A bench-scale study on the removal and recovery of phosphate by hydrous zirconia-coated magnetite nanoparticles

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ABSTRACT

Owing to the easy magnetic separation from water for reuse, magnetic nanoparticles have drawn great interest as adsorbents. Herein hydrous zirconia-coated magnetite nanoparticles ($Fe_3O_4@ZrO_2$) were created by a facile method and a bench–scale study was undertaken to evaluate its effectiveness and mechanism to remove phosphate at low concentrations. Results indicated that phosphate removal by $Fe_3O_4@ZrO_2$ was fast (95% of phosphate removal within 10 min) and nearly complete removal could be achieved at the adsorbent dosage > 0.6 g/L. In tap water or wastewater where competitive anions coexist, regulation of pH was found to be quite effective to augment the performance of phosphate removal. In pH–lowered adsorption systems, phosphate removal followed a good pattern similarly to pure water, i.e., a continuous high efficiency removal followed by a rapid saturation. Adsorption–desorption–regeneration studies showed that $Fe_3O_4@ZrO_2$ could be repeatedly used for phosphate removal and adsorbed phosphate could be stripped for recovery. The fractionation of adsorbed phosphorus suggested that NaOH-P fraction was dominant. We also found that the adsorption reaction of phosphate with $Fe_3O_4@ZrO_2$ shifted the isoelectric point of $Fe_3O_4@ZrO_2$ from ~9.0 to ~3.0. FTIR measurements further showed the direct coordination of phosphate onto zirconium by replacement of hydroxyl groups. The formation of the monodentate $(ZrO)PO_2(OH)$ complex was proposed.

1. Introduction

Phosphorus is an important component for all living organisms and its application in agriculture as a fertilizer is essential for production of food we need. The mining and use of phosphate rock had begun around the mid-to-late 19th century and increased dramatically since 1950 s [1,2]. Currently around 15 million tonnes of phosphate rock per year are used as fertilizer [2]. However, phosphate rock is a non-renewable resource. It is estimated that global commercial phosphate rock reserves will be depleted in 50–100 years based on the current rates of extraction [2,3]. More seriously, there is no substitute for P in the world, thus sustainable P supply is essential to ensure our food security.

The data of Substance Flows Analysis (SFA) through the food system by Cordell et al. [2] revealed that only one-fifth of applied phosphate fertilizer is incorporated into the foods of plants and animals that humans consume. Therefore, most of the P is lost along the way of flow through the food production and consumption system, causing serious environmental problems particularly the worldwide eutrophication of lakes, reservoirs, estuaries, and parts of the oceans [4,5]. Therefore, investigation on the recovery and reuse of the lost P is in

urgent demand to recycle the finite resource and to protect our environment.

Of the lost P, soil runoff and the excreta from animal and human beings are the main fractions, accounting for about 35% and 42%, respectively [2]. The former has a non-point source character with high volume and low concentration, making recovery of P technically and economically difficult. However, the latter has limited volume and relatively high P concentration; P recovery may be accomplished in tandem with conventional wastewater treatment process that decomposes organic matter.

Adsorption is one of the most investigated technologies for removal and recovery of phosphate from wastewater as recently reviewed [5–8]. In this technique, phosphate is removed from wastewater via selective adsorption to a solid phase (adsorbent). Then, the adsorbed P is stripped from the solid adsorbent and the stripped P may be chemically precipitated as a high-purity fertilizer which could be conveniently transported for use in agriculture. The adsorbent may be reused again for phosphate capture after regeneration. However, desorption and regeneration processes require easy separation of solid adsorbent from aqueous media.

In recent years, magnetic nanoparticles have drawn great interest

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as adsorbents for removal and recovery of pollutants from water because the use of a magnet provides a very simple and effective method of separating the particles from water. For instance, magnetite nanoparticles have been investigated for pollutants removal recently [9–13]. But due to the possible oxidation of Fe^{2+} in magnetite structure in air, the limited kind of pollutants for which magnetite has affinity, and the relatively low adsorption capacity, surface modification of magnetite for use as magnetic adsorbents have been more interested and intensively investigated [14–27].

In our previous study, we have reported the one-step synthesis and the preliminary application of a novel magnetic adsorbent, hydrous zirconia coated magnetite nanoparticles (expressed as $Fe_3O_4@ZrO_2$ for convenience), for the removal and recovery of phosphate from synthetic water with relatively high P concentrations [28]. Results revealed that the material had high adsorption performance for phosphate in terms of adsorptive capacity, selectivity, as well as kinetics. However, its mechanism is still poorly understood and its potential application in real natural and wastewater, whose phosphate concentrations are relatively low, has not been explored.

In our current study, we wish to report our research on the removal and recovery of phosphate at low concentration levels typically found in wastewaters, using a bench-scale device. To our best knowledge, bench-scale study on application of magnetic adsorbent for pollutants removal from water/wastewater has rarely been conducted yet. For the assessment of the real effectiveness of the developed adsorbent, the magnetic $Fe_3O_4@ZrO_2$ was applied in tap water and real effluent of municipal wastewater treatment plant which contained other ions and dissolved species. In addition, the adsorption mechanism was investigated and the performance of $Fe_3O_4@ZrO_2$ under different operation conditions such as contacting time and pH were examined.

