



Effective removal of phosphate from aqueous solution using humic acid coated magnetite nanoparticles



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ABSTRACT

Effective removal of excess phosphate from water is critical to counteract eutrophication and restore water quality. In this study, low cost, environmentally friendly humic acid coated magnetite nanoparticles (HA-MNP) were synthesized and applied for the remediation of phosphate from aqueous media. The HA-MNPs, characterized by FTIR, TEM and HAADF-STEM showed the extensive coating of humic acid on the magnetite surface. The magnetic nanoparticles with diameters of 7–12 nm could be easily separated from the reaction mixture by using a simple hand held magnet. Adsorption studies demonstrate the fast and effective separation of phosphate with maximum adsorption capacity of 28.9 mg/g at pH 6.6. The adsorption behavior follows the Freundlich isotherm suggesting the formation of non-uniform multilayers of phosphate on the heterogeneous surface of HA-MNP. The adsorption kinetic fits the pseudo-second order model well with rate constants of 0.206 ± 0.003 , 0.073 ± 0.002 and $0.061 \pm 0.003 \text{ g mg}^{-1}\text{min}^{-1}$ for phosphate (P) concentrations of 2, 5 and 10 mg/L respectively. The removal of phosphate was found higher at acidic and neutral pH compared to basic conditions. The nanoparticles exhibit good selectivity and adsorption efficiency for phosphate in presence of co-existing ions such as Cl^- , SO_4^{2-} and NO_3^- with some inhibition effect by CO_3^{2-} . The effect of temperature on the adsorption reveals that the process is endothermic and spontaneous. HA-MNPs are promising, simple, environmentally friendly materials for the removal of phosphate from aqueous media.

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1. Introduction

Phosphate is a primary nutrient required for the normal functioning of many organisms in the ecosystem (Zeng et al., 2004). However, presence of excess phosphate into the aquatic systems leads to eutrophication which can promote harmful algal growth and decrease the amount of dissolved oxygen in water (Chouyyok et al., 2010; Pan et al., 2014; Yan et al., 2010). Recent study shows the significant rise of lakes and streams containing higher amounts of total phosphorous (TP) which exacerbate the concern about the deterioration of water quality and overall ecological balance (Stoddard et al., 2016). Municipal and industrial wastewaters are the major point sources for phosphate discharges while agricultural run-off is considered the dominant non-point source (Almeelbi and Bezbaruah, 2012; Karageorgiou et al., 2007). The commonly used methods to remove phosphates from water include biological

treatment (Oehmen et al., 2007), chemical precipitation (De-Bashan and Bashan, 2004), reverse osmosis (Kumar et al., 2007), adsorption (Almeelbi and Bezbaruah, 2012; Liu et al., 2008a; Seida and Nakano, 2002) etc. Among these, adsorption is the most widely accepted method for phosphate removal because of its high efficiency, minimum cost, easy and simple operation and applicability at lower concentrations (Zhang et al., 2009). In this study, we have used adsorption to remove phosphate from the aqueous solutions using humic acid coated magnetic iron oxide (magnetite) nanoparticles as adsorbent.

In recent years, iron based nanoparticles have been widely applied for environmental remediation. The strong magnetic properties of such nanoparticles enables separation of adsorbent and adsorbate by using a simple magnet (Qu et al., 2013; Xu et al., 2012). Magnetite, an iron (Fe_3O_4) material shows the highest magnetism among all the naturally available minerals (Harrison et al., 2002). Application of bare magnetite nanoparticles (MNP) for the removal of toxic water contaminants have been reported in the literature (Mayo et al., 2007). However, the susceptibility to auto-oxidation, tendency to agglomerate and concerns over

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toxicity are the main challenges for the real life water treatment applications of bare MNP (Huang et al., 2016; Liu et al., 2008b; Maity and Agrawal, 2007). The coating of natural organic matter (NOM) on the bare MNP surface has been found useful in making the nanoparticles less toxic and more environmental friendly. Such thin coatings can also inhibit the agglomeration and auto-oxidation, the primary drawbacks associated with the use of bare MNP. Furthermore, the coating with NOM can potentially increase the adsorption capacity and selectivity of the nanoparticles.

Humic acid (HA), a ubiquitous natural organic matter (NOM), is derived from plants and microbial residues. HA possesses a number of organic functional groups including carboxylic acids, carbonyl groups and phenolic hydroxyl groups which can promote its complexation with a variety of metal oxides (Hankins et al., 2006). HA has a high affinity for magnetite (Fe_3O_4) and effectively coats bare MNP most likely through the surface complexation ligand exchange reactions (Gu et al., 1994; Illés and Tombácz, 2003). Limited studies have been reported on the removal of water contaminants using HA-MNP with primary focus on the removal of metal cations (Liu et al., 2008b; Yang et al., 2012). However, our research group recently demonstrated the potential use of HA-MNP to successfully remove metal oxyanions (chromate) from the aqueous media (Jiang et al., 2014). Herein, we report the application of the nanoparticles (HA-MNP) for the efficient removal of anionic phosphate from water. The natural protective coating of humic acid plays a crucial role in the phosphate-HA-MNP complexation while preserving the magnetic property of magnetite imperative for the final separation step in the treatment process.

