices, in constructed artificial wetlands, and, in gravel bed reactors
	Sediment dredging	• Dry or wet excavation • Hydraulic and pneumatic dredging
✓ ***Control of the physical and biological structure***		
Physical manipulation	**Destratification**	• Introduction of compressed air by diffusers, perforated pipe or filters
Biological manipulations	**Food web manipulations**	• Introduction of piscivorous fish and/or removing planktivorous fish • Temporarty drainage of lake
	Macrophyte biomass control	• Water-level drawdown • Mechanical harvesting and sediment covers • Aquatic herbicides • Biological control

2.1. Reduction of in-lake P concentrations

- **Reduction of external P loading**

As it has been stated before, in order to reverse the eutrophication of lakes, much effort should be paid on reducing P external loading. Although some lakes may respond rapidly to such reductions, these measures have frequently not, as expected, led to a decrease in lake water P concentrations (Marsden, 1989; Sas, 1989). Therefore, after P external loading reduction, there are compiled in the literature different responses of in-lake P concentrations which have been generally classified in three types by Cooke et al. (2005). These authors classified the probable response of lakes to external load reduction in: (i) ”sufficient to change trophic category” (type I) (e.g. Lake Washington, USA), (ii) ”reduction in lake P and Chl a but insufficient to change trophic category” (type II) (e.g. Lake Norviken, Sweden) and (iii) ”small or no obvious improvement or reduction in lake P, and with little reduction in Chl a” (type III) (e.g. Lake Sammamish, USA).

From the large number of cases reported in the literature, we have selected two lakes which drastically differ in their response after reducing P external loading: Lake Washington (USA) and Lake Albufera (Spain). Lake Washington (USA) is a typical case of fast, straightforward and complete recovery occurred after external P load reduction. After diversion of secondary treated domestic wastewater, during the period from 1964 to 1967, a significant total phosphorus (TP) reduction (from 64 µg L^{-1} to 17 µg L^{-1}) was observed. The main reasons for so fast recovery were: (i) its relatively great depth, (ii) fast renewal rate, (iii) its oxic hypolimnion and (iv) its relatively short history of enrichment.

On the opposite site, Lake Albufera (Natural Park of Albufera, Spain) is an illustrative example of a shallow Mediterranean lake, which represents the predominant lentic aquatic ecosystems typology located in the Mediterranean area. It is the largest Spanish coastal lake with a surface area of 23.2 km^2, a mean depth of 1.2 m and a high water renewal rate of about 10 $year^{-1}$ (Romo et al., 2005). Nine years after sewage diversion (which caused a reduction in 77% and 24% of P and nitrogen (N) external loading, respectively), annual mean TP concentration decreased from 0.5 to 0.3 mg L^{-1}, Chl a concentration was reduced by half (annual mean of 180 µg L^{-1}) and cladoceran abundance increased and reached peaks twice a year. However, the reduction in P external loading was insufficient to change trophic category as in-lake P concentration was still too high. In fact, it is generally accepted that, in northern temperate shallow lakes, significant and sustaining changes in the biological community and water transparency cannot be expected to appear unless the TP concentrations has been reduced to a level below 0.05-0.1 mg L^{-1} (Jeppesen et al., 2000). Even more, experimental evidence suggests that critical thresholds are expected to be lower in warmer than in northern shallow lakes (Romo et al., 2004; Bécares et al., 2008).

On the other hand, resistance to water quality improvement may also be related to "biological" changes (Jeppesen et al., 2005). A comprehensive analysis based on a long-term data set of northern Europe shallow lakes reveals how changes in fish community structure and biomass, caused by the reduction in external P loading, may drastically affect top-down control on phytoplankton (see Jeppesen et al., 2005a; Jeppesen et al., 2005b; Jeppesen et al., 2007a; Søndergaard et al., 2007, among others), preventing, in the majority of cases, water clearance. A typical example, deeply studied, is Lake Søbygård (Denmark) which was considered to be strongly affected by changes in the zooplankton community structure. The results showed that, for a short-term, the changes in Chl a were influenced by the changes in the abundance of planktivorous fish. Nevertheless, the studies for a long-term evidenced a failure in the recovery of the lake due to the high internal P loading (Jeppesen et al., 1998).

Finally, it is important to consider that there are essential differences in biological interactions in temperate versus subtropical-tropical lakes and, therefore, different responses to external P loading reductions are expected to occur. As suggested by Jeppesen et al. (2007b), warm lakes have often prolonged growth seasons with a larger risk of long-lasting algal blooming and dense floating plant communities, higher dominance and abundance of small fish, higher fish aggregation in vegetation (loss of zooplankton refuge), more fish cohorts per year, more omnivory by fish and less specialist piscivory. Therefore, it will eventually result in a weaker response after reductions in external P loading in these kinds of lakes.

- **Reduction of internal P loading**

  - ***Chemical inactivation***

Apart from reducing external P loading, it has been frequently proved the need for reducing internal P loading. P inactivation by chemical treatment with aluminum (Al), calcium (Ca) or iron (Fe) salts is arguably one of the most frequently applied methods for increasing P retention in lake sediments and it has attracted considerable attention because of its relatively simplicity, convenience and efficiency. Metal salts, such as ferric salts and Al, Ca and nitrate (NO_3^-) have been used as P-binding substances because they can effectively precipitate P

(Hupfer and Hilt, 2008; Jeppesen et al., 2009). These substances supply new sorption sites for P, but each substance has their own advantages and disadvantages.

***Calcium treatment**:* Ca compounds induce the process of calcite ($CaCO_3$) precipitation that leads to sorption of P at the $CaCO_3$ surface (Hupfer and Hilt, 2008), being this process extremely dependent on P concentrations in the solution (Koutsoukos and Nancollas, 1981; Moreno and Varughese, 1981; De Rooij et al., 1983; House, 1990). House (1990) studied the P co-precipitation with $CaCO_3$ in freshwater and he found that inorganic P inhibits the crystal growth and, even, may stop the growth completely, depending on the supersaturation. This means that as eutrophication of a lake increases, this method is expected to be less effective as the precipitation reaction is progressively inhibited (House, 1990). In addition, pH and reaction time also play an important role. $CaCO_3$ seeds increase the crystallization rate and efficiency of crystallized P, especially after a reaction time of 1 day (Song et al., 2006) and it is dissolved for pH below 7.5 (Jeppesen et al., 2009). Apart from the pH dependence, the solubility of $CaCO_3$ is highly sensitive to redox changes. It is known that the equilibrium reaction of carbonic acid (H_2CO_3) in lake water is as follows:

$CO_{2(aq)} + H_2O \leftrightarrow H_2CO_{3(aq)} \leftrightarrow H^+ + HCO_3^- \leftrightarrow H^+ + CO_3^{2-}$

And if there exists Ca^{2+}, $CaCO_3$ will be formed,

$Ca^{2+} + CO_3^{2-} \leftrightarrow CaCO_3$

In this basis, Cooke et al. (1993) established that when CO_2 concentration increases and pH falls, a rapid dissolution of $CaCO_3$ occurs (i.e., the equilibrium reaction moves to the left), resulting in a continuous release of P to the lake water. This is especially important for eutrophic lakes, because during thermal stratification, pH is typically lower in hypolimnetic than in epilimnetic waters due to higher CO_2 concentrations caused by higher mineralization rates (i.e. CO_2 production) and no CO_2 consumption by photosynthesizer organisms. As a result, P dissolution from P bound to $CaCO_3$ compounds is a typical problem in hypolimnetic waters. In fact, liming experiments with $Ca(OH)_2$ and $CaCO_3$ in enclosures carried out on the eutrophic subalpine Lake Alserio (Italy) have confirmed that lime addition is not a long-time efficient method for trapping P in hypolimnetic waters as it strongly depends on pH values (Rogora et al. 2002). Accordingly, in this case, Ca treatment is recommended to be accompanied by other techniques such as hypolimnetic withdrawal that break the thermal stratification of lake and, therefore, avoid the conditions mentioned above. Nonetheless, it is always a necessary and a previous step to know the characteristics of lake before considering any other technique. As a way of illustration of some successful whole-lake Ca treatments, Prepas et al. (1990) observed that the addition of lime ($CaCO_3$ or calcium hydroxide) to a hardwater lake (Alberta, Canada) enhanced the natural occurrence of $CaCO_3$ precipitation, causing a summer reduction of TP and Chl a of 30% and 12%, respectively. Similarly, Babin et al. (1994) reported that mean summer Chl a and TP decreased from 61 µg L^{-1} to 24 µg L^{-1} and from 120 µgP L^{-1} to 68 µgP L^{-1}, respectively, in a thermally stratified lake (Alberta, Canada). They attributed this event to a higher winter dissolved oxygen concentrations which enhanced sediment Ca, and, consequently, avoided P release.It is important to consider that the increase in water temperature and in pH characterizing summer thermal stratification period, promotes the natural occurrence of $CaCO_3$ precipitation and, thus, it may reduce TP and Chl a concentrations (Koschel et al., 1998). Therefore, the present technique is based on promoting this natural process by adding Ca.

***Aluminum treatment**:* Al salt is another compound that has been widely used in USA and in northern Europe to combat eutrophication due to its strong affinity for P (i.e. Hansen et al., 2003; Cooke et al., 2005; Reitzel et al., 2003, 2005). Despite the high efficiency of Al for binding P, Al treatments are generally difficult to handle because of their acidity. Application of Al to a lake results in the formation of an Al hydroxide ($Al(OH)_3$) that cause a release of H^+ ions, leading to a sharp decrease in pH (Berkowitz et al., 2005; Hupfer and Hilt., 2008; Anderson and Berkowitz, 2010). This may consequently lead to the formation of toxic species of Al such as Al^{3+} and $Al(OH)^{2+}$ when pH is below 6 (Cooke et al., 2005; Hupfer and Hilt, 2008; Jeppesen et al., 2009). Additionally, an increase in the pH above 8 may result in the re-release of the P from the Al flocs (Lewandowski et al., 2003). These changes in Al speciation as a function of pH can be observed in Figure 2 (Stumm and Morgan, 1996).

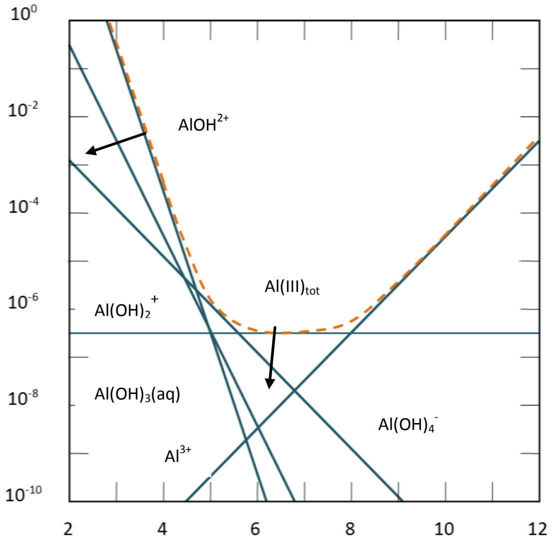


Figure 2. Distribution of Al species as function of pH (modified from Stumm and Morgan, 1996).

Although Al application for P inactivation is a widely used technique for recovery of eutrophic lakes, little is known about its long-term effects. Several few cases have been reported in the literature (see Cooke et al., 1993). For example, long-term datasets have shown that hypolimnetic Al treatment had retarded internal P loading for at least 12 years in alkaline Mirror and Shadow Lakes (WI, USA). Shallow West and East Twin Lakes (OH, USA) are also some of the few examples of long-term success experiences as hypolimnetic Al application caused a reduction in P concentrations even after 14 years. Smeltzer, (1990) reported that Lake Morey (Vermont, USA) had achieved long-term control over internal P loading after Al treatment. In this lake, with moderately low alkalinity, the long-term P control was ensured by adding an alkaline substance (sodium aluminate) as buffering capacity to avoid pH reduction and Al toxicity. However, for shallow Kezar Lake (NH, USA), which is very soft water lake, P concentrations returned to near pretreatment values after 5 years of Al application despite the use of sodium aluminate.

More recently, Egemose et al. (2011) reported the response of Lake Nordborg (Denmark) to both an external P loading reduction and to P inactivation, by adding $AlCl_3$. In particular, external P loading was reduced by 40% by using precipitation ponds in two inlets and $AlCl_3$ was added for reducing internal P loading (90-94%). As a result, in-lake P concentrations were drastically reduced (73%) even 4 years after Al addition (Figure 3). However, it was concluded that a further reduction in external P loading was needed to obtain the full effect of the Al treatment in the lake. Another important conclusion of this study was that, unambiguously, the addition of Al to lake water influences not only P cycling but also the cycling of silica. In fact, lower silica concentrations were observed one year after Al treatment, thus corroborating the findings of de Vicente et al. (2008b).

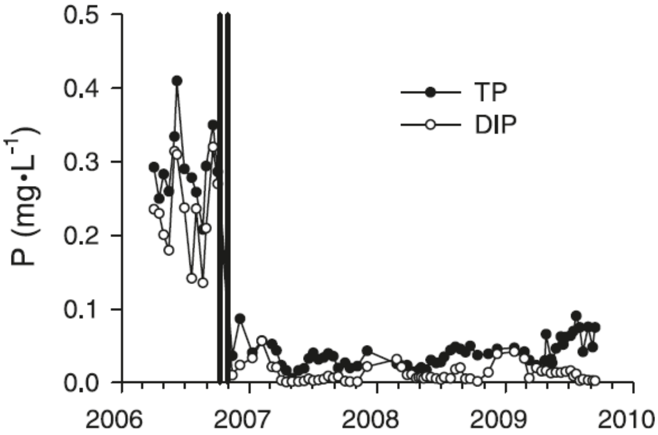


Figure 3. Temporal development in total P (filled circles) and dissolved inorganic P (open circles) in the water phase of Lake Nordborg before and after the Al treatment in October 2006 (treatment period indicated by the two vertical lines), given as average concentrations in the whole water column (Egemose et al., 2011).

Next, we would like to stress two of the main disadvantages of using Al salts for lake restoration. Firstly, the fast reduction in maximum P adsorption capacity when $Al(OH)_3$ flocs are aged. In particular, de Vicente et al. (2008a) quantified a reduction of 76% in the maximum P adsorption capacity when the fresh $Al(OH)_3$ flocs were aged for 3 months as a result of the increase over time in their crystallinity, lastly causing the transformation of amorphous $Al(OH)_3$ to gibbsite, which was accompanied by a decrease in surface area. Similar results were also found by Berkowitz et al. (2006) who measured half of the maximum P adsorption capacity when Al flocs were aged for 6 months. The use of air dried instead of fresh $Al(OH)_3$ flocs by Berkowitz et al. may have increased crystallization in their experiment with the consequence of underestimation of the adsorption capacity. These results are crucial for lake restoration as they suggest that repeated dosing of smaller Al-aliquots may be more efficient than adding a single big dose. Secondly, and in order to get the right dose of Al for trapping P, it is necessary to consider the existence of chemical interferences that may affect the adsorption of P on $Al(OH)_3$ in natural lake water. Hence, de Vicente et al. (2008b) found that, using single-ion experiments, silicate (>200 µM) and humic acids significantly decreased the effectiveness of P adsorption to $Al(OH)_3$ by 10–13% at 450 µM Si and 17% at 1 mM C, respectively; while no effect of NaCl was observed.

***Iron treatment**:* Although Fe has higher affinity for P than Al, its efficiency strongly depends on the redox conditions in the water (Hupfer and Hilt, 2008; Jeppesen et al., 2009). It is well-known that under strongly reductive conditions, a portion of ferric hydroxides ($Fe(OH)_3$) can be reduced to Fe^{2+}, being the previously sorbed P again released to the dissolved phase (Mortimer, 1941; Mortimer, 1971). Accordingly, the Fe-P complex is only stable under oxic conditions. Boers et al. (1994) showed that treatment of lake sediments with ferric chloride ($FeCl_3$) was potentially an effective method to decrease internal P loading, but the durability of this method still needs to be proven. Indeed, it has been shown that the availability of sorption sites for P on Fe is correlated with the surface sediment Fe:P ratio and, hence, it controls the retention (Fe:P>15) or release (Fe:P<15) of P under oxic conditions (Jensen et al., 1992).

- **Aeration and oxygenation**

Hypolimnetic aeration (air injection) and oxygenation (pure oxygen injection) is applied to counteract hypolimnetic anoxia which is formed during summer stratification of deep eutrophic lakes (Liboriussen et al., 2009). Among the main problems caused by anoxic prolonged periods are sediment P release, due to the redox-dependent release from Fe hydroxides and bacteria, solubilization of metals that are undesirable in water supplies and limitation of fisheries, especially cold water species (Cooke et al., 2005; Liboriussen et al., 2009).

Thereby, the specific objectives of this method are:

1. To raise the oxygen content of the hypolimnion without destratifying the water column or warming the hypolimnion.
2. To provide an increased habitat and food supply for coldwater fish species.
3. To reduce P internal loading, if the sediment-water exchange of P is controlled by iron redox.
4. To reduce other constituents that reach high and possibly undesirable concentrations under anaerobic conditions, such as NH_4^+, Mn and Fe.

Liboriussen et al. (2009) have observed different responses in five eutrophic dimictic Danish lakes (Hald, Viborg, Vedsted, Torup and Fure) after hypolimnetic oxygenation were conducted for 4-20 years. The most marked effects in TP concentrations were observed in Lake Hald (TP decreased from 800 µg P L^{-1} to 200 µg P L^{-1}) where reduction of the external P loading, during the oxygenation period, was highest. By contrast, Lake Fure experienced the highest increase in hypolimnetic oxygen concentration (mean summer increase from 1.4 to 8.9 mg O_2 L^{-1}). A striking result is that in one of the studied lakes (Lake Vedsted), mean summer dissolved oxygen concentration decreased from 3.0 to 2.2 mg L^{-1} after hypolimnetic oxygenation. This result may be explained by a stimulation of the mineralization rate (Cooke et al., 1993). Another possible negative effect of hypolimnetic oxygenation could be an increase in sediment P release from organic P pool (due to the mineralization enhancement) when there is not enough adsorption sites (Fe:P<15) . Accordingly, there is a risk that oxygenation will create an increased mobile P pool that might be released when oxygenation is stopped (Gächter and Müller, 2003).

Documentation is mostly lacking for the effect of more distributed zooplankton populations on phytoplankton control in lakes after aeration. It has been observed that large *Daphnia pulex* became very abundant in Hemlock lake following hypolimnetic aeration (Cooke et al., 1993). It reached an abundance nearly 90 times greater than during the pretreatment time. Encouragement of the large zooplankters could lead to greater phytoplankton loss rates and lower biomass. If that effect can be proved, hypolimnetic aeration could offer much greater benefits for restoring eutrophic lakes than hitherto believed.

- **Nitrate addition**

Similarly to hypolimnetic oxygenation, NO_3^- addition (“Riplox method”) to anoxic hypolimnion focuses on improving redox-sensitive sorption of P to Fe in the surface sediment (Hupfer and Hilt, 2008). As we have already stated, it is well-known that, under anoxic conditions, P which is incipiently bound to $Fe(OH)_3$ can be released as a consequence of the partial reductive dissolution of the Fe^{3+} solid phases (Stumm and Morgan, 1996). In this sense, NO_3^- enhances mineralization of organic matter by denitrifying bacteria, and, thereby, restores the oxidized state of sediment (Cooke et al., 1993), maintaining a high redox potential where Fe is still in its oxidized form (Fe^{3+}) (Jeppesen et al., 2009) (Table 2). The main advantage of using NO_3^- instead of oxygen is that much higher oxidation equivalents can be added because being a salt, NO_3^- is more soluble than oxygen (a gas). Thus, NO_3^- will penetrate into the sediment more readily and to a greater depth than oxygen (Cooke et al., 1993; Jeppesen et al., 2009).

Table 2. Standard redox potential for some environmentally important redox half-cell reaction (take from Benjamin, 2002).

Reaction	*E_H^0 (mV)*
$2NO_3^- + 10e^- + 12H^+ \leftrightarrow N_2(g) + 6H_2O$	1241
$MnO_2(s) + 2e^- + 4H^+ \leftrightarrow Mn^{2+} + 2H_2O$	1227
$O_2\ (g) + 4H^+ + 4e^- \leftrightarrow 2H_2O$	1226
$NO_3^- + 8e^- + 10H^+ \leftrightarrow NH_4^+ + 3H_2O$	878
$NO_3^- + 2e^- + 2H^+ \leftrightarrow NO_2^- + H_2O$	843
$Fe^{3+} + e^- \leftrightarrow Fe^{2+}$	769
$SO_4^{2-} + 8e^- + 10H^+ \leftrightarrow H_2S(aq) + 4H_2O$	299
$SO_4^{2-} + 8e^- + 9H^+ \leftrightarrow HS^- + 4H_2O$	248
$2H^+ + 2e^- \leftrightarrow H_2(g)$	0

In the literature, there are reported several study cases of NO_3^- addition (Cooke et al., 1993). For example, Foy (1986) showed the effectiveness of NO_3^- for inhibiting Fe reduction and, as a consequence, reducing P release from the anoxic sediments of a small dimictic lake. However, the addition of NO_3^- did not alter the rate of hypolimnetic deoxygenation and the treatment was not able to reduce Mn and NH_4^+ release. When comparing the costs of using NO_3^- or Fe/Al salts to suppress sediment P release, it is recognized that NO_3^- addition is at least 80% more expensive. More recently, SØndergaard et al. (2000) found that maximum concentrations of dissolved inorganic P in the hypolimnion ranged from 1.6 to 2.9 mg P L^{-1} in untreated years in a Danish lake, while after adding NO_3^- a reduction to 0.8 -1.2 mg P L^{-1} in treatment years was observed.

For getting better results by using the “Riplox Method”, lake managers have often used a combination of several adsorbents. Cooke et al. (1993) reported the first application of this method in Lake Lillesjö (Sweden). Firstly, $FeCl_3$ was applied to the sediments and a very low pH was created there (pH=3). Secondly, $CaCO_3$ was added in a quantity so as to create an optimal pH for denitrification (usually between 7.0-7.5). Finally, calcium nitrate was injected into the top 30 cm of sediments to oxidize and break down organic matter and denitrify the sediments. Successful results were observed as oxygen concentrations and Secchi disk transparency increased and P concentrations drastically decreased.

- **Increasing of P export**

  - **Hypolimnetic withdrawal**

It involves removing nutrient-enriched hypolimnion water and therefore, improving the redox conditions in the lake as the hypolimnetic water is characterized by a high oxygen deficiency and an accumulation of reduced substances (Hupfer and Hilt, 2008; Jeppesen et al., 2009). According to Cooke et al. (2005), the advantages of hypolimnetic withdrawal are threefold: (i) relatively low capital and operational costs, (ii) evidence of effectiveness in a large fraction of cases, and (iii) potentially long-term and even permanent effectiveness. However, the main inconvenience of this method is the potential pollution of downstream systems (high loading of TP, ammonia, low oxygen concentration and occasionally an obnoxious smell of hydrogen sulfide) (Jeppesen et al., 2009).

2.2. Control of the physical and biological structure

- **Physical manipulation**

Physical manipulation mainly involves breaking lake thermal stratification (destratification) when the air is artificially circulated through the water column by using devices such as pumps, jets or bubbled air (Cooke et al., 1993; Lawson and Anderson, 2007). Unlike hypolimnetic aeration, the temperature of the whole lake is raised with complete circulation; the greatest increase in temperature occurs at depths that were previously part of the hypolimnion. Therefore, as a result of this artificial circulation, dissolved oxygen conditions across the lake are improved (i.e. the oxygen reaches the anoxic bottom waters). Accordingly, it is expected that complexation and precipitation of metals such as NH_4^+, Mn and Fe occur under oxic conditions, preventing the release of sedimentary P.

On the other hand, circulation can also directly control phytoplankton growth by increasing the depth of mixing and, thus, causing light limitation. In addition, changes in phytoplankton composition have also been observed (Cooke et al., 1993). For example, it has been found a shift from dominance by bloom forming blue-green algae to one by diatoms or green algae. There actually exist at least three hypothesis for explaining those changes in phytoplankton composition: (i) epilimnetic CO_2 increase and pH decrease, (ii) distribution of buoyant cells and (iii) grazing by zooplankton.

A clear disadvantage of artificial circulation is that it is not recommended for the case of shallow lakes as it may conduct to sediment resuspension (Cooke et al., 1993). Indeed, in the shallow (mean depth = 3 m) Crystal Lake (MN, USA) a phytoplankton increase was observed right after destratification.

Apart from basin morphology and depth, the design and operation conditions of the devices play an important role in this technique. In the Crystal Lake, internal P loading was substantially increased following circulation due to insufficient air-flow rate employed (Cooke et al., 1993). Lawson and Anderson (2007) observed that stratification and a large area of anoxic sediments persisted despite pump operation in the shallow Lake Elsinore (California, USA) due to lack of a well-defined design of axial flow pump.

- **Biological manipulation**

This method is based on manipulating fish populations in a lake in order to change algal biomass (Cooke et al., 1995). There has been a considerable spectrum of biomanipulation experiences throughout the world and some of these go back longer than we hitherto believed. Indeed, Caird (1945) described a case in which, in 1940, 1000 largemouth bass (a piscivorous fish) were added to Round Pond (USA). Up to that time the lake had severe algal problems but it apparently improved soon after. Later, these observations, led Shapiro et al. (1975) to propose the term "biomanipulation" which was defined as "*a serie of manipulations of the biota of lakes and of their habitats to facilitate certain interactions and results which we as lake users consider beneficial –namely reduction of algal biomass and, in particular, of blue-green*". In fact, it is generally expected that a reduction of predation pressure on herbivorous zooplankton, by reducing planktivorous fish community and/or enhancing piscivorous fish, will be followed by an increased abundance and size of zooplankton, particularly Daphnia and as a consequence, a higher grazing pressure on phytoplankton. Accordingly, a discernible improvement on water clarity will be observed (Hansson et al., 1998).

In the literature, there exist a large number of illustrative examples with different outcomes after applying biomanipulation. Cooke et al. (2005) recognized the difficulty in generalizing the success of any biomanipulation application as there are many factors involved. Jeppesen et al. (1997), based on data from 233 Danish lakes, indicated that biomanipulation may be more successful in shallow lakes due to the frequent colonization of large areas by submerged macrophytes which act as a refuge for cladocerans, protecting them from fish predation and, thereby, helping to maintain a higher grazing pressure on phytoplankton. On the other hand, Gulati et al. (2005) recognized that there are several reasons for explaining biomanipulation failures, such as: (i) inadequate reduction of external P loading and increase of internal P loading, (ii) poor edibility of colonial cyanobacteria to daphnids, (iii) inadequate coverage of the lake area by macrophytes due to foraging on the macrophytes by both fish and birds, (iv) ineffective reduction of planktivorous fish biomass and inability to maintain the fish mass to a low level for longer periods, (v) failure of piscivorous fishes (i.e. *Esox lucius*) transplantation to lakes to control planktivorous fishes.

But, apart from causing a general reduction in phytoplankton biomass, several secondary effects may occur after biomanipulation (Hansson et al., 1998). Among them, we would like to remark the risk of increased recruitment of young-of-the-year fish (YOY). The high recruitment YOY due to a reduced competition for food, may exert a strong predation on zooplankton (*Daphnia*) and hence counteract the effect of biomanipulation.

Finally, Hansson et al. (1998) included some practical recommendations for achieving the success after lake biomanipulation, such as (i) the reduction in the biomass of planktivorous fish should be 75% or more, (ii) the fish reduction should be performed efficiently and rapidly (within 1-3 years), (iii) efforts should be made to reduce the number of benthic feeding fish, (iv) the recruitment of YOY fish should be reduced, (v) the conditions for establishment of submerged macrophytes should be improved and (vi) the external input of nutrients (P and N) should be reduced as much as possible before the biomanipulation.

Next, we present two cases reported in the literature which illustrate the variety of lake responses after biomanipulation (Hansson et al., 1998). Firstly, Lake Vesijärvi (Finland), which was biomanipulated by cyprinid removal in combination with piscivore addition is an example of long-term successful results (see Figure 4). After biomanipulation, there was a notable decrease in TP and Chl a concentrations and a concomitant increase in water transparency (Secchi disk) and this water quality improvement was observed even 6 years after biomanipulation (Figure 4).

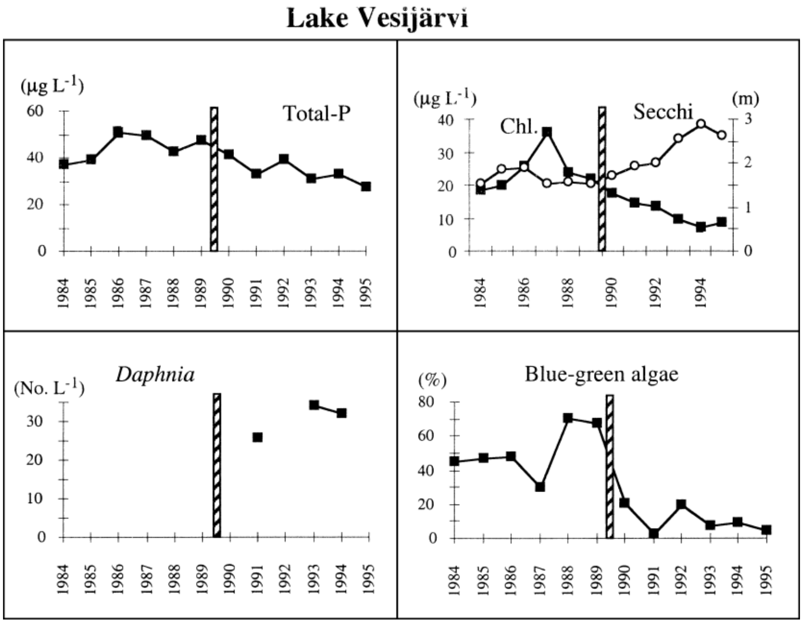


Figure 4. Temporal fluctuations in chemical and biological variables in Lake Vesijärvi (Finland). The striped bar indicates the start of the biomanipulation. The variables are total phosphorus (µg L^{-1}). Secchi depth (m), chlorophyll a (µg L^{-1}), Daphnia abundance (number. L^{-1}), and blue-green algae as proportion (%) of total algal biomass.

Contrarily to Lake Vesijärvi, most of lakes where biomanipulation has been applied experienced changes mainly on short term but later on, water quality starts to deteriorate. That is the case of the Danish Lake Væng, where a cyprinid fish removal was carried out. As a result, a rapid decrease in TP and Chl a concentrations with a subsequent increase of Secchi depth (Figure 5). *Daphnia* biomass showed an increase the year after the treatment, but then decreased to very low values, suggesting that zooplanktivorous community exerted a strong predation pressure on those organisms. On the other hand, the percentage of piscivorous fish increased from 20% to almost 80% of total fish biomass 2 years after the biomanipulation, and the submerged macrophytes expanded and covered almost 80% of the sediment surface after 4 years. However 5 years after biomanipulation, TP concentrations and Chl a gradually increased concomitantly to a Secchi disck depth and submerged macrophyte cover decline. The reason behind this failure was the insufficient reduction in planktivorous fish biomass (50% compared to 85% in the Lake Vesijärvi) which had negative cascading grazing effects. Indeed, the higher abundance of planktivorous fish could likely have caused an increased recruitment of YOY with their negative effect on lake water quality, as it has been mentioned above.