2. Materials and methods

2.1. Reagents, water samples and materials

$ZrOCl_2 \cdot 8H_2O$ used in this study was purchased from Aladdin Industrial Corporation (Shanghai, China) and had a > 98% purity. Other reagents were all analytical grades and purchased from Sinopharm Chemical Reagent Co. Ltd (Shanghai, China).

Three kinds of water samples were used in this study including pure water, tap water and real effluent of Minhang waste water treatment plant, Shanghai, China. Pure water was used for comparison purposes or for the study of adsorption mechanism. Though effluent sample would be the most preferable to assess the performance of $Fe_3O_4@ZrO_2$ for phosphate capture from wastewater, a large part of experiments were done using easily available tap water because a large amount of water sample was needed for bench-scale experiment carried out in our laboratory. Tap water was also used in previous studies to mimic the mineral composition of wastewater [29,30]. The phosphate concentration of effluent sample was 0.60 mg/L and was spiked to 2 mg/L with KH_2PO_4 for study because this phosphate concentration of 2 mg/L was in the range of the average concentration in real waste streams and similar phosphate concentrations were used by other workers for investigating phosphate removal from waste stream [31,32]. For a better comparison, experiments in pure water and tap water were also done using the same initial phosphate concentration (2 mg/L). Chemical compositions of tap water and effluent are listed in Table 1. Not surprisingly, the concentration of soluble species of the latter was much higher than the former.

The detailed preparation techniques of $Fe_3O_4@ZrO_2$ with different Fe/Zr molar ratios and the characterization of $Fe_3O_4@ZrO_2$ (XRD, TEM, BET surface area and saturation magnetization) have been described in detail in a companion paper [28]. Briefly $FeSO_4 \cdot 7H_2O$, $FeCl_3 \cdot 6H_2O$ and $ZrOCl_2 \cdot 8H_2O$ were dissolved in water to give the molar ratio of $Fe^{2+}/Fe^{3+}/Zr = 1.33/2.66/1$, i.e., the $Fe_3O_4@ZrO_2$ used in this study had the Fe/Zr molar ratio of 4/1. This solution was titrated with

Table 1
Soluble species in waste water and tap water.

Species (mg/L)	Waste water	Tap water
Na^+	79.75	54.80
K^+	16.44	6.81
Ca^{2+}	65.24	49.20
Mg^{2+}	13.86	10.80
Cl^-	91.43	5.95
SiO_4^{2-}	14.49	5.82
NO_3^-	13.31	1.09
SO_4^{2-}	107.74	10.07
Alkalinity[a]	62.65	40.85

[a] Alkalinity was expressed by amount of CaO.

6 M NaOH solution to the pH end point of 7.6 and further aged at 60 ℃ for 18 h. The solid product was then rinsed and dried. Some important physicochemical characteristics of the material with respect to this study are: BET surface area 152.46 m^2/g; saturation magnetization 23.65 emu/g; and Langmuir adsorption maxima for phosphate 42.19 mg/g. According to the result of TEM image, the magnetite core of $Fe_3O_4@ZrO_2$ is ball-like or hexagonal particles with diameter ranging from 10 to 50 nm, while the ZrO_2 shell is aggregate wrapped outside the core. The size of the particle depends on the amount of ZrO_2 aggregates swathed on the magnetic particles, varying from tens to hundreds of nanometers.

2.2. Performances of removal and recovery of phosphate

2.2.1. Effect of contacting time and adsorbent dosage on phosphate removal

To understand the adsorption kinetics of phosphate at a concentration similar to real water/waste stream, $Fe_3O_4@ZrO_2$ was mixed with phosphate solution having the concentration of 2 mg/L which was prepared from tap water. The adsorbent dosage was fixed at 1 g/L and the reaction device was described in Section 2.2.3. After reacted for a given time with stirring (400 rpm), the propeller was stopped and the mixture was magnetically separated whereas the supernatant was analyzed for phosphate concentration. The amount of adsorbed phosphate was calculated by the difference between initial and final phosphate concentration in solution. The experiment was conducted in triplicate and the mean data as well as the standard deviations are reported.

The effect of $Fe_3O_4@ZrO_2$ dosage on phosphate removal was explored at different dosages from 0.06 to 1 g/L. The initial phosphate concentration was 2 mg/L, prepared from tap water, and the reaction time was 30 min with stirring (400 rpm) using the reaction device described in Section 2.2.3. After magnetic separation, the phosphate concentration in the supernatant was analyzed. The experiment was conducted in triplicate and the mean data as well as the standard deviations are reported.

2.2.2. Repeated contacting experiments for P adsorption

$Fe_3O_4@ZrO_2$ was reacted with 2 mg/L phosphate solution with stirring (400 rpm) at the dosage of 1 g/L using the reaction device described in Section 2.2.3. Because the purpose was to examine the potentiality of $Fe_3O_4@ZrO_2$ for phosphate removal at a low concentration, the long reaction time of 24 h was adopted to fully assure that no further adsorption would take place. After 24 h, the mixture was magnetically separated and the supernatant was analyzed for phosphate concentration to calculate the amount of adsorbed P. A fresh 2 mg/L phosphate solution was added and removal experiment was again done. The adsorption experiment was repeated until the removal efficiency was less than 5%, which was regarded as that the material was saturated with phosphate and that no further uptake of phosphate by the materials could be detected any more.