



# Synthesis and characterization of magnetic chitosan microspheres as low-density and low-biototoxicity adsorbents for lake restoration



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## HIGHLIGHTS

- Magnetic chitosan particles by reverse-phase suspension cross-linking method.
- Multicore particles homogeneously distributed within the biopolymer matrix.
- Maximum P adsorption capacity of 4.84 mg g<sup>-1</sup> at pH = 7.
- Excellent candidates to remove P mobile from the upper sediment layers.
- They present lower density and biotoxicity than carbonyl iron microparticles.

## GRAPHICAL ABSTRACT



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## ABSTRACT

We propose a novel magnetic adsorbent for optimal Phosphorus (P) removal from the upper sediment layers. For this aim, magnetic chitosan microparticles were prepared using a reverse-phase suspension cross-linking technique. The resulting particles and suspensions were characterized using scanning electron microscopy, X-ray powder diffraction, Fourier transform infrared spectroscopy, magnetometry, thermogravimetric analysis, electrophoretic mobility and turbidity measurements. The hybrids are multicore particles consisting of well dispersed magnetite nanoparticles (approx. 10% w/w) homogeneously distributed within the biopolymer matrix. These microparticles can be easily separated from the water column and sediment using magnetic field gradients. Their P adsorption capacity is evaluated in batch conditions resulting in a maximum P adsorption capacity of  $M_L = 4.84 \text{ mg g}^{-1}$  at pH = 7. We demonstrate that these particles are excellent candidates to remove P from water column and also P mobile from the upper sediment layers due to two main reasons: they sediment slower and present lower potential toxicity (due to a their larger size) than conventional iron/iron oxide microparticles previously proposed for lake restoration.

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## 1. Introduction

Enrichment of phosphorus (P) is considered the main cause of eutrophication of inland waters (Carpenter, 2005). In situations in which P release from sediment (internal P load) impedes lake

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recovery once external P load has been reduced, in-lake addition of P-binding adsorbents appears as an advisable alternative for lake management (Cooke et al., 2005; Søndergaard et al., 2003). Z2G1 or Aqual-P<sup>®</sup>, Phoslock<sup>®</sup>, calcium, iron (Fe) or alum salts have been demonstrated to increase sediment P-sorption capacity (Cooke et al., 2005; Dittrich et al., 2011; Gibbs et al., 2011; Robb et al., 2003; Søndergaard et al., 2003). Although some of these techniques could represent a long-lasting sink for P, changes in physicochemical conditions or resuspension events can lead to undesirable P release to water column along with toxic substances stemming from the adsorbents composition (Egemose et al., 2009; Zamparas and Zacharias, 2014).

In the last decades, magnetic nano- and microparticles have attracted special attention to adsorb contaminants from waters and soils due to their easy separation and recovery from the medium for further reuse. This obviously leads to cost savings and to the reduction of the contact time with biota (Crane and Scott, 2012; Gómez-Pastora et al., 2014; Huber, 2005; Lu et al., 2007; Tang and Lo, 2013). With this in mind, more recently, these magnetic particles have been successfully used for P removal in the context of lake restoration and improvement of water quality (Choi et al., 2016; Daou et al., 2007; de Bashan and Bashan, 2004; de Vicente et al., 2010; Funes et al., 2016, 2014; Lai et al., 2016; Long et al., 2011; Shaikh and Dixit, 1992).

Apart from high P adsorption capacity and reusability, magnetic particles must meet other stringent requirements for lake restoration applications. Particle size has very important implications not only in adsorption capacity but also in biological toxicity. Small (nano) particles are preferred to enhance adsorption capacity (because of their large surface area) (Yavuz et al., 2006). However, there are evidences of toxicological effects on aquatic organisms (Oberdörster, 2004); because cladocerans such as *Daphnia* sp. filter large volumes of water, considerable amounts of nanoparticles can be ingested by them, having negative consequences in their physiology and also in upper levels of the food chain (Lovern and Klaper, 2006; Zhu et al., 2010). Unfortunately, nanoparticles can also negatively affect aquatic biota by adsorption on their carapaces and filtrations apparatus (Baumann et al., 2014). Finally, Fe dissolution is another indirect effect of using Fe based nanoparticles which can lead to phytotoxicity (Keller et al., 2012).

Of outstanding importance in this work is particle density. Actually, particle density is a key factor driving adsorbent distribution through the sediment profile and determines its availability for P adsorption. It is worth to stress here that sedimentary P mobile, which is the target P pool, mostly concentrates within the first 10 cm of sediment and decreases rapidly with depth (Reitzel et al., 2005). From this perspective, very large density particles are not desirable because they sink deeper in sediment being not available for P adsorption. Moreover, sinking of magnetic particles into deeper layers may contribute to intense sediment resuspension when removing the magnetic particles with the magnet causing undesirable effects (Søndergaard et al., 1992). In addition, large density particles may sink into the deepest sediment layers where magnetophoretic forces exerted by the magnets could not be large enough to overcome opposing surface (cohesive) forces within the sediment making the recovery process inefficient (Yavuz et al., 2006). Thus, a balance between high P removal efficiency (high affinity and large surface area), low bio-toxicity (biocompatible components and large particle size to difficult the ingestion by biota) and low density (to remain in the first 10 cm of sediment) must be pursued (Philippova et al., 2011; Reddy and Lee, 2013).