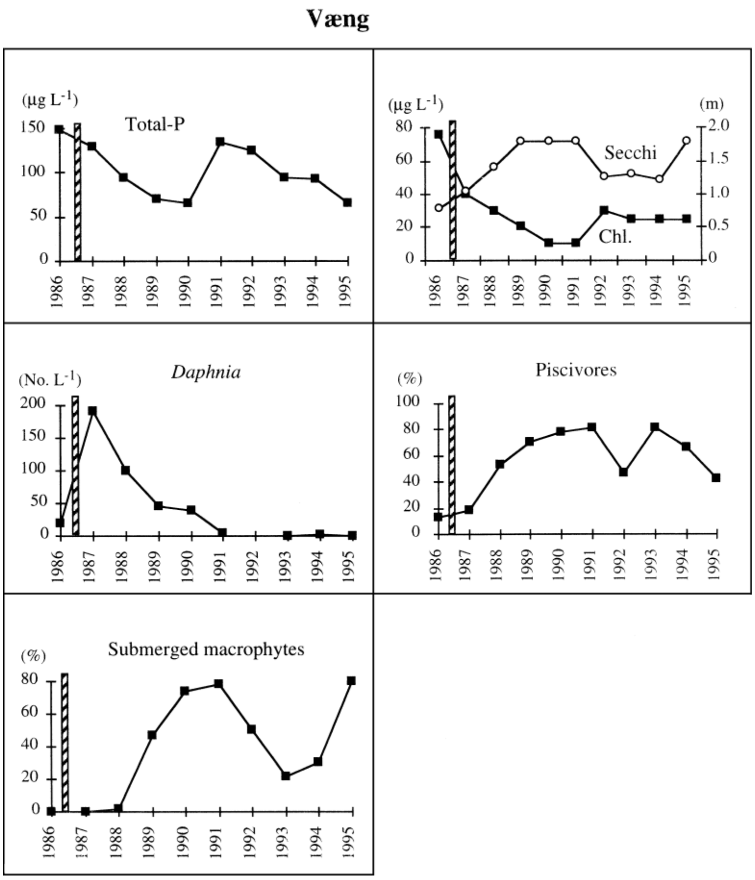


Figure 5. Temporal fluctuations in chemical and biological variables in Lake Væng (Denmark). The striped bar indicates the start of the biomanipulation. The variables are total P (µg L^{-1}), Secchi depth (m), chlorophyll a (µg L^{-1}), Daphnia abundance (no. L^{-1}), piscivorous fish as proportion (%) of total fish biomass, and the cover of submerged macrophytes (% of total bottom area).

- **New ecotechnological measures**

From the above mentioned failures characterizing lake biomanipulation, new and complementary measures have been recently proposed (Gulati et al., 2008). They are considered as ecotechnological measures which include: (i) reduction of sediment resuspension, (ii) water-level management and (iii) the use in shallow lakes of bivalve mussels as effective grazers.

With respect to the use of bivalve mussels as restoration tool, they have suggested their use as complementary grazers to crustacean zooplankton when Cyanobacteria are dominant in lakes. In fact, Gulati et al. (2008) reviewed the use of zebra mussels (*Dreissena polymorpha*) as substitute grazers to control algal populations and they found that there exist a great discrepancy in the impact that bivalve and zooplankton could have on phytoplankton.

Experimental results have evidenced that *Dreissena polymorpha* has higher filtration rates of Cyanobacteria than *Daphnia spp*. However, despite the high clearance rate characterizing bivalve mussels, it is essential to consider that using bivalves for lake restoration also has several and relevant disadvantages, such as: (i) the substrate for settlement of mussel larvae is not always adequate, (ii) the zebra mussels may spread and expand their territory causing uncontrolled impacts on the entire lake ecosystem, and (iii) zebra mussels may also negatively affect the biodiversity of native fauna through competition for food resources and habitat. Hence, further studies should be focused on the use of native mussels instead of the zebra mussel as an alternative tool for lake restoration.

3. New and promising methods: the case of magnetic particles

As it can be concluded from the previous section, there is no a management tool as panacea for eutrophicated inland waters. Although chemical adsorbents such as Fe, Al and Ca salts seem to be the most convenient, they are very sensitive to changes in physicochemical conditions. In order to by-pass these difficulties, great attention has recently been paid for developing new and efficient adsorbents that are able to reduce P levels in water bodies. Next, we outline some examples.

A new lanthanum-modified clay (bentonite) mineral with high cation exchange capacities (Phoslock) was developed in the 1990s by the Commonwealth Scientific and Industrial Research Organisation (CSIRO) of Australia. Lürling and Tolman (2010) studied its effects on Daphnia and showed that it had no harmful effects on these organisms and was highly efficient in P removal from the water column. Ross et al. (2008) and Haghseresht et al. (2009) studied the removal of P by Phoslock under controlled conditions. These studies revealed that: (i) the maximum adsorption capacity is achieved at pH 5-7 and decreases rapidly at higher pHs. This decrease can be attributed to the formation of the hydroxyl species of the lanthanum ions, decreasing the number of phosphorus binding sites on the Phoslock surface; (ii) the smaller particles aggregate at pH 9 causing both a reduction in surface area and a faster settling (shorter contact time with the solution) and (iii) the Zeta potential of Phoslock is more negative at high pH values. This also contributes to the decrease in P adsorption capacity of Phoslock at high pH values.

Karapinar et al. (2009) suggested the use of naturally occurring hydrated aluminosilicate minerals (zeolites) for the removal of ammonium and then as a seed material for the precipitation of phosphate in the form of Ca-phosphate. Their study highlights that zeolites can be suitably used as an adsorbent/seed material for the removal of both nutrients.

Albeit, the precipitation is highly dependent on pH, i.e., an increase of pH makes the solution conditions favorable for precipitation. In addition, this method has only been tested in wastewater. Further investigation is required with focus on experiments in natural lake water where the water chemistry is widely different.

Recently, a new and commercial titanium dioxide based adsorbent (Metsorb) has been used for dissolved reactive phosphorus (DRP) removal from fresh and marine waters in combination with diffusive gradients using a thin film technique (DGT). Panther et al. (2010) presented a study at scale-laboratory about the effect of adsorbent capacity in deployment time. This work demonstrated that the capacity of the Metsorb binding decreased at longer deployment times. Moreover, they highlighted that adsorbent selectivity is also an important factor that must be considered when the DGT is used in the presence of competing major ions; a high-capacity adsorbent with limited selectivity would quickly become saturated in natural waters and may be rendered ineffective.

In this dissertation, we propose the use of magnetic colloidal particles as a valuable restoration tool for removing P from eutrophicated inland waters. Our interest in these particles was motivated by their specific physicochemical properties that confer important advantages. As will be seen in section 4 of this introduction, magnetic particles can be (and in fact are) relatively cost-effective, in comparison with others adsorbents. This is due to the fact that their magnetic response makes them suitable to be recovered from the solution, hence reducing economic costs as well as secondary effects in the aquatic biota. However, their physicochemical characteristics need to be carefully tuned and interrogated to provide an appropriate basis for their development into effective restoration tools for eutrophicated aquatic systems. Hence, a comprehensive study regarding their synthesis and characterization can be seen throughout this dissertation.

3.1. Colloidal systems: theoretical background

3.1.1. Concept of colloidal system

Water dispersions of magnetic particles employed in this dissertation constitute a colloidal dispersion. It can be defined as a dispersion of one phase (dispersed phase) into another one (continuous phase). Depending on the nature of the dispersed and the continuous phase different types of colloidal dispersions can be distinguished. For example, a dispersion of solid or liquid particles in a gas is called aerosol whereas a liquid dispersed in other liquid is an emulsion. Likewise, if the dispersed phase represents a solid and this is distributed into a liquid, the system formed is called colloidal suspension (Hunter, 1993).

Anyway, the system will be colloidal if the dispersed phase has some linear dimension between 10^{-9}m (10 Å) and 10^{-6}m (μm). However, it should be emphasized that there is no unanimity about the size boundaries and these are rather arbitrary.

Traditionally, colloids are divided into two classes: lyophilic and lyophobic, depending on the ease with which the system can be redispersed (Hunter, 1993). Thereby, lyophilic colloids are spontaneously dispersed in the continuous phase, i.e., they feel attraction toward the solvent. In the absence of chemical changes or changes of temperature, this dispersion is stable indefinitely. On the other hand, lyophobic colloids are dispersed with difficulty due to the fact that they are not attracted by the solvent. In this case, particles tend to join together because of the attractive van der Waals forces, forming aggregates. When water is the medium or solvent, the terms hydrophilic or hydrophobic are often used (Hiemenz and Rajagopalan, 1997).

Undoubtedly, the most interesting property of a colloidal system is the high surface-to-volume ratio that is related with a high adsorption capacity of other species. Likewise, a large number of other unique properties are associated to these systems such as optical, rheological or electrokinetic. Also, the inherent magnetic feature of the particles employed in this dissertation provides new and especial properties.

3.1.2. Brownian motion

Colloidal particles, immersed in a fluid, undergo Brownian motion. This is due to the fact that solvent molecules (much smaller than the molecules in colloidal particles) undergo continuous fluctuations because of thermal energy. In this scenario, the colloidal particles suffer ceaseless jiggling and their surface pressures are continuously varying. Consequently, the net force provokes a random displacement of the particles within the continuous medium (Hunter, 1993; Hiemenz and Rajagopalan, 1997).

3.1.3. Concept of stability in colloidal systems

Stability of colloidal systems is understood as no aggregation of the particles, i.e., the particles of the dispersed system phase remain uniformly distributed throughout the suspension over very long periods of time. This is due to the fact that the system is thermodynamically stable as occurs in lyophilic colloids.

On the contrary, in unstable colloidal systems, particles collide with one another because of their Brownian motion, remaining stuck together due to the attractive van der Waals forces. This collisions lead to the formation of aggregates as it is the most stable thermodynamic state. It occurs in lyophobic colloids.

The main mechanisms of colloidal systems destabilization are:

- Coalescence: It is the process by which two (or more) particles merge together to form a single larger particle. Here, the total interfacial area is reduced, and hence, there is a reduction of the total free energy of the system. It is an irreversible process.
- Aggregation, coagulation or flocculation: These are the processes by which particles clump together without merging into a new particle. There is no reduction of surface and it is generally a reversible process. Depending on the density of the two phases we can observe two phenomena:
  i) Creaming: the dispersed phase possesses a smaller density than continuous phase, and therefore, the dispersed phase floats to the top of the continuous phase.
  ii) Sedimentation: the dispersed phase possesses a higher density than continuous phase, and particles sink to the bottom.

3.1.4. Electrical double layer

A colloidal particle, immersed in water, will develop a surface charge due to a number of mechanisms. One of the most common processes arises from the ionization or dissociation of the surface groups. This mechanism is based on the interaction of these surface groups with hydrogen (H^+) or hydroxyl (OH^-) ions, depending on pH of solution. As a result, the surface acquires a positive or negative charge. These ions are called potential-determining ions because they dramatically affect the electric potential of the diffuse part of the double layer (see below). Specifically adsorbed ions (other than H^+ and OH^-) can also provide charge to the surface. These groups are located in the inner part of the double layer and affect the potential of the diffuse part, although they are not called potential-determining ions. Other possibility for a colloidal particle to acquire electrical charges is by isomorphic substitution, i.e., the electrical charge comes from atom replacement of another ion with different valence. This charge is independent of pH and is permanent since it cannot be modified by the environment. Lastly, a differential dissolution of surface ions can take place, in a similar manner to the ionization of the surface groups.

Because of all the above mentioned mechanisms the particle surface will have a specific charge that, consequently, will affect the distribution of ions within the liquid. In a common situation (see Figure 6), the charged surface attracts ions of opposite charge and they will be strongly adsorbed by electrostatic or van der Waals forces until a surface charge balance is reached. This region is known as Stern layer. On the other hand, the counter-ions, which are not adsorbed on the particle surface, but keep being under the influence of opposite charge, stay freely distributed in a close region under the influence of electrostatic forces and thermal motion. This is called diffuse layer. These two charged layers are called diffuse double layer.

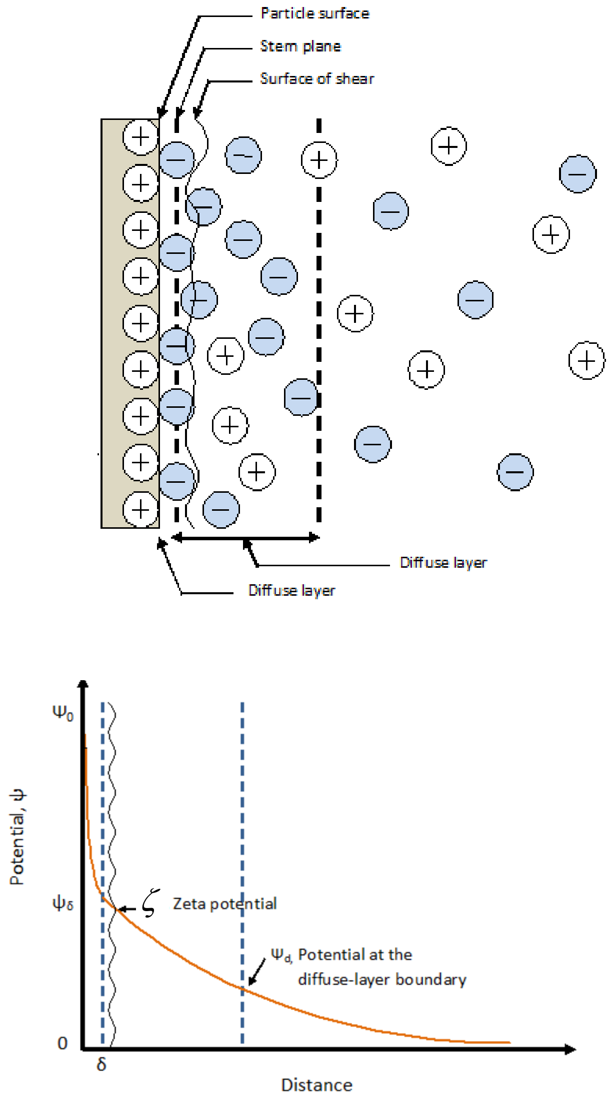


Figure 6. Schematic illustration of the electrical double layer and of the variation of potential with distance (taken from Hiemenz and Rajagopalan, 1997).

When two different electrical phases approach each other, an interface, with an electrical potential difference (Ψ), is created. This potential is maximum at the particle surface and drops off linearly with distance from the surface (as described in Figure 6).

An important parameter in the theory of the diffuse double layer is the Debye-Hückel parameter (k), defined as:

$$k = \left(\frac{e^2 \Sigma n_i^0 z_i^2}{\varepsilon K T} \right)^{1/2} \tag{1}$$

where ze is the charge of the ion, n_i^0 is the number of ions of type i per unit volume in the bulk solution far from the surface, ε is the permittivity of the solution, K is the Boltzmann constant and T is the temperature (in Kelvin). The inverse of this parameter (k^{-1}) is called the "thickness" of diffuse double layer and has units of length. As can be seen from equation 1, the "thickness" depends on the ionic strength of the solution. Hence, as the ionic concentration increases, the "thickness" of the double layer decreases, a process referred to as compression of the double layer. This situation provokes a reduction in the repulsive barrier (see below) between particles and, therefore, a lesser kinetic stability of the particles which favors the formation of aggregates.

From Figure 6, one can also observe a surface near the Stern plane called surface of shear. This marks the boundary between particle surface and the moving liquid. It should be pointed out that motion of ions within this region is impeded. The electrostatic potential in this plane, relative to the potential in the bulk solution is called the Zeta potential (ζ). Although the precise location of the surface of shear is not known, it is accepted that this is close to the Stern layer for smooth particles.

The Zeta potential has a direct impact on the colloid stability since it indicates the magnitude of the potential energy of interaction between a pair of particles.

3.1.5. Electrophoresis as electrokinetic technique for assessing the electrostatic potential

The electrostatic potential at the particle surface cannot be experimentally measured. Nevertheless, in practice we can approximate this by the measurement of the Zeta potential. It is important to note that this is only an approximation since the Zeta potential is localized on the surface of shear.

There are a number of different techniques by which the Zeta potential can be determined. They are referred as electrokinetic techniques and combine effects of motion and electrical phenomena. These techniques are:

- Electrophoresis: motion of a charged surface in solution relative to a stationary liquid under the influence of an external applied electric field.

- Electro-osmosis: motion of liquid (solution) through a charged surface under the influence of an external electric field.
- Streaming potential: creation of an electric field when a liquid is forced to flow past a charged surface.
- Sedimentation potential: creation of an electric field by charged particles sedimenting in a liquid.

Among these techniques, the most frequently used is electrophoresis. It measures velocity of particle motion by effect of its charge, under the influence of an external electric field; the direction of motion depends on the charge of the particles with a negative particle migrating to the cathode and positively charged particle moving towards the anode. This velocity is called electrophoretic mobility and Zeta potential can be indirectly calculated from it. We will explain, in more detail, the determination of electrophoretic mobility in Chapter III.

The establishment of a quantitative relationship between the electrophoretic mobility (μ_e) and Zeta potential (ζ) was pioneered by Smoluchowsky, Hückel and Henry (Lozada-Cassou and González-Tovar, 2001).

When the thickness of the double layer is negligible compared to the radius of curvature of the surface (R), i.e. k R>> 1, then, the Helmholtz-Smoluchowski equation applies that is expressed as follows:

$$\mu_e = \frac{\varepsilon_o \varepsilon_r \zeta}{\eta} \qquad (2)$$

where ε_o is the dielectric constant of vacuum, ε_r is the relative dielectric constant and η the viscosity of the dispersing medium. This theory assumes a spherical particle with a constant surface potential and the surface conductivity of the electrical double layer is small enough to have negligible influence on the field-induced potential distribution (Delgado, 2002).

When the values of k R are small (i.e., k R << 1), the relation between μ_e and ζ is well described by Hückel equation:

$$\mu_e = \frac{2}{3} \frac{\varepsilon_o \varepsilon_r \zeta}{3\eta} \qquad (3)$$

The Hückel´s theory also assumes a spherical particle. This is considered to be nonconducting and with a dielectric permittivity much smaller than that of the dispersion medium (Delgado, 2002).

The relationship between Zeta potential and electrophoretic mobility for intermediate values of k R is given by the Henry theory. It incorporates the electrokinetic retardation effect, this is, counter-ions are moved in opposite direction with respect to the charged particle due to the applied electrical field. The Henry equation is expressed as:

$$\mu_e = \frac{2\varepsilon_o \varepsilon_r}{3\eta} f(\alpha) \tag{4}$$

where, $\alpha = kR$ and $f(\alpha)$ is known as Henry function:

$$f(\alpha) = \left(1 + \frac{1}{16}\alpha^2 - \frac{5}{48}\alpha^3 - \frac{1}{96}\alpha^4 - \frac{1}{96}\alpha^5 - \left[\frac{1}{8}\alpha^4 - \frac{1}{96}\alpha^6 \right] \exp(\alpha) \int_\infty^\alpha \frac{e^{-t}}{t} dt \right) \tag{5}$$

This function is used for k R < 1. When k R > 1, the function $f(\alpha)$ becomes:

$$f(\alpha) = \left(\frac{3}{2} - \frac{9}{2}\alpha^{-1} + \frac{75}{2}\alpha^{-2} - 330\alpha^{-3} \right) \tag{6}$$

These equations were evolved into the classical theory of the electrophoretic motion of a particle by O´Brien and White. This model takes into account that the application of electrical field generates, besides the movement of the particle, the distortion of the diffuse double layer (or relaxation effect). Here, electrophoretic mobility and Zeta potential are defined by their reduced electrophoretic mobility and reduced Zeta potential, respectively, these equations are as follows:

$$\overline{\mu_e} = \frac{3\eta e \beta}{2\varepsilon_o \varepsilon_r} \mu_e \tag{7}$$

$$\overline{\zeta} = e\beta\zeta \tag{8}$$

where, e is the protonic charge and β is defined as:

$$\beta = \frac{1}{k_B T} \tag{9}$$

The model is satisfactory for any value of k R and considers only spherical particles (Lozada-Cassou and González-Tovar, 2001).

The point of zero charge (pzc) is defined as the pH at which the net surface charge is zero. On the other hand, isoelectric point (iep) is the pH at which there is no motion of the particle in the electric field μ_e=0. If there is no specific adsorption, the iep is the same as the pzc of the surface. These parameters are specific to every kind of colloidal particle and depend on several factors. The most important of these are the temperature and the ion concentrations in the suspension (Cornell and Schwertmann, 1996).

3.1.6. Intermolecular forces between colloidal particles

A good approach to understand the stability of colloidal systems is to study the net interaction forces between the colloidal particles. These forces are of attractive and repulsive nature and determine the possible coagulation or separation of particles:

(i) Attractive forces:

The most important attractive forces in colloidal systems are, namely, the van der Waals forces (Hunter, 1993; Hiemenz and Rajagopalan, 1997). These forces, which occur between any two particles immersed in a medium are called the long-range van der Waals force. The term “long-range” has been assigned because these forces are additive, i.e, it is the sum of attractive interactions between atoms and attractive interactions between molecules of each particle. The result is a force which has a much longer range than the attractive force between individual atoms (Hunter, 1993). The long-range van der Waals force decreases as the inverse square of the separation, therefore, the force is stronger at short interparticle separations. On the other hand, in atoms, the force decreases as the inverse sixth-power of the separation (Hunter, 1993; Hiemenz and Rajagopalan, 1997).

The three major types of van der Waals forces are:

- Instantaneous dipole/induced dipole interactions (London or Dispersion Force):

The electrons of an atom or molecule can fluctuate randomly, and momentarily, and concentrates on a specific region. This electron motion converts a non-polar molecule into polar molecule and produces an instantaneous dipole. Consequently, the electrons of a neighboring atom or molecule are also displaced and an induced dipole is created. These two processes provoke an intermolecular weak force between them known as London or Dispersion Force (Hunter, 1993; Hiemenz and Rajagopalan, 1997; Petrucci et al., 2003).

- Permanent dipole/permanent dipole interactions (Keesom interactions):

Many molecules consist of atoms with different electronegativity. For example, in the HCl molecule, the chlorine atom tends to draw the hydrogen´s electron toward itself, and this molecule therefore has a permanent dipole moment. Such molecules are called polar molecules (Israelachvili, 2011). The electric dipole creates two regions into the molecule, one with partial negative charge and other with partial positive charge. As a result, there exists an electrostatic attraction between the positive region of a molecule and the negative region of a second molecule. The greater the difference of electronegativity of atoms, the higher the attractive force between dipoles. Hydrogen bond is a special kind of permanent dipole/permanent dipole interaction (Hunter, 1993; Hiemenz and Rajagopalan, 1997; Petrucci et al., 2003).

- Permanent dipole/induced dipole interactions (Debye interactions):

A polar molecule, with a permanent dipole, induces a dipole in a non-polar molecule. This produces an attraction force between both molecules (Hiemenz and Rajagopalan, 1997).

(ii) Repulsive forces:

Repulsive forces between particles are due to electrostatic interactions. This is, the particles have an electric charge (positive or negative) and if all have the same charge then they will repel one another on close approach (Hunter, 1993). The range of repulsion depends on the thickness of diffuse double layer, the ionic strength, radius of particle and dielectric constant of medium.

These forces are due to the overlap between the diffuse double layers of the particles, i.e., when colloidal particles approach one another, the diffuse double layer with ions of same charge, provokes repulsive forces between particles. Thereby, the smaller is the ionic strength, the larger is the thickness of the diffuse double layer. As a consequence, the repulsive force will be greater. When the thickness of diffuse double layer is broad enough, aggregation due to van der Waals forces is prevented.

3.1.7. DLVO theory

The stability of colloidal dispersions can be explained according to the theory elaborated by Derjaguin and Landau (1941) in Russia and, independently, by Verwey and Overbeek (1948) in Holland. This is the celebrated DLVO theory, which describes the interaction between two colloidal particles as a balance between repulsive and attractive potential energies of interaction between the particles. Hence, the total potential energy of interaction (V_T) is calculated as the algebraic sum of two terms: an attractive one (V_A) and a repulsive one (V_R):

$$V_T = V_A + V_R \tag{10}$$

V_A is due to London-van der Waals (dispersion) energy and decays according to a power law with the distance of separation, whereas V_R is due to the overlap between the diffuse double layers surrounding the particles, which are similarly charged, and decays almost exponentially (Ortega-Vinuesa et al., 1996).

The non-simplified expression for V_A is given by:

$$V_A = -\frac{A}{6}\left[\frac{2a^2}{H(4a+H)} + \frac{2a^2}{(2a+H)^2} \ln\frac{H(4a+H)}{(2a+H)^2}\right] \tag{11}$$

where A is the Hamaker constant for particles interacting with the medium (water), a is the radius of the particle and H is the distance between the surface boundary of the particles, considering these particles as spheres (Hidalgo-Álvarez et al.,1996).

The repulsive electrostatic interaction (V_R), without considering ion size, can be expressed as:

$$V_R = 2\pi\varepsilon_R\varepsilon_o\left(\frac{4K_BT}{z_ie}\gamma\right)^2 e^{-kH} \tag{12}$$

where again ε_o is the permittivity of the vacuum, ε_R is the dielectric constant of the electrolyte solution, e is the elementary charge, K_B is the Boltzmann constant, T is the absolute temperature, k is the Debye parameter referred to as the reciprocal double-layer thickness, and γ is defined as:

$$\gamma = \tanh\left(\frac{z_ie\psi_d}{4k_BT}\right) \tag{13}$$

being ψ_d the diffuse potential (Hidalgo-Álvarez et al., 1996).

The total potential energy of interaction is usually plotted against the distance between particles, obtaining potential energy curves (Figure 7). By convention, the potential energy associated with repulsion is defined to be positive, while the attraction is negative (Hiemenz and Rajagopalan, 1997).

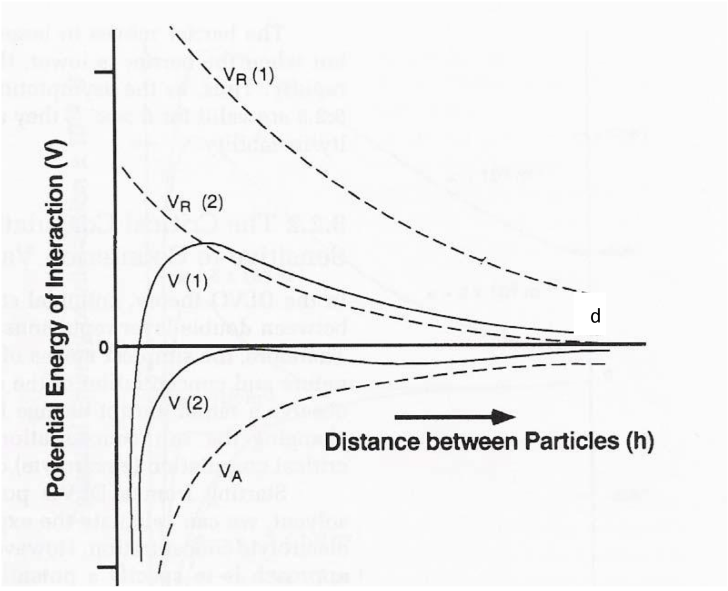


Figure 7. Potential energy of interaction between particles as a function of the distance of separation between them. V_R and V_A show the repulsive and attractive forces, respectively

Figure 7 suggests that the attraction energy becomes infinitely negative on contact so that particles once in contact could never be separated. Although redispersion is sometimes difficult, it is not normally impossible and other forces come into play at these small distances. Another feature that deserves attention: at very large distances the van der Waals force always dominates over the repulsion. The long range minimum (called secondary minimum) can be of outstanding depth for large colloidal particles.

The DLVO theory allowed to explain and to predict a series of phenomena related with the electrostatic stabilization of colloidal systems. However, it started to fail when it was applied to different systems where other interactions (apart from electrostatic or van der Waals) took place. Hence, it was necessary to modify the original DLVO theory by adding other effects, turning it into what is known today as the “extended DLVO” theory. For example, it has been necessary to incorporate the effect of ion size, hydrodynamic (viscous), electrosteric and elastic compression effects, and hydration forces, depending on the systems under study.

In the case of magnetic colloids, it is especially important to include the magnetic interparticle interaction. de Vicente et al. (2000) introduced the magnetic contribution in terms of a potential energy function, V_M , as follows:

$$V_M = -\frac{8\pi}{9}\frac{\mu_0 M^2 a^3}{\left({}^{S}\!\big/_{a+2}\right)^3} \tag{14}$$

where M is the magnetization of the material, a is the radius of the particles, S is the distance between the surfaces of two interacting particles, and μ_0 is the magnetic permeability of the vacuum (de Vicente et al. 2000; Viota et al., 2005).

As seen in the previous section, a repulsion barrier is created between two particles. Only when the particles have enough kinetic energy to surpass this repulsion barrier the suspension coagulates and becomes unstable. The magnitude of the surface charge of the particles and the length of the diffuse double layer determine the “height” of the repulsion barrier and, hence, the difficulty for surpassing it. For achieving the colloidal stability, there exist two main possibilities: Electrostatic and steric stabilization.

3.2. Magnetic particles as a kind of colloidal particle

3.2.1. Main properties of magnetic particles

The size of a magnetic material strongly determines its magnetic properties, and this is particularly of utmost importance in the nanoscale domain (Chatterjee et al., 2003).

For large enough particles (micronsized), the application of a magnetic field results in the magnetization of the particles. Concretely, magnetic domains within the particles start to grow and rotate under the field until the magnetic field strength is large enough to magnetically saturate the material (Huber, 2005). When the particles are smaller in size (nanosized), an energetic analysis demonstrates that every particle can only accomodate one single domain (Lu et al., 2007). In this case the referred domain has a permanent magnetic moment and therefore the magnetization mechanism changes (from a Brownian a Neel relaxation process). The limiting diameter separating the multi- to monodomain regimes is dependent on the material (Morrish and Haneda, 1983), but it is generally around 10-20 nm (Huber, 2005; Lu et al., 2007).

In this dissertation, we study two different magnetic particles, namely ferromagnetic (iron) and ferrimagnetic (magnetite) particles that display a multi-domain structure. These materials have a high room-temperature value of saturation magnetization and behave as soft magnetic materials (i.e. they do not possess remanent magnetization when the external magnetic field is removed).

3.2.2. Uses of magnetic particles

A great number of technological fields have recognized the especial properties of magnetic particles, and a heyday of their use in innovative applications can be seen. Next, we show a summary about some applications of magnetic particles.

Biomedical area is one which has received an intense interest by scientists. In 1970s began to studying “magnetically directed drug delivery” for cancer treatment. This approach involves the intravenous injection of the magnetic particles to which drug molecules are attached, followed by the application of a magnetic field gradient in the area where delivery is desirable. Shortly after accumulation in the targeted region, drug molecules are gradually released, thus improving the therapeutic efficiency of the drugs by lowering the collateral toxic side effects on the healthy cells or tissues (Huber, 2005; Lu et al., 2007; Philippova et al., 2011).

Other technique is hyperthermia, considered as a supplementary treatment to chemotherapy, radiotherapy, and surgery in cancer therapy. The idea of using magnetic particles in hyperthermia is based on the fact that when these particles are exposed to a varying magnetic field, it loses energy due to hysteresis property. This energy expenditure manifests itself as heat and if particles are appropriately localized, an area of tissue can be selectively heated (Huber, 2005; Lu et al., 2007; Philippova et al., 2011).

