



Removal of phosphate using calcium and magnesium-modified iron-based adsorbents



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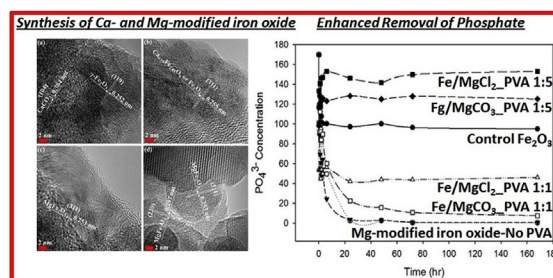
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HIGHLIGHTS

- Magnetic Ca and Mg-modified iron oxide adsorbents were synthesized.
- PVA imparted magnetism to the adsorbents for easy separation.
- Batch adsorption experiments were carried out to gain insights on the adsorption kinetics and equilibrium.
- The adsorbents effectively removed phosphates from water at a capacity of nearly 17 mg g⁻¹.

GRAPHICAL ABSTRACT



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ABSTRACT

Magnetic calcium (Ca) and magnesium (Mg)-modified iron oxide adsorbents were synthesized using CaCl₂, CaCO₃, MgCl₂, or MgCO₃ by a simple combustion method for the remediation of phosphate. Modification with Ca and Mg significantly improved the phosphate adsorption capacity of the magnetic iron oxide adsorbents. Additionally, polyvinyl alcohol (PVA) was incorporated during synthesis to aid in the magnetism of the samples, making the adsorbents easy to separate from solutions. Physicochemical properties of the adsorbents were determined by characterization with X-ray diffraction (XRD), particle analyzer, scanning electron microscopy (SEM), transmission electron microscopy (TEM), and high resolution TEM (HR-TEM). Batch adsorption experiments were carried out to gain insight on the materials' ability to remove phosphate from water supplies. Samples without the addition of PVA had higher phosphate capacities (ranging from 16.92 to 16.97 mg g⁻¹) compared to PVA-containing samples (ranging from 12.39 to 16.74 mg g⁻¹), yet the PVA-containing samples were magnetic and thus, easily separable.

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1. Introduction

Phosphorous (P) is one of the essential elements for all life as it is significantly associated with the DNA/RNA structure, cell membrane formation, energy storage/transfer, as well as enzyme activation or deactivation [1,2]. Phosphorus is commonly found in

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sources of drinking water due to an inflow of urban and industrial wastewater and agricultural run-offs, which contain phosphates [3–7]. Phosphates entering into the nutrient limited aquatic environment are significantly involved in eutrophication, which is associated with the formation of massive algal blooms, excessive growth of microorganisms, and depletion of dissolved oxygen [8–10]. Moreover, massive algal blooms containing cyanobacteria can be a potential hazard to humans and animals because some species of cyanobacteria produce and release toxins, known as cyanotoxins [11–13]. Therefore, it is of great interest to develop reliable technologies for the removal of phosphates from water.

Currently, chemical precipitation [14], biological processes [15], and adsorption [16] have been widely used for removing phosphate from water, yet both chemical precipitation and biological processes have disadvantages. While chemical precipitation has been shown to reduce phosphorus concentrations by 60–95%, depending on many factors including influent water parameters and coagulant dosage [17]; these methods involve high operating costs as well as the production of large amounts of sludge, and the efficiency of this method depends on the types of chemicals used for phosphate removal [18,19]. Biological processes have several drawbacks as well. In order to achieve maximal phosphate removal, operating conditions and water quality parameters must be very specific. For example, the system only functions optimally when phosphate concentrations are ≥ 5 – 10 mg L^{-1} and when the ratio of BOD to P is at least 35:1 [16]. Therefore, in order to improve the efficiency of phosphate removal by chemical precipitation and biological processes, enhanced biological phosphorus removal (EBPR) has been extensively studied [20–22]. The removal of phosphate was significantly improved by applying EBPR, which employs designed communities of microorganisms (aka, phosphorus accumulating organisms (PAO)). High concentrations of calcium (Ca) and magnesium (Mg) were recommended to achieve high efficiency removal of phosphate in EBPR. The Ca attributes to the formation of hydroxyapatite ($\text{Ca}_5(\text{PO}_4)_3\text{OH}$), which is about 39% of the phosphate precipitation in EBPR and Mg is associated with precipitation of struvite ($\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$) or newberyite (MgHPO_4) [20,23–25]. However, the formation of phosphate precipitates during EBPR operations have caused significant problems including pipe blockage and precipitate accumulation on the surface of equipment such as pumps and centrifuges in the treatment system [26]. Also, ranges of phosphate accumulation vary widely (i.e., from 20 to 80%) based on the PAO used [27]. Therefore, adsorption has attracted much attention for phosphate removal because of its simplicity, inexpensiveness, and low sludge production. Also, adsorption is an appropriate method for removing low concentrations of phosphate [28]. Thus, the use of Ca- and Mg-modified adsorbents were explored as they have been shown effective at improving the EBPR process and can form phosphate precipitates.

