



Kinetic, equilibrium and thermodynamic studies for phosphate adsorption to magnetic iron oxide nanoparticles



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HIGHLIGHTS

- Phosphate sorption to magnetic iron oxide nanoparticles had a maximum sorption capacity of 5.03 mg P g⁻¹.
- Phosphate sorption was relatively constant at an acidic solution pH.
- Phosphate sorption to magnetic nanoparticles showed endothermic nature of sorption process.
- Magnetic nanoparticles could be used as adsorbents for phosphate removal with regeneration and repeated use.

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ABSTRACT

Phosphate (P) removal by magnetic iron oxide nanoparticles was investigated using kinetic, equilibrium and thermodynamic experiments. The results demonstrate that phosphate sorption to the magnetic nanoparticles reached equilibrium at 24 h with the maximum sorption capacity of 5.03 mg P g⁻¹ under given experimental conditions (initial P concentration range = 2–20 mg P L⁻¹; adsorbent dose = 0.6 g L⁻¹; reaction time = 24 h). The phosphate removal was relatively constant at an acidic solution pH (3.0–3.1 mg P g⁻¹ at pH 2.0–6.0), whereas the phosphate removal decreased sharply as the solution pH approached a highly alkaline condition (0.33 mg P g⁻¹ at pH 11.1). Thermodynamic tests indicate that phosphate sorption to the magnetic nanoparticles increased with increasing temperature from 15 to 45 °C, indicating the spontaneous and endothermic nature of sorption process ($\Delta H^0 = 39.17 \text{ kJ mol}^{-1}$; $\Delta S^0 = 156.35 \text{ J K}^{-1} \text{ mol}^{-1}$; $\Delta G^0 = -5.88 \sim -10.57 \text{ kJ mol}^{-1}$). The results indicate that the pseudo second-order model was most suitable for describing the kinetic data. Regarding the equilibrium data, the Freundlich and Redlich–Peterson isotherms were fitted well. This study demonstrates that magnetic iron oxide nanoparticles could be used for phosphate removal from aqueous solutions with regeneration and repeated use.

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1. Introduction

The synthesis and application of magnetic nanoparticles to water and wastewater treatment have attracted considerable attention in recent years [1]. Magnetic nanoparticles can be used as adsorbents for water and wastewater treatment and separated from aqueous medium through magnetic separation [2–4], and among the various magnetic nanoparticles, maghemite ($\gamma\text{-Fe}_2\text{O}_3$) and magnetite (Fe_3O_4) are the iron oxides observed to be useful [5]. Several researchers applied magnetic iron oxide nanoparticles

to remove contaminants from aqueous solutions [1,6,7]. Pan et al. [8] removed mercury from an aqueous solution by mercapto-functionalized magnetite nanoparticles. Badruddoza et al. [9] fabricated magnetite nanoparticles functionalized with carboxymethyl- β -cyclodextrin to remove copper ions. Wang et al. [10] investigated the sorption kinetics and mechanism of copper to nanoscale magnetite. Iram et al. [11] removed neutral red dye from an aqueous solution using magnetite hollow nanospheres. Wang et al. [12] synthesized the composites of magnetite nanoparticles and gellan gum to adsorb heavy metals.

Phosphate is an essential macronutrient in aquatic environments, but in excessive amounts, it causes eutrophication of reservoirs, lakes and coastal areas [13]. Effluent concentration of phosphate from wastewater treatment facilities and industrial

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plants must be controlled through chemical and biological techniques to meet the discharge limits [14,15].

Researchers have used magnetic iron oxide nanoparticles for phosphate removal. For use as adsorbents to remove phosphate in batch and fixed-bed experiments, Zach-Maor et al. [16,17] impregnated magnetite nanoparticles (<4 nm) to granular activated carbon. They performed kinetic and equilibrium isotherm model analyses of the batch sorption data. Pan et al. [18] synthesized nano-sized magnetite particles (40.3 nm) stabilized with sodium carboxymethyl cellulose to immobilize phosphate in soils; they observed the adsorption kinetics of phosphate on the magnetite nanoparticles along with the transportability of the nanoparticles in soils. de Vicente et al. [19] used magnetite nanoparticles (90.6 ± 1.2 nm) to adsorb phosphate from aqueous solutions and examined the adsorption isotherms and the reusability of the nanoparticles. Daou et al. [20] investigated the phosphate adsorption mechanisms of magnetite nanoparticles (40 nm) via infrared spectra, X-ray photoelectron spectroscopy and Mössbauer spectrometry analyses. Further studies are required to definitively determine the phosphate removal capability of magnetic iron oxide nanoparticles.

The aim of this study was to investigate the removal of phosphate from aqueous solutions using magnetic iron oxide nanoparticles. Kinetic, equilibrium and thermodynamic experiments were performed to characterize the phosphate to the magnetic nanoparticles. Sorption kinetic and equilibrium isotherm models were used for the data analysis.