2. Experimental section

2.1. Materials

Di-potassium hydrogen phosphate (>99.9%), ammonium hydroxide (29.15%), sulfuric acid (>95.6%), ferric chloride hexahydrate (98.8%), sodium carbonate (100.4%) and sodium bicarbonate (99.7%) were purchased from Fisher. Humic acid sodium salt and ferrous chloride tetrahydrate ($\geq 99.0\%$) were obtained from Sigma. In all cases, Millipore filtered water (18 M Ω .cm) was used to prepare the solutions.

2.2. Synthesis of humic acid coated magnetite nanoparticles (HA-MNP)

An established method (Jiang et al., 2014) was followed to prepare the humic acid coated magnetite nanoparticles (HA-MNP). Briefly, 3.0 g of ferrous chloride tetrahydrate ($\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$) and 6.0 g of ferric chloride hexahydrate ($\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$) were dissolved in 100 mL of water in a three-neck round bottom flask connected with a reflux condenser. The mixture was then heated with magnetic stirring until the temperature reached to 90 °C. At this temperature, 10 mL of 25% ammonium hydroxide and 50 mL of 1% humic acid sodium salt were added simultaneously into the reaction mixture and kept at 90 ± 5 °C for additional 30 min. The solution was then allowed to cool, washed with water several times to separate the nanoparticles from the free iron and humic acid. Finally, the dried (in a vacuum oven at 40 °C), ground magnetic nanoparticles [Fig. S1(a)] were stored in a desiccator.

2.3. Material characterization

Fourier transform infrared spectroscopy (FTIR) was performed at room temperature using PerkinElmer FTIR 100. Spectral scans of the synthesized nanoparticles were obtained from 550–4000 cm^{-1} (64 scans per spectrum). Transmission electron microscopy (TEM)

and high angular annual dark field (HAADF-STEM) images were collected to determine the surface morphology and microstructure of the HA-MNP. The samples were sonicated for 30 min prior to dipping onto a silicone monoxide substrate grids, dried at room temperature and then analyzed using a FEI TITAN G2 80–300 instrument operated at 300 kV. The leaching of HA was determined by measuring total organic carbon (TOC) in solutions at different pH after the separations of the synthesized. Shimadzu TOC-VCSH analyzer was used for TOC analysis.

2.4. Adsorption experiments

Stock solution of phosphate (P) with concentration of 1000 mg of P/L (ppm) was prepared from di-potassium hydrogen phosphate (K_2HPO_4). A series of standard and working solutions with concentrations ranging from 0.05 to 100 mg/L were prepared by dilution of the stock solution. The adsorption studies were carried out in capped plastic bottles with 50 mL of phosphate solution as adsorbate and 0.05 g of HA-MNP (1.0 g/L) as adsorbent. To ensure efficient mixing and proper mass transfer, the samples were placed in the orbit shaker (Lab-line instrument Inc., model 3520) and shaken at 250 rpm for a specific time period. All the experiments were conducted at room temperature (298 K) with a pH 6.6 ± 0.1 except the studies investigating the temperature and pH effects. For the pH experiments, 0.1 M NaOH and 0.1 M HCl were used to adjust the initial solution pH, confirmed in the pH meter (Mettler Toledo, model: SevenEasy). In case of thermodynamic study, sample solutions were placed in the thermostated waterbath (Lauda-Brinkman, model: RM20) to maintain the desired temperature. In all instances, the sample solutions were separated from the adsorbent nanoparticles using a simple handheld magnet [Fig. S1(b)]. To determine the residual concentration of phosphate, the magnetically separated solutions were filtered further using 0.45 μm syringe filter (to insure removal of any trace amount of suspended particles from the solution) and the filtrates were analyzed in the ion chromatography (761 Metrohm compact IC) equipped with a compact auto sampler (model: 813). The equilibrium of phosphate adsorption was calculated by using the following equation,

$$Q_e = \frac{(C_o - C_e)}{m} V \quad (1)$$

Where Q_e is the amount of phosphate adsorbed (mg/g) at equilibrium, C_o and C_e corresponds to the initial and equilibrium concentration of phosphate in solution respectively, expressed in mg/L; m is the mass (g) of the adsorbent (HA-MNP) and V is the total volume (L) of the solution. Reproducibility of the collected data were ensured by taking the average of triplicate run of the experiments with accepted standard deviation not more than 5%.

3. Results and discussions

3.1. Characterization of the synthesized nanoparticles

From FTIR spectra (Fig. S2), the band at 1598 cm^{-1} in HA-MNP corresponds to the C=O stretching of carboxylate anion of HA due to its interaction with the iron oxide surface of magnetite (Jiang et al., 2014). The same band appears at 1638 cm^{-1} in humic acid (Fig. S2) along with the band for amide C=O stretch at 1564 cm^{-1} . The appearance of another strong band in the synthesized HA-MNP at 1398 cm^{-1} can be assigned to the scissoring of $-\text{CH}_2$ group of HA. The band at 3331 cm^{-1} in HA is attributed to O–H stretching of alcohol and/or phenol which largely disappeared in HA-MNP indicating the complexation between the magnetite core and the humic acid shell. The band at 1090 and 1009 cm^{-1} in HA can be

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