In this work, we fabricate hybrid magnetic particles (magnetic chitosan microspheres, MCMs) that accomplish the three requirements discussed in paragraph above. We follow a novel approach that consists in the encapsulation of magnetic multicores

within a biopolymer spherical matrix that prevents Fe dissolution, is non-toxic and less dense (than traditional magnetic adsorbents), but still exhibiting a large adsorption capacity for lake restoration applications. Furthermore, by using a chitosan matrix we introduce versatile adsorption properties (apart from the traditional specific adsorption mechanism between P and Fe oxides) that can be controlled through the cross-linker concentration due to the presence of amine and hydroxyl groups and therefore pH dependent electrostatic interactions.

## 2. Materials and methods

All reagents were of analytical grade and used without further purification. FeCl<sub>3</sub>·6H<sub>2</sub>O, ethylene glycol (EG) and sodium acetate (NaAc) were supplied from VWR (AnalaRNormapur). Trisodium citrate (Na<sub>3</sub>Cit) was obtained from Carlo Erba. Chitosan (low molecular weight; 75–80% deacetylated), glutaraldehyde (8%), mineral oil, Span 80 and petroleum ether were acquired from Sigma Aldrich. Acetic acid (5%) and acetone were obtained from Panreac. Finally, carbonyl Fe microparticles were obtained from BASF (grade HQ, average diameter = 800 nm, Germany).

### 2.1. Synthesis of magnetite (Fe<sub>3</sub>O<sub>4</sub>) nanoparticles

There are several routes for the synthesis of Fe<sub>3</sub>O<sub>4</sub> depending on the particle size to be obtained. For instance, Fe<sub>3</sub>O<sub>4</sub> nanoparticles of typical sizes in the range ~10 nm can be prepared by the Massart's method (Massart, 1981). In this case, Fe<sup>+2</sup> and Fe<sup>+3</sup> are coprecipitated in an alkaline solution. Another option to obtain Fe<sub>3</sub>O<sub>4</sub> particles in the micronized range, ~1000 nm, is to follow Sugimoto and Matijević (1980). In this case, Fe<sup>+2</sup> oxidation is slowed down by a nitrate salt allowing the particles to grow larger. In this particular work, we are interested in particles having an intermediate particle size (~100 nm): large enough to respond to magnetophoretic forces and small enough for a large surface activity and hence adsorption capacity.

We used a solvothermal method following the recommendations by Liu et al. (2009a) with slight modifications. Briefly, 3.38 g of FeCl<sub>3</sub>·6H<sub>2</sub>O (0.25 mol L<sup>-1</sup>) and 0.5 g of Na<sub>3</sub>Cit (34 mmol L<sup>-1</sup>) were dissolved in 50 mL of ethylene glycol by using a centrifugal mixer (3 min at 1000 rpm). NaAc (3 g) was then added and the suspension was mixed again (15 min at 1000 rpm). Next, the mixture was sealed in a Teflon-lined stainless-steel autoclave (125 mL capacity) and heated at 215 °C for 10 h. The obtained magnetic nanoparticles were washed several times with ethanol and dried at 50 °C for 4 h.

### 2.2. Preparation of magnetic chitosan microspheres (MCMs)

MCMs were fabricated by a reverse-phase suspension cross-linking technique following Jiang et al. (2005) with slight modifications. First, previously synthesized Fe<sub>3</sub>O<sub>4</sub> powder (0.082 g) was dispersed via ultrasonication in a solution of chitosan (0.25 g) in 5% acetic acid (10 mL) for 10 min. The Fe<sub>3</sub>O<sub>4</sub>:chitosan ratio (by weight) was 1:3. Next, 10 mL of this suspension were added drop-wise to a mixture of mineral oil (37.5 mL) and Span 80 (2.5 g) as a surfactant. During all the process, the formed emulsion was stirred with a mechanical stirrer at 2500 rpm for 30 min. Then, 5 mL of glutaraldehyde were added dropwise and the dispersion was stirred for another 1 h at 40 °C to promote the cross-linking. Finally, the magnetic microspheres were separated from the oil phase by applying a magnet for 30 min and washed several times with petroleum ether and acetone. MCMs were then dried at 50 °C for 4 h and stored until use. Chitosan microspheres (CMs) were prepared following the same procedure as MCMs without addition of Fe<sub>3</sub>O<sub>4</sub>. CMs were separated from oil phase by centrifugation at 3000 rpm

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