2. Materials and methods

2.1. Synthesis of magnetic iron oxides nanoparticles

Magnetic iron oxide nanoparticles were synthesized by a coprecipitation method. An alkali solution of sodium hydroxide (NaOH, 6 mol) was added drop-wise with intensive stirring at room temperature into a 500 mL solution of $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ (0.25 M) and $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ (0.5 M) to obtain a pH of 7.6. The resulting precipitates were aged at 60°C for 18 h and then washed thoroughly with deionized water to remove any excess sodium. The washed precipitates were then oven-dried at 150°C for 6 h and then pulverized in a ball mill. The synthesized particles were nano-sized particles with magnetic properties (Fig. 1a). The nanoparticles were predominantly comprised of maghemite (spherical) with goethite (long rod-type), as shown in Fig. 1b. The nitrogen gas (N_2) adsorption–desorption experiments were performed using a surface area analyzer (BELSORP-max, BEL Japan Inc., Japan) after the samples were pretreated at 120°C . The nanoparticles had a specific surface area of $82.2\text{ m}^2/\text{g}$. The magnetic properties were measured using a vibrating sample magnetometer (VSM 5-15, Toei Industry Co., Japan) at room temperature with a field measurement range of ± 5.0 kOe. The saturation magnetization of the nanoparticles was 43.29 emu/g , whereas the coercivity of the nanoparticles was 26.27 Oe .

2.2. Phosphate removal experiments

Phosphate removal by the magnetic nanoparticles was conducted under batch conditions. The desired phosphate (P) solution was prepared by diluting the stock solution (1000 mg P L^{-1}) that had been made from potassium dichromate (KH_2PO_4). The batch experiments were performed at 30°C using 50 mL polypropylene conical tubes, unless otherwise stated. All of the batch experiments were performed in triplicate.

The first set of experiments examined phosphate removal as a function of adsorbent dosage. The experiments were conducted at an initial P concentration of 2 mg P L^{-1} with an adsorbent dose

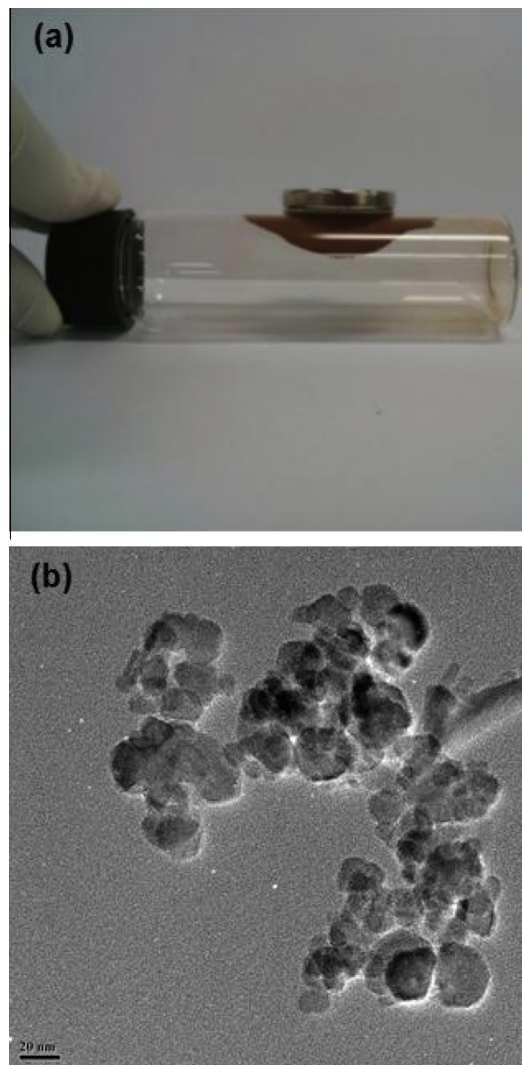


Fig. 1. Magnetic iron oxide nanoparticles used in the experiments: (a) attraction by a magnet (≈ 1.18 Tesla) and (b) TEM image (bar = 20 nm).

of $0.1\text{--}2.0\text{ g L}^{-1}$ in 30 mL of solution. The tubes were shaken at 100 rpm using a shaking incubator (Daihan Science, Seoul, Korea). After 24 h, the samples were collected and filtered through a 0.45- μm membrane filter. The phosphate concentration was analyzed by the ascorbic acid method [21]. The phosphate concentrations were measured at a wavelength of 880 nm using a UV–vis spectrophotometer (Helios, Thermo Scientific, Waltham, MA, USA). Before and after the phosphate sorption experiments, the infrared spectra of the magnetic nanoparticles were obtained using a Nicolet 6700 (Thermo scientific, USA) Fourier-transformed infrared (FTIR) spectrometer in the attenuated total reflectance (ATR) mode.

The second set of experiments was performed as a function of reaction time (adsorbent dose = 0.6 g L^{-1} ; initial P concentration = 2 mg P L^{-1}). The tubes were shaken using a shaking incubator, and the samples were collected after various reaction times. The additional experiments were performed at 15 and 45°C to examine the effect of temperature on phosphate removal. The third set of experiments was conducted as a function of the initial P concentration. Magnetic nanoparticles (0.6 g L^{-1}) were added to 30 mL of phosphate solution (initial concentration = $2\text{--}20\text{ mg P L}^{-1}$), and the samples were collected 24 h later.

The fourth set of experiments was conducted to examine the repeated use of magnetic nanoparticles for phosphate removal

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