Likewise, magnetic resonance imaging (MRI) contrast, used in diagnostics, clinical medicine and biomedical research, involves target-specific magnetic particles as contrasting agents, becoming a tool of biologic processes study (Huber, 2005; Philippova et al., 2011).

The application of magnetic particles for the in vitro separation of cells or biomolecules is another important application. For example, magnetic iron oxide nanoparticles grafted with dopamine have been used for protein separation. Also, the isolation of various macromolecules such as enzymes, enzyme inhibitors, DNA, RNA, antibodies, antigens etc, has been performed (Philippova et al., 2011).

Since iron has a high catalytic activity, it has been used as catalyst in processes of synthesis such as conversion of nitrogen compounds to N_2 during coal pyrolisis, hydrogenation of naphthalene or growth of carbon nanotubes, among others. Nonetheless, a promising application is their use as catalyst in the Fischer-Tropsch synthesis which consists in converting a gas (CO and H_2) into hydrocarbons (Huber, 2005).

Another developing technology, which has taken advantage of magnetic particles, is the electrical industry. Thus, the largest commercial applications can be found in magnetic tapes used in, such as, computer backup tapes and camcorders (Huber, 2005).

Oil industry has also demonstrated special interest for the use of magnetic particles. In particular, for blocking water flow in a productive well. Here, a gel plug with embedded magnetic microparticles is formed and this is accumulated inside a tube near a magnet. Through a short time, the flow becomes completely blocked by the magnetic gel plug. Then, the magnet can be removed, and the gel plug remains in its place (Philippova et al., 2011).

3.2.2.1. Use of magnetic particles in wastewater treatments

Based on an analysis of publications, we have observed that the use of magnetic particles in wastewater treatment is one of the most widespread applications.

The first researches about this topic go back to the end of 70´years when Kolarik et al. (1977) studied by first time the use of magnetite particles as coagulant-adsorbent material in water purification processes. Afterwards, seeing the advantages of magnetite over traditional compounds, the Commonwealth Scientific and Industrial Research Organization (CSIRO) in Australia was developing, during the 80´years, a new process called “Sirofloc process”, involving the use of these particles (Bolto, 1990; Broomberg et al., 1999). This process was designed for the removal of turbidity and color from water.

Conventional coagulants present small specific surface area and show a poor surface activity. They are not able to adsorb small particles and hence a subsequent clarification stage has always been required. Likewise, their very low kinetic of flocculation hinders sedimentation and therefore limits the recovery of flocs settle for their later regeneration and reuse. The use of magnetite solves plenty of these complications (Kolarik, 1981; Bolto, 1990).

In the Sirofloc processes, magnetite particles, in the size range from 1 to 10 µm, are treated with alkali, giving them positive surface charge. A basic procedure consisted in adding the alkali-treated magnetite, diluted in a sodium hydroxide solution 0.1 M, inside of a stirred tank where the sewage is placed. Therein, impurities of the water, which in general present negative charge, are adhered to the positive surfaces of the magnetite particles. Afterwards, the magnetite particles are magnetized with a permanent magnet and they are quickly and easily separated from the sludge in a clarifier. The flocculates, i.e., the magnetite particles with the bound impurities, settle and these are pumped from the bottom of the clarifier toward magnetic drum separators where they are separated and regenerated for their subsequent use (Bolto, 1990). Adsorption is generally performed at pH 4-6, and regeneration was achieved in a weak (0.1 M) NaOH solution (Broomberg et al., 1999).

It also has been seen that creating appropriate pH conditions in the aqueous medium, algae, bacterium and viruses will carry a net charge on their surface. Thereby, they can strongly bind to magnetite and be removed from the medium by the method described above (Atherton and Bell, 1983a; Atherton and Bell, 1983b; Bolto, 1990).

Magnetite particles can be used alone but also in conjunction with other coagulants. Several works have focused into this topic. For instance, Anderson et al. (1980) studied the coagulation process with composite particles containing magnetic iron oxides in an insoluble polymeric matrix and Anderson et al. (1987) studied this process with soluble cationic polyelectrolytes. Both authors found an enhancement in the efficiency.

The use of magnetic particles to treat wastewater has been broadly spread. For example, a great number of publications reveal the use of magnetic particles for the removal of heavy metals pollutants (Bolto, 1990; Chang et al., 2004; Hu et al., 2005; Afkhami and Norooz-Asl, 2009; Ambashta and Sillanpää, 2010). Indeed, researches have been driven towards the functionalization of magnetic particles surfaces to increase the efficiency in the removal of pollutants. Bayramoglu and Arica (2007) synthesized new magnetic functional polymeric beads, p(GMA-MMA-EGDMA) for removal of Hg(II) ions. Huang and Hu (2008) synthesized a sorbent which comprises silica-coated magnetic nanoparticles (SCMNPs) modified with γ-mercaptopropyltrimethoxysilane (γ-MPTMS) for solid phase extraction of trace amounts of Cd, Cu, Hg and Pb from biological and environmental samples. Huang and Chen (2009) developed a magnetic nano-adsorbent by the covalent binding of polyacrylic acid (PAA) on the surface of magnetite nanoparticles followed by amino-functionalization using diethylenetriamine (DETA). This permits adsorption of various metal cations (Ag^+, Cu^{2+}, Ni^{2+}, Co^{2+}, Cd^{2+}, Fe^{2+}, Fe^{3+}) and anions ($AuCl_4^-$, $PdCl_4^{2-}$, $HCrO_4^-$). Suleiman et al. (2009) studied the separation of trace amounts of Cr, Cu and Pb in environmental samples with Bismuthiol-II-immobilized magnetic nanoparticles. Yong-Mei et al. (2010) developed a novel magnetic nano-adsorbent by the covalent binding of 1,6-hexadiamine on the surface of magnetite nanoparticles ($MNP-NH_2$) for removal of Cu^{2+} ions from aqueous solution. Faraji et al. (2010) used the decanoic acid-coated magnetite nanoparticles as an adsorbent for the extraction of trace amounts of Cd, Co, Cr, Ni, Pb and Zn from environmental water samples. Badruddoza et al. (2011) fabricated carboxymethyl-β-cyclodextrin modified magnetite nanoparticles (CMCD-MNPs) for removal Cu ions from aqueous solution. More recently, Shin et al. (2011) synthesized nitrogen-doped magnetic carbon nanoparticles (N-MCNPs) for adsorption of heavy metal ion.

Functionalized magnetic particles have also been designed for the removal of radionuclides from solutions (Ambashta and Sillanpää, 2010). For example, Kaminski et al. (2000) manufactured magnetic microparticles containing embedded silicotitanate powders for separate ^{137}Cs from contaminated milk. They achieved a 90-98 % of ^{137}Cs removal. Watson and Ellwood (2003) showed that magnetic iron sulphide is a good adsorbent for pertechnetate ion (^{99}Tc) and actinides as it can effectively remove them from radioactive waste streams. Lastly, Grüttner et al. (2005) synthesized magnetic particles coated with dendrimers. These dendrimers present terminal amino groups which are used to bind radionuclides.

Pollution of wastewaters by dyes, coming from textile, paper, food or cosmetic industries, have also been treated with magnetic particles (Bolto, 1990; Ambashta and Sillanpää, 2010). Safarik (1995) fabricated a compound which consisted in the incorporation of fine particles of magnetite into the chitosan structure. Hydroxyl groups of magnetite stay free on the surface and are responsible of retaining organic dyes. Safarik et al. (2007) designed a magnetic biocompound that consisted in modifying fodder yeast (Kluyveromyces fragilis) cells by placing them in contact with water-based magnetic fluid. They showed that the new biosorbent was efficient for removal of water-soluble dyes.

As an alternative to traditional fixed-bed ion exchange resins, a magnetic ion exchange resin (MIEX) was developed jointly by Orica Watercare, Commonwealth Scientific Industrial Research Organization, and South Australian Water Corporation. It was designed specifically to remove dissolved organic carbon (DOC) from natural water (Boyer and Singer, 2006). MIEX was an anionic exchanger and kept traditional anion exchange properties, such as a polyacrylic matrix in the chloride form, a macroporous structure and strong-base functional groups. Magnetized iron oxide was incorporated into the polymer matrix in the form of beads and every bead acted as an individual magnet. This resulted in an agglomeration and subsequent faster settling. The diameter of the MIEX resin was 2-5 times smaller than traditional ion exchange resins, and therefore the surface area to volume ratio increased. Lastly, the new MIEX resin was designed to be used in a suspended manner in a completely mixed flow reactor and therefore removal of DOC was much faster than traditional fixed-bed ion exchange resins

(Boyer and Singer, 2005). Another advantage of the magnetic component added to these sorbents was the capacity of recovery of the resin for its regeneration and reuse (Ambashta and Sillanpää, 2010). In addition, the application of MIEX to retire other compounds has been numerous. For example, MIEX was used for removal alkalinities and bromide concentrations (Boyer and Singer, 2005), and Johnson and Singer (2004) proposed the utilization of the MIEX prior to ozonation in drinking water treatment and showed that this resin lowers the ozone demand and formation of bromated.

Lastly, magnetic polymer particles with high voidage have been developed and have also found applications in the wastewater treatment field. One of them is in the filtration stage. Magnetic filters offer considerable advantages over traditional filtration carried out by sand bed. For example, the conventional filter is dependent on the quantity of suspended solids, i.e., this reaches the saturation, being unusable and hence, increasing the cost. Recoverable magnetic filter overcomes this problem (Bolto, 1990). With this magnetic polymers it would also be possible the oil spill remediation. In this scenario, they must be hydrophobic and contain a high fraction of pores for magnetic material floats on the water surface (Bolto, 1990; Machado et al., 2006). The action protocol is simple. The unmagnetised material is distributed over the oil spill and the oil is retained in the voids. Then, the polymer-oil sludge is magnetized and collected on rotating magnetic discs. With the aid of a scraper, the sludge is removed and collected in a container. Later, this is pumped to a holding tank (Bolto, 1990).

4. An economic approach for comparing P adsorbents

Before making any whole-lake application it is essential to gain also some knowledge about the economic balance. This is especially important for the case of reducing internal P loading, as different P adsorbents can be used. In Table 2, we compare some crucial characteristics (price and P removal efficiency) of magnetic particles and some of the most commonly used and already mentioned P adsorbents for lake restoration such as $AlCl_3 \cdot 6H_2O$ (i.e. Rydin et al., 2000; Reitzel et al., 2005; Egemose et al., 2011) and Phoslock (i.e. Robb et al., 2003; Lürling and Tolman, 2010). P binding properties of these adsorbents have been reported in the recent literature. In particular, de Vicente et al. (2008a) suggested that total Al-dosage ($AlCl_3 \cdot 6H_2O$) should be calculated relative to the pool of potential mobile P in the lake with a molar ratio not less than 10 Al: 1 P. In this PhD dissertation (see Chapter V), we have found that maximum P adsorption capacity of Fe magnetic particles was 18.8 mg P g^{-1} Fe; and more recently, Jensen and Reitzel (unpublished) have estimated that P binding capacity by Phoslock is 100 Phoslock: 1 P (in mass). As it is shown in Table 3, our results evidence that the cheapest adsorbent is Phoslock and the most expensive is $AlCl_3 \cdot 6H_2O$. As magnetic particles can be re-used (see Chapter V), we can conclude that when re-using Fe particles more than 2 times it is economically worthy to use this adsorbent instead of Phoslock.

Table 3. Economic cost and P removal efficiency of some P adsorbents.

	Price (€ kg^{-1} product)	**Premoval efficiency (g product g^{-1} P)**	**Economic cost (€ kg^{-1} P)**
$AlCl_3 \cdot 6H_2O$	**72**	**66.4**	**4780**
Phoslock	**6.4**	**100**	**640**
Fe	**30**	**53**	**1590**

As a way of illustrative example, next we compare the economic cost when applying the three different adsorbents for reducing internal P loading in a hypertrophic shallow lake (Lake Honda, South Spain). Based on published data related to sedimentary P concentrations (de Vicente et al., 2003), we have estimated the mobile P pool (as the sum of Fe bound P and alkali and acid organic P pool obtained by using EDTA method, Golterman 1996) in the top 5 cm at the deepest station. Assuming a density of 1.1 kg ww L^{-1}, we got an average mobile P content of 121 g P m^{-3} (standard deviation of 32 g P m^{-3}) or 6.07 g P m^{-2} (in these top 5 cm). If we consider an even distribution over the whole sediment surface (94000 m^2) we get an average total mobile P quantity of 571 kg P (in the top 5 cm; and a maximum mobile P quantity of 781 kg P). As the binding capacity (in mass) of $AlCl_3 \cdot 6H_2O$, Phoslock and Fe particles to P is 66.4, 100 and 53:1, respectively, it gets a final economic cost of $2.7 \cdot 10^6$ € for $AlCl_3 \cdot 6H_2O$, 365.440 € for Phoslock and about 907.890 € for Fe particles. So, comparing Phoslock and Fe particles, we can conclude that when re-using magnetic particles more than 2 times, we get the less economic cost. In conclusion, these results evidence the economic suitability of using magnetic particles for lake restoration.

Chapter II. *Objectives*

Chapter II

0BJECTIVES

The general objective of this study was to evaluate the feasibility of using magnetic particles for phosphorus (P) removal from natural and artificial aqueous solutions, identifying the best operating conditions under both batch and continuous mode.

In more detail, the specific objectives are as follows:

- To quantify the P maximum adsorption capacity under batch conditions using both synthesized magnetite and commercial iron particles (Chapter V).
- To identify the more appropriate conditions to achieve the maximum efficiency under batch mode (*Chapter V*). To achieve this goal, different sets of experiments were planned, the main objectives of these experiments were:
    - (i) To study the effect of pH.
    - (ii) To test the possible reutilization of magnetic particles.
    - (iii) To interrogate the effect of surface functionalization in the adsorption capacity.
- To set-up a laboratory-scale High Gradient Magnetic Separation (HGMS) device for separating P from water under continuous flow conditions and to identify the best working conditions by investigating the effects of a set of four different experimental variables: sonication time, flow rate, magnetic field strength, and the Fe particles/P concentration ratio (*Chapter VI*).
- To examine the chemical interferences of the typical dissolved ions in natural waters on P removal and to quantify the possible adsorption of other dissolved ions in natural waters on Fe particles (*Chapter VII*).
- To determine and quantify the single-effect of some of the major ions present in natural waters such as sulphate and calcium as well as humic acid and reactive silicate on the P removal efficiency by Fe particles (*Chapter VIII*).

Chapter III. *Experimental details*

Chapter III

EXPERIMENTAL DETAILS

1. Synthesis of magnetic particles

The synthesis of magnetic particles, with a flexible control of size distributions and a feasibility scaling-up process, has been intensively developed not only for its fundamental scientific interest but also for many technological applications. Hence, to date, a large number of efficient synthetic pathways to produce these particles with traits-controlled can be found in the literature (Huber, 2005; Lu et al., 2007; Wu et al., 2008; Laurent et al., 2008). Below some of the most common methods of preparation of magnetic particles are outlined.

For example, one of these methods consists in the thermal decomposition of organometallic compounds in high-boiling organic solvents containing stabilizing surfactants. It provides a very good shape and morphology control and resulting particles are highly monodispersive (i.e. narrow size distribution). However, the reactions used are kinetically and mechanistically very complicated and require high temperatures (e.g. 100-400 °C for the case of magnetite) (Lisitsyn et al., 1989; Cornell and Schwertmann, 1996; Huber, 2005; Lu et al., 2007; Wu et al., 2008).

Another method is the sonochemical synthesis, in which the application of ultrasounds causes acoustic cavitation, i.e., the formation, growth and subsequent collapse of bubbles in a liquid by the pressure fluctuations of a simple sound wave. Each bubble collapse generates a localized hotspot with extreme conditions (i.e. transient temperatures of 5000 K, pressures of 1800 atm, and cooling rates in excess of 10^{10} K s^{-1}). These conditions permit that chemical reactions take place. The method produces ultra-small (1-2 nm) and highly monodispersive nanoparticles with unusual magnetic properties (Grinstaff et al., 1992; Suslick et al., 1995; Huber, 2005; Wu et al., 2008).

Hydrotermal synthesis involves wet-chemical reactions of crystallizing substance in a sealed container with aqueous solution at high temperature (generally in the range from 130 to 250 °C) and at high vapor pressure (generally in the range from 0.3 to 4 MPa). This method presents good control of the particle shape with narrow size distribution, too. Albeit, the yield is lower compared to the methods mentioned above (Wang et al., 2005; Liu et al., 2007; Lu et al., 2007; Wu et al., 2008).

Magnetic particles can be also formed into a water-in-oil microemulsion. The water droplets provide a restricted reaction media, i.e., by the addition of the desired reactants, particles are precipitated. Then, the precipitate can be extracted by filtering or centrifuging the mixture. With the microemulsion technique, many types of small particles and relatively narrow size distribution can be obtained. However, compared to others techniques, the ambient conditions are very complicated and the yield is low. In addition, in spite of the presence of surfactants, the aggregation of the produced particles usually needs several washing processes and further stabilization treatments (Solans et al., 2005; Vidal-Vidal et al., 2006; Lu et al., 2007; Wu et al., 2008).

The most conventional and easiest method to use in large-scale industrial production of magnetic particles is the co-precipitation technique. This method consists of mixing ferrous and ferric hydroxides in aqueous media, under inert atmosphere at elevated or room temperature. Then, a base is added. Thereby, the precipitation and subsequent aging of particles take place. The properties of the magnetic particles can be fully reproducible and only small amount of compounds are needed to initiate the reaction. There are several experimental variables to take into account: concentration of the reacting components, pH, ionic strength, reaction temperature and nature of constituent anions and cations in the aging system (Sugimoto and Matijevic, 1980; Lu et al., 2007; Wu et al., 2008; Philippova et al., 2011). An inconvenient is that particles tend to be rather polydisperse. This could be overcome by the use of organic additives (e.g. polyvinlyacohol, carboxylate ions, hydroxy carboxylate ions, oleic acid) as stabilization and/or reducing agents. Organic ions prevent nucleation and a slow growth of the particles takes place, being crucial to produce monodisperse particles (Lu et al., 2007; Wu et al., 2008). On the other hand, Dauo et al. (2007) have reported that a good monodispersity of magnetite can be obtained by co-precipitation, followed by a hydrothermal treatment.

1.1. Synthesis of carbonyl iron particles

Carbonyl iron particles, supplied by the chemical company BASF, were used in our study. Their synthesis is achieved by a thermal decomposition of iron pentacarbonyl ($Fe(CO)_5$). This molecule is easy to decompose due to their low standard enthalpy of formation (i.e. – 185 kcal mol^{-1}) (Huber, 2005). However, the decomposition reaction is extraordinarily complicated due to their low boiling point (103 °C) and the high temperature required for the decomposition (approximately 200 °C) (Huuppola et al., 2012).

In this synthesis exists a broad range of intermediate iron carbonyls (Huber, 2005; Huuppola et al., 2012) which play a significant role in $Fe(CO)_5$ decomposition, e.g. $Fe(CO)_4$ may react with $Fe(CO)_5$ to form $Fe_2(CO)_9$, which in turn may react with another $Fe(CO)_4$ or $Fe(CO)_5$ to form CO and $Fe_3(CO)_{12}$ (Huber, 2005). Likewise, $Fe(CO)_5$ decomposition can be catalyzed or promoted by a number of compounds, such as amine (Smith and Wychlck, 1980; Huuppola et al.,2012), cobalt chloride (Albers and Coville, 1980) and iron particles (Smith and Wychlck, 1980).

The first syntheses with polymeric surfactants was done by Smith and Wychlck (1980). In their work, they compared the thermal decomposition of $Fe(CO)_5$ in solvent alone, in the presence of active polymers (i.e. the react directly with $Fe(CO)_5$) and in the presence of passive polymers (i.e. they react with intermediates such as $Fe(CO)_4$). They found that the decomposition reaction was much faster in the presence of the active polymers.

A typical synthesis procedure could consist in placing $Fe(CO)_5$ compound in a reactor and heating the sample until temperature range of 170-220 °C is reached. The heating is achieved by keeping high CO pressure into the reactor. During heating, the high CO pressure prevents the decomposition of $Fe(CO)_5$. Afterwards, at the desired temperature, the CO gas release valve of the reactor is closed and the pressure is rapidly dropped to a desired decomposition pressure. This induces the decomposition of the $Fe(CO)_5$ and consequently the nucleation and growth processes. Then, the pressure in the reactor begins to increase gradually due to release of CO gas according to the reaction:

$$Fe(CO)_5 \rightarrow Fe^0 + 5CO(g)$$

This reaches a constant level when no more gas is evolved indicating that the reaction is complete (Huuppola et al.,2012).

1.2. Synthesis of magnetite particles

In this dissertation, magnetite particles were synthesized following the described method by Sugimoto and Matijevic (1980). This consisted in a sol-gel precipitation and re-crystallization involving an iron hydroxide gel formation followed by slow aging.

We used a reactor of 1 L of capacity with five necked and sealed jacketed (Photograph 1). This synthesis requires inert atmosphere which was achieved through displacement of dissolved oxygen by nitrogen. The reaction temperature was fixed at 85 ºC.

Figure 8. Reactor used for the synthesis of magnetite particles (Laboratory of Department of Applied Physics, University of Granada).

The detailed experimental procedure was as follows. Firstly, we prepared three stock solutions: (i) 50.55 g of KNO_3 0.2 M in 250 mL of water, (ii) 3.117 g of KOH 0.005 M in 250 mL of water, and (iii) 8.34 g of $FeSO_4{\cdot}7H_2O$ 0.03 M in 100 mL of water. Water used in the preparation of the stock solutions was previously subjected to nitrogen flow in order to displace dissolved oxygen.

Secondly, we mixed 250 mL KOH, 100 mL KNO_3 and 550 mL H_2O solutions in the reactor under agitation and nitrogen flow. Then, 100 mL $FeSO_4{\cdot}7H_2O$ were added.

Just immediately after Fe^{2+} salt addition, the color of the solution turned black due to the formation of iron hydroxide (Photograph 2). The reaction remained for 4 h, without agitation, at 85 °C and under nitrogen flow.

Figure 9. Dissolution when Fe^{2+} salt is added.

Once finished the reaction, the particles were washed for removing of unreacted ions. The washing consisted in the magnetic decantation of the supernatant in the presence of a permanent magnet (405 mT) and re-dispersion in Milli-Q water. This process was repeated 5 or 6 times. The last washing was carried out with ethanol and finally magnetite/ethanol dispersions were placed in Petri disks in a convection oven at 60 ºC for 24 h. The yield of this reaction was 1.4 g of magnetite per litre of initial solution.

As is indicated in the study of Vereda and co-workers (Vereda et al., 2013), magnitudes of particles, such as size and morphology, can be controlled in a relatively easy manner if the reactive concentrations are handled in the synthesis process. Major or minor excess of Fe^{2+} in the synthesis reaction is essential for the growth of particles and, hence, for its size. An excess of Fe^{2+} can be achieved if the $[FeSO_4]$ is larger than [KOH]/2.

The excess of $[Fe^{2+}]$ is assessed with the expression:

$$\left[Fe^{2+}\right]_{Exc} = \left[FeSO_4\right] - \left[KOH\right]/2 \tag{15}$$

In this work, magnetite particles were synthesized at $[Fe^{2+}]_{Exc} = 0.0024$ M.

2. Characterization of magnetic particles

2.1. Particle size distribution characterization

Morphology, size, and size distribution of magnetic particles were measured. Firstly, the particle morphology was determined using the Scanning Electronic Microscope (SEM) technique. The device used was a LEO Gemini 1530 field-emission scanning electron microscope (FESEM) operating in a secondary electron (SE) mode. The basic principle of electron microscopy consists in an electron gun that is used to generate an electrons beam that, with the help of two focusing electromagnetic lenses and deflection coils, is driven to the particle surface. These electrons interact with surface atoms, removing their electrons. These reflected electrons are collected by a photo-detector, creating a three-dimensional image (e.g. see the Figure 8) of very high magnification on a screen (Hiemenz and Rajagopalan, 1997).

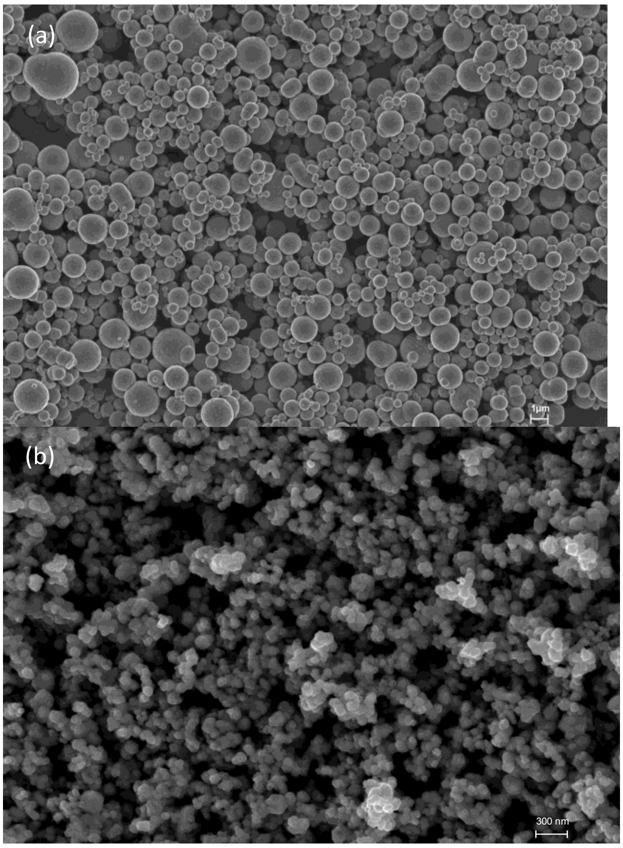


Figure 10. SEM micrographs of iron (a) and magnetite (b) particles.

Using the micrographs, the diameters of magnetite particles can be determined applying a statistical analysis, i.e., class ranges are made with the observed size data and, then, the data are fitted to a Log-normal distribution with a density function given by:

$$f(x) = \frac{A}{\sqrt{2\pi}x\sigma} \exp \frac{-(\ln x - \mu)^2}{2\sigma^2} \tag{16}$$

where μ and σ are the mean and standard deviation of the variable´s natural logarithm, respectively.

For the case of iron particles, it is applied a Normal Gaussian distribution. The normal distribution is the most important distribution in statistics. We used this distribution to ascertain the mean diameter of our iron particles and applied the statistical analysis to about 280 observed particles. Its density function takes the form:

$$f(x) = \frac{1}{\sigma\sqrt{2\pi}} \exp\left[-\frac{1}{2}\left(\frac{x-\mu}{\sigma}\right)^2 \right] \tag{17}$$

again, μ and σ are the mean and standard deviation, respectively.

Lastly, the resulting data can be plotted as a histogram, as is depicted in the Figure 11.

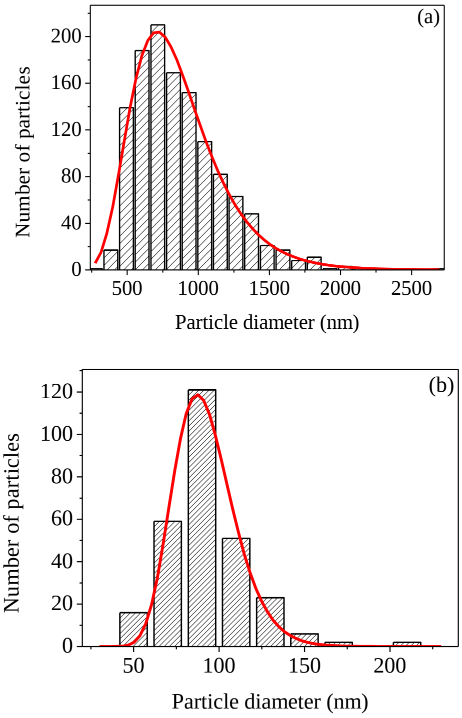


Figure 11 Histogram for magnetic iron (a) and magnetite (b) particles.

2.2. Magnetic characterization

The magnetization of magnetic particles was determined using a Quantum Design (San Diego, CA) MPMS-XL 5.0 Tesla Magnetometer. This device is equipped with a Superconducting

Quantum Interference Devices (SQUID) sensor which allows characterizing magnetic properties of a material with high detection sensitivity. In addition, this magnetometer works in a broad temperature range, i.e., from 2 K (-271 ºC) to 400 K (127 ºC).

Magnetic Properties Measurement System (MPMS) consists of a superconducting detection coil positioned at the center of a superconducting magnet. The detection coil is a single piece of superconducting wire wound in a set of three coils configured as a second-order (second-derivative) gradiometer. When an external magnetic field is applied, the sample, mounted in a sample holder, is moved through the detection coil. Superconducting detection coil is connected to a SQUID sensor which functions as current-to-voltage convertor, i.e., the SQUID electronics produces an output voltage which is strictly proportional to the current flowing in the SQUID input coil. During the measurement the sample is stopped at a number of positions over the specified scan length, and at each stop, several readings of the SQUID voltage are collected and averaged. The output signal is analyzed using a computer.

This technique is able to make rapid measurements of the magnetization as a function of field. We obtained the saturation magnetization by extrapolation to zero the magnetization values in the high field range versus the inverse of the applied field strength (1/H). Experiments were run at room temperature and a magnetic hysteresis curve was obtained for our magnetic particles:

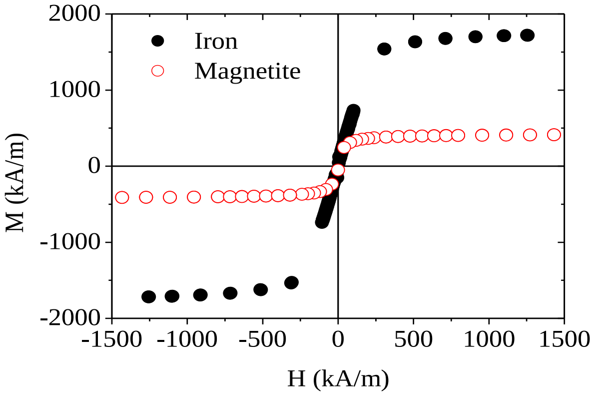


Figure 12. Magnetic hysteresis curves for iron and magnetite particles.

2.3. Electrokinetic characterization

In order to characterize the surface electrical state of magnetic particles, we carried out electrokinetic measurements by the specific experimental technique referred as (micro)electrophoresis. It measures the motion of charged particles suspended in a liquid, under the influence of an applied electric field. We outline below in which consist this technique, but, before, it is necessary to have some background in the general area of electrical transport phenomena.

Following the explanation of Hiemenz and Rajagopalan, (1997), an isolated particle in an electric field experiences a force directed toward the oppositely charged electrode. This force is given by the product of the charge of the particle (q) times the electric field (E):

$$F_{el} = qE \tag{18}$$

however, an opposing force due to the viscous resistance of the medium increases as the particle velocity increases:

$$F_{vis} = fv \tag{19}$$

where f is the friction factor. A stationary-state velocity is established quite rapidly in which these two forces are equal:

$$v = \frac{qE}{f} \tag{20}$$

The friction factor can be substituted for the value which is given by Stokes´s law to obtain:

$$v = \frac{qE}{(6\pi\eta R_s)} \tag{21}$$

where R_s is the radius of the particle, assumed to be a sphere by this substitution. The charge of a simple particle can be written as the product of its valence z times the electron charge e :

$$q = ze \tag{22}$$

Substitution of this result into equation (21) yields:

$$v = \frac{zeE}{(6\pi\eta R_s)} \tag{23}$$

The velocity per unit field is defined as the electrophoretic mobility (μ_e) of the particle:

$$\mu_e = \frac{v}{E} \tag{24}$$

The μ_e can be employed to calculate the zeta potential (ζ) by means of the Henry equation, given by:

$$\mu_e = \frac{2\varepsilon\zeta f(k_a)}{3\eta} \tag{25}$$

where ε is the dielectric constant, η the viscosity of the dispersing medium and $f(k_a)$ the Henry´s function (see Chapter II).

