Phosphorus adsorption onto green synthesized nano-bimetal ferrites: Equilibrium, kinetic and thermodynamic investigation

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HIGHLIGHTS

- A green technique for manufacturing $CuFe_2O_4$ was developed from industrial sludge.
- The synthesized $CuFe_2O_4$ is fast and effective in removing P from polluted water.
- The inner-sphere mechanism is importantly involved with P adsorption onto $CuFe_2O_4$.
- The nano-$CuFe_2O_4$ can be rapidly recovered by a magnet because of its magnetism.
- The results imply that 0.001 N NH_4OH is sufficient for P desorption from $CuFe_2O_4$.

ARTICLE INFO

ABSTRACT

Phosphorus (P) in natural aquatic environments is one of the most critical elements for causing eutrophication. On the other hand, it is also an essential nutrient for organisms in broad ecosystems. Therefore, it has become an important issue in environmental and ecological sciences to remove and recover efficiently of P in various water bodies. This study investigates the feasibility of P removal/recovery using nano-bimetal ferrites ($CuFe_2O_4$), manufactured from industrial sludge. These new results reveal that a rapid P removal, from 9.9% to 99.9%, was observed when the solution pH decreased from 9.06 to 2.64. The maxima P adsorption capacity was found to be 13.5 mg g^{-1} at pH 2.64 (318 K), which is much higher than other available adsorbents. The observed negative changes in the standard free energy (ΔG = −4.99, −5.47, −6.12, −7.21 kJ mol^{-1} at 288, 298, 308, and 318 K, respectively) and the positive value of ΔH (1.92 kJ mol^{-1}) demonstrate that the adsorption reaction is spontaneous and endothermic. Moreover, we observed also that the P adsorption increases with the increased of ionic strength from 0.001 to 1.0 N, suggesting important involvement of some inner-sphere mechanisms.

1. Introduction

Phosphorus (P) is an essential and limiting nutrient for organism growth in most environments and ecosystems [1–3]. Most lifes require phosphorus in the form of phosphate, which plays a critical role in RNA/DNA and in cellular metabolism [4]. However, geological phosphate (the main source of phosphorous in nature) is a non-renewable resource and could be completed consumed due to the steadily increased demands by various industrial and agricultural applications [5,6]. On the other hand, excess phosphate (or phosphorus) in aquatic system could induce significant eutrophication and caused overgrowth of aquatic plants, as well as depletion of dissolved oxygen, and subsequently leads to a serious damage of aquatic life [3,7,8].

It is well known that phosphorus would enter water bodies from phosphorus rich bedrock, wastes generated from agricultural (fertilizer in runoff), household (laundry), and industrial (semiconductor effluents) [7,9–12]. The phosphorus in wastewater is in the form of phosphate ($H_2PO_4^-$, HPO_4^{2-}, and PO_4^{3-}), polyphosphate and organic phosphate [1]. These dissolved species were easily adsorbed by plants and algae while polyphosphates and organic phosphate could be hydrolyzed into the phosphate form [13,14]. Therefore, efficient removal/recovery of phosphate from water bodies can prevent not only the loss of a precious resource but also protect natural waters from contamination.

Popular methods including biological or chemical treatments have been employed for removing high concentration (hundreds to thousands mg L^{-1}) of phosphate in wastewater. Chen et al. [15] found that La(III)-loaded granular ceramic could efficiently

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remove P from water. Under the conditions pH 7 and 313 K, the maxima saturated P adsorption capacity could reach 0.9 mg g^{-1}. Another La-EDTA coated Fe$_3$O$_4$ adsorbent has been reported by Yang et al. [8] for P removal from water. The result indicated that the maxima saturated P adsorption capacity could reach 4.2 mg g^{-1} under the conditions pH 6 and 298 K. Nevertheless, the above adsorbents displayed very low P adsorption capacity in water system. In addition, the high price of La coated adsorbents may limit their development when conducting in factories.

Nano-bimetal ferrite (CuFe$_2$O$_4$), with spinel structure, has a cubic close-packed arrangement of oxygen ions with Cu^{2+} and Fe^{3+} at two different crystallographic sites [16]. It was reported that CuFe$_2$O$_4$ has large potential to remove some toxic ions from wastewaters [17,18]. However, the price of CuFe$_2$O$_4$ generated from sol–gel method, co-precipitation, or auto-combustion [19–21] is rather high if the raw materials of pure chemical reagents were used for producing CuFe$_2$O$_4$. Inversely, the cost could be considerably decreased if the raw materials were replaced by the industrial sludge.
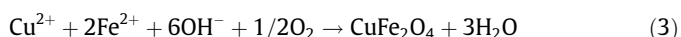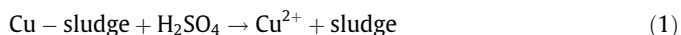
This research focuses on evaluating the P removal efficiency using the nano-bimetal ferrites manufactured from the printed circuit board (PCB) sludge. Our earlier investigation has successfully recycled Cu from PCB sludge by acid leaching and chemical exchange procedures [22]. Following these technologies, ferrite process was carried out to make sure both the supernatant and the sludge meet the limits of environmental regulation.

The sludges generated from ferrite process were used as an adsorbent and a series of batch experiments were conducted to examine the feasibility of nano-bimetal ferrites for P removal in aqueous solutions. The adsorbent properties and the adsorption mechanism of these nano-particles were studied in detail. Additionally, adsorption kinetics and thermodynamics of P adsorption on nano-bimetal ferrites were investigated. The information gained here reveals great potential for designing a fast and effective adsorbent for removing/recovering P in aqueous solutions using nano-bimetal ferrites.

