



One-step synthesis of magnetite core/zirconia shell nanocomposite for high efficiency removal of phosphate from water



Zhe Wang, Mingchao Xing, Wenkan Fang, Deyi Wu*

School of Environmental Science and Engineering, Shanghai Jiao Tong University, No. 800 Dongchuan Rd., Shanghai 200240, China

ARTICLE INFO

Article history:

Received 12 October 2015

Received in revised form 6 January 2016

Accepted 7 January 2016

Available online 11 January 2016

Keywords:

Magnetite
Zirconia
Phosphate
Removal
Mechanism
Nanoparticles

ABSTRACT

A self-assembled magnetite core/zirconia shell ($\text{Fe}_3\text{O}_4@\text{ZrO}_2$) nanoparticle material was fabricated by the one-step co-precipitation method to capture phosphate from water. $\text{Fe}_3\text{O}_4@\text{ZrO}_2$ with different Fe/Zr molar ratios were obtained and characterized by XRD, TEM, BET surface area and magnetization. It was shown that, with the decreasing of Fe/Zr molar ratio, magnetization decreased whereas surface area and adsorption capacity of phosphate increased. $\text{Fe}_3\text{O}_4@\text{ZrO}_2$ with the ratio of higher than 4:1 had satisfactory magnetization property (>23.65 emu/g), enabling rapid magnetic separation from water and recycle of the spent adsorbent. The Langmuir adsorption capacity of $\text{Fe}_3\text{O}_4@\text{ZrO}_2$ reached 27.93–69.44 mg/g, and the adsorption was fast (90% of phosphate removal within 20 min). The adsorption decreases with increasing pH, and higher ionic strength caused slight increase in adsorption at $\text{pH} > 5.5$. The presence of chloride, nitrate and sulfate anions did not bring about significant changes in adsorption. As a result, $\text{Fe}_3\text{O}_4@\text{ZrO}_2$ performed well to remove phosphate from real wastewater. These results were interpreted by the ligand exchange mechanism, i.e., the direct coordination of phosphate onto zirconium by replacement of hydroxyl groups. Results suggested that phosphate reacted mainly with surface hydroxyl groups but diffusion into interior of zirconia phase also contributed to adsorption. The adsorbed phosphate could be desorbed with a NaOH treatment and the regenerated $\text{Fe}_3\text{O}_4@\text{ZrO}_2$ could be repeatedly used.

© 2016 Elsevier B.V. All rights reserved.

1. Introduction

Nowadays eutrophication has already become a globalized environmental problem in relatively stagnant water bodies such as lakes, reservoirs, and estuaries. Eutrophication can cause comprehensive ecological crisis of aquatic environment, such as the decrease of biological diversity, the loss of landscape function and the potential health risk to human beings [1]. Phosphorus is well recognized as the limiting factor for eutrophication. To protect against nuisance algal blooms in lakes, average phosphorus concentration should not surpass 0.02 mg/L [2]. Thus, the removal of phosphate, the main species of phosphorus, from wastewater before discharge is one of the most effective ways for eutrophication control [3–5].

Adsorption is a promising technology for the removal of phosphate. Therefore, in recent years, investigations on adsorbents for immobilizing phosphate from water have been undertaken. Among the large number of adsorbents, zirconium-containing materials

have been widely investigated for phosphate removal from water, such as mesoporous zirconia [6], hydrous zirconia [7–9], the binary oxides of Fe–Zr [10] and Ce–Zr [11], and Zr loaded materials [12–17]. Regarding the use of zirconium in phosphate removal, of the utmost importance is the high affinity of zirconium for phosphate because this transition metal cation, which has hard Lewis acid property, exhibit strong ligand adsorption for phosphate which behaves as a Lewis base. In addition, zirconium is widely distributed in nature and the concentration within the Earth's crust is about 130 mg/kg [18–20], which is even more abundant than zinc and copper. The resources of zircon, the principal commercial source of zirconium, exceed 60 million tons worldwide and annual worldwide zirconium production is approximately 900,000 tons [18–20]. Zirconium is also found in all biological systems. The human body contains, on average, 250 mg of zirconium, and daily intake is approximately 4.15 mg (3.5 mg from food and 0.65 mg from water), depending on dietary habits [21]. Therefore, zirconium is relatively cheap, non-toxic and environmentally friendly. Other advantages of zirconium are its resistance to oxidant agents and acid/base and low solubility in water [7–9].

Amorphous hydrous zirconia could be prepared mainly via a co-precipitation method from an aqueous solution of zirconium salts.

* Corresponding author.

E-mail address: dywu@sjtu.edu.cn (D. Wu).

From the amorphous hydrous zirconia, crystalline zirconia could be obtained by a crystallization process, which could be carried out by one of two methods: hydrothermal treatment or solid-state reaction [22,23]. Hydrothermal treatments are accomplished by increasing the temperature of an aqueous suspension of amorphous hydrous zirconia particles. In contrast, solid-state crystallization is achieved by removing the amorphous material from the suspension (usually via filtration) followed by high temperature calcination. It is known that crystalline zirconia can exist in three different polymorphic forms: a monoclinic (*m*-ZrO₂), tetragonal (*t*-ZrO₂), or cubic (*c*-ZrO₂) crystal structure. Since chemisorption of anions by metal oxide is highly related to surface hydroxyl groups, amorphous hydrous zirconia with more hydroxyl groups on its surface and higher specific surface area is thought to be more effective for the capture of anionic pollutants.