The two values generally used as approximations for the $f(k_a)$ determination are: 1.5 and 1.0. For particles larger than about 0.2 µm dispersed in aqueous media and moderate electrolyte concentration, it is possible to determine the ζ with the value of 1.5. This is referred to as the Smoluchowski model. On the other hand, for small particles in dilute salt solutions, the Henry´s function is 1.0. This is referred to as the Hückel model and non-aqueous measurements generally use this.

In our experiments, the surface electrical charge of magnetic particles was measured with a Zeta-PALS (Brookhaven). Here an incident beam is made to cross the capillary cell containing the particles suspension (see Figure 13). At same time, an electric field is applied to the cell and particles are moved. Their velocity is the measured using Laser Doppler Velocimetry (LDV) technique. The light scattered at an angle of 17º is combined with the incident beam. This produces a fluctuating intensity signal where the rate of fluctuation is proportional to the velocity of the particles. A digital signal processor is used to extract the characteristic frequencies in the scattered light. From this, it constructs the mobility spectrum (i.e. the frequency of particles with a given mobility).

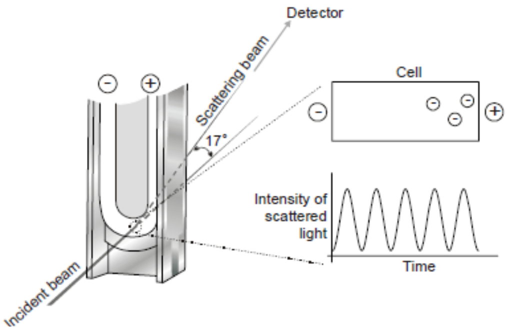


Figure 13. Schematic representation of the incident beam through the capillary cell.

In this dissertation, we measured the electrophoretic mobility as function of pH. The protocol consists in taking every mobility data point as the average of 10 measurements taken for the same sample in the course of a “run”. According to the features of our system, we selected the Smoluchowski´s approximation.

2.4. Kinetic stability

The study of the stability of magnetic particles suspensions has been done using a Turbiscan Classic (Formulaction, France). This instrument enables to identify the different instability phenomena of colloidal systems (i.e. creaming, sedimentation, flocculation and coalescence) in a faster and more reliable way than just visual observation.

The sample to be analyzed is placed in a flat-bottom cylindrical glass and is scanned from the bottom to the top with a near-infrared light source (λ = 850 nm) (Figure 14). There exists two synchronous detectors in order to monitor the light transmitted through the sample (180º from the incident light, transmission sensor), and light backscattered by the sample (45º from the incident radiation, backscattering detector) along the height of the cell. The Turbiscan makes scans at various pre-programmed time, acquiring transmission and backscattering data every 40 µm. Each scan provides a curve which depicts the transmitted and backscattered light flux as a function of the sample height (in mm) (Figure 13) and all curves are overlaid on one graph to show stability over time (Figure 13) (Mengual et al., 1999a; Mengual et al., 1999b; Bordes et al., 2003). Transmission is used to analyze clear to turbid dispersions while backscattering is used to analyze opaque dispersions.

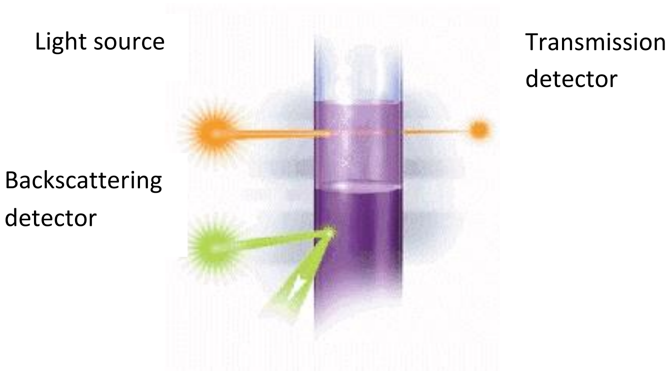


Figure 14. Measurement principle of the Turbiscan.

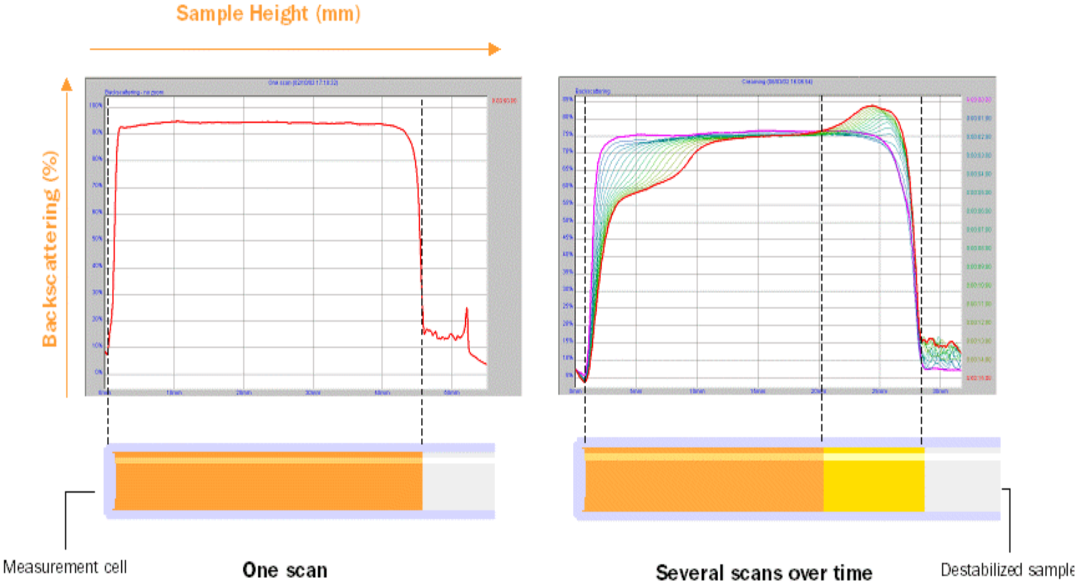


Figure 15. Turbiscan backscattering profiles.

The intensity of both transmission and backscattering light is related with the mean diameter and volume fraction of particles present in the suspension. Therefore, any change in these light levels shows destabilization phenomena. Thus, a decrease of the backscattering level over total height of the cell is characteristic of a particle size increase, and hence a coalescence or flocculation phenomenon is taking place. On the other hand, the increase of backscattering level indicates that the particle concentration at the top is increasing (i.e. creaming phenomenon). Lastly, in the case we are dealing, an increase of backscattering level in the bottom of the cell means an increase of particles in the bottom (i.e. sedimentation phenomenon).

In this dissertation, we measured several suspensions of magnetic particles in P solutions, previously sonicated at different times, in the Turbiscan Classic to detect the transmitted intensity signal and, thereby, to ascertain when the sedimentation phenomena takes place.

3. Adsorption experiments

3.1. Adsorption mechanisms

Adsorbates can absorb onto the adsorbent by two mechanisms:

- Physisorption (physical adsorption): the adsorbate is bound to the adsorbent surface by weak physical interactions such as van der Waals forces. When the molecules are bound, they are not distorted, i.e., they maintain their geometric and electronic identity. Hence, the adsorption is not specific and can occur in any site of the surface. This kind of bounding enables an adsorption in multilayer, where successive layers of adsorbate are adsorbed onto the first layer. The adsorption energy is lower than in the case of chemisorption. Physical adsorption increases as the temperature is lowered.

- Chemisorption: a chemical bond such as ionic, covalent or metallic is formed between the adsorbate and the underlying adsorbent. Chemisorption differs from physisorption in that, here, electron exchange between the adsorbent and the adsorbate occurs. Therefore, it transforms into other different molecule. The adsorption will be specific, existing active sites on the surface. The adsorption energy involved (usually of the order of several hundred kiloJoules per mole) is significantly higher than for physisorption. In this case, the adsorption is restricted to one monolayer. Chemical adsorption decreases at low temperature because this requires activation energy to break chemical bonds.

Next, we consider our case, that is, the chemical adsorption of a solid (P) from solution (water) onto a solid surface (Fe). In this scene, it is necessary to keep in mind that the adsorbent (Fe) surface is already covered with the solvent molecules, existing a very strong interaction among both. It can occur two different situations: the adsorbate (P) competes with water molecule for a place at the surface (competitive reaction) or an exchange process takes place (ligand exchange reaction) (Hunter, 1993). Numerous studies show that adsorption of P on Fe particles occur by an exchange process (Cornell and Schwertmann, 1996; Arai and Sparks, 2001; Antelo et al., 2005; Chitrakar et al., 2006; Daou et al., 2007; Zhang et al., 2009).

The presence of water molecules at the Fe surfaces provides them with surface hydroxyl groups (OH^-) that are the functional groups, i.e., the chemically reactive entities. They possess a double pair of electrons together with a dissociable hydrogen atom which enable them to react with both acids and bases molecules (they are amphoteric molecules) (Cornell and Schwertmann, 1996).

These surface hydroxyl groups can be coordinated to one, two or three underlying Fe atoms and are known as singly, doubly and triply coordinated groups, respectively. Also, there exists a fourth group where two OH^- groups are attached to one Fe atom (it is called germinal group) (Figure 16) (Cornell and Schwertmann, 1996).

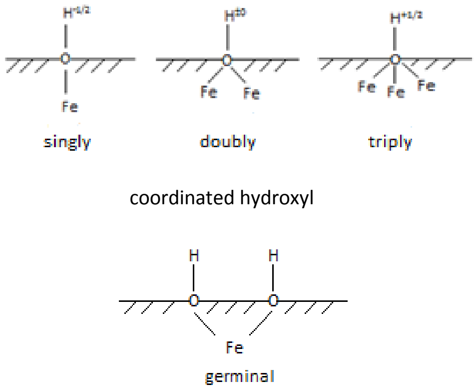


Figure 16. Singly coordinated, doubly coordinated, triply coordinated and germinal surface hydroxyl groups on iron oxides (Cornell and Schwertmann, 1996).

The adsorption of P on the Fe surface occurs by a process of replacement of surface hydroxyl groups by the P, resulting in the formation of inner-sphere surface complexes at the water/oxide interface.

3.2. Equilibrium isotherm models

In order to optimize the design of magnetic particles adsorbents in P removal from eutrophic inland waters, it is important to identify the most appropriate relationship between the maximum adsorption capacity and the minimum amount of adsorbents required. Adsorption isotherms are presented as efficient tools for this purpose.

Adsorption isotherm is a graph which relates the amount of a compound adsorbed (e.g. in units of mmol kg^{-1} or mg kg^{-1}) to the equilibrium solution concentration of the compound (e.g. in units of mmol L^{-1} or mg L^{-1}) at fixed temperature, pressure and solution chemistry (e.g. pH and ionic strength) (Essington, 2004).

A typical procedure for determining the equilibrium adsorption capacity (q) of a substance into a dilute solution would consist on putting in contact the adsorbent with different initial concentrations of the adsorbate during an enough time for ensuring the adsorption. Before this, temperature and pH of the solution are fixed. The solution, once filtered, with the final concentration of the compound of interest (C_{eq}) is analyzed. The difference, between initial and final concentrations, is assumed to have been adsorbed onto the solid surface and q can be assessed by:

$$q = \frac{C_o - C_e}{M_a} V \tag{26}$$

where C_o is the initial adsorbate concentration in solution (mg L^{-1}), C_e is the final or equilibrium concentration (mg L^{-1}), M_a is the mass of adsorbent used in grams and V is the total volume of solution (L). Lastly, q (the y-axis variable) is plotted against C_e (the x-axis variable). We determined the adsorption isotherm of P adsorbed onto our magnetic particles so the procedure will be explained in detail below.

Traditionally, experimental adsorption isotherm has been classified into one of the four types shown in Figure 15 (Giles et al., 1974; Essington, 2004).

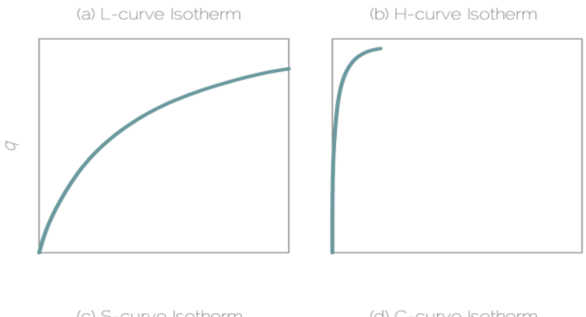


Figure 17. Isotherm types commonly observed: (a) L-type; (b) H-type; (c) S-type; (d) C-type (Essington, 2004).

The type I (Figure 15-a) is called L-curve isotherm and it indicates that adsorbate has a relatively high affinity for the surface at low surface coverage (this concept will be explained below). However, as coverage increases, the affinity of the adsorbate for the surface decreases until a plateau is reached and the adsorbent not adsorbs any more, i.e., it has reached its saturation value in the solvent. The plateau is interpreted as indicating monolayer coverage (low values of q) and decreases with increasing surface coverage. This type of behavior implies a sufficiently specific interaction between adsorbate and adsorbent and it is more typical of chemisorption than physical adsorption.

The second type (Figure 15-b), the so-called H-curve isotherm, shows that adsorbate has a very high affinity for the adsorbent surface at very low surface coverage. It indicates the formation of inner-sphere surface complexes by physical adsorption and is interpreted to mean multilayer adsorption.

On the other hand, the type III (Figure 15-c), the called S-curve isotherm, has a small slope at low surface coverage that increases with adsorbate concentration.

Finally, the fourth type (Figure 15-d), is called C-curve isotherm and is associated with cases where the initial slope remains independent of the surface coverage until some maximum adsorption capacity is achieved. This type of adsorption behavior is also called constant partitioning.

There exist several mathematical models to describe adsorption isotherms. Following, we describe the most commonly employed isotherm equations.

3.2.1. Langmuir isotherm model

Irving Langmuir was pioneering in developing a theoretical model to describe adsorption isotherm. He began studying the gas adsorption on a solid and found a direct relation between adsorbed gas on a substrate and the gas pressure at a particular temperature, i.e, the amount of adsorbed gas increases when the pressure enhances. This behavior is typical of L-type isotherm.

We analyze the Langmuir equation from Kinetic Theory (Viñes, 2008). First, the extent of adsorption is measured by the coverage (θ), which is defined as the fraction of surface sites filled (X) with regard to the total number of surface sites ($X_{\max}$):

$$\theta = \frac{X}{X_{\max}}$$

(27)

For the adsorption of a compound (A) and existing a number of bare sites (i.e., available sites ($*$), the process can be outlined as:

$$A + * \leftrightarrow A*$$

The velocity of the adsorption process (V_a) and of the desorption process (V_d)

is given by:

$$V_a = k_a[A][*] \tag{28}$$

$$V_d = k_d[A*] \tag{29}$$

being k_a and k_d the adsorption and desorption rate constants, respectively.

According to Langmuir, this situation is defined to be in equilibrium so V_a is the same as V_d :

$$k_a[A][*] = k_d[A*] \tag{30}$$

Now, the gas concentration $[A]$ is expressed as its gas pressure (P_A); the adsorbed gas concentration $[A*]$ as the coverage (θ_A); and the available sites concentration $[*]$ as $(1-\theta_A)$, hence the expression has the following form:

$$k_a p_A(1-\theta_A) = k_d(\theta_A) \tag{31}$$

The ratio k_a/k_d is defined as the Langmuir adsorption coefficient (b) and is a measure of the intensity of the adsorption:

$$b = \frac{k_a}{k_d} \tag{32}$$

Finally, replacing the equation (31) for the equation (32) and rearranging, the Langmuir equation for the adsorption of a gas on a solid is:

$$\theta_A = \frac{k_a p_A}{k_d + k_a p_A} = \frac{bp_A}{1+bp_A} \tag{33}$$

Langmuir assumed the following (Essington, 2004):

i. Adsorption occurs at specific locations (or sites) on a surface, i.e., the adsorbates are adsorbed in sites where its potential energy is minimum.
ii. All adsorption sites are identical in character; the surface is homogeneous.
iii. A monolayer of adsorbed molecules is formed on the surface (i.e., $\theta = 1$) and an adsorption maximum is achieved as the monolayer becomes filled by the adsorbate.
iv. The heat or energy of adsorption is constant over the entire surface.
v. The volume of the monolayer and the energy of adsorption are independent of temperature.
vi. Equilibrium is attained.

The equation (33) can be used for the case of adsorption of solid-liquid, therefore, the Langmuir equation can be given by:

$$q = \frac{K_L M_L C_e}{1+K_L C_e}$$

(34)

where K_L and M_L are empirical constants. K_L is related to the binding energy (L g^{-1}) and M_L is the adsorption maxima, having the units of q (mg g^{-1}).

The Langmuir adsorption isotherm can be expressed in linear form as:

$$\frac{C_e}{q} = \frac{1}{M_L K_L} + \frac{C_e}{M_L} \tag{35}$$

A method for obtaining the numerical values for the adsorption constants is plotting a graph, C_e / q (y-axis variable) vs C_e (x-axis variable), and, then, a straight line will be obtained with slope m and y-intercept b. The expression has the form:

$$y = mx + b \tag{36}$$

where x and y are the independent and dependent variables, respectively.

If doing a linear regression, a good correlation coefficient (R^2) is obtained, i.e., $R^2 \cong 1$, then, the values of m and b can be assigned a physical significance, i.e., the slope would be:

$$m = \frac{1}{M_L} \tag{37}$$

and, the y-intercept:

$$b = \frac{1}{M_L K_L} \tag{38}$$

3.2.2. BET isotherm model

As seen in the previous section, the Langmuir isotherm assumes that only a first layer is filled, involving chemisorption, and thereby a surface saturation at high pressures is reached. However, it ignores the possibility that successive layers are formed. If this last condition is admitted, then layer growth will be indefinite until the condensation of the vapor as a liquid onto the solid is produced (Hunter, 1993).

The model more suitable for analyze the multilayer adsorption was developed by Brunauer, Emmett and Teller in 1938 and is known by the initials of the authors: BET. It is an extension of Langmuir´s arguments in which successive layers are independently formed by physisorption.

The BET model is described by:

$$\frac{V}{V_m} = \frac{cx}{(1-x)[1+(c-1)x]} \tag{39}$$

where V is the total volume of gas adsorbed, V_m is the volume adsorbed at monolayer coverage, that is, the volume of gas that would be adsorbed if a monolayer were formed, c is a constant related to the adsorption and desorption rate constants and x is expressed by:

$$x = \frac{p}{p_o} \tag{40}$$

where p is the vapor pressure of the adsorbate and p_o is the equilibrium vapor pressure of the adsorbate. The BET equation encompasses both type II and type III isotherms.

The assumptions for this equation are (Hiemenz and Rajagopalan, 1997):

i. Like in the Langmuir isotherm, the adsorption is localized.
ii. There is no limitation as to the number of layers of molecules that may be adsorbed (multilayer adsorption with θ >1), hence, there is no saturation of the surface with increasing pressure.
iii. The energy of adsorption is constant over the entire surface, as in the Langmuir case.
iv. Homogeneous surface.
v. Adsorption or desorption can occur from a particular layer only if that layer is exposed, that is, provided no additional adsorbed layers are stacked on top of it.

The linear form for BET equation is given by:

$$\frac{1}{V}\frac{x}{1-x} = \frac{c-1}{cV_m}x + \frac{1}{cV_m} \tag{41}$$

The parameters V_m and c can be assessed by plotting (1/V)[x /(1- x)] against x . A straight line is supplied with slope m and y-intercept b , where:

$$m = \frac{c-1}{cV_m} \tag{42}$$

and

$$b = \frac{1}{cV_m} \tag{43}$$

Equations (42) and (43) may be solved to supply values of V_m and c from experimental results:

$$V_m = \frac{1}{m+b} \tag{44}$$

$$c = \frac{m}{b} + 1 \tag{45}$$

3.2.3. Freundlich isotherm model

The following model is the Freundlich isotherm model. It has broad application to L-, H-, and C-type isotherms. The model is based on a process of reversible multilayer adsorption, but, in this case, with heterogeneous surface where each site has different binding energy.

The Freundlich equation is:

$$q = K_F C_e^N \tag{46}$$

where K_F and N are positive-valued adjustable parameters.

N is a measure of the heterogeneity of adsorption sites on the adsorbent surface and it lies between 0 and 1. As N approaches 0, surface site heterogeneity increases, indicating that there is a broad distribution of adsorption site types. Conversely, as N approaches unity, surface site homogeneity increases, indicating that there is a narrow distribution of adsorption site types (Essington, 2004).

The assumptions of this equation are (Crini and Badot, 2008):

i. Multilayer adsorption.
ii. The model applies to adsorption on heterogeneous surfaces with interaction between adsorbed molecules.
iii. The adsorption energy exponentially decreases on completion of the sorptional centres of an adsorbent.
iv. This is an empirical equation employed to describe heterogeneous systems.

The linear expression for Freundlich equation is:

$$\log q = \log K_F + N \log C_e \tag{47}$$

As in the two previous cases, the constants in the Freundlich isotherm can be determined by plotting $\log q$ (y-axis variable) vs $\log C_e$ (x-axis variable) that will yield a straight line with slope N and a y-intercept $\log K_F$.

3.2.4. Temkin isotherm model

This model is used in the cases of heterogeneous surface on which the adsorption energy decreases as the coverage increases (Cornell and Schwertmann, 1996).

The Temkin equation uses a logarithmic relationship:

$$\theta = a \ln(bp) \tag{48}$$

where a y b are constants which, in similar manner of models above, its values can be assessed plotting θ vs $\ln p$. The slope of the straight line is the constant a and y-intercept is b .

3.2.5. Linear isotherm model

The linear or Henry isotherm model assumes that the amount of adsorbed solute (q) is proportional to equilibrium concentration of solute (C_e) and is quantified using the expression:

$$q = KC_e \tag{49}$$

where K is adsorption constant.

This model is known as Linear Partition Theory (Essington, 2004) and the behavior of sorption is associated with the following characteristics:

1. Equilibrium sorption isotherms are linear (C-type) up to relatively high adsorbate concentrations.
2. The extent of compound sorption is highly correlated to the equilibrium concentration of solute. K increases with increasing C_e .

iii. The sorption of a compound is not influenced by the presence of a second compound (no apparent competition between the compounds for the surface, which implies that specific adsorption sites are not involved in compound retention).

In this dissertation, we carried out an experimental procedure for determining the adsorption isotherm of P adsorbed onto our magnetic particles, working in batch mode and room temperature. The procedure consisted on adding 1 mL of the stock magnetic particles suspensions (50 mg L^{-1}) to 45 mL of 3 mM $NaHCO_3$ buffer. Afterwards, the samples were shaken for 24 h and later, 1 mL of stock P solutions with concentrations ranging from 5 to 60 mM P was added. The pH of the solution was adjusted at pH 7 and again, the samples were shaken for 24 h to ensure that the equilibrium is attained. Finally, the samples were filtrated and the concentrations of P in the solution were measured.

The amount of P adsorbed onto the magnetic particles was assessed according to the expression (26) mentioned above:

$$q = \frac{C_0 - C_e}{M_a} V$$

where q is the equilibrium adsorption capacity of P, C_0 represents the initial P concentration in solution (mg L^{-1}), C_e is the final or equilibrium concentration (mg L^{-1}), M_a is the mass of adsorbent used in grams and V is the total volume of solution (L). Then, q (the y-axis variable) was plotted against C_e (the x-axis variable) (Figure 16).

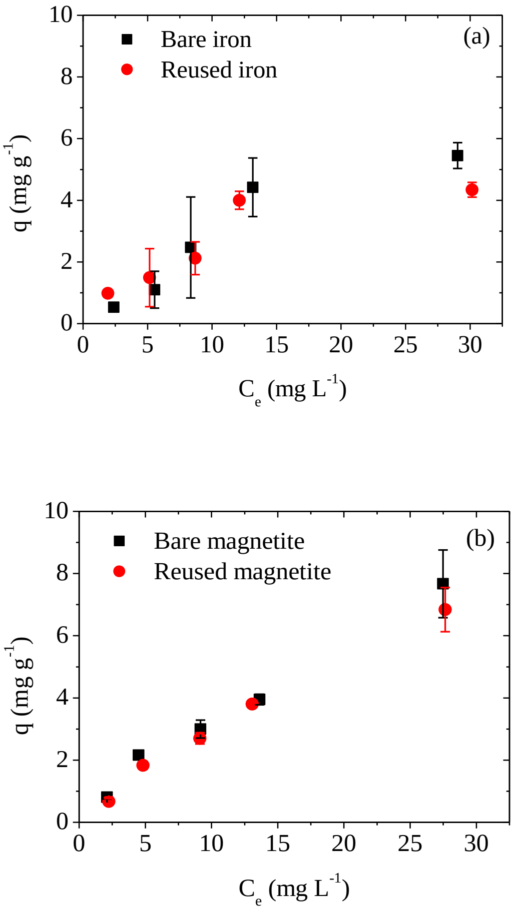


Figure 18. Adsorption isotherm of bare and reused iron (a) and magnetite (b) particles.

From the graphs, it can be observed that there exists a steep increase in the adsorption capacity with the rise of adsorbate concentration (indicating a great affinity of the adsorbent for the adsorbate), until a plateau, corresponding to saturation of all surface sites, is reached. Hence, the experimental data can be fitted to the one layer Langmuir isotherm model for estimating the maximum adsorption capacity and whose equation is described by equation (34):

$$q = \frac{K_L M_L C_e}{1 + K_L C_e}$$

where, K_L is an adsorption constant related to the binding energy (L g^{-1}) and M_L is an empirical saturation constant, that is the maximum mass of solute adsorbed per unit mass of adsorbent (adsorption capacity) (mg g^{-1}).

3.3. Adsorption kinetic

An ideal P adsorbent for lake restoration, such as magnetic Fe particles, may not only have a great adsorbate capacity but also a fast adsorption rate. Therefore, the adsorption rate is another important factor for the adsorbent selection and adsorption kinetics must be taken into account since they explain how fast the chemical reaction occurs and also provides information on the factors affecting the reaction rate (Crini and Badot, 2008).

In the present study we conducted an experiment for studying the effect of contact time on P adsorption onto magnetic Fe particles. In detail, we ran an adsorption experiment in batch mode where four suspensions were prepared by adding 1 mL of the stock Fe solution (50 g L^{-1}) to 45 mL $NaHCO_3$ (3 mM). Afterward, they were shaken for 24 h (150 rpm) and later, 1 mL of KH_2PO_4 solution (1 mM P) was added to each sample. The pH´s were adjusted to 7 with the addition of HCl 1 M. The suspensions were transferred to 50 mL volumetric flasks, made up to volume with 3 mM $NaHCO_3$. Then, each suspension was shaken for 2, 5, 10 and 24 h, respectively. The next step was the filtration of the suspensions and the equilibrium P concentrations into the filtered samples were determined using the spectrophotometric method described by Murphy and Riley. The analytical results are the averages of three replicates.

The amount of P (µg P g^{-1} Fe) adsorbed, which was calculated from the difference between initial and equilibrium P concentrations, to magnetic Fe particles (1g) to 2, 5, 10 and 24 h is represented in Figure 19. It shows a fast adsorption rate of P on magnetic Fe particles as P was removed by 97.55% in only 2 h, reaching 100% in 24 h. These results confirm the convenience of using magnetic particles for lake restoration.

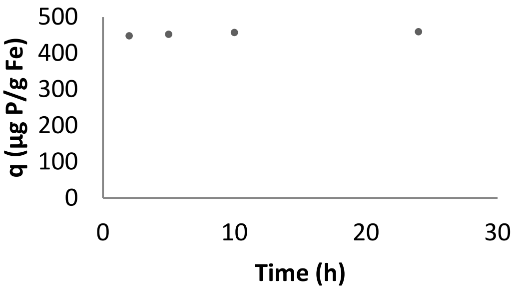
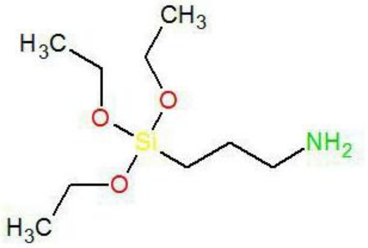


Figure 19. P adsorption kinetic on Fe particles.

4. Functionalization of magnetic particles

In order to avoid the possible aggregation of magnetic particles and to improve the kinetic stability, the surface of magnetic particles can be modified by attaching different stabilizer compounds. Some stabilizers used include: polymers, phospholipids, carboxylic acids, surfactant, clay minerals, etc (Cornell and Schwertmann, 1996; Laurent et al., 2008; Zhu et al., 2008; Hajdú et al., 2009; Girginova et al., 2010; Jang and Lim, 2010; Pan et al., 2010; Zhao et al., 2010; Ge et al., 2012).

We carried out an experiment for coating the magnetic particles with aminopropyltriethoxysilane (APTS) (see Chapter V). The schematic representation and linear formula of the molecule can be seen in the Figure 18.



NH_2-C_3H_6-$Si(OC_2H_5)_3$

Figure 20. Schematic representation and linear formula of APTS molecule.

APTS are bifunctional molecules that containing an alkoxysilane, $Si(OC_2H_5)_3$, which is bound covalently to the free –OH groups at the surface of the particles, and an organic head-group functionality, i.e., an amine group (NH_2) that determines the final chemical character of the modified surface (del Campo et al., 2005). NH_2 provides positive charge to magnetic particles.

The protocol followed was according to the method described in del Campo et al. (2005). The experiment consisted in the dispersion of 1.25 g of magnetic particles in 25 mL of APTS (2% v/v). In order to reach the maximum density of active amine groups, the suspensions of magnetic particles were shaken during 24 h. Afterwards, suspensions were centrifuged and the pellets were washed as follow: firstly, it is added 25 mL of 3 mM $NaHCO_3$, secondly, the samples were sonicated for 5 min and shaken for 10 min. Then, the samples were centrifugated for 5 min. This washed procedure was carried out 5 times. Lastly, the final pellet was diluted and sonicated in 30 mL of 3 mM $NaHCO_3$ and were shaken for 24 h.

5. High Gradient Magnetic Separation set up in continuous flow mode

The development of a device for removing P from waters under conditions of continuous flow involves an innovative step forward in the restoration of inland eutrophicated waters, due to large volumes of water can be handled because of decreasing retention times. All in all, in this dissertation, we set up a prototype laboratory-scale device for separating P from water under continuous flow and using the High Gradient Magnetic Separation (HGMS) technique.

The experimental design is depicted in the Figure 21 (for more detail, see Chapter 6). It basically, consists in the following: an aqueous solution is enriched with magnetic particles and P. Under sonication conditions, the magnetic suspension is passed through the HGMS column by using a peristaltic pump. The magnetic material, i.e. magnetic particles + adsorbed P, is retained on the magnetized wire and the nonmagnetic fraction (treated water) is collected to the output.