2. Materials and methods

Herein, Ca- and Mg-modified ferrites as phosphate adsorbents were synthesized by a simple combustion method using polyvinyl alcohol (PVA). Iron(III) nitrate ($\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, certified ACS, Fisher Scientific), calcium or magnesium precursors, and PVA (MW 89,000–98,000, 99+% hydrolyzed, Sigma-Aldrich) were mixed together using 5 mL of milli-Q grade water. Then, the mixtures were calcined in a muffle furnace (Ney Vulcan, A-550) at $300 \text{ }^\circ\text{C}$ for 1 h. Calcium carbonate (CaCO_3 , $\geq 99.0\%$, Sigma-Aldrich) or calcium chloride ($\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$, 74.27%, Fisher Scientific), and magnesium carbonate (MgCO_3 , Sigma-Aldrich) or magnesium chloride ($\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$, ACS reagent, J. T. Baker) were used to prepare Ca-ferrite and Mg-ferrite, respectively. Control iron oxide (Fe_2O_3) was

synthesized without Ca and Mg precursors or PVA. The detailed information of the ingredients for the synthesis of Ca- and Mg-modified ferrite are summarized in Table 1. Synthesized samples were characterized by X-ray diffraction (XRD, Panalytical X'pert 2-theta diffractometer, obtained from Panalytical, Almelo, Netherlands at a wavelength of 1.54 \AA and at 2-theta range 2 – 90° under CuK_α radiation), porosimetry (using a Tristar 3000 porosimeter analyzer, obtained from Micromeritics), scanning electron microscopy (SEM, model Philips XL 30 ESEM-FEG, at an accelerating voltage of 30 kV), transmission electron microscopy (TEM, a FEI CM20 TEM operated at 200 kV was employed), and high resolution TEM (HR-TEM, model JEM-2010F, obtained from JEOL, was employed with a field gun emission gun at 200 kV). Prior to HR-TEM characterization, the adsorbents were prepared and dispersed by ultrasonication (2510R-DH, Branson) in 99.8% pure isopropyl alcohol, obtained from Pharmco-AAPER for 30 min. Then, on a carbon-coated copper grid (LC325-Cu, EMS), a drop of the supernatant was fixed and dried at room temperature. The images obtained from the HR-TEM were analyzed using ImageJ, an image processing software (National Institutes of Health, Maryland, USA). To evaluate the phosphate adsorption capacity of the prepared samples, batch equilibrium experiments at pH 7 were conducted using the buffer 3-(N-morpholino) propanesulfonic acid (MOPS), obtained from Sigma-Aldrich. Variable dose isotherm studies were conducted using different masses of adsorbent (ranging from 0.1 to 1.5 g) in 125 mL Nalgene polypropylene bottles with 100 mL of phosphate solution. The stock phosphate solution was prepared by dissolving 3 g of sodium phosphate monohydrate ($\text{NaH}_2\text{PO}_4 \cdot \text{H}_2\text{O}$, Sigma-Aldrich), obtained from Fisher Scientific, in 11 L of deionized water at a target phosphate concentration of 200 mg L^{-1} . The concentrations of phosphate were measured by a standard colorimetry EPA Method 365.1 [29].

3. Results and discussion

3.1. Adsorbent characterization

XRD characterization of the samples are shown in Fig. 1. The XRD patterns of synthesized Ca- and Mg-modified samples were identified with JCPDS 00-036-0398 for magnesioferrite (MgFe_2O_4), 00-006-0502 for hematite ($\alpha\text{-Fe}_2\text{O}_3$), 00-025-1402 for maghemite ($\gamma\text{-Fe}_2\text{O}_3$), 00-047-1743 for calcite (CaCO_3), 00-005-0628 for halite (NaCl), 00-019-0629 for magnetite (Fe_3O_4), and 00-046-0291 for calcium iron oxide ($\text{Ca}_{0.15}\text{Fe}_{2.85}\text{O}_4$). As seen in Fig. 1(c), all peaks corresponding to non-magnetic hematite were detected. This indicates that PVA is necessary to convert non-magnetic iron oxide to magnetic iron oxide (i.e., maghemite, magnetite, and ferrite). Unfortunately, no peaks corresponding to Ca or Mg were found.

Table 1
Ingredients for the synthesis of Ca- and Mg-modified ferrite.

Sample	$\text{Fe}(\text{NO}_3)_3$ (g)	Ca (g)	Mg (g)	PVA (g)
Control Fe_2O_3	25	0	0	0
Fe/ CaCl_2 -No PVA	40.4	11.0	0	0
Fe/ MgCl_2 -No PVA	40.4	0	9.5	0
Fe/ CaCO_3 -No PVA	64.6	8.0	0	0
Fe/ MgCO_3 -No PVA	64.6	0	6.7	0
Fe/ CaCO_3 -PVA 1:1	40.4	7.4	0	47.8
Fe/ CaCl_2 -PVA 1:1	40.4	11.1	0	51.5
Fe/ CaCO_3 -PVA 1:5	4.04	0.74	0	23.9
Fe/ CaCl_2 -PVA 1:5	4.04	1.11	0	25.8
Fe/ MgCO_3 -PVA 1:1	20.2	0	4.2	24.4
Fe/ MgCl_2 -PVA 1:1	20.2	0	5.1	25.3
Fe/ MgCO_3 -PVA 1:5	4.04	0	0.8	24.2
Fe/ MgCl_2 -PVA 1:5	4.04	0	1.0	25.3

Note: 5 mL of water was used to prepare all samples.

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