However, to recycle the adsorbents for repeated use, we must recover adsorbents from water first and then desorb the adsorbed phosphate. Adsorbents in its powder form are generally not easily recovered once put into water. Granulation of powder adsorbents as filter media for flow-through use is a common way but this substantially reduces the surface area and resultantly the phosphate removal capacity. It is known that finer particles have higher adsorption capacity and faster kinetics because of the higher specific surface area, shorter intraparticle diffusion distance and larger number of surface reaction sites [24]. Therefore, an adsorbent would be the most efficient provided that it is employed in its powder form.

One of the recent approaches to overcome the difficulty in the recovery of adsorbents is to prepare nano-sized magnetic composites as adsorbent material, because they are capable to be collected from water by providing an external magnetic field. A number of novel magnetic nanoparticles have recently been developed [24–30]. In them two research groups have successfully obtained magnetite core/zirconia shell nanocomposite for high efficiency removal of phosphate from water. But their preparation methods were not easy and required three steps, i.e., (1) preparation of nanoscale Fe₃O₄; (2) coating of Fe₃O₄ by silica and (3) consequent grafting functional material as shells [25,26]. The procedure is obviously time-consuming and not cost-effective, which limit its practical application.

Our current study attempted to combine magnetite and zirconia together as a recyclable adsorbent for phosphate capture from water, through a facile process. For this purpose, the one step co-precipitation method was tried and it was shown to be quite successful because magnetite and zirconia could be bound together through self-assembling to form magnetite core/zirconia shell (Fe₃O₄@ZrO₂) structure. This structure was confirmed by the measurements of TEM, BET surface area and phosphate adsorption capacity. The properties of Fe₃O₄@ZrO₂ with different Fe/Zr molar ratios were characterized and their performances and mechanisms for adsorption and desorption of phosphate were explored.

2. Materials and methods

2.1. Reagents

ZrOCl₂·8H₂O used in this study was purchased from Aladdin Industrial Corporation and had a >98% purity. The humic acid was supplied by Aldrich Chemical in the form of sodium salt which was extracted from waters draining from an open pit mine in Oberhessen, Germany. Other reagents were all analytical grades and purchased from Sinopharm Chemical Reagent Co. Ltd. The phosphate solutions were prepared with KH₂PO₄, and all the concentrations were expressed in element P.

2.2. Preparation of Fe₃O₄@ZrO₂

In previous literatures dealing with the removal of phosphate by magnetite, the synthesis of magnetite from stoichiometric divalent and trivalent iron salts in basic medium was done under an anoxic atmosphere [31,32] or air [33]. It must be noted that the contact with air may lead to partial formation of non-magnetic iron hydroxide. But from the engineering application angle, the synthesis under air could be easily controlled and thus the product would be more cost-effective when compared with the synthesis under inert atmosphere. We did a preliminary experiment to compare the saturated magnetization of magnetite prepared under inert atmosphere (solutions were prepared with degassed pure water and nitrogen gas was bubbled during synthesis process) or under an aerobic condition. Results indicated that the former had a higher saturation magnetization (32.90 emu/g) than the latter (31.72 emu/g), but the difference was small probably due to our relatively short reaction time (<30 min). In the present study, the preparation of Fe₃O₄@ZrO₂ was carried out without the control of inert atmosphere.

First, 0.125 mol FeSO₄·7H₂O, 0.25 mol FeCl₃·6H₂O as well as a given amount of ZrOCl₂·8H₂O were dissolved in a 500 ml doubly distilled (DD) water. A 6 M NaOH solution was then added dropwise until the pH reached 7.6. A stirring rate of 400 rpm was maintained during the titration process. The mixture was further aged at 60 °C for 18 h without stirring. After this, the solid product was recovered and washed with DD water twice and ethanol twice. The separation of solid phase and liquid phase was done by applying an external magnetic field or by centrifugation, depending on the magnetization strength of the solids. Finally, the product was dried at 45 °C for 24 h, ground to pass through an 80-mesh sieve, and stored in airtight containers for later experiments. The amounts of ZrOCl₂·8H₂O added were 0.0417, 0.0938, 0.1875 and 1.5000 mol, in order to achieve Fe₃O₄@ZrO₂ with Fe/Zr molar ratios of 9:1, 4:1, 2:1, 1:4, respectively. The obtained materials were noted as M(9)Z(1), M(4)Z(1), M(2)Z(1) and M(1)Z(4), respectively. For comparison purposes, magnetite and hydrous zirconia were separately synthesized through the same procedure but without the addition of iron or zirconium salts.

2.3. Characterization

The X-ray diffraction (XRD) profiles were recorded using D8 ADVANCE (BRUKER-AXS) with the Cu-Kα filtered radiation (30 kV, 15 mA). TEM images of the materials were obtained with a Tecnai G2 F20 (FEI) electron microscope (200 kV, point-to-point resolution 0.24 nm). BET surface area was determined by ASAP 2010 M+C (Micromeritics Inc.) using the nitrogen adsorption method. The saturated magnetizations of the materials were obtained through magnetization curves using a vibrating sample magnetometer (Lakeshore). The soluble components in the effluent from Minhang waste water treatment plant, Shanghai, China were analyzed by Inductively Coupled Plasma Mass Spectrometer (Agilent 7500a) and ion chromatography (METROHM, MICI).

2.4. Batch adsorption experiments

Batch adsorption experiments were performed in 50 ml centrifuge tubes. An exact amount of about 0.1 g adsorbents was put into the centrifuge tubes containing 40 ml of phosphate solutions. The suspensions were shaken at 25 °C under 180 rpm. After a given time intervals, the suspensions were centrifuged or magnetically separated, depending on the magnetization strength of the solids. The phosphate concentrations in the supernatants were determined by the molybdenum-blue ascorbic method [34]. The

Download English Version:

<https://daneshyari.com/en/article/5353171>

Download Persian Version:

<https://daneshyari.com/article/5353171>

[Daneshyari.com](https://daneshyari.com)