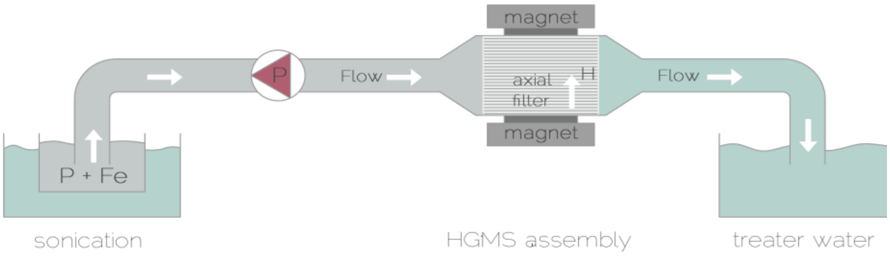


Figure 21. Experimental set-up. P+Fe – phosphorus + iron suspenson; P – peristaltic pump; H – magnetic field strength.

The theory behind 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 particle flow. The field gradient exerts a force on the magnetic particles which causes them to be trapped by the wires. This force is given by:

$$\underline{F_m} = V\chi\nabla\left(\frac{1}{2}\underline{B}\cdot\underline{H}\right) \tag{50}$$

where V is the particle volume, χ is the magnetic susceptibility of the particles, B is the magnetic induction and H is the magnetic field strength (de Vicente et al., 2010b).

We designed a laboratory prototype HGMS filter and choose an axial configuration as the most suitable. This consisted in two magnets of variable separation, between which a reservoir filled with a very soft magnetizable wire matrix is placed. The wire was composed of Fe 70%, Cr 25% and Al 5% and has a diameter of 0.5 mm and a total length of 2 m. This had the long axes in the direction of the flow velocity and perpendicular to the magnetic field applied. When an external magnetic field is applied, magnetic particles + adsorbed P are retained by the matrix, and once the magnets are removed, the wire is demagnetized and thereby magnetic particles can be recovered. This is possible due to, as can be seen in their hysteresis curve (Figure 22), there are no remnant magnetization.

Figure 22. Magnetization curve of wire used in the HGMS assembly.

A balance of magnetic and stokesian drag forces on the particles results in the following criterion for capture when the external magnetic field is not large enough to saturate the wire:

$$v_m = \frac{4x\mu_0 H^2 b^2}{9\eta a} \succ v_0 \qquad (51)$$

where v_m is the so-called magnetic velocity, v_0 is the linear flow average velocity through the filter, μ_0 is the permeability of vacuum, b is the particle radius, a is the wire radius and η is the viscosity of the continuous phase (Watson, 1973).

Likewise, the loading number N_L of the wire is defined as:

$$N_L = \frac{2x\mu_0 H^2 b}{v_0^{3/2} (\rho\eta a)^{1/2}} \qquad (52)$$

here ρ is the density of the continuous phase. Capture is expected for N_L > 25 (Nesset and Finch, 1980).

Finally, the filling factor of the filter can be expressed as:

$$F = n\pi a^2 \qquad (53)$$

where n is the number of wires intersecting a unit area of filter cross-section and a is the radius of the wire. The performance of the filter was determined by $F \approx 0.16$.

In addition, we carried out several experiments for identifying the best working conditions which allowed obtaining the greatest efficiency in the P removal. Particularly, we investigated four different operational variables:

i. Sonication time: this parameter must have considerable attention since magnetic particles tend to aggregate when they are near of their i.e.p. The aggregation causes a reduction in the specific surface area and in the free interfacial energy, thereby, adsorption properties are drastically affected.
ii. Flow rate: this parameter has also a great importance since it determines the retention time of the particles in the magnetic field.
iii. Magnetic field strength.
iv. Fe/P concentration ratio: to find out the minimum dose of magnetic particles necessary for removing the larger possible amount of P.

Chapter IV. *Summary of the presented papers*

Chapter IV

SUMMARY OF THE PRESENTED PAPERS

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. Among them, eutrophication is the most important global challenge to water quality scientists. It is caused by an excessive amount of inorganic nutrients in a water body, which finally promotes a deterioration of the whole lake ecosystem. About 30-40% of lakes and reservoirs worldwide are affected by unnaturally high nutrient concentrations. The sequence of ecological changes is extremely complex, finally conducting to a reduction in species diversity and drastically affecting anthropogenic water uses such as drinking water supply, fishery and recreation. It is worldwide accepted that among inorganic nutrients, phosphorus (P) is the minimum factor controlling the degree of eutrophication so a reduction of phosphorus availability in the water column is essential for improvement lake water quality. The P availability in the lake water can be decreased by reducing P input, increasing P retention in the sediment or increasing P export. Among them, the careful management and control of P loading has been adopted worldwide as the keystone and centerpiece of eutrophication management. New and innovative methods are of great importance to devise technologies for dealing with environmental problems. The application of magnetic particle technology to solve environmental problems is one of these methods that have received considerable attention in recent years.

This Thesis deals with evaluating the convenience of using magnetic nano- and micronsized particles as P absorbents and their later removal from solution by magnetic separation. Magnetic nanoparticles are recommended as seeding adsorbent material for P removal because of both (i) their high surface/ volume ratio, which is lastly responsible for their major chemical reactivity, and (ii) their potential reusability, because after the adsorption is carried out, the adsorbent can be separated and recovered from the medium by a simple magnetic separation.

Next, we will present the most important results obtained in the 4 papers compiling the present Thesis.

Paper I ***(published in Journal of Hazardous Material)*** focuses on selecting the more apropriate conditions for increasing the efficiency of P adsorption onto two types of magnetic particles (micronsized iron and nanosized magnetite particles) having a controlled shape and size well in the colloidal domain. Magnetite particles adsorbed more P (empirical saturation constant = 27.15 mg P g^{-1} Fe) than iron (Fe) particles (empirical saturation constant = 18.83 mg P g^{-1} Fe) as a consequence of the different particle size (average values for particle diameters of 90.6 ± 1.2 and 805 ± 10nm for magnetite and for Fe, respectively). A protocol was established for the successful reutilization of these magnetic particles by repeated washing with NaOH and therefore, optimizing the economic cost of this technology. Magnetic particles were also surface treated with amino silane groups (APTS) to counteract magnetic and van der Waals attractive interactions and promote kinetic stability. APTS-coated iron particles experienced a notable increase in P maximum adsorption capacity which could be explained by a remarkable increase in electrophoretic mobility. We proposed the use of APTS-coated Fe particles which are less-expensive and easy to obtain as a promising technique for lake restoration.

Paper II ***(published in Journal of Hazardous Material)*** is based on using highly magnetic particles as the seeding adsorbent material and their later removal from solution by High Gradient Magnetic Separation (HGMS). Contrarily to other methods based on batch conditions, large volumes of water can be easily handled by HGMS because of decreasing retention times. This study identifies the best working conditions for removing P from solution by investigating the effects of a set of four different experimental variables: sonication time, flow rate (as it determines the retention time of particles in the magnetic field), magnetic field strength distribution and the iron (Fe) particles/ P concentration ratio. Additionally, the change of P removal efficiency with time and the possibility of reusing magnetic particles were also studied. Our results evidenced that while flow rate does not significantly affect P removal efficiency, sonication time, magnetic field strength distribution and the Fe particles/ P concentration ratio are the main factors controlling magnetic separation process.

Paper III ***(published in Journal of Hazardous Material)*** is related to the analysis of the chemical interferences affecting the effectiveness P removal by magnetic seeding. As sodium, calcium, magnesium, silicate, sulfate, dissolved organic carbon and many other ions are naturally occurring in freshwater and brackish lakes, it is of major importance to understand their effects on P removal by magnetic seeding. In fact, due to the extreme seasonal variability in rainfall patterns characterizing Mediterranean climate and the frequent endorheic character of Mediterranean ponds (a close drainage basin), most of the Mediterranean ponds present high mineralized waters. Accordingly, studying the interference of the typical ions dissolved in lake waters on P removal by magnetic seeding represents a crucial and necessary task. 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. This objective was explored by collecting water from 20 Mediterranean shallow lakes, widely differing in their water chemistry. Our results evidence the strong ionic strength dependence of P removal efficiency. Although high P removal efficiencies (>80%) have been found in freshwater lakes (conductivities < 600 µS cm^{-1}), a drastic reduction in P removal was observed for extremely high mineralized waters. Correlation analysis has shown that major cations (Ca^{2+}, Mg^{2+}, Na^{+} and K^{+}) and anions (SO_4^{2-} and Cl^{-}) present in lake water as well as dissolved organic carbon (DOC) were the driving factors controlling the effectiveness of P removal. Complementary analysis has shown that after adding Fe particles, a notable reduction in DOC concentration, apart from the P reduction, is also observed. Our results confirm that P removal by magnetic seeding in not purely based on electrostatic attraction as negatively charged Fe particles still do adsorb a very significant amount of P. We have also found that negative charge of Fe particles dramatically decrease when increasing conductivity of lake waters.

Paper IV ***(submitted to Water Resources Reseach)*** is focused on determining and quantifying the single-effect of each ion on P removal efficiency by conducting experiments in artificial lake water where adding specific anions. In particular we studied the effect of HA (used as an indicator of DOC), SO_4^{2-} and Ca^{2+} on P removal efficiency by magnetic Fe particles using in-flow HGMS technique. 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 up to 35.5 mg HA L^{-1} and 10 mg Si L^{-1}, respectively. By contrast, SO_4^{2-} and Ca^{2+} did not significantly reduce P removal by adsorption on magnetic Fe particles. In this basis, we conclude that before using magnetic particles for restoring eutrophied aquatic ecosystems, in a whole-lake addition experiment, it is essential to make a throughout chemical analysis of the lake water in order to dose the right Fe concentration for getting the highest P removal efficiency.

Chapter V. *On the use of Magnetic Nano and Microparticles for Lake Restoration* (Paper I)

On the use of Magnetic Nano and Microparticles for Lake Restoration (Paper I)

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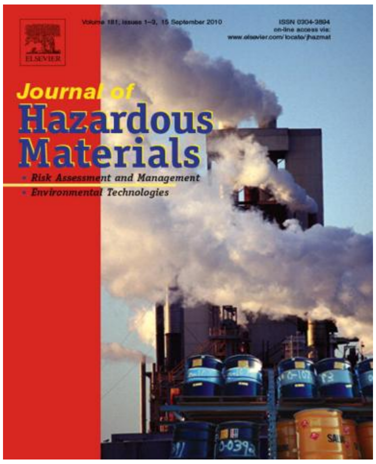
Published in:

Journal of Hazardous Materials. Volume 181, Issue 1-3, September 2010, Pages 375-381.



Abstract

Innovative approaches are of outstanding importance to devise technologies for dealing with eutrophication of inland waters. This study provides a quantitative estimate showing the convenience of using magnetic nano- and micronsized particles as phosphate absorbents and their later removal from solution by high gradient magnetic separation. Two different materials are investigated (iron and magnetite) having a controlled shape and size well in the colloidal domain. Magnetite particles adsorb more phosphate (empirical saturation constant = 27.15 mg P g^{-1} Fe) than iron particles (empirical saturation constant = 18.83 mg P g^{-1} Fe) as a consequence of the different particle size (average values for particle diameters of 90.6 ± 1.2 nm and 805 ± 10 nm for magnetite and for iron, respectively). A protocol is established for the successful reutilization of these magnetic particles by repeated washing with NaOH and therefore, optimizing the economic cost of this technology. Magnetic particles are also surface treated with amino silane groups (APTS) to counteract magnetic and van der Waals attractive interactions and promote kinetic stability. APTS-coated iron particles experience a notable increase in phosphate maximum adsorption capacity which could be explained by a remarkable increase in electrophoretic mobility. We propose the use of APTS-coated iron particles which are less-expensive and easy to obtain as a promising technique for lake restoration.

Keywords: Phosphorus, magnetic particles, lake restoration, eutrophication

1. Introduction

Eutrophication, an increased primary productivity (trophy) in a water body due to enhanced availability or usage nutrients, has resulted in a deterioration of lake ecosystems worldwide [1, 2, 3]. Visible indications of eutrophication are high turbidity caused by algal blooms, reduced or absent submerged vegetation, mass development of harmful cyanobacteria (blue green algae), reduced species diversity, oxygen depletion, formation of hydrogen sulfide, fish kills and smell nuisance [4]. As a consequence, changing lake´s productivity, the biology of the lake is drastically affected as a whole. In most inland waters the nutrient phosphorus (P) is the minimum factor controlling the degree of eutrophication and, due to the strong relationship between total P concentrations and chlorophyll in lake water, reducing the P concentrations in the lake water is the most important strategy for eutrophication control.

The P availability in the lake water can be decreased by reducing P input, increasing P retention in the sediment or increasing P export. Among them, the careful management and control of P loading has been adopted worldwide as the keystone and centerpiece of eutrophication management [5]. Additionally, to reinforce recovery, various physical and chemical methods have been employed to combat the internal P loading, including sediment dredging and oxygenation of the hypolimnion with pure oxygen or nitrate, among others. Finally, biological tools such as biomanipulation comprising removal of planktivorous fish and/or stocking of piscivorous fish, are frequently used for lake restoration especially in North Europe [6, 7, 8]. Overall, reduction in P inputs is essential for lake restoration before considering increasing P retention in the sediment or increasing P export. In fact, the absence of long-term effects (>8-10 years) of lake restoration are frequently caused to insufficient external P loading reduction.

New and innovative methods are of great importance to devise technologies for dealing with environmental problems. The application of magnetic particle technology to solve environmental problems is one of these methods that have received considerable attention in recent years [i.e. 9, 10]. Magnetic particles can be used to adsorb contaminants from aqueous or gaseous effluents and after the adsorption is carried out, the adsorbent can be separated from the medium by a simple high gradient magnetic separation process. Some examples of this technology are the use of magnetite particles to accelerate the coagulation of sewage [11], the removal of divalent metals from wastewater [9, 10], the use of magnetite-coated functionalized polymer such as resin to remove radionuclides from milk [12], the use of poly(oxy-2,6-dimethyl-1,4-phenylene) for the adsorption of organic dyes [13], and the use of polymer-coated magnetic particles for oil spill remediation [14].

Hence, as an alternative technology, magnetic separation of precipitated P could be considered as a promising tool for lake restoration. Several outstanding advantages of using these particles for lake restoration can be suggested: (i) the recovery of magnetic particles from the solution, reducing both the effects in the aquatic biota and the economic costs and (ii) the reusability of the particles, thus reducing economic costs.

In this context, the main purpose of the present paper was to achieve the convenience of using well controlled magnetic adsorbents to retain P and its later removal from lake water by a simple magnetic separation procedure after saturation is reached. To do so, a set of laboratory experiments were carried out in order to select the more appropriate conditions for increasing the efficiency of P adsorption onto two types of magnetic particles (micronsized iron and nanosized magnetite particles). Firstly, the P adsorption capacity of bare magnetic particles is evaluated and the effect of particle size investigated. Since the applicability of magnetic particles as adsorbents depends not only on their adsorption capacity but also on their reusability, a protocol is established here to desorb P from the particles. Finally, particles are functionalized by using aminopropyl-triethoxysilane (APTS), and hence positively charging the particles, to ascertain the effect of electrostatic interactions in the adsorption process.

2. Magnetic Separation Technique

The behavior of a small piece of magnetic material under the presence of a magnetic field strongly depends on the typical size. Very small particles (less than a few nanometers diameter) behave as magnetic monodomains. Since Brownian motion is very significant for such small systems, particles are stable in a magnetic field gradient and do not aggregate.

On the other hand, larger magnetic particles consist of magnetic multidomains. In the presence of an external magnetic field, these particles become magnetized. As a consequence two kinds of interactions come into play: particle-particle and particle-field interactions [15]. In this work we are concerned about the second kind of interaction, particle-field interactions, which are described by the following equation:

$$\underline{F_m} = \left(\underline{m} \cdot \underline{\nabla}\right)\underline{B} \tag{1}$$

where $\underline{B}$ is the magnetic induction, and $\underline{m}$ is magnetic particle dipole moment. Assuming that the particles are dispersed in a non magnetic medium, their magnetic dipole moment can be written as $\underline{m} = V\chi\underline{H}$, where V is the particle volume, $\underline{H}$ is the magnetic field strength and χ is the magnetic susceptibility of the particles.

For the case of a dilute suspension, the permeability of the suspension is not too different from the one of vacuum and $\underline{B} = \mu_0 \underline{H}$. Bearing this in mind, the magnetic force on the particle can be written as:

$$\underline{F_m} = \frac{V\chi}{\mu_0}(\underline{B} \cdot \underline{\nabla})\underline{B} \tag{2}$$

If there are no time-varying electric fields or currents in the medium, $\underline{\nabla} \times \underline{B} = 0$ and the magnetic force can be manipulated to give:

$$\underline{F_m} = V\chi\nabla\left(\frac{1}{2}\underline{B} \cdot \underline{H}\right) \tag{3}$$

where $\frac{1}{2}\underline{B} \cdot \underline{H}$ is the magnetostatic field energy density. Thus, if $\chi > 0$ the magnetic force acts in the direction of steepest ascent of the energy density scalar field. This is the reason why iron filings are brought near the pole of a magnet, they are attracted towards that pole. It is also the basis for any magnetic separation application. As observed from equation (3), larger forces are achieved for larger particles having large magnetic susceptibility. Hence, one may think that large magnetic particles are the most convenient ones.

Magnetic separation is always a two-step process, involving i) the adsorption, tagging or labeling of the desired material with magnetic particles, and ii) the separating out of these entities via a magnetic separation device. The simplest magnetic separator is a permanent magnet. However, faster accumulation rates can be obtained by using other more complicated devices [16, 17].

3. Experimental

3.1. Materials

Micronsized iron (Fe) particles were kindly supplied by BASF (Germany) and used without further treatment to make the suspensions. According to the manufacturer, the composition of this powder is 97.5 % iron, 0.9 % carbon, 0.5 % oxygen, and 0.9 % nitrogen.

All chemicals were analytical quality. KOH (90% purity), KNO_3, $FeSO_4.7H_2O$ (extra pure), and APTS were obtained from Sigma-Aldrich (Spain), KH_2PO_4, $NaHCO_3$, NaOH and HCl were obtained from Panreac (Spain). Deionized and filtered water (Milli-Q Academic, Millipore, France) was used in the preparation of all the suspensions

3.2. Synthesis of magnetite nanoparticles

Nanometer sized magnetite (Fe_3O_4) particles are frequently prepared by stoichiometric coprecipitation of Fe^{2+} and Fe^{3+} salts in basic medium [18]. Unfortunately such small particles are not interesting for us since thermal Brownian motion overcomes magnetic forces [19], which means that these particles could not be magnetically separated from solution. However, larger magnetite particles can be prepared from slow oxidation of $Fe(OH)_2$ by nitrate ions under controlled atmosphere [20]. This approach has been successfully applied in the past for the preparation of other iron oxides as well [21].

Magnetite particles having a typical size of 100 nm diameter were prepared following a sol-gel precipitation and re-crystallization method involving an iron hydroxide gel formation followed by aging under nitrate ions. To this end a 1L five-necked sealed jacketed reactor was used to accurately control experimental conditions. The synthesis requires inert atmosphere and this is achieved through displacement of dissolved oxygen by nitrogen. The reaction temperature was fixed at 85 ºC.

Several stock solutions were initially prepared consisting of 0.2 M KNO_3, 0.005 M KOH and 0.03 M $FeSO_4.7H_2O$. Water used in the preparation of the stock solutions was previously subjected to nitrogen flow in order to displace dissolved oxygen. The synthesis process involved the mixing of 250 mL KOH, 100 mL KNO_3 and 550 mL H_2O solutions in the reactor under agitation and nitrogen flow. Then, 100 mL $FeSO_4.7H_2O$ were added. Just immediately after Fe^{2+} salt addition, a sudden color change was observed due to the formation of iron hydroxide. After 4 hours under nitrogen flow at 85 ºC, the reaction was stopped in ice water. Decantation in the presence of a permanent magnet (405 mT) placed at the bottom of the container, and redispersion in Milli-Q water, was the method used to clean the suspension of unreacted ions. This process was repeated 5 or 6 times until the supernatant thus obtained was transparent and had low electric conductivity (<2 μS/cm). Particles were kept in a fridge in ethanol for later use. In order to get the dry weight, magnetite/ethanol dispersions were placed in Petri disks in a convection oven at 60 ºC for 24 hours. The black sediment obtained was later analyzed. The yield of this reaction is 1.4 grams of magnetite per litre of initial solution.

3.3. Electron microscopy of the magnetic particles

Particle morphology was studied in a LEO Gemini 1530 field-emission scanning electron microscope (FESEM) operating in a secondary electron (SE) mode. Microscope samples were prepared by drying on top of a glass substrate a droplet of a suspension of the magnetic particles dispersed in ethanol. A thin (ca. 20 nm) coating of carbon was then applied.

3.4. Magnetic characterization of Fe and Fe_3O_4 powders

The magnetization (M) of the powder magnetic particles was measured as a function of the external applied magnetic field (H) using a Quantum Design (San Diego, CA) MPMS-XL 5.0 Tesla Magnetometer. The external field was swept from -4000 to 4000 kA/m. Experiments were run at room temperature. Saturation magnetization was obtained by extrapolation to zero the magnetization values in the high field range versus the inverse of the applied magnetic field strength.

3.5. Electrokinetic characterization

Electrophoretic mobility (μ_e) was measured with a Zeta-PALS (Brookhaven) at 25.0 ± 0.5 ºC. Measurements were carried out 24 h after preparation of the suspensions, and the pH was readjusted immediately before measuring mobility. Every mobility data point presented in this work is the average of 10 measurements taken for the same sample in the course of a 'run'. The error bars are given by the standard deviation of those five measurements. Because of the high density of the particles and therefore their tendency to sediment under gravity, the samples were sonicated for 5 minutes and the measuring cell was turned over a couple of times before every run. As a preliminary step, the dependence of the measured mobility on the solid-phase concentration of our suspensions was first investigated. At low solid concentration, mobility increased with particle concentration and then remained practically constant for concentrations over 0.05 g L^{-1}. Results shown here correspond to suspensions having 1 g L^{-1} of particles content.

3.6. Preparation of magnetic suspensions

The preparation of the suspensions consisted of the following steps. i) 10 g of magnetic powder and 200 mL of purified water were mixed in a polyethylene container. ii) The mixture was stirred first by hand, and then in an ultrasonic bath. iii) Step ii) was repeated several times and, finally, the sample was immersed in a Branson sonifier (model 450) to ensure the required final homogeneity. The gradual homogenization of the samples was confirmed by the disappearance of the aggregates initially observed in the container bottom. As 1 mL of the stock Fe solution (50 g L^{-1}) was added up to a final volume of 50 mL, the final Fe concentration was 1 g L^{-1}, similarly to that reported by Karapinar et al. [22].

3.7. Effect of pH in the adsorption by Fe particles

Firstly, the effect of pH on P adsorption by Fe particles was investigated. To this end, 1 mL of the stock Fe suspension (50 g L^{-1}) and 1 mL of 5 mM KH_2PO_4 solution were added to 40 mL of 3 mM $NaHCO_3$ (acting as pH buffer) in 50 mL centrifuge tubes. Afterwards, pH was adjusted to the desired value, and then the suspensions were left for shaking in a horizontal shaker during 24 h at 20 ºC (150 rpm). After that time, pH was readjusted and made up to 50 mL of volume with 3 mM $NaHCO_3$. Thus, the initial Soluble Reactive Phosphorus (SRP) concentration in the centrifuge tube was fixed to 100 µM P. Next, magnetic particles were separated from the suspension by applying a magnetic field gradient of approximately 12,400 kA m^{-2} during 5 minutes (PASCO scientific; EM-8641). The supernatant was pipetted off and filtered (Whatman GFF) to be analyzed for molybdenum reactive P using the spectrophotometric procedure by Murphy and Riley [23]. The whole process was repeated for different pH's in the range from pH = 5 to pH = 9.

3.8. Adsorption isotherm for Fe and Fe_3O_4

Adsorption experiments were carried out in batch mode by adding 1 mL of the stock Fe or Fe_3O_4 suspensions to 45 mL 3 mM $NaHCO_3$ in 50 mL centrifuge tubes. Afterwards, the samples were shaken for 24 h and later, 1 mL of KH_2PO_4 solutions with concentrations ranging from 5 to 60 mM P was added to each tube. Once the pH of the suspensions was adjusted to 7.0 ± 0.3, they were shaken for 24 h. After adjusting again the pH to 7.0 ± 0.3, suspensions were transferred to 50 mL volumetric flasks and made up to volume with 3 mM $NaHCO_3$. Thus, the initial SRP concentrations varied between 0.1 and 1.2 mM. The next step was the filtration of the suspension in order to evaluate the amount of P adsorbed onto the magnetic particles. This process closely follows that described in section above.

3.9. Reusability of magnetic micro and nanoparticles

A new set of adsorption experiments was performed to test the possible reutilization of iron and magnetite particles. Once a typical adsorption experiment is carried out as described above, magnetic particles were separated and later washed twice with 1 M NaOH and three more times with 3 mM $NaHCO_3$. Resulting particles were then dried in Petri disks in a convection oven at 60 ºC for 24 hours and ready for later usage.

3.10. Adsorption by magnetic functionalized particles

Magnetic particles were surface treated to improve P adsorption at neutral pH following a similar procedure as described by del Campo et al. [24]. Concretely, 1.25 g of magnetic particles were dispersed in 25 mL of APTS (2% v/v). As del Campo et al. [24] noticed, there exists a clear change in the density of active amine groups with the reaction time, reaching the maximum density after 20 hours shaking. Accordingly, in this study, suspensions of magnetic particles were left for shaking during 24 hours. Afterwards, suspensions were centrifuged (20,000 rpm, 5 minutes) and the supernatants withdrawn. Pellets were washed 5 times as follows: i) addition of 25 mL of 3 mM $NaHCO_3$, ii) sonication for 5 minutes, iii) shaking for 10 minutes and iv) centrifugation for 5 minutes (20,000 rpm). The final pellet was diluted and sonicated in 30 mL of 3 mM $NaHCO_3$. Once the suspensions were shaken for 24 hours, they were ready for being used for adsorption experiments by following the same methodology explained in sections above.

4. Data analysis

4.1. Adsorption models

The equilibrium adsorption capacity of phosphorous, q, is calculated as follows:

$$q = \frac{C_0 - C_e}{M_a} V \tag{4}$$

where C_0 represents the initial P concentration in solution (mg L^{-1}), C_e is the final or equilibrium concentration (mg L^{-1}), M_a is the mass of adsorbent used in grams (in this case Fe or Fe_3O_4) and V is the total volume of solution (L).

The maximum adsorption capacity was estimated here according to the one layer Langmuir model [25]:

$$q = \frac{K_L M_L C_e}{1 + K_L C_e} \tag{5}$$

where, K_L is an adsorption constant related to the binding energy (L g^{-1}) and M_L is an empirical saturation constant, that is the maximum mass of solute adsorbed per unit mass of adsorbent (adsorption capacity) (mg g^{-1}). K_L and M_L were empirically determined from the linear forms of the Langmuir model. It is important to note that assumptions used to derive the Langmuir equation are rather stringent [26]. For example, ideal behaviour on the surface implies a homogeneous surface that lacks dislocations or any other structural nonidealities that might induce preferred adsorption. In addition, it assumes that a monolayer of adsorbed molecules is formed on the surface and an adsorption maximum is achieved as the monolayer becomes filled by the adsorbate. Although it is difficult to realize these conditions in practice, the Langmuir isotherm provides a conceptual basis for thinking about surface adsorption as well as a basis for modelling the adsorption process. Furthermore, the equation makes a convenient form for fitting data because it accommodates many situations in which the Langmuir model assumptions do not strictly apply [27].

4.2. Statistical analysis

All experiments reported in this work were run in triplicates. Comparison of mean values was done using t-student test and, unless otherwise stated, $p < 0.05$ is considered statistically significant. Statistical analyses were performed using Statistica 6.0 Software [28].

4. Results and Discussion

4.1. Particle size distribution

As observed in SEM images (Fig. S1), magnetic particles used in this work are spherical in shape and relatively polydisperse. Table 1 contains results from fitting experimental size data to a Log-normal distribution:

$$f(x) = \frac{A}{\sqrt{2\pi} x\sigma} \exp \frac{-(\ln x - \mu)^2}{2\sigma^2} \tag{6}$$

where, μ and σ represent the mean and standard deviation of the variable’s natural logarithm, respectively. From this, average values for particle diameters are estimated as follows: 805 ± 10 nm for iron and 90.6 ± 1.2 nm for magnetite. Histograms corresponding to magnetic particles are shown in Fig. S2.

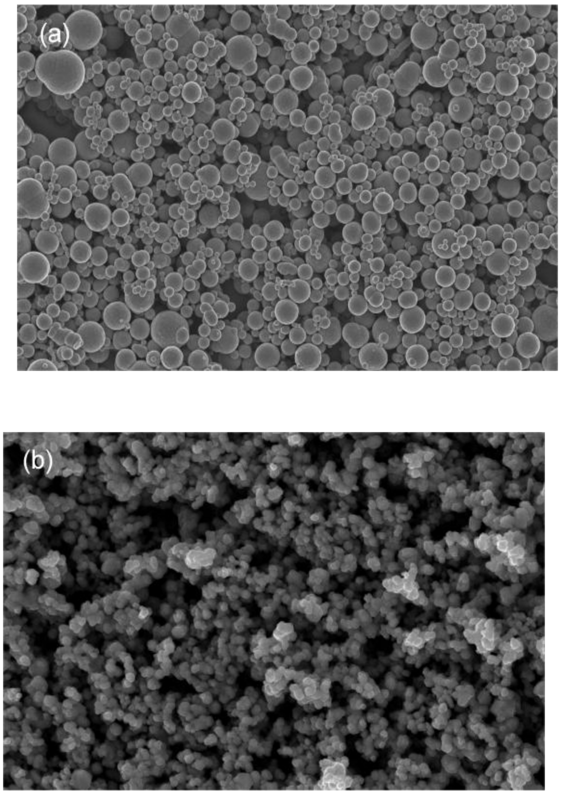


Figure S1. SEM images for iron (a) and magnetite (b) particles

Table 1. Fitting parameters to a Log-normal distribution. e^{μ} represents the center of the distribution and σ represents the width of the distribution.

	Median, e^{μ} (nm)	Standard deviation, σ (nm)
Iron	805 ± 10	0.36 ± 0.01
Magnetite	90.6 ± 1.2	0.194 ± 0.012

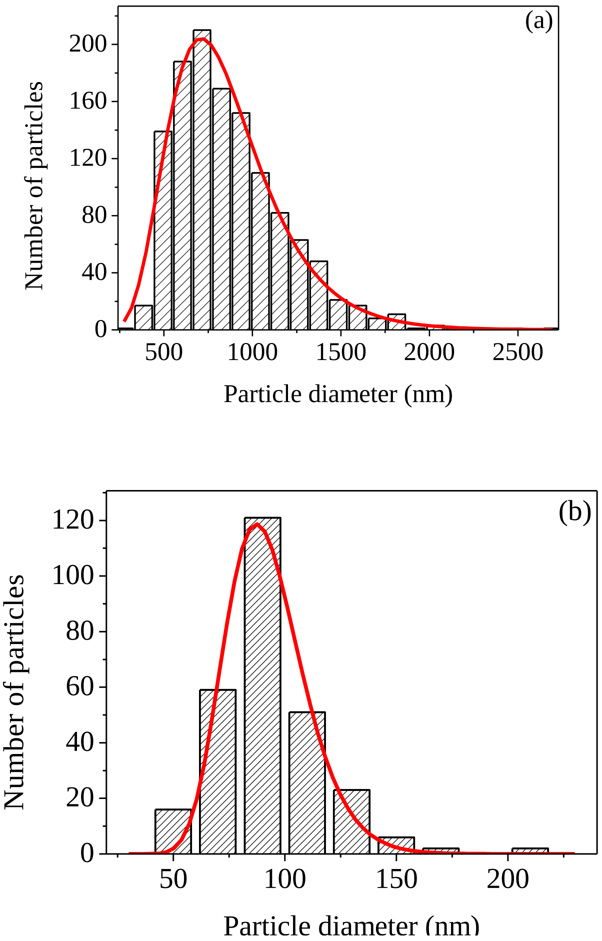


Figure S2. Histograms for iron (a) and magnetite (b) particles. Solid lines represent best fit Log-normal distributions.