2. Materials and methods

2.1. Preparation of nano-bimetal ferrites

The nano-bimetal ferrite manufactured from PCB industrial sludge was followed the same procedures as a previous study, where the detailed characterization of the nano-bimetal ferrites were also described [22]. Briefly, the nano-bimetal ferrites were synthesized from PCB sludge by a combination of acid leaching, chemical exchange, and ferrite process. The acid leaching was carried out using 500 g PCB sludge and 10 L diluted sulfuric acid was added for extracting Cu from solids. Fe^0 was used as sacrificed metal to substitute Cu^{2+} in the liquid during chemical exchange. To ensure the supernatant fulfill the effluent standards, ferrite process was performed after chemical exchange. The novel low-cost adsorbents, nano-bimetal ferrites, were thus synthesized after the ferrite process. The main corresponding reactions of these processes (acid leaching, chemical exchange, and ferrite process) are described as Eqs. (1)–(3), respectively.

$$Cu - sludge + H_2SO_4 \rightarrow Cu^{2+} + sludge \tag{1}$$

$$Fe^0 + Cu^{2+} \rightarrow Fe^{2+} + Cu^0 \tag{2}$$

$$Cu^{2+} + 2Fe^{2+} + 6OH^- + 1/2O_2 \rightarrow CuFe_2O_4 + 3H_2O \tag{3}$$

The point of zero charge (PZC) was analyzed by using Zeta Potential Analyzer (Zetasizer 2000, USA). The crystal phases were determined by XRD (D8 Advance, Bruker, Germany) using graphite

monochromatic copper radiation over the 2θ range 20–80°. The Brunauer–Emmett–Teller (BET) surface areas and the porosity of the adsorbents were obtained from nitrogen adsorption isotherms at 77 K using an ASAP 2010 analyzer (Micromeritics, USA). The surface morphology and particle size were examined by scanning electron microscopy (SEM, JSM-6330, Japan). The saturation magnetization of the nano-particles was measured using a Superconducting Quantum Interference Device (MPMS-XL7, Quantum Design, USA) at 298 ± 1 K.

The physical/chemical properties of the synthesized adsorbent were summarized in Table S1 in the Supplementary Material. Briefly, the point of zero charge (PZC) and the primary particle size of the nano-bimetal ferrites were found to be at 7.3 and 30–110 nm, respectively. Not only with the heavy density of 5.2 g cm^{-3}, nano-bimetal ferrites also have the high saturation magnetization of 62.3 emu g^{-1}. The BET surface area, pore volume, and average pore diameter of the adsorbent was determined to be 69.1 m^2 g^{-1}, 0.11 cm^3 g^{-1}, and 18.57 Å, respectively. The XRD spectra (Fig. S1) show main diffraction peaks at d-spacing of 4.790, 2.960, 2.517, 2.100, 1.613, 1.479, 1.272, 1.087, and 0.964 Å, matched well with the CuFe$_2$O$_4$ crystals (JCPDS file number 00-025-0283). Additionally, the synthesized novel low-cost adsorbent was collected using a magnetic separation method by taking advantage of its strong magnetism. The nano-bimetal ferrites were then washed with Milli-Q water at least 5 times until the solution pH reached near neutral. The solids were then dried at 323 K for 24 h in an oven and stored for further investigation.

2.2. Batch adsorption experiments

The batch adsorption experiments were carried out in order to evaluate the evolving process and the equilibrium states of phosphate mobilization. The stock solution of phosphorus was prepared by dissolving a fixed quantity of KH$_2$PO$_4$ (Merck, Germany). All batch adsorption experiments were performed according to the following procedures: (1) 10 mL P solution and fixed amount of nano-bimetal ferrites were poured into 15 mL centrifuge tubes. (2) The centrifuge tubes were then put on the shaft of a rotary shaker after the caps were tightened.

To evaluate the influence of the solution pH and the ionic strength on the P adsorption, various experiments were performed by adding 0.03 g of the adsorbent containing 50 mg L^{-1} P solution at 298 ± 1 K. The pH of the solutions was adjusted using 0.1 N HNO$_3$ or NaOH solution to the designated values (2.64 ± 0.01, 3.44 ± 0.01, 4.53 ± 0.01, 5.51 ± 0.01, 7.02 ± 0.01, 9.06 ± 0.01, and 10.92 ± 0.01) and the ionic strength of the solutions was designed at 0.001, 0.01, 0.05, 0.1, 0.5, and 1.0 N by adding 1.0 N NaCl solution.

All equilibrium adsorption experiments were individually conducted by shaking 0.03 g of the nano-bimetal ferrites with 50 mg L^{-1} P solution using a thermostated shaker at a speed of 30 rpm for 2 h. Adsorption kinetics for P were measured by taking 50 mg L^{-1} P solution with 0.03 g of the nano-bimetal ferrites and shaking the mixture at pH 2.64 (temperature was controlled at 288 ± 1 to 318 ± 1 K). The P uptake rate of q_t (mg g^{-1}) was determined by Eq. (4):

$$q_t = \frac{(C_o - C_t) \times V}{m} \tag{4}$$

where C_o and C_t are the metal concentration in liquid phase at the initial and at time t (mg L^{-1}), respectively; m is the adsorbent amount (g); V is the volume used in the adsorption process (L).

The solid and liquid phases were magnetically separated using a magnet with 4000 Gauss. The P concentrations in the filtrate were determined by ICP-OES (iCAP 6500, Germany). The amount of P adsorbed on the nano-bimetal ferrites was determined using the concentration differences between the initial and the equilibrium in solutions. Prior to analysis, the supernatant were acidified with