Particle size affects in different ways to adsorption and magnetic separation phenomena. On the one hand, a large particle size is required to enhance magnetic separation under the presence of a magnetic field; large particles interact more strongly under the presence of the field moving towards magnetic field gradients. On the other hand, an important drawback comes from the fact that these particles are expected to quickly sediment under gravity. As a way of example, according to Stokes equation, an isolated one micronsized iron particle (density 7,500 kg m^{-3}) immersed in water (25 ºC, 1 mPa·s) reaches a terminal velocity of 3.6 μm s^{-1}. Furthermore, another important challenge is the fact that a larger adsorption requires small absorbents since surface/volume ratio strongly increases when decreasing the particle size. In conclusion, from a particle size investigation, bare magnetite particles are expected to have larger adsorption capacity if compared to iron ones. However, larger magnetic field gradients would be required for magnetite removal from solution.

4.2. Magnetic characterization

Typical hysteresis curves obtained for iron and magnetite powders are shown in Fig. S3 for magnetic fields in the range from -1,500 to 1,500 kA m^{-1}. As observed, for iron particles a ferromagnetic behavior is found with a negligible remnant magnetization as expected from a soft magnetic system. This result suggests that particles are multidomain having a saturation magnetization of 1,725 kA m^{-1} in close agreement with the bulk value 1,720 kA m^{-1} [29]. Qualitatively similar results are obtained for magnetite (Fe_3O_4) because of its ferrimagnetic order due to an inverse spinel crystalline structure. As expected, magnetite saturation magnetization is about three times lower than iron (477 kA m^{-1} at 300 K).

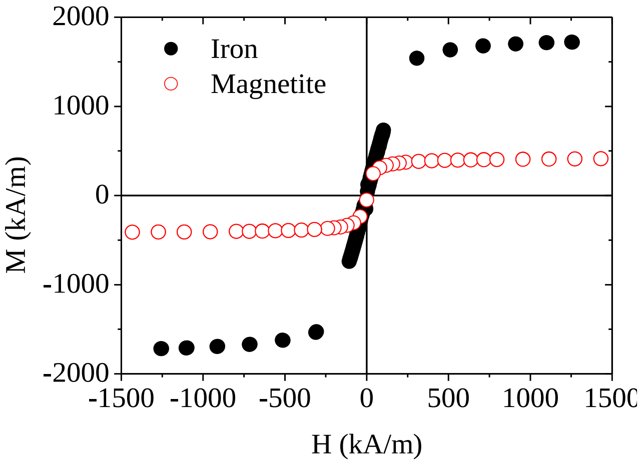


Figure S3. Magnetic histeresis curves for iron and magnetite particles.

4.3. Electrokinetic behavior

Iron particles used here do present a thin oxide surface layer [30] and hence behave as amphoteric solids with surface charges controlled by the pH in the aqueous medium [31]. Fig. 1 shows electrophoretic mobility of iron particles as a function of pH. An isoelectric point around pH = 6.5 is found, in good agreement with previously reported data on iron oxide-based colloids [32, 33]. At low pH values the particles are expected to be positively charged. On the contrary, at high pH values they are expected to bear a negative charge. As a consequence, in the case that the adsorption process is dominated by electrostatic interactions, low pH's would be required for phosphate removal from solution.

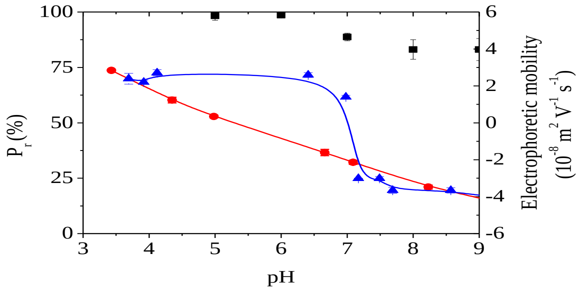


Figure 1. Effect of pH on the efficiency of P removal, P_r (%) and on the electrophoretic mobility of iron particles. Squares indicate P removal. Circles and triangles indicate electrophoretic mobility for bare and APTS-coated iron particles, respectively. The standard deviation is represented by vertical bars. Lines are plotted to guide the eye.

4.4. Effect of pH on P removal from Fe-based aqueous solution

P removal is an index frequently used for quantifying the efficiency of an adsorption method [34, 35]. P removal efficiency (in %), P_r, is defined as the ratio between the adsorbed P concentration to the initial P concentration:

$$P_r = \frac{C_0 - C_e}{C_0} \times 100 \quad (7)$$

In Fig. 1 we show results for P_r at different pH's for Fe suspensions. As observed, iron magnetic particles do behave as excellent adsorbents for phosphate; whatever the pH, the efficiency is larger than 80 % (very similar results were found for magnetite). These values are in the range of those reported in the literature for similar pH conditions using other P adsorbents. For example, Robb et al. [34] estimated an average P reduction around 90% when using Phoslock (a modified clay) for P removal from wastewaters. Similarly, Dixon [36] quantified P removal efficiencies near 85% when using magnetite. And, more recently, Ou et al. [35] found that lanthanum-doped mesoporous SiO_2 was able to remove nearly 100% of the initial P. However, it is worthy to note that the last authors used initial P concentrations 3 times lower than that used in the present study. Finally, much lower P removal efficiencies are also reported in the literature. Therefore, Shaikh and Dixit [37] quantified P removal efficiencies down to 10% at pH = 7 when using aluminium sulphate and magnetite as adsorbents, measuring the highest efficiencies at pH = 4 (~90%).

Our results showed a slight decrease in P removal efficiency with increasing pH (cf. Fig. 1). They are in agreement with those observed by Dixon [36] from pH = 6 to pH = 9, while a notable decrease in P removal was detected by this author at higher pH´s. The slight decrease in P removal observed in this study, from pH = 5 to pH = 9, could be qualitatively explained through electrophoretic mobility curves shown in Fig. 1. These results suggest that the adsorption mechanism is not purely electrostatic [38] since negatively charged Fe particles still do adsorb a very significant amount of P. However, the investigation of the mechanisms governing the adsorption of P on the particles is out of the scope of this paper (for more information see [38]). Similarly to our results, Illés and Tombácz [39] observed that magnetite was an excellent adsorbent for humic acids despite of the electrostatic repulsion at pH ~ 9. More recently, Borgnino et al. [40] showed that despite the negative electrophoretic mobility of two Fe (III)-modified montmorillonites, they were good P adsorbents. The fact the P adsorption is so efficient independently on the pH reinforces the idea of using magnetic particles as P adsorbents for lake restoration. As natural waters are commonly from neutral to basic, it is difficult to find good adsorbent materials, mainly because the isoelectric points of most frequently oxides are around this value. In our case, magnetic particles do behave exceptionally well even at pH = 7 where the P removal efficiency was larger than 85%.

4.5. Adsorption isotherms: comparing P adsorption capacity between Fe and Fe_3O_4 particles

Adsorption isotherms (q vs C_e plots) were measured for bare iron and magnetite particles. Results are shown in Fig. 2. P maximum adsorption capacity (M_L) was estimated by fitting the experimental data to Langmuir isotherm, and revealed interesting differences between the two particles employed. Comparison between micronsized iron and nanosized magnetite particles evidenced the higher P adsorption capacity of magnetite (M_L = 27.15 mg g^{-1}) if compared to iron particles (M_L = 18.83 mg g^{-1}). In particular for an initial SRP concentration of 35 mg P L^{-1}, the P adsorption was 1.4 times higher for the magnetite than for iron particles. These results could be explained in terms of the different particle size between iron and magnetite (cf. Fig. S2). A larger adsorption is expected for magnetite if compared to iron because magnetite particles are smaller than iron ones, hence increasing the available surface for adsorption. For practical applications, it is essential to remark that as Daou et al. [38] observed, phosphatation does not modify the structure and the magnetization of magnetite assuring its efficient removal once added to aqueous solutions.

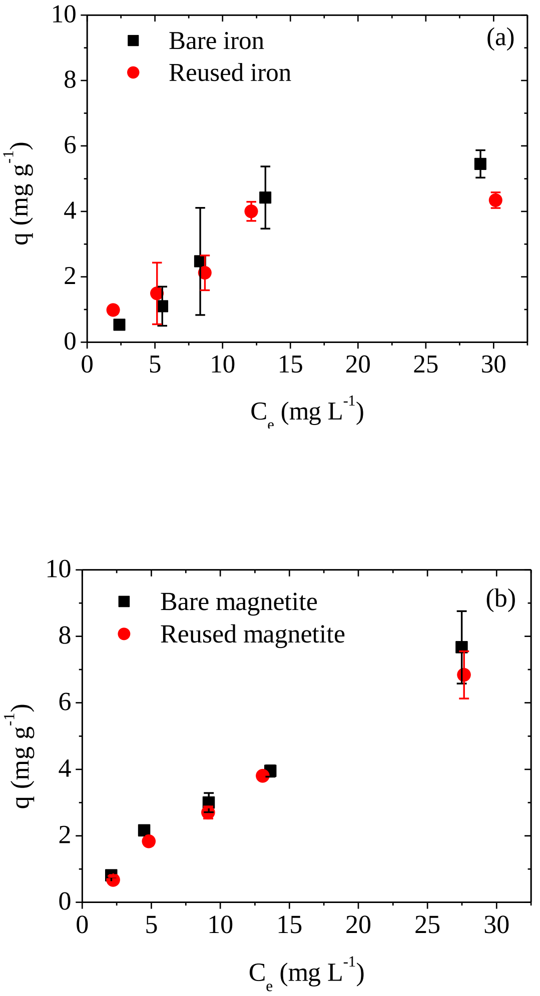


Figure 2. P adsorption on bare and reused iron (a) and magnetite (b) particles.

4.6. Reusability of magnetic micro- and nanoparticles

A new challenge for using magnetite particles is their reutilization and therefore, optimizing the economic cost. In fact, although the use of both iron and magnetite particles could not be cost-effective in a full-scale process, the particles reutilization makes this method especially interesting for lake restoration due to the large water volume to be treated.

Results obtained in this work suggest that when re-using particles that had already adsorbed P, by washing them with NaOH, P adsorption capacity of reused particles experienced a slight change whatever the magnetic particles involved (Fig. 2). In particular, a slight decrease in the empirical saturation constant is observed for iron particles (from 18.83 to 15.80 mg g^{-1}) and for magnetite particles (from 27.15 to 23.83 mg g^{-1}). Indeed, for an initial

SRP concentration of 35 mg P L^{-1}, the P adsorption was reduced 20% for reusable iron particles and for an initial SRP concentration of 3 mg P L^{-1}, the P adsorption was reduced 18% for reusable magnetite particles. In conclusion, the possibility of reusing magnetic particles opens new perspectives in the search for practical applications significantly reducing economic costs.

4.7. Adsorption and P removal efficiency by using magnetic functionalized particles

One of the main difficulties facing almost all the novel techniques based on using magnetic nanoparticles is their tendency to aggregate [41]. As aggregation reduces the specific surface area and the interfacial free energy [42, 43], it is expected that adsorption properties are likely to be diminished. The principal cause of aggregation is generally assumed to be the short-range van der Waals attraction and/or remnant magnetisation forces between the particles. To counteract these attractive interactions and promote kinetic stability, the surface of magnetite and iron particles can be modified by attaching polymers, organic long-chain molecules or designing more complex composite materials to improve the affinity of the particles for specific target species [26, 44-46].

In this work, to further understand the effect of electrostatic interactions in the adsorption mechanism, magnetite and iron particles were coated with amino silane groups as detailed in the experimental section. These $-NH_2$ groups would provide the particles with a positive charge hence increasing adsorption capacity. Actually, preliminary electrophoretic mobility measurements demonstrate that particles become positively charged over a larger pH range having also a larger net surface charge (see Fig. 1).

Adsorption tests show that when coating iron particles with APTS, a notable increase in P maximum adsorption capacity (M_L) is found from 18.83 mg g^{-1} (uncoated iron particles) to 25.06 mg g^{-1} (APTS-coated iron particles) (Fig. 3). Indeed, the higher P adsorption properties of APTS-coated iron particles compared to uncoated particles could be explained by a notable increase in electrophoretic mobility, as it is mentioned above. Therefore, uncoated particles experienced electrophoretic mobility values of -2.14×10^{-8} m^2 V^{-1} s^{-1} at pH = 7.09 while APTS-coated iron particles show electrophoretic mobility values of 1.4×10^{-8} m^2 V^{-1} s^{-1} at pH = 6.98 (Fig. 1). The effect of APTS-coating on P maximum adsorption capacity was less pronounced for the case of magnetite particles, where similar maximum adsorption capacities were observed in uncoated and coated particles.

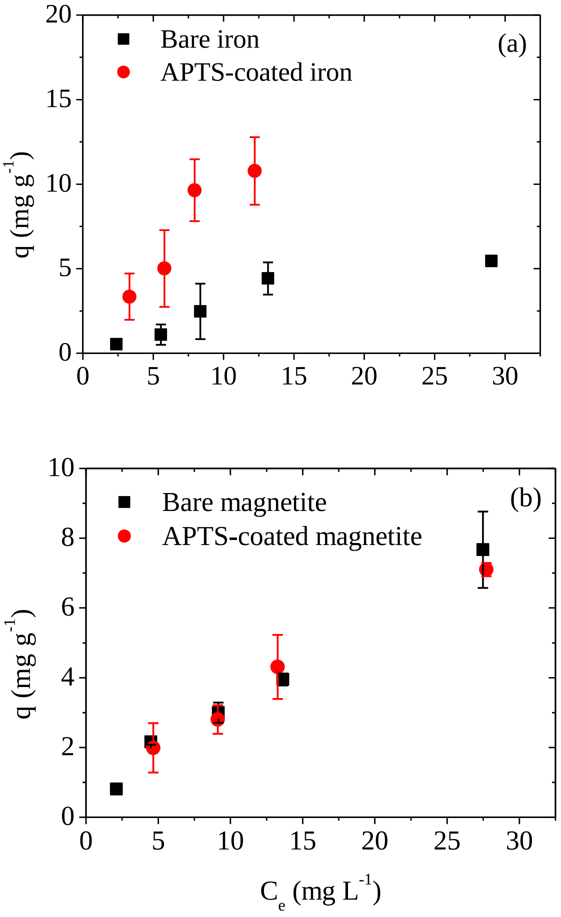


Figure 3. P adsorption on bare and on APTS-coated iron (a) and magnetite (b) particles.

5. Conclusions

This study provides a quantitative estimate showing the convenience of using iron and magnetite particles for removing P from solution. An important requisite for the magnetic components is their biocompatibility and low toxicity. Iron and magnetite are well known magnetic materials that accomplish this requirement. Although magnetite particles adsorb more P than iron particles as a consequence of the different particle size, APTS-coated iron particles were especially efficient for P removal. In addition, the existence of similar P adsorption capacities in bare and in reused magnetite and iron particles makes this method especially interesting for applying in a full-scale process for lake restoration. In particular, we think that the use of magnetic separation technology could be useful for decreasing P external loading to aquatic ecosystems by constructing artificial ponds where adding iron particles and retaining P before entering the lake. However, we put forward the need for future research focused on a better understanding of the adsorption mechanisms involved as well as the study of the potential interference in P adsorption caused by anions and cations present in solution.

Acknowledgements

The authors would like to thank F. Galisteo-González for providing the Bool2k software used for the generation of particle-size distributions from SEM micrographs. This work was supported by an Integrated Action Project "Acción Integrada (2953/07)" from the University of Granada and MICINN MAT 2009-14234-C03-03 project (Spain).

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Chapter VI. *Setting up High Gradient Magnetic Separation for combating eutrophication of inland waters*

(Paper II)

Setting up High Gradient Magnetic Separation for combating eutrophication of inland waters

(Paper II)

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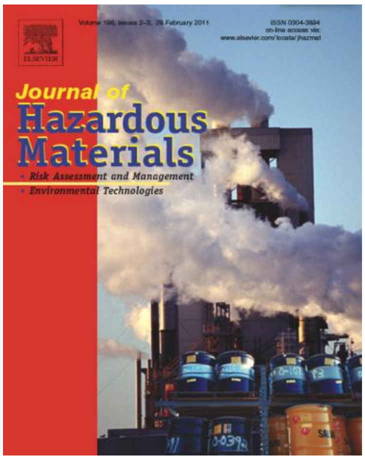
Published in:

Journal of Hazardous Materials. Volume 186, Issue 2-3, February 2011, Pages 2068-2074.



Abstract

To find new approaches to devise technologies for handling with eutrophication of inland waters is a global challenge. Separation of the P from water under conditions of continuous flow is proposed as an alternative and effective method. This work is based on using highly magnetic particles as the seeding adsorbent material and their later removal from solution by High Gradient Magnetic Separation (HGMS). In contrast to other methods based on batch conditions, large volumes of water can be easily handled by HGMS because of decreasing retention times. This study identifies the best working conditions for removing P from solution by investigating the effects of a set of four different experimental variables: sonication time, flow rate (as it determines the retention time of particles in the magnetic field), magnetic field strength and the iron (Fe) particles/ P concentration ratio. Additionally, the change of P removal efficiency with time (build up effect) and the possibility of reusing magnetic particles were also studied. Our results evidenced that while flow rate does not significantly affect P removal efficiency in the range 0.08 – 0.36 mL s^{-1}, sonication time, magnetic field strength and the Fe particles/ P concentration ratio are the main factors controlling magnetic separation process.

Keywords: High Gradient Magnetic Separation, phosphorus, magnetic particles, lake restoration, eutrophication

1. Introduction

Currently eutrophication, which is caused by an excessive amount of inorganic nutrients, is the most important global challenge to water quality scientists [1, 2, 3]. About 30-40% of lakes and reservoirs worldwide are affected by unnaturally high nutrient concentrations [4]. The sequence of ecological changes is as follows: nutrients stimulate phytoplankton growth increasing the zooplankton biomass, causing drastic oxygen depletions as a result of the bacterial decomposition of the organic matter [5]. In addition, other visible indications of eutrophication are mass development of harmful cyanobacteria (blue green algae) and reduced species diversity, causing a strong influence on anthropogenic water uses such as drinking water supply, fishery and recreation [4].

Among inorganic nutrients, it is worldwide accepted that phosphorus (P) is the most important limiting nutrient of primary production in inland waters [6, 7]. Accordingly, reducing the P concentrations in the lake water is frequently the key strategy for eutrophication control. To deplete P in lake concentrations, it is crucial to reduce external P loading to aquatic eutrophic ecosystems before considering any other technique such as increasing P retention in the sediment or increasing P export. Among the most promising and innovative methods for lake restoration, the use of highly magnetizable model colloidal particles as a seeding adsorbent material for P removal has been recently investigated by de Vicente et al. [8] in batch mode. Highly magnetic iron oxide/carbonyl iron nanoparticles are recommended as seeding adsorbent material for P removal from aqueous solutions because of (i) their high surface/volume ratio, which is lastly responsible for their major chemical reactivity, (ii) the specific adsorption of P on the magnetic particles as demonstrated in a shift of the isoelectric point of adsorbent at a low pH value, and (iii) their potential reusability, because after the adsorption is carried out, P can be desorbed by simply increasing the alkalinity of the medium and the magnetic particles can be separated and recovered from the medium by a simple High Gradient Magnetic Separation (HGMS) process [8, 9].

Once it has been proved the high P adsorption capacity of carbonyl iron particles under batch conditions [8], in the present paper we aim on setting up a laboratory-scale device for separating P from water under continuous flow conditions by using HGMS [10].

2. High Gradient Magnetic Separation as a promising technique for lake restoration

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 in accordance with:

$$\underline{F_m} = V\chi\nabla\left(\frac{1}{2}\underline{B}\cdot\underline{H}\right) \tag{1}$$

where, V is the particle volume, χ is the magnetic susceptibility of the particles, B is the magnetic induction and H is the magnetic field strength [8]. According to eq. 1, the highest efficiency in magnetic particles removal can be achieved by (i) increasing the applied magnetic field (e.g. using powerful magnets and hence, increasing the economic cost), by (ii) increasing the field gradient (e.g. employing a magnetically soft HGMS filter) or by (iii) using highly magnetizable particles with large magnetic susceptibility (e.g. carbonyl iron) [11]. For a discussion on the effect of particle size we refer to de Vicente et al. [8].

Usually, one differentiates between three geometric configurations of HGMS filters which have been designated as transverse, longitudinal and axial [12]. In the axial filter configuration (sometimes referred to as a *parallel stream filter*) the wire axis and the fluid flow are mutually parallel and the magnetic field is perpendicular to them. This configuration has several advantages: the capturing magnetic force scarcely competes with the hydrodynamic drag force; mechanical capture is reduced; filter washing can be performed efficiently; and the fluid dynamics can be treated most easily as demonstrated by the existence of both potential and laminar flow analytical models [12, 13, 14].

A necessary (but not sufficient) condition to trap the magnetic particles is that the magnetic force $\underline{F_m}$ has to overcome other competitive forces, namely gravitational, hydrodynamic, centrifugal and inertial forces [15]. According to the earlier work by Watson [16], a balance of magnetic and stokesian drag forces on the particles results in the following criterion for capture when the external magnetic field is not large enough to saturate the wire, $H < M_{sw}/2\mu_0$, being M_{sw} the saturation magnetization of the wire.

$$v_m = \frac{4\chi\mu_0 H^2 b^2}{9\eta a} > v_0 \tag{2}$$

Here, v_m is the so-called *magnetic velocity*, v_0 is the linear flow average velocity through the filter, μ_0 is the permeability of vacuum, b is the particle radius, a is the wire radius and η is the viscosity of the continuous phase.

Also, Nesset and Finch [17], by considering a balance between magnetic and Blasius-type drag forces around the wires, developed a loading number N_L, where:

$$N_L = \frac{2\chi\mu_0 H^2 b}{v_0^{3/2}(\rho\eta a)^{1/2}} \tag{3}$$

Here, ρ is the density of the continuous phase. Capture is expected for $N_L > 25$.

Since 1970s, HGMS has been widely applied for removing heavy metals ions from industrial and municipal wastewaters as well as in the mineral processing and the recycle industries [18]. In fact, in recent years magnetic separation has undergone considerable progress and HGMS has become a powerful technique for the handling of finely dispersed weakly magnetic particles [15]. Other practical applications of the HGMS have been in the steel, paper and power industries [10]. Numerical models to simulate the capture process and to select test conditions in a HGMS do actually exist [19, 20]. Despite HGMS is a well-known process, up to date, the application of HGMS for treating wastewaters has been mainly based on the combination of coagulation and magnetic seeding techniques. Hence, metal ions or dissolved nutrients (i.e. P) are removed from liquids by using hydroxide flocs and later, these flocs combined with magnetic seeds (typically magnetite) are separated from the water by using magnetic separation [10, 11, 21]. Many examples can be found in the literature [11, 22].

For HGMS to be an efficient technique for removing P in a full-scale process of lake restoration, it is crucial to reduce economic costs. Accordingly, in the present paper we aim on (i) setting up a laboratory-scale HGMS device for removing P from aqueous solutions by simply adding carbonyl iron colloidal particles as adsorbent material, and (ii) identifying the best working conditions. In particular, we focus on investigating the effects of a set of four different operational variables: sonication time, flow rate, magnetic field strength and the P/ magnetic particles concentration ratio.

3. Materials and Methods

3.1. Materials

Because of their large magnetic dipole moment, micronsized carbonyl iron (Fe) particles (BASF, Germany) were used as seed material. Fe particles, with a mean particle diameter of ~ 1 μm, are chemically characterized as follows: 97.5 % iron, 0.9 % carbon, 0.5 %

oxygen, and 0.9 % nitrogen. More details about the physico-chemical characterization of these particles can be found in de Vicente et al. [8].

All chemicals were analytical quality. KH_2PO_4, $NaHCO_3$, NaOH, H_2SO_4 and HCl were obtained from Panreac (Spain). Distilled water was used for the preparation of all suspensions.

3.2. Preparation of the magnetic suspensions

Simulated inland water was prepared by adding 0.2 mL of 10 mM KH_2PO_4 solution and 2 mL of the stock Fe solution (50 g L^{-1}) in 100 mL of 3 mM $NaHCO_3$. Hence, final Fe concentration was 1 g L^{-1} in the same way as Karapinar et al. [23]. It is also important to note that the P concentrations considered in the present study are among those naturally observed in highly eutrophic inland waters [24] where the potential application of this technique is crucial. Similarly to de Vicente et al. [8] the pH of the solution was adjusted to pH = 7 by adding HCl. All magnetic suspensions were always prepared right before use and experiments were carried out in triplicates.

3.3. Electrokinetic characterization

The electrokinetic characterization of Fe particles was investigated measuring their electrophoretic mobility with a Zeta-PALS (Brookhaven) at 25.0 ± 0.5 ºC. For this purpose, a solution was prepared by adding 2 mL of the concentrated Fe solution (50 g L^{-1}) to 100 mL of 3 mM $NaHCO_3$. Measurements were carried out 24 h after preparation of the suspensions, and the pH was readjusted to pH = 7 immediately before measuring mobility. Every mobility data point presented in this work is the average of 10 measurements taken for the same sample in the course of a ‘run’. The error bars are given by the standard deviation of those measurements. 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. As a preliminary step, the dependence of the measured mobility on the solid-phase concentration of our suspensions was first investigated. At low solid concentration, mobility increased with particle concentration and then remained practically constant for concentrations over 0.05 g L^{-1}. Results shown here correspond to suspensions having 1 g L^{-1} of particles content.

3.4. Magnetic characterization of the particles and wire matrix

The magnetization (M) of both the magnetic particles and the magnetizable wire was measured as a function of the external applied magnetic field (H) using a QuantumDesign (San

Diego, CA) MPMS-XL5.0 Tesla Magnetometer. The external field was swept from −1500 to 1500 kA m^{-1}. Experiments were run at room temperature. Saturation magnetization was obtained by extrapolation to zero the magnetization values in the high field range versus the inverse of the applied magnetic field strength.

3.5. High Gradient Magnetic Separation set-up

3.5.1. Experimental device:

A laboratory prototype HGMS axial filter has been designed and built that consists of a reservoir, filled with a very soft magnetizable wire matrix with the long axes in the direction of the flow velocity and perpendicular to the magnetic field applied (see Fig. 1c). The chemical composition of the Aluchrom wire is Fe 70%, Cr 25% and Al 5% with a diameter of 0.5 mm and a total length of 2 m. This wire is bended to get shorter wires of ~ 5 cm length. The performance of the filter is described by the filling factor $F = n\pi a^2 \approx 0.16$ where, n is the number of wires intersecting a unit area of filter cross-section and a is the radius of the ferromagnetic wire.

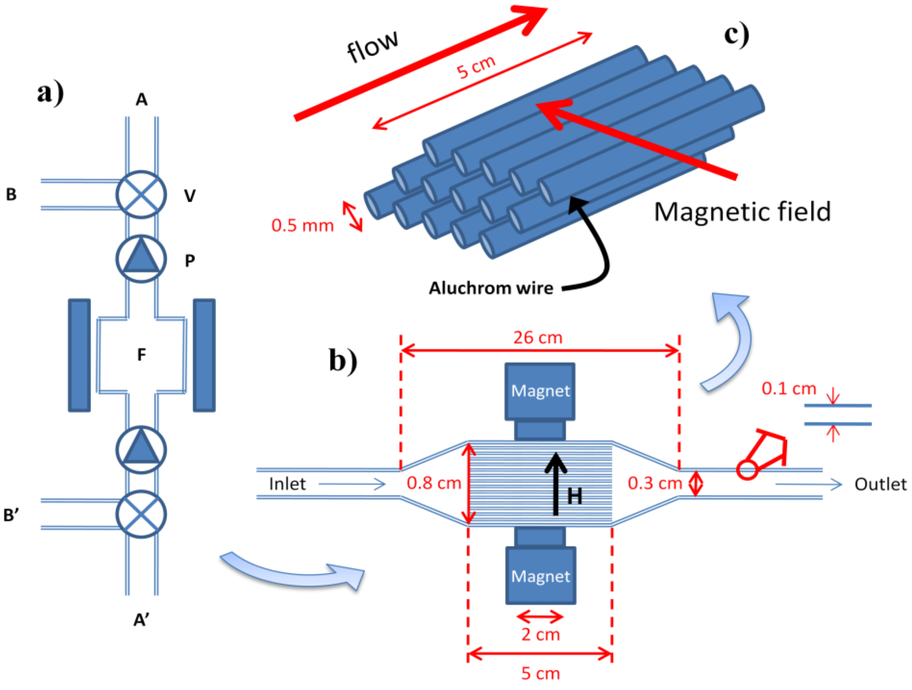


Figure 1. a) Experimental set-up. A.- Feeder (Fe + P suspension), V.- Valve, P.- Peristaltic pump, F.- Axial filter, A'.- Treated water, B.- Rinse water, B'.- P enriched distilled water. b) HGMS assembly. c) Detail of the axial filter.

$2\rho_p b^2/9\eta = 4.3\times10^{-7} << 1$, being ρ_p = 7.8 g cm^{-3} the density of the iron particles. Particle magnetization (M) calculations were carried out using Frölich-Kennelly equation [25]:

$$M = \frac{\mu_i H}{1 + \mu_i H / M_s} \tag{4}$$

where $\mu_i = 40$ is the initial magnetic permeability of the particles and $M_s = 1550\ kAm^{-1}$ is their saturation magnetization. Once the magnetization is obtained for a given magnetic field strength, the magnetic susceptibility is calculated as $\chi = M/H$.

In Fig. 2 we show results obtained for the magnetic velocity v_m as a function of the external magnetic field applied H according to eqs 2 and 4. Also included are horizontal lines corresponding to the linear flow velocity v_0. As expected, the magnetic velocity increases with the magnetic field. Only for large enough magnetic fields the magnetic velocity overpasses the linear velocity hence trapping the magnetic particles on the array of wires. The minimum magnetic field required to trap the particles increases as we increase the linear velocity and flow rate. From these calculations we see that the minimum magnetic field strengths to be applied should be around 30 - 90 kA/m for the carbonyl iron particles to be trapped under flow velocities up to 51 mm s^{-1}.

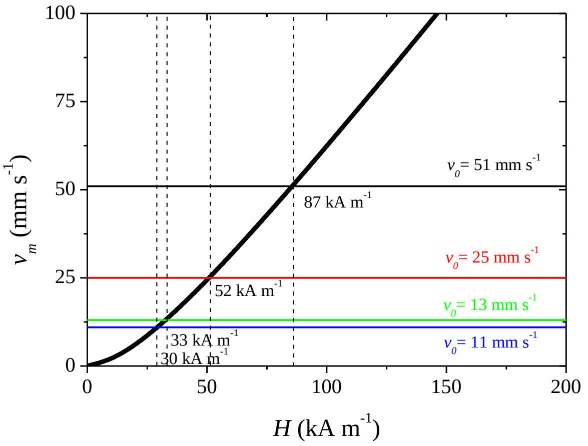


Figure 2. Operating regime of the axial filter. $v_m > v_0$ is needed for the particles to be trapped in the filter.

In Table 1 we show the magnetic field strength required for N_L = 25 at different flow rates. As observed, the restriction on the N_L number is easily accomplished for magnetic fields larger than ~ 10 kA m^{-1}.

Table 1. Minimum magnetic field necessary for $N_L = 25$ (eq 3) corresponding to different flow rates C and linear flow velocities v_0.

C **(mL s^{-1})**	v_0 **(mm s^{-1})**	**H (kA m^{-1})**
0.08	11	3.2
0.09	13	3.5
0.18	25	6.1
0.36	51	10.7

To generate magnetic fields of the order of a few tens of kA m^{-1} we used a special design involving permanent magnets. The magnetic field is generated by the use of two strong neodymium magnets with variable gap separation. The magnetic field strength at midpoint between poles when the separation is 1 cm corresponds to H = 450 kA m^{-1}. The effective filter length is 2 cm which is determined by the diameter of the pole pieces of the magnet (Fig. 1).

In a typical experiment, first, magnetic (Fe) particles are added into a P enriched aqueous solution under sonication conditions (A) (Fig. 1). By using a peristaltic pump (P), the magnetic suspension is passed through the HGMS column (F, Fig. 1b). The magnetic material, i.e. magnetic particles + adsorbed P, is then retained on the magnetized wire and the nonmagnetic fraction (treated water) passes through the matrix (A΄). Finally, the treated water is filtered through a fiber filter (Whatman GFF) and analyzed for P concentration by using the spectophotometric method described by Murphy and Riley [26]. In this work P removal efficiency (in %), P_r, is defined as the ratio between the adsorbed P concentration to the initial P concentration:

$$P_r = \frac{C_0 - C_e}{C_0} \times 100 \tag{5}$$

Here C_0 represents the initial P concentration in solution (mg L^{-1}) and C_e is the final or equilibrium concentration (mg L^{-1}).

In a subsequent step the magnetic field was removed, distilled water (B) was passed through the HGMS column (F) and the particles were washed from the matrix being recovered in the container B´. This recovery was only possible due to the negligible remnant magnetization of the wire (the magnetization of the wire became zero when the magnetic field was removed as shown in Fig. 3).

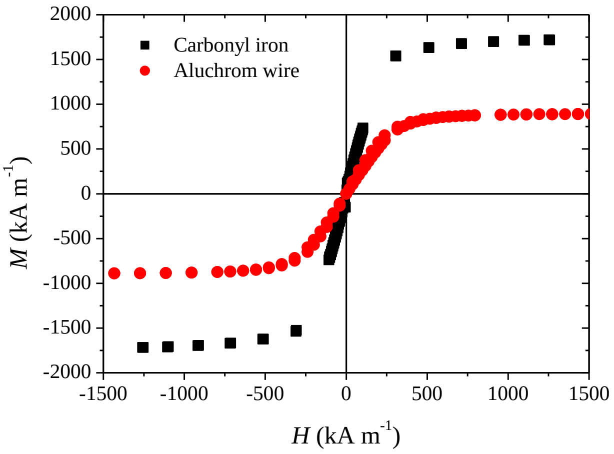


Figure 3. Magnetization curve of the carbonyl Fe powder and Aluchrom wire used in the HGMS assembly.

3.5.2. Experiments:

A first experiment was carried out in order to clarify the role of magnetic seeding on the P removal by HGMS. A suspension containing 0.2 mL of 10 mM KH_2PO_4 solution in 100 mL of 3 mM $NaHCO_3$ but without the addition of Fe particles, was passed through the HGMS. We did not observe any P retention in the HGMS filter.

Testing the effect of sonication time: The magnetic suspensions prepared as it was described above, were sonicated at different times: 1, 2, 3, 4, 5, 10 and 15 minutes. Then, they were pumped through the device using a peristaltic pump under continuous sonication condition. The other experimental variables such as flow rate, distance between the magnets and magnetic particles/P concentration ratio were fixed to 0.36 mL s^{-1}, 1 cm and 1.61 g Fe mg^{-1} P, respectively.

Testing the effect of flow rate: Magnetic suspensions prepared as stated above were passed through the HGMS column similarly as previously described: sonication time of 5 min, distance between magnets of 1 cm and magnetic particles/phosphorus concentration ratio of 1.61 g Fe mg^{-1} P. The experiment was repeated at different flow rates: 0.36, 0.18, 0.09 and 0.08 mL s^{-1}.

Testing the effect of magnetic field strength: To investigate the influence of magnetic field strength on P removal, suspensions were passed through the device under sonication condition, applying different distance between magnets: 1, 1.8, 2.6, 3.3, 4.1, 4.6 and 5 cm. The other operational variables such as sonication time (5 minutes), flow rate (0.36 mL s^{-1}) and Fe/P concentration ratio (1.61 g Fe mg^{-1} P) were kept constant.

Testing the effect of Fe/P concentration ratio: Here we check the effect of different Fe/ P concentration ratios (0.19, 0.40, 0.81, 1.61, 3.23, 4.03 and 4.84 g Fe mg^{-1} P) on the P removal. The experimental design was similar as described above and the other experimental variables such as sonication time (5 min), flow rate (0.36 mL s^{-1}) and distance between the magnets (1 cm) were kept constant.

Testing the particle buildup effect in P removal efficiency: To study the change on time of P removal efficiency, 2 mL of the 10 mM KH_2PO_4 solution and 20 mL of the concentrated Fe solution (50 g L^{-1}) were added to 1 L of 3 mM $NaHCO_3$ (pH adjusted to 7). After the suspension sonication (5 min), it was passed through the device and outflow was collected at different times: 1, 3, 5, 10, 15, 20, 25 and 30 min. Again, the other experimental variables such as flow rate (0.36 mL s^{-1}), distance between the magnets (1 cm) and magnetic particles/ phosphorus concentration ratio (1.61 g Fe mg^{-1} P) were constant.

3.6. Reusing magnetic particles

Magnetic fraction (Fe particles + specifically adsorbed P) of the suspensions recovered in the distilled water of the alternative system (B´ in Fig. 1a) was transferred to 50 mL volumetric flasks. Suspension was centrifuged (4000 rpm, 5 min) and the supernatant withdrawn. Pellet was dried in a convection oven at 60 ºC for 24 hours. The dry particles were subsequently washed with 1 N NaOH according to de Vicente et al. [8]. Finally, recovered magnetic particles were diluted in 3 mM $NaHCO_3$ and then reused for removing P from suspensions following the same methodology as described above.

4. Results and Discussion

In the literature there are few examples about the combination of chemical precipitation and HGMS for removing P from wastewaters [11]. However up to date, there are no studies related to P removal only applying HGMS, which would otherwise drastically reduce the economic costs when applying at full-scale. The present study shows the convenience of using carbonyl Fe particles as seeding agents in combination with HGMS, without any addition of coagulants, for P removal from aqueous solutions. At the optimal operating conditions, P removal efficiencies are higher than 90%. In the present study and similarly to Karapinar [27], we have proved that no P removal by the magnetized wire occurs by itself. By contrast, only when adding Fe particles, high P removal efficiencies were achieved. Since P without the addition of Fe particles can not be separated magnetically, magnetic seeding technique was found to be essential for the separation of P by HGMS but no addition of any other coagulant was needed. Next, we will present and discuss the results of the different experiments carried out to select the most optimal operating conditions for P removal by HGMS.

4.1. Electrokinetic behavior

All suspensions were adjusted to pH = 7 as it is the most frequently pH observed in aquatic ecosystems. At this pH, and similarly to de Vicente et al. [8], Fe particles are negatively charged (Electrophoretic mobility, $\mu_e = (-3.01 \pm 0.01) \times 10^{-8}\ m^2\,V^{-1}\,s^{-1}$). The result suggests that P is specifically adsorbed on Fe particles by interactions that basically are not electrostatic since negatively charged Fe particles still do adsorb a very significant amount of P (see below). Similarly to our results, Illés and Tombácz [28] observed that magnetite was an excellent adsorbent for humic acids despite of the electrostatic repulsion at pH $\sim$ 9. More recently, Borgnino et al. [29] showed that despite the negative electrophoretic mobility of two Fe (III)-modified montmorillonites, they were good P adsorbents. The fact that the P adsorption is so efficient independently on the pH reinforces the idea of using magnetic particles as P adsorbents for lake restoration.

4.2. Magnetic characterization

In Fig. 3 we show the magnetic hysteresis curves corresponding to the carbonyl Fe particles and Aluchrom wire used in the HGMS assembly. As observed, both the particles and the wire behave as ferromagnetic materials. Initial permeability and saturation magnetization of the particles were obtained by fitting Frölich-Kennelly equation (eq 4) to the experimental data.

4.3. Effect of the sonication time

A crucial physical property of magnetic particles is their tendency to aggregate. Encounters between particles dispersed in liquid media occur, and the stability of a suspension is determined by the interaction between the particles during these encounters. Since the aggregation causes a reduction in the specific surface area but also in the free interfacial energy, adsorption properties are drastically affected. To counteract these attractive interactions and promote kinetic stability, the samples were sonicated.

Table 2 shows the effect of different sonication times of the magnetic suspensions on P removal efficiency. Based on this data, we can conclude that the optimal sonication time is 5 min, showing a drastic reduction in P removal efficiency when sonication time increased up to 10 or 15 min. To further investigate this finding we performed measurements in a Turbiscan Classic to ascertain the transmitted and backscattered intensity signal. Higher settling rates were measured in suspensions sonicated for longer times (Fig. 4). In fact, when increasing sonication time, a sharp reduction in transmission is observed at low heights (< 10 mm) while a concominant increase in transmission occurred at higher heights. This result suggests that Fe particles sediment under gravity during long sonication times, presumably resulting in a larger P removal efficiency. However, a reduction in P removal efficiency was observed that may be ascribed to a reduced P adsorption on Fe particles caused by thermal effects

Table 2. Effect of the sonication time on P removal efficiency. Calculations correspond to a distance between magnets of 1 cm (H = 450 kA m^{-1}), Fe/P concentration ratio of 1.61 gFe mg^{-1} P, and flow rate C = 0.36 mL s^{-1}.

Sonication time (min)	P removal (%)	Standard deviation
1	65	2.4
2	72	1.3
3	74	3.0
4	72	4.8
5	100	1.5
10	52	2.7
15	24	3.9

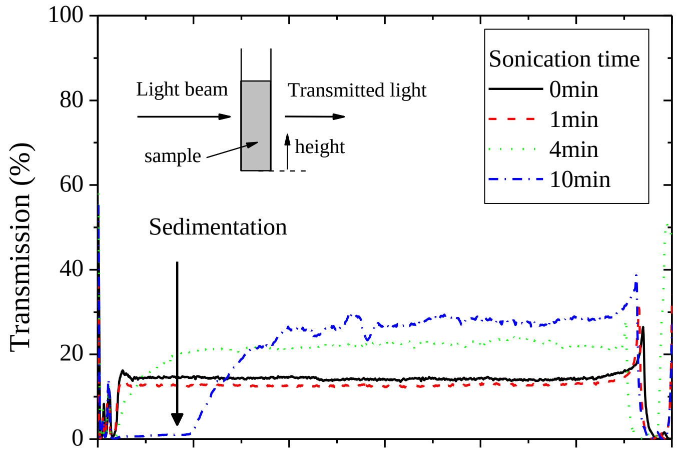


Figure 4. Transmission profile corresponding to the Fe suspensions after being sonicated different times (0, 1, 4 and 10 min). Distance between magnets 1 cm (H = 450 kA m^{-1}). Fe/P concentration ratio 1.61 gFe mg^{-1} P. Flow rate C = 0.36 mL s^{-1}.

4.4. Effect of the flow rate on P removal efficiency

The flow rate is a key variable when designing HGMS as it determines the retention time of the particles in the magnetic field [11]. In the present study we do not observe any significant effect of the flow rate (in the range from 0.08 to 0.36 mL s^{-1}) mainly because of the slow rate employed on P removal efficiency as expected from the large relative capture cross section for our HGMS filter [13] (Table 3). This is reinforced by calculations that reveal that the linear velocity is smaller than the magnetic velocity when the flow rate is smaller than 2.54 mL s^{-1}. Currently, experiments are being done in this direction to check this point. Regardless the flow rate, P removal efficiency was always higher than 80%. These results evidence the convenience of using HGMS for removing P from large volumes of aqueous suspensions. According to the present results, all subsequent experiments were run considering a flow rate of 0.36 mL s^{-1} in order to achieve a high efficiency for treating large water volumes.

Table 3. Effect of the flow rate on P removal efficiency. Calculations correspond to a distance between magnets of 1 cm (H = 450 kA m^{-1}), Fe/P concentration ratio of 1.61 gFe mg^{-1} P, and sonication time of 5 min. The minimum flow rate for $v_0 > v_m$ is as large as 2.54 mL s^{-1}.

C **(mL s^{-1})**	**P removal (%)**	**Standard deviation**
0.08	94	3.5
0.09	88	2.9
0.18	98	2.4
0.26	100	1.7
0.36	100	1.5

Our results are similar to those reported by Shaik and Dixit [11] who did not note any effect of flow velocity on the magnetite removal efficiency. Similarly to magnetite [11], Fe particles are highly magnetic and firmly attach to the magnetized wire. Accordingly, even the highest flow rate tested in this study was not able to detach it from the matrix. By contrast, Karapinar [27] found that increasing flow rate (from 0.57 to 3.00 L min^{-1}) resulted in a reduction in the Fe and magnetite removal efficiency. Hence, the author proposed to intensify magnetic field for getting higher efficiencies at high flow rates, but only when flow rates were always lower than 2.00 L min^{-1}.

4.5. Effect of the magnetic field strength on P removal efficiency

Apart from the hydrodynamic force, the magnetic force $\underline{F_m}$ is the other dominant external force in a magnetic separator, increasing particle capture with increasing magnetic field [15]. In the axial filter the magnetic field decreases when increasing the distance between the magnets and consequently the particles are less effectively attached to the magnetized wire.

Our results evidenced that as a consequence of increasing the distance between the magnets, Fe particles passed through the HGMS instead of being retained on the magnetized wire (Fig. 5). In fact, we have measured, in the outlet, total Fe concentrations around five times higher for distances larger than 4 cm compared to shorter distances. Accordingly, P removal efficiency experienced a drastic reduction when the distance between magnets was higher than 4 cm. These results are in agreement with theoretical calculations for the largest distance between the magnets (3.4 cm) and the minimum magnetic field strength (87 kA m^{-1}).

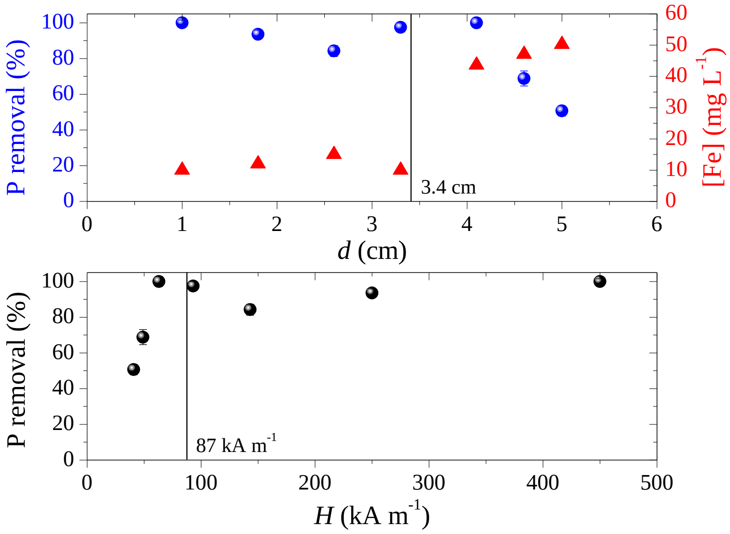


Figure 5. Effect of magnetic field strength in the P removal efficiency (blue circles) and outlet Fe concentration (red triangles). Vertical lines correspond to theoretical calculations for the minimum magnetic field strength and maximum gap distance. Sonication time 5 min. Fe/P concentration ratio 1.61 gFe mg^{-1} P. Flow rate C = 0.36 mL s^{-1}.

To find out the right dose of magnetic particles necessary for removing a certain amount of P and then, get the highest efficiency, different Fe/P concentrations ratios were considered. Interestingly, results showed that the separation efficiency of P by HGMS strongly depends on the ratio of Fe concentration to P dosage (Fig. 6). Keeping constant the other operating conditions, highest P removal efficiency (100%) was obtained when applying ~ 1.5 g Fe mg^{-1} P.

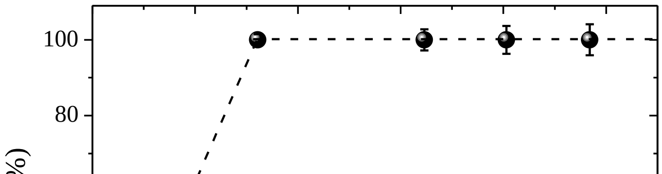


Figure 6. Effect of Fe/P ratio in the P removal efficiency. Dashed lines are plotted as a guide for the eyes. Distance between magnets 1 cm (H = 450 kA m^{-1}). Sonication time 5 min. Flow rate C = 0.36 mL s^{-1}.

Since the basic property that determines the effectiveness of magnetic separation is the magnetic force exerted on the particles, a possible reason for the reduced effectiveness with lower ratios can be the decreasing of the magnetization of the precipitate [27]. In addition, the saturation of the binding sites for P adsorption can be also a likely explanation.

4.7. Change of P removal efficiency with time

From a practical point of view, the effect of buildup of magnetic particles onto the wire (i.e. the maintenance performance of the filter) is an important property to be examined [30]. This study shows that P removal efficiency remained larger than 80 % up to 30 minutes operation (Table 4). A detailed understanding of the temporal evolution in P removal efficiency is out of the scope of this work and requires further investigations. In general, these results suggest that the HGMS is an efficient method for recovering P from wastewater even when considering large volumes of water. In fact, we observed that even after passing more than 500 mL (648 mL) of the wastewater through the HGMS column, the outlet contained less than 15 % of the initial P concentration implying that most of the Fe particles entering in the HGMS assembly were retained by the filter. Accordingly, HGMS could be recommended for being used when treating larger volumes of aqueous suspensions.

Table 4. Effect of the buildup on P removal efficiency. Calculations correspond to a distance between magnets of 1 cm (H = 450 kA m^{-1}), Fe/P concentration ratio of 1.61 gFe mg^{-1} P, and flow rate C = 0.36 mL s^{-1}.

Time (min)	P removal (%)
1	99
3	88
5	80
10	82
15	84
20	86
25	88
30	90

4.8. Reutilization

To do economically attractive the method, the particles reutilization was studied. Our results suggest that when re-using particles that had already adsorbed P, by washing them with NaOH, P adsorption capacity of reused particles decreased 36%. These results are slightly lower than those obtained by de Vicente et al. [8]. Although adsorption capacity experienced a little decrease, the possibility of reusing magnetic particles continues being effective.

5. Conclusions

We design an axial HGMS filter for removing P from P enriched waters using magnetic particles as the seeding absorbent material and identify the best operating conditions under continuous flow. The best conditions are: (i) sonication time: 5 minutes; (ii) flow rate: as it does not affect so much to P removal efficiency, it is better to use the higher we can; (iii) distance between magnets: 1 cm or the closer we can and (iv) magnetic particles: P ratio: 1.5 g mg^{-1}.

Magnetic field strength and flow rate effects are in good agreement with theoretical predictions for model axial filters.

The high P removal efficiency obtained by adding only carbonyl Fe particles and the possibility of both using a high flow rate and of reusing magnetic particles makes the process economically attractive. Hence, magnetic particles as the seeding absorbent material combined with the HGMS emerge as a promising technique for removing P from both wastewaters and also from the P enriched waters discharging to inland waters.

Acknowledgements

This work was supported by Junta de Andalucía project No. RNM-6630 (Proyecto de Excelencia, 2010, Spain), MICINN MAT 2009-14234-C03-03 and MAT-2010-15101 projects (Spain) and by the European Regional Development Fund (ERDF).

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Chapter VII. *Chemical interferences when using High Gradient Magnetic*

Separation for phosphate removal: consequences for lake restoration

(Paper III)

Chemical interferences when using High Gradient Magnetic Separation for phosphate removal: consequences for lake restoration

(Paper III)

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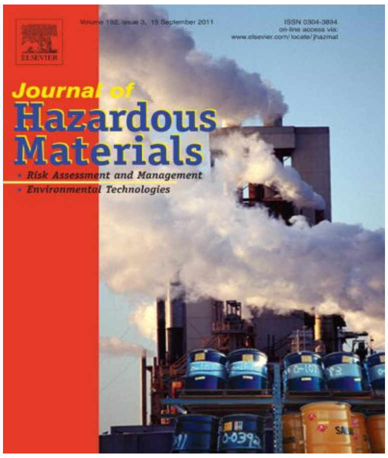
Published in:

Journal of Hazardous Materials. Volume 192, Issue 3, September 2011, Pages 995-2001.



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 µS cm^{-1}). However, a significant reduction in P removal was observed for extremely high mineralized waters. Correlation analysis showed that major cations (Mg^{2+}, Na^+ and K^+) and anions (SO_4^{2-} and 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.

Keywords: High Gradient Magnetic Separation, phosphorus, eutrophication, magnetic particles, chemical interferences.

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

Table 1. Chemical composition of the studied lakes. nd= under detection limit.

Lake	TDS (mg/l)	DOC (mg/l)	TP (µg/l)	NT (mg/l)	N-NO_3^- (mg/l)	Si (mg/l)	Mn^{2+} (mg/l)
Agia	3860	22.19	35.2	2.29	0.65	2.5	0.53
Canales	100	1.28	25.2	0.10	0.05	nd	0.09
Güejar Sierra	840	53.05	380.2	4.92	0.63	4.2	0.50
Quentar	278	1.37	23.5	0.30	0.33	0.7	0.04
Fco Abellán	467	2.32	18.5	0.26	0.22	nd	0.08
Cubillas	543	2.80	33.5	1.51	1.14	0.3	0.07
Colomera	518	3.28	23.5	4.31	3.46	0.6	0.05
La Laguna	970	14.78	2642.5	18.49	0.07	3.5	0.51
Loja	294	22.84	559.2	3.63	0.31	3.0	0.27
Grande	5500	11.23	95.2	2.08	0.08	10.2	0.56
Chica	30520	41.71	70.2	4.37	1.67	5.5	0.56
Zafarraya	412	16.92	1500.8	7.46	0.23	3.2	0.37
Rico	324	16.00	934.2	4.03	0.53	1.2	0.37
Alhama	269	1.29	75.2	0.67	0.35	1.1	0.03
Bermejales	366	1.92	41.8	0.67	0.32	0.2	0.04
Honda	258000	136.00	545.8	37.34	8.02	0.6	5.88
Ruidera	485	3.70	3.5	10.15	10.55	1.8	0.07
Doñana	15960	274.5	1542.5	30.32	11.65	1.4	0.32
Beznar	294	1.49	15.2	0.66	0.45	3.0	0.043
Torrente	392	1.32	323.5	1.00	0.83	6.2	0.037

Table 1. Continued.

	Na^+ (mg/l)	K^+ (mg/l)	Mg^{+2} (mg/l)	Ca^{+2} (mg/l)	Cl^- (mg/l)	SO_4^{-2} (mg/l)
Agia	17.0	2.4	213.3	449.2	63.5	2922.6
Canales	4.2	0.8	12.5	18.9	24.9	25.2
Güejar Sierra	31.0	23.6	59.5	102.7	62.1	410.3
Quentar	1.7	0.7	28.0	29.5	2.0	38.2
Fco Abellán	12.4	2.9	31.4	50.6	20.0	217.5
Cubillas	17.9	4.2	19.2	81.3	29.9	357.2
Colomera	26.9	3.9	15.2	76.9	42.5	296.9
La Laguna	56.4	14.8	57.0	71.2	88.5	298.6
Loja	3.1	14.7	3.3	52.1	5.0	5.5
Grande	210.5	7.7	198.7	502.4	327.6	2621.0
Chica	4119.5	41.1	1978.5	576.6	8397.0	12237.0
Zafarraya	18.8	10.1	12.0	27.8	46.2	12.3
Rico	6.7	30.6	10.7	32.4	19.1	7.9
Alhama	2.4	1.1	16.6	32.4	2.4	6.2
Bermejales	3.4	2.3	23.3	47.0	5.1	165.4
Honda	23601.2	703.6	15050.2	346.9	60138.2	70265.8
Ruidera	14.6	2.5	14.0	57.63	7.4	58.4
Doñana	2828.7	93.5	132.0	104.5	6028.9	51.8
Beznar	10.5	2.3	24.3	27.2	16.6	73.7
Torrente	14.0	3.7	27.7	45.2	20.3	95.2

2.2. Chemical analysis

The filtered water was analyzed for P [31], nitrate (NO_3^-) and ammonium (NH_4^+) 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^{2+}) was analyzed following APHA [34]. The determination of sodium (Na^+). potassium (K^+). calcium (Ca^{2+}). magnesium (Mg^{2+}). sulphates (SO_4^{2-}) and chlorides (Cl^-) 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 ºC 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 ~ 800 nm [24]. A stock Fe suspension was prepared by dispersing 5 g Fe particles in 100 mL distilled H_2O. A stock 1 mM P solution was prepared by adding 136 mg KH_2PO_4 (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^{-1}) 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^{-1} in T1 and T2. and 25.81 g mg^{-1} 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].

Table 2. Experimental set-up for studying the chemical interferences of coexisting ions on P adsorption on Fe particles.

	Fe/ P (g mg^{-1})	**P (µM)**	**Fe (g l^{-1})**
T 1	6.45	5	0.25
T 2	6.45	10	0.50
T 3	25.81	5	1.00

Fe + P suspensions were firstly sonicated for 5 minutes 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^{-1}. The flow rate (0.36 mL s^{-1}) 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^{-1} 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 analysed 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:

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

where A_{λ} 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^{-1}) 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 minutes 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 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].

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].

Table 3. pH. electrophoretic mobility (μ_e). Zeta potential and conductivity of Fe particles suspended in different lake waters.

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

(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 x 10^{-8} m^2 V^{-1} s^{-1}) was measured when Fe particles were dissolved in the lowest mineralized lake water (Canales. 0.18 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.

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.

Indep Var	**Fe/ P ratio (g mg^{-1})**	**Fitting equations**	r^2	***p* level**
Cond	6.45 (T 1)	y=2.23-0.19x	0.50	<0.005
	6.45 (T 2)	y=1.94-0.09x	0.26	<0.05
	25.81 (T 3)	y=2.08-0.13x	0.40	<0.01
Na^+	6.45 (T 1)	y=1.84-0.15x	0.54	<0.01
	6.45 (T 2)	y=1.79-0.08x	0.41	<0.01
	25.81 (T 3)	y=1.81-0.11x	0.51	<0.005
K^+	6.45 (T 1)	y=1.74-0.17x	0.29	<0.05
	6.45 (T 2)	y=1.75-0.11x	0.32	<0.05
	25.81 (T 3)	y=1.79-0.19x	0.59	<0.005
Mg^{2+}	6.45 (T 1)	y=1.97-0.20x	0.52	<0.005
	6.45 (T 2)	y=1.84-0.10x	0.33	<0.05
	25.81 (T 3)	y=1.88-0.14x	0.39	<0.05
Cl^-	6.45 (T 1)	y=1.88-0.15x	0.61	<0.005
	6.45 (T 2)	y=1.80 -0.08x	0.42	<0.01
	25.81 (T 3)	y=1.83-0.10x	0.47	<0.05

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.

Indep Var	**Fe/ P ratio (g mg^{-1})**	**Fitting equations**	***r^2***
pH	6.45 (T 1)	y=2.02-0.05x	0.01
	6.45 (T 2)	y=2.14-0.06x	0.03
	25.81 (T 3)	y=1.93-0.03x	0.00
NO_3^-	6.45 (T 1)	y=1.58-0.12x	0.10
	6.45 (T 2)	y=1.65-0.06x	0.06
	25.81 (T 3)	y=1.60-0.15x	0.23
NH_4^+	6.45 (T 1)	y=1.47-0.95x	0.10
	6.45 (T 2)	y=1.60-0.03x	0.03
	25.81 (T 3)	y=1.49-0.10x	0.21
Si	6.45 (T 1)	y=1.62-0.09x	0.03

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.

Indep Var	**Fe/ P ratio (g mg^{-1})**	**Fitting equations**	r^2	***p* level**
Ca^{2+}	6.45 (T 1)	y=2.34-0.38x	0.52	<0.005
	6.45 (T 2)	y=1.92-0.13x	0.17	ns
	25.81 (T 3)	y=1.96-0.16x	0.16	ns
DOC	6.45 (T 1)	y=1.74-0.16x	0.25	<0.05
	6.45 (T 2)	y=1.73-0.07x	0.15	ns
	25.81 (T 3)	y=1.75-0.13x	0.25	<0.05

In all treatments. P removal was significant ($p < 0.05$) and inversely related to Na^+. K^+. Mg^{2+}. Cl^-. SO_4^{2-}. Mn^{2+} and conductivity (Table 4). On the contrary. the correlation was not significant for pH. NH_4^+. NO_3^-. Si and TA as $p > 0.05$ (Table 5). and a complex scenario appears for DOC and 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 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 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 ± 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 ± 12 %. only for the significant relationships except for 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 Mg^{2+} and 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 unhydrolised cations at pH equal or lower that the isoelectric point. Contrarily to these observations. Stachowicz et al. [40] did not find any effect of Mg^{2+} and Ca^{2+} on arsenite adsorption on goethite in the pH range relevant for natural waters (pH 5-9).

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 Cl^-. SO_4^{2-} and CO_3^- 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 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 μM) significantly decreased the effectiveness of P adsorption to $Al(OH)_3$ by 10–13% at 450 μM 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 μM) identified by de Vicente et al. [19].

From these experiments we cannot conclude that anions or cations by theirselves 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 preferently 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 $Al(OH)_3$ by the presence of humic acids. In relation to humic acid adsorption on magnetite. Illés and Tombácz [44] observed that humic acid has high affinity to magnetite surface especially at lower pH. where interacting 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).

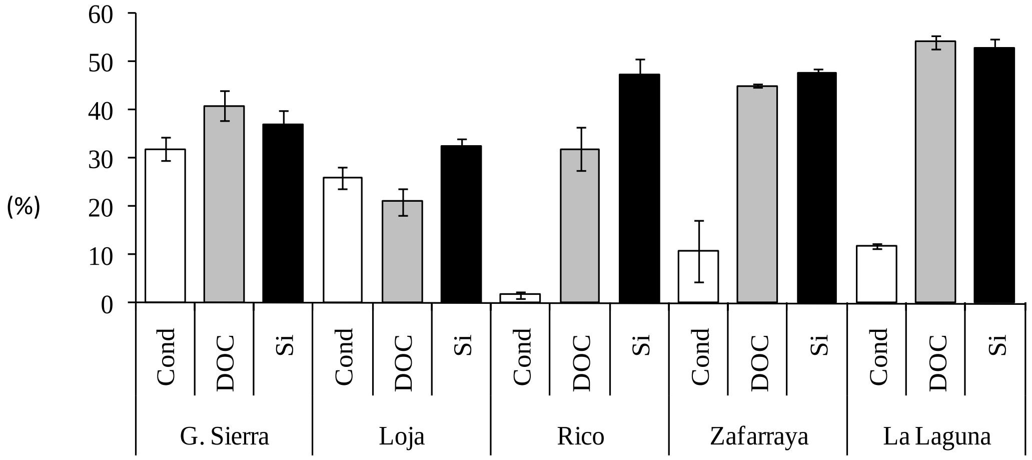


Figure 1. Reduction (%) of conductivity. dissolved organic carbon (DOC) and total dissolved silicate (Si) by magnetic seeding (Fe/P ratio 1.61 g mg^{-1}).

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.

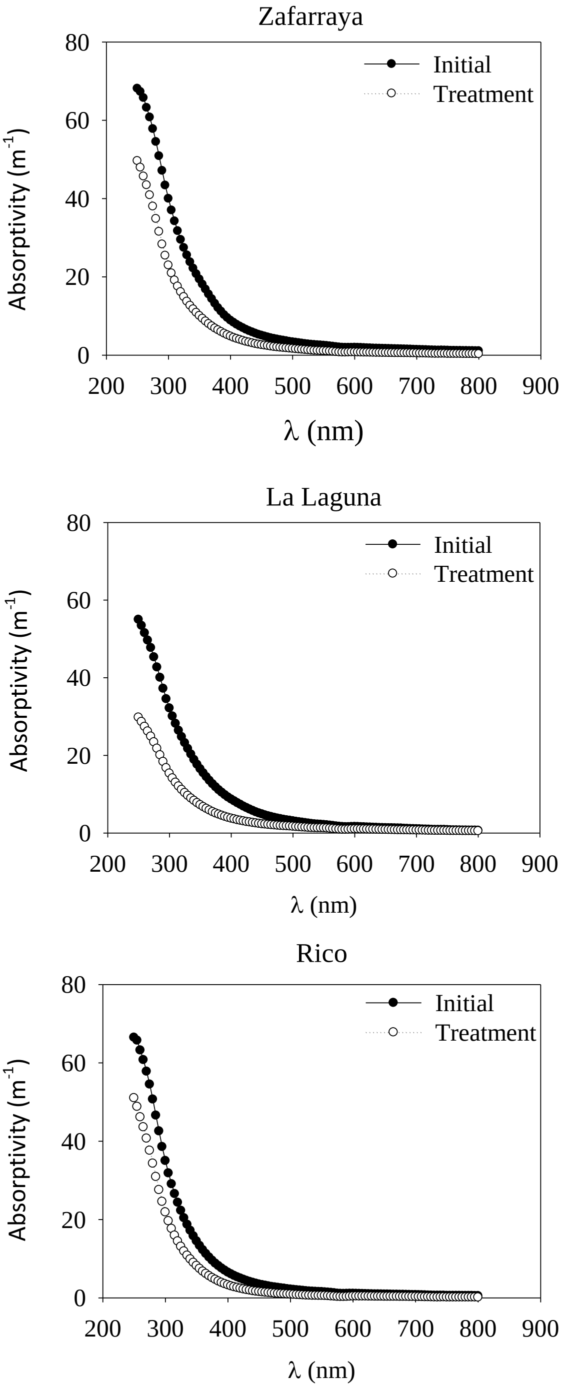


Figure 2. Absorptivities from 250 to 800 nm of lake waters before adding Fe particles (initial) and after the addition of Fe particles and once passed through the HGMS device (treatment. Fe/P ratio 1.61 g mg^{-1}) in some selected lakes.

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 µS cm^{-1}). However. a drastic reduction in P removal was observed for extremely high mineralized waters. Correlation analysis has shown that major cations (Mg^{2+}. Na^+ and K^+) and anions (SO_4^{-2} and Cl^-) were the driving factors controlling the effectiveness of P removal. By contrast. no significant effect of pH. NO_3^-. NH_4^+. Si and TA was observed. Additionally. interesting results related to the effect of Ca^{2+} on P removal efficiencies were observed. Hence. 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 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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Chapter VIII. *Single-ion interferences when using magnetic microparticles for phosphorus removal in aquatic ecosystems* (Paper IV)

Single-ion interferences when using magnetic microparticles for phosphorus removal in aquatic ecosystems
(Paper IV)

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Abstract

The specific adsorption of phosphate (P) on strongly magnetizable carbonyl iron (Fe) particles and their subsequent removal using in-flow High Gradient Magnetic Separation (HGMS) techniques is actually being considered as a promising tool for restoring eutrophied waters. A previous study has evidenced the existence of chemical interferences in natural waters reducing P removal efficiency but that study could not fully account for the direct effect of each single-ion on P removal efficiency (de Vicente et al. 2011). On this basis. in this manuscript we assess the single-effect of some of the major ions present in natural waters such as sulphate (SO_4^{2-}) and calcium (Ca^{2+}) as well as humic acid (HA) and reactive silicate (Si) on P adsorption to magnetic Fe particles in artificial lake waters. The results show that HA (used as an indicator of DOC) 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 up to 35.5 mg HA L^{-1} and 10 mg Si L^{-1}. respectively. By contrast. SO_4^{2-} and Ca^{2+} did not significantly reduce P removal by adsorption on magnetic Fe particles. To conclude. before using magnetic particles for restoring eutrophied aquatic ecosystems. in a whole-lake addition experiment. it is essential to make a throughout chemical analysis of the lake water in order to dose the right Fe concentration for getting the highest P removal efficiency.

Keywords: Phosphate removal. magnetic particles. High Gradient Magnetic Separation. chemical interferences

1. Introduction

Eutrophication is one of the most important and long lasting water quality problems in the European Union. Since at least two decades. several policies have been adopted to tackle nutrient pollution and its consequences. Water Framework Directive (WFD. 2000/60/EC) establishes an integrated and co-ordinated framework for the sustainable management of water. including prevention of deterioration of water bodies (lakes. rivers. coastal and transitional. groundwater). promotion of sustainable water use. and ensuring "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 'good status' by 2015.

Eutrophication is basically caused by an excessive inorganic nutrient loading (e.g. Hupfer and Hilt. 2008). In particular. phosphorus (P) has been identified as the main nutrient responsible for eutrophication (Hupfer and Hilt. 2008; Jeppesen et al.. 2009; Smith. 2009). Concurrently. the demand for good quality freshwaters 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 resources managers (Jeppesen et al.. 2009). Hence. new adsorbents have been developed in the recent years for the treatment of polluted water (Hsu et al.. 2008; Panther et al.. 2011; Zhang et al.. 2011). One of these adsorbents that is being increasingly used for trapping P in lake sediments is aluminum hydroxide ($Al(OH)_3$) (e.g.. Smeltzer et al. 1999; Welch and Cooke 1999; Reitzel et al. 2005. Egemose et al.. 2011). It adsorbs and precipitates both phosphate (PO_3^{4-}) and dissolved organic P-compounds (Reitzel et al. 2009) but it is well known that the resulting Al phases and floc quality are pH dependent (e.g.. Kennedy and Cooke. 1982). Phoslock is another promising P adsorbent (Robb et al.. 2003; Reitzel et al.. 2013a. 2013b). It is made from a modified bentonite clay containing an active rare earth ingredient Lanthanum (La) within its chemical structure. It is precisely at the La sites where dissolved P becomes adsorbed. Phoslock is most effective at pH values between 5 and 7. and the adsorption capacity decreases above pH 9 (Ross et al. 2008). Also recently. natural and modified zeolites. consisting of a three-dimensional framework structure bearing SiO_4 and AlO_4 tetrahedra. are being used for P removal from aqueous solution (i.e. Karapinar. 2009; Gibbs and Özkundakci. 2011). They are demonstrated to be highly effective P-inactivation agents in both aerobic and anaerobic conditions.

Despite of all these novel effective adsorbents. an alternative technology based on the use of magnetic particles could be considered in 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 have been already suggested: (i) the recovery of magnetic particles from the solution. reducing both the effects in the aquatic biota and (ii) the reusability of the particles. thus reducing economic costs. In this context. the high P adsorption capacity of micronsized carbonyl iron particles under batch conditions was tested and the most favorable 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 handling large volumes of water because of decreasing retention times. In brief. this method is based on the use of highly magnetizable 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 color. turbidity and metals for water clarification (Chang et al.. 2004; Dixon. 1984; Girginova et al.. 2010). chemical interferences in P removal by magnetic seeding in natural waters were studied by de Vicente et al. (2011). In particular. these authors reported an extensive investigation on the 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 µS cm^{-1}). while a drastic reduction in P removal was observed for extremely high mineralized waters. Although correlation analysis showed that major cations (Mg^{2+}. Na^+ and K^+) and anions (SO_4^{2-} and Cl^-) were the driving factors controlling the effectiveness of P removal. from these experiments authors could not conclude whether anions or cations by themselves were 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 was just an indirect consequence of the positive relationship between cation and anion concentrations. As a result. further experimental research focused on artificial lake waters using specific anions are currently 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 increasing 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 in-flow HGMS technique. In order to quantify single-ion interferences when adding magnetic particles it is an essential preliminary task to determine the appropriate Fe dose to achieve the highest P removal efficiency.

2. Materials and Methods

2.1. Preparation of magnetic particles. phosphate and specific-ion solutions

Carbonyl iron powder. supplied by BASF (Germany). was used for Fe suspensions preparation by dispersing 5 g Fe particles in 100 mL distilled H_2O. A detailed physicochemical description and the elemental composition of these particles can be found in de Vicente et al. (2010).

A stock 1 mM P solution was prepared by adding 136 mg KH_2PO_4 (Panreac. Spain) to 1 L of distilled water.

Humic acid (HA). from Sigma-Aldrich. was used as an indicator of lake dissolved organic carbon (DOC). The content of carboxylic groups of this particular humic acid is around 3.1 mmol g^{-1} (de Vicente et al.. 2008). HA stock solution was prepared according to the procedure recommended by de Vicente et al. (2008) in which 1.4 g humic acid was added to 1 L 3 mM $NaHCO_3$ solution. Then the pH of the resulting solution was adjusted to pH = 8.3. Next. the stock solution was stirred for 12 hours and filtered through fiber 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 Schimadzu TOC-V CSH. The DOC concentration in the HA stock solution was 35.5 mg L^{-1}.

A stock sulphate solution was prepared by adding 18.14 g K_2SO_4 (Panreac. Spain) to 1 L distilled water. Final SO_4^{2-} concentration was 10000 mg L^{-1}. Silicate and calcium commercially available standard solutions (Merck. Spain) with concentrations of 1000 mg L^{-1} were used.

2.2. Laboratory experiments

A set of laboratory single-ion experiments was conducted to study the interference of specific ions on PO_4^{3-} adsorption by carbonyl Fe particles. Each test consisted in adding 2 mL of the stock Fe solution (50 g L^{-1}) and 2 mL of P solution (1 mM). 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 1M or NaOH 1M and left under shaking overnight. After 24h the pH was again re-adjusted to pH = 7. and suspensions were finally transferred to 100 mL volumetric flasks. making the total volume to be 3 mM $NaHCO_3$. Fe/P concentrations ratios used in all treatments were those identified by Merino-Martos et al. (2011) as necessary for getting the highest P removal efficiency.

Testing the interference with humic acid: For testing the effect of HA on P removal efficiency. two suspensions containing Fe. P and two different concentrations of HA (17 and 35.5 mg C L^{-1}) were prepared. These suspensions were obtained by adding 2 mL of the stock Fe solution (50 g L^{-1}) and 2 mL of P solution (1 mM) to 100 mL of the HA stock solution. getting a final HA concentration of 35.5 mg C L^{-1}. and to 50 mL of the HA stock solution and adding

$NaHCO_3$ up to 100 mL. in this case final HA concentration was 17 mg C L^{-1}. Then. suspensions were passed through the HGMS as it was described below. and PO_4^{3-} 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_4^{2-} solution were added to different magnetic suspensions (containing 2 mL of the 50 g Fe L^{-1} and 2 mL of 1 mM P solution in 100 mL $NaHCO_3$ for giving final SO_4^{2-} concentrations of 100. 250. 500. 1000 and 5000 mg L^{-1}. respectively. Suspensions were treated as described below and filtered samples were analyzed for PO_4^{3-} and SO_4^{2-}.

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 prepared as described earlier. The final silicate concentrations were 5. 10. 25 and 50 mg L^{-1}. respectively. Suspensions were treated as described below and filtered samples were analyzed for PO_4^{3-} and dissolved reactive silicate (Si).

Testing the interference with calcium: Different aliquots (1. 5. 10 and 50 mL) of the stock Ca^{2+} solution were added to each magnetic suspension prepared as stated above. The final Ca^{2+} concentrations were 10. 50. 100 and 500 mg L^{-1}. respectively. Each sample was subjected to HGMS treatment described below and filtered samples were analyzed for PO_4^{3-} and Ca^{2+}.

The experimental set-up was similar for all 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 axial HGMS filter design and the standard protocol can be found in Merino-Martos et al. (2011). In brief. Fe + P + ion suspensions were first sonicated for 5 min and then passed through the axial HGMS filter. The magnetic field strength in the filter was fixed at 450 kA m^{-1}. The experiments were performed under optimal conditions. The treated samples coming from the HGMS device were filtered through a fiber filter (Whatman GFF) and P. Si. SO_4^{2-} and Ca^{2+} concentrations were determined in the filtered samples. In particular. equilibrium P concentrations were determined using the spectrophotometric method described by Murphy and Riley (1962). Dissolved reactive silicate (Si) was determined by using a spectrophotometric method described by Koroleff (1983). The determination of calcium (Ca^{2+}) and sulphates (SO_4^{2-}) 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 ºC until analysis. DOC was analyzed by high-temperature catalytic oxidation on a Shimadzu TOC-V CSH.

Finally. to examine the effect of HA. SO_4^{2-}. Si and Ca^{2+} on carbonyl Fe particles. the similar adsorption experiment described above was conducted without adding PO_4^{3-}.

2.3. Statistical analysis

All experiments reported in this study were carried out in triplicates. Comparison of mean values was done using Student's t-test and. unless otherwise stated. $p < 0.05$ is considered statistically significant. Statistical analyses were performed using Statistica 6.0 Software.

3. Results and discussion

3.1. 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 analyzed changes in P removal efficiency in the presence of different HA concentrations (17 and 35.5 mg L^{-1}). 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^{-1}). In fact. P removal efficiency decreased from 94 % to 12 % when HA concentrations increased from 17 to 35.5 mg L^{-1} (Table 1).

Table 1. Effect of HA on P removal efficiency. including standard deviations (SD). The values reported are the average of three replicates.

HA(mg C L^{-1})	P removal (%)	SD
0	97.0	1.3
17	94	9
35.5	12	7

From these results. we conclude that the organic molecules of HA are 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 ligand exchange reaction on the oxide surface that is consistent with the specific adsorption mechanism in P adsorption on Fe particles. Consequently. there is a 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 the ability of HA to bind metals under the entire pH range (Zhang et al.. 2009a). Cornell and 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 dominated by electrostatic effects. However. ligand exchange and hydrophobic bonding may also be involved at pH´s above the pzc. More recently. Illés and Tombácz (2004. 2006) investigated the pH-dependent adsorption of HA on magnetite and revealed that the adsorption capacity was severely influenced by the pH as well as the 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 to previous literature.

Similar findings have been observed for other oxides and hydroxydes. Sibanda and Young (1986) observed that organic matter in solution strongly decreased P adsorption by aluminum 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 $Al(OH)_3$ by the presence of HA. More recently. Zhang et al. (2009b) indicated the reduction in 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 negative charge to nanoparticle surfaces and increase their surface electrostatic potentials.

However. there are also publications demonstrating a negligible interaction between HA and P adsorption. For example. Borggaard et al. (1990. 2005) studied the effects of HA and fulvic acids on P adsorption by aluminum and iron oxides in soil samples and they found that organic matter did not compete with P for adsorption site of oxides. This observation is similar to that previously described by Gerke and Hermann (1992) that reported P bounding onto humic-Fe complexes via ligand exchange by substitution of H_2O and OH^-. This reaction was found to be dependent upon pH. as well as the presence of Ca^{2+} ions. Ca^{2+} adsorbed on negative charged groups reduces electrostatic repulsion of the P anions and. therefore. P adsorption is increased at pH above 5.2.

3.2. Effect of sulphate ions on P adsorption by carbonyl Fe particles

Using a combination of solutions ($Fe+P+SO_4^{2-}$ and $Fe+SO_4^{2-}$) we observed that there was not a significant ($p > 0.05$) effect of SO_4^{2-} anions on P adsorption by magnetic Fe particles (Table 2). In fact. an increase in SO_4^{2-} concentrations from 100 to 5000 mg L^{-1} caused a slight but not significant reduction in P removal efficiency (from 100 to 92 %). These results are 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_4^{2-} causes only a small reduction in P adsorption per surface area unit of goethite. Zhang et al. (2009a) found that the presence of

SO_4^{2-} had no significant effect on P removal by a Fe-Mn binary oxide adsorbent. Notable differences exist. however. between our experimental design and that proposed by Zhang et al. (2009a). Among others. in the present study we have used P initial concentrations much lower (0.62 mg L^{-1} instead of 5 mg L^{-1}) and SO_4^{2-} concentrations much higher (from 100 to 5000 mg L^{-1} instead of from 96 to 960 mg L^{-1}) than Zhang et al. (2009a). This means that even in our scenario. with low P and high SO_4^{2-} concentrations. which is likely to be more amenable for the existence of chemical interferences. no significant interactions occurred.

Table 2. Results of P removal and SO_4^{2-} removal. by magnetic Fe particles. at different initial concentrations of SO_4^{2-}. in the presence and in the absence of P. The values reported are the averages of three replicates.

	P+Fe+SO_4^{2-}				**Fe+SO_4^{2-}**	
SO_4^{2-} (mg/L)	**PO_4^{3-}removal (%)**	**PO_4^{3} removal (mgP/gFe)**	**SO_4^{2-} removal (%)**	**SO_4^{2-} removal (mgSO_4^{2-}/gFe)**	**SO_4^{2-} removal (%)**	**SO_4^{2-} removal (mgSO_4^{2-}/gFe)**
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

Our results also evidenced that adsorption of SO_4^{2-} by magnetic Fe particles is strongly controlled by the presence or absence of P in solution (Table 2). Hence. for the case of the highest SO_4^{2-} concentration. a notable (three-fold) significant increase in SO_4^{2-} removal (in mg SO_4^{2-} g^{-1} Fe) was measured when no P was present in solution compared to when P was dissolved in the bulk. Our results are consistent with those reported by Geelhoed et al. (1997) who observed that P experienced a higher affinity for adsorption sites on goethite than SO_4^{2-} over a wide range of pH (2.5. 4.0. 5.5. 7.0 and 8.5) and. therefore. it is a stronger competitor. It is important to note that adsorption of SO_4^{2-} by Fe oxides may be nonspecific involving ion pair formation. dominated by the electrostatic interaction (Cornell and Schwertmann. 1996). In fact. there exists a strong dependence of SO_4^{2-} adsorption on pH being maximum at low pH and decreasing when pH rises. up to negligible adsorption above the pzc (Cornell and Schwertmann. 1996). In this sense. it is important to emphasize that all 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 around 6.5. so it is expected that at pH 7 there exists a minor adsorption of SO_4^{2-} ions by Fe particles. Also in agreement with our results. Boukhalfa (2010) found that SO_4^{2-} removal from aqueous solutions by hydrous Fe oxide was extremely 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_4^{2-} 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_4^{2-} was observed for 10 mM concentration as a result of the strong interaction of P with the surface of the hydroxide relatively to SO_4^{2-}. All in all. these results are explained by the fact that both ions compete for the same sorption sites as suggested above.

3.3. Effect of silicate on P adsorption by carbonyl Fe particles

Single-ion experiments using Fe+P+Si and Fe+Si suspensions were carried out to test the effectiveness of P adsorption by magnetic Fe particles in the presence of Si. Our results evidenced that there exists a significant reduction in P adsorption by Fe particles when Si concentration increases (Table 3). In fact. P removal efficiency was reduced from 81 % to 35 % when Si concentration increased from 5 to 50 mg L^{-1}. These findings are coherent with previous studies which pointed out that Si and P have the same specific adsorption behavior and so. competition for adsorption sites should occur (Sigg and Stumm. 1981; Cornell and Schwertmann. 1996; Hartikainen et al.. 1996). A similar behavior was observed by de Vicente et al. (2008) when using $Al(OH)_3$ as P adsorbents. These authors concluded that Si (at similar concentrations used in the present study) significantly decreased the effectiveness of P adsorption by $Al(OH)_3$ 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 are also coherent with those obtained by Hartikainen et al. (1996) who analyzed sediment samples from Lake Vesijärvi (southern Finland). These authors observed that P oxyanions compete directly with Si compounds for sorption sites but their results indicate that Si retention on the oxide surface is relatively less effective than that of P. They justified it as a result of the high pK_a value of silicic acid (9.7). which implies that Si sorption is at maximum at 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 and Stumm (1981) reported the dependence of pK values on the surface charge of α-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 behavior than P. when Si concentration was higher than 1 mg L^{-1} and the pH was greater than 5. For example. they found that. in the presence of 10 mg L^{-1} Si and at a pH of approximately 6.8. the adsorption capacity of ferric hydroxide for Arsenite was reduced from 116 µg mg^{-1} to 23 µg mg^{-1} Fe.

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 three replicates.

	P+Fe+Si				Fe+Si	
Si (mg/L)	PO_4^{3-} removal (%)	PO_4^{3-} removal (mgP/gFe)	Si removal (%)	Si removal (mgSi/gFe)	Si removal (%)	Si removal (mgSi/gFe)
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

To get a better understanding of the effect of Si concentration on P removal efficiency. we have performed a linear regression fitting to the experimental data in the range 5-25 mg L^{-1}. As a result. an increase in Si concentration from 5 to 25 mg L^{-1} would cause a reduction in P removal from 61 % to 17 % and therefore. an increase in Fe dose would be needed for sequestering P. So. these results are essential to be considered when dosing Fe to be added in whole-lake restoration projects.

For completeness. we also investigated the adsorption behavior of Si by magnetic Fe particles in the presence and in the absence of P (Table 3). We have found that Si removal (in mg Si g^{-1} Fe) 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 confirmed. again. 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 getting values for r^2 higher than 0.8. Our results have evidenced that for an initial Si concentration of 10 mg L^{-1}. Si removal decreased from 12.2 % to 8.2 % in the presence of P. However. if we compare P and Si removal. we could conclude that. despite the competition among both anions. P is clearly preferentially adsorbed than Si by Fe particles

(Table 3). As a way of illustration. for initial Si concentrations of 10 mg L^{-1}. P removal was significantly higher (22%. 6.1 mg P g^{-1} Fe) than Si removal (6.3%. 0.6 mg Si g^{-1} Fe).

All in all. at this stage it is necessary to remark that most of natural waters present Si concentrations lower than 10 mg L^{-1}. In fact. an extensive sampling performed by de Vicente et al. (2011) in 20 inland aquatic ecosystems. widely differing in their chemical composition. revealed that 19 over 20 presented Si concentrations lower than that threshold. Hence. according to Table 3. for such a low Si concentration a minor competition between P and Si is likely to occur. Only 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.

3.4. Effect of calcium ions on P adsorption by carbonyl Fe particles

To assess the role of Ca^{2+} ions in controlling the effectiveness of P removal by Fe particles. single-ion experiments were performed using Fe+P+Ca^{2+} suspensions. The results showed that Ca^{2+} did not significantly affect P removal efficiency by Fe particles denoting no competition for adsorption sites (Table 4). In fact. in a wide Ca^{2+} concentration range (10-500 mg L^{-1}). resembling Ca^{2+} concentration in inland waters typical from Southeastern Spain (i.e. de Vicente et al.. 2011). we have measured P removal efficiency always higher than 93 %.

Table 4. Results of P removal and SO_4^{2-} 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 three replicates.

	Fe+P+Ca^{2+}				**Fe+Ca^{2+}**	
Ca^{2+} (mg/L)	**PO_4^3 removal (%)**	**PO_4^{3-} removal (mgP/gFe)**	**Ca^{2+} removal (%)**	**Ca^{2+} removal (mgCa^{2+}/gFe)**	**Ca^{2+} removal (%)**	**Ca^{2+} removal (mgCa^{2+}/gFr)**
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

Stachowicz et al. (2008) studied the interaction between Ca^{2+}-PO_4^{3-} and Mg^{2+}-PO_4^{3-} on goethite. Specifically in the Ca^{2+}-PO_4^{3-}. they found that there exists P adsorption. as well as Ca^{2+} adsorption in pH range 3-11. in spite of the fact that Ca^{2+} had much lower affinity for goethite than PO_4^{3-}. This result was explained by electrostatic interactions as negative charge of the adsorbed PO_4^{3-} ions on goethite stimulates the binding of the positively charged Ca^{2+} ion. However. contrarily to these observations. we have not found any Ca^{2+} 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 and Murray. 1982; Cornell and Schwertmann. 1996; Gao and Mucci. 2003; de Vicente et al.. 2011). Nevertheless. adsorption behavior can be affected by factors such as pH. concentrations and ionic strength (Kim and Walker. 2001). It has been reported in the literature that the extent of adsorption of cations on Fe oxides depends on pH (Dixon. 1984). Indeed. there is a narrow pH range where the adsorption of cation goes from near zero adsorption to 100 % adsorption and is commonly called the adsorption edge (Balistieri and Murray. 1982). As a way of example. Gao and Mucci (2003) observed that the addition of Ca^{2+} increases P adsorption on goethite slightly at pH < 8.5 and extensively at pH > 9. Ca^{2+} cations adsorb on goethite and make the Fe oxides surface more positively charged. thus promoting P adsorption. Again. we have to point out that all experiments were run at pH = 7 so a secondary effect of Ca^{2+} on P removal was occurring in our experiments.

Next. we aim on studying Ca^{2+} adsorption by the Fe particles both in the presence and in the absence of P (Table 4). Although we have not found a clear tendency as a function of Ca^{2+} concentrations. Ca^{2+} removal was generally higher when P was not present in solution. In particular. for the highest Ca^{2+} concentration (500 mg L^{-1}). it has been measured Ca^{2+} removal up to more than 50 mg Ca g^{-1} Fe in the absence of P while no Ca^{2+} removal was achieved in the presence of P. Gao and Mucci (2003) studied Ca^{2+} adsorption on goethite in absence of P and they found that Ca^{2+} adsorption was zero at pH=7.5 but it increased to close to 50% at pH=10. Again. it is important to note that cation adsorption not only depends on pH but also on ionic strength. As a way of illustration. Gao and Mucci (2003) compared P adsorption on goethite in a 0.7 M NaCl solutions and an artificial seawater solutions. They found that P adsorption was slightly lower in 0.7 M NaCl solution compared to artificial seawater. In relation to pH. Kanungo (1994) found that Mn^{2+} adsorption increased from 2 to 92 % in the narrow pH range of 6.75-7.40 in a 0.5 M NaCl solution.

4. Conclusions

This study has shown 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 SO_4^{2-} and Ca^{2+} did not significantly affect P removal efficiency. In particular. single-ion experiments have evidenced that P adsorption by Fe particles at high HA concentrations (35.5 mg L^{-1}) was significantly reduced. On the other hand. Si suppressed P adsorption at the highest concentrations tested (10. 25 and 50 mg L^{-1}) but showed no significant effect at the lowest concentration (5 mg L^{-1}).

Acknowledgments

This work was supported by Junta de Andalucía projects P10-RNM-6630 and P11-FQM-7074 (Proyectos de Excelencia. Spain). and MINECO MAT 2010-15101. MAT 2013-44429-R project (Spain).

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Chapter IX. *CONCLUSIONS*

Chapter IX

CONCLUSIONS

1. Under batch mode, P adsorption by magnetic Fe particles is efficient independently on the pH. However, a slight decrease in P removal efficiency was found with increasing pH. These results suggest that P is specifically adsorbed on Fe particles by interactions that basically are not electrostatic since negatively charged Fe particles still do adsorb a very significant amount of P.

2. Maximum P adsorption capacity by bare iron (18.83 mg P g^{-1} Fe) was lower than that by magnetite particles (27.15 mg P g^{-1} Fe) as a consequence of the different particle size (average values for particle diameters of 90.6 ± 1.2 and 805 ± 10 nm for magnetite and for Fe, respectively).

3. The reutilization experiments have shown a slight decrease in the empirical saturation constant for iron particles (from 18.83 to 15.80 mg g^{-1}) and for magnetite particles (from 27.15 to 23.83 mg g^{-1}), evidencing the convenience of using these particles in several adsorption processes which reduces economic costs.

4. The surfaces of iron and magnetite particles were modified by APTS-coated. Adsorption tests showed that APTS-coated iron particles experienced a notable increase in P maximum adsorption capacity from 18.83 mg g^{-1} (uncoated iron particles) to 25.06 mg g^{-1} (APTS-coated iron particles) which could be explained by a remarkable increase in electrophoretic mobility.

5. The effect of APTS-coating on P maximum adsorption capacity was less pronounced for the case of magnetite particles. where similar maximum adsorption capacities were observed in uncoated and coated particles.

6. An axial HGMS filter for removing P from P enriched waters using magnetic particles as the seeding absorbent material was designed and the best working conditions were investigated. The results showed that sonication time. magnetic field strength

distribution and the Fe particles/P concentration ratio are the main factors controlling HGMS process. In particular. the best identified operating conditions under continuous flow were:

1. Sonication time: 5 minutes
2. Distance between magnets: 1 cm or the closer we can
3. Magnetic particles/P ratio: 1.5 g mg^{-1}

7. Flow rate does not significantly affect P removal efficiency. in the range 0.08-0.36 mL s^{-1}. so very large water volumes can be efficiently treated.

8. The change of P removal efficiency with time (i.e. the effect of buildup of magnetic particles onto the wire) was investigated. This study showed that P removal efficiency remained larger than 80% up to 30 minutes operation. This suggests that the HGMS is an efficient method for recovering P from wastewater even when considering large volumes of water.

9. The particles reutilization was studied. The results suggested that when re-using particles that had already adsorbed P. P adsorption capacity of reused particles decreased 36%. Although adsorption capacity experienced a little decrease. the possibility of re-using magnetic particles continues being effective.

10. High P removal efficiencies (>80%) were found in freshwater lakes (conductivities <600 µS/cm). However. a significant reduction in P removal was observed for extremely high mineralized waters.

11. Correlation analysis has shown that major cations (Ca^{+2}. Mg^{+2}. Na^{+} and K^{+}) and anions (SO_4^{-2} and Cl^{-}) played an essential role in P removal efficiency.

12. After adding Fe particles. a notable reduction in DOC and Si concentrations. as well as a change in water color is observed.

13. The electrophoretic mobility of Fe particles decreases when increasing conductivity of lake waters.

14. The single-effect of some of ions present in natural waters on P adsorption to magnetic Fe particles in artificial lake waters was studied. The results has shown that the main drivers of P removal by adsorption on magnetic Fe particles were HA (as an indicator of DOC) and Si while other ions typically present in lake waters such as SO_4^{2-} and Ca^{2+} did not significantly affect P removal efficiency.

Chapter X. *References*

Chapter X

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