

Research Paper

Preparation of uniform magnetic iron oxide nanoparticles by co-precipitation in a helical module microchannel reactor

Sen Lin^{a,b}, Kuangfei Lin^{b,*}, Diannan Lu^{a,*}, Zheng Liu^a^a Department of Chemical Engineering, Tsinghua University, Beijing 100084, China^b State Environmental Protection Key Laboratory of Environmental Risk Assessment and Control on Chemical Process, East China University of Science and Technology, Shanghai 200237, China

ARTICLE INFO

Article history:

Received 15 August 2016

Received in revised form 7 November 2016

Accepted 7 December 2016

Available online 8 December 2016

Keywords:

Microchannel reactor

Magnetic iron oxide nanoparticles

Co-precipitation

Hazard compounds

Waste water treatment

ABSTRACT

A helical module microchannel reactor (MR) was developed for the preparation of magnetic iron oxide nanoparticles (MIONPs) by co-precipitation. The product properties were characterized by TEM, XRD, XPS and BET, which showed that the MIONPs obtained from MR appeared a more uniform size distribution, a better crystallinity, a smaller size but larger specific surface area, as compared to their counterpart obtained from conventional stirred reactor (SR). The workability of the synthesized MIONPs using MR in waste water treatment was examined using aqueous arsenite, arsenate and chromate as samples. The results obtained in the present study showed the advantages of using MR to fabricate MIONPs with high conversion yield and high productivity. The fabricated MIONPs is promising for a rapid and complete removal of aqueous hazard compounds.

© 2016 Elsevier Ltd. All rights reserved.

1. Introduction

The proven advantages of nanoparticles in terms of high specific surface area, unique physio-chemical properties and derivative functionalities make them attractive for unlimited applications in aerospace machinery, electronic products, biotechnology, chemical engineering, environmental engineering and so on [1]. Among these nanoparticles, magnetic nanoparticles, e.g. magnetic iron oxide nanoparticles (MIONPs) composing of Fe_3O_4 and $\gamma\text{-Fe}_2\text{O}_3$, are of particular interest to chemical engineering practices for their convenience of operation and recovery [2]. One of the most extensively studied areas of MIONPs is waste water treatment, in which MIONPs are applied as adsorbents to remove heavy metal ions [3–7]. For example, Shen et al. used Fe_3O_4 of 8 nm in diameter to remove aqueous Cr(VI) and achieved an adsorption capacity of 35.46 mg/g, which was significantly higher than the bulky adsorbents such as diatomite (11.55 mg/g), activated carbon (15.47 mg/g), anatase (14.56 mg/g) [8]. On the other hand, various preparation methods for MIONPs have been proposed, including co-precipitation [9], hydrothermal decomposition [10,11], biosynthesis [12], micro-emulsion [11], and other improved combined methods [10,13–18]. Among these methods, co-precipitation is the

most frequently used one, particularly for the preparation of MIONPs as adsorbents for the removal of heavy metals in waste water because it yields the MIONPs products with more hydroxyls on the surface [19–21]. The process and economic advantages are also important reasons for the popularity of this synthetic scheme [22]. These virtues have embodied well in our previous study, in which $\gamma\text{-Fe}_2\text{O}_3$ synthesized by co-precipitation has showed excellent adsorption performance for As(III) and As(V) [18]. However, the conventional co-precipitation process in a stirred tank often failed to provide a uniform product on a large scale. The crystallization degree and uniformity of MIONPs drop significantly particularly in large volume reactor due mainly to unsatisfying mixing during precipitation process and agglomeration occurred simultaneously during the precipitation. These problems thus have hindered the application of MIONPs [23–25].

The recent years have witnessed the development of micro-fluidics reactors as a powerful tool to enhance the mass and heat transfer and thus resulting in an enhanced reaction process [26,27]. These advantages have enabled application of microfluidics reactor in the synthesis of various products and materials with predefined size and shape [28]. For instance, Verma *et al.* set up a three-dimensional multi-helical microchannel system, which can improve liquid mixing efficiency effectively [29]. Singh *et al.* reported a four-fold enhancement was offered in heat transfer depending on a micro coiled flow inverter [30]. With our appreciation of the above mentioned advantages of micro-fluidics

* Corresponding authors.

E-mail addresses: kflin@ecust.edu.cn (K. Lin), ludiannan@tsinghua.edu.cn (D. Lu).

reactor, we directed our efforts towards the preparation of MIONPs by co-precipitation process conducted in a microfluidics reactor. As the first step towards this objective, we established a helical module microchannel reactor and tested its workability for the co-precipitation process. The MIONPs products obtained using this microchannel reactor and the conventional stirred reactor were analyzed with FTIR, XRD, XPS, in addition to TEM observation. The adsorption capacities of MIONPs for aqueous heavy metals were examined to confirm the effectiveness of the MIONPs as adsorbents.

2. Materials and methods

2.1. Materials

All reagents were of chemically pure grade and used without further purification. Ferrous chloride ($\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$), ferric chloride ($\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$), sodium hydroxide (NaOH), hydrochloric acid (HCl) and nitric acid (HNO_3) were all purchased from Modern Oriental Fine Chemicals Co., Ltd. All sample solutions were prepared with the deionized water. Ferrous chloride ($\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$) and ferric chloride ($\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$) were used as the source of Fe^{2+} and Fe^{3+} in the feed solution, respectively. Sodium arsenate ($\text{Na}_2\text{HAsO}_4 \cdot 12\text{H}_2\text{O}$), sodium arsenite (NaAsO_2) and sodium dichromate ($\text{Na}_2\text{Cr}_2\text{O}_7 \cdot 2\text{H}_2\text{O}$) served as the source of arsenite (As(III)), arsenate (As(V)) and chromate (Cr(VI)) solutions, respectively, provided by Sinopharm Chemical Reagent Co., Ltd. All glassware was soaked in 15% HNO_3 before use.

2.2. Synthesis of MIONPs

The MIONPs were prepared by co-precipitation in different reactors with optimal working conditions. The synthesis in a stirred reactor, noted as SR hereafter, was according to our previous method [31]. Briefly, 5 ml solution containing 0.03 mol/L Fe^{3+} and 0.015 mol/L Fe^{2+} was mixed with 2 ml 0.5 mol/L NaOH solution rapidly, followed by 3 h incubation at 60°C at a stirring rate of 1000 rpm. At last the MIONPs were collected from suspension with a permanent magnet.

The synthesis of MIONPs in a helical module microchannel reactor, noted as MR hereafter, was shown in Scheme 1. Firstly, the feed solution containing 0.1 mol/L Fe^{3+} and 0.05 mol/L Fe^{2+} and 0.5 mol/L NaOH solution were pumped through different tubes at a

flow rate of 5.0 ml/min and 2.5 ml/min, respectively. Then the two streams mixed in the T shape tube connector rapidly to form crystal nuclei of MIONPs. And the mixed streams continued flow into the polytetrafluoroethylene (PTFE) tube of 12 m in length and 0.5 mm in diameter, which was wrapped in a helical module with diameter of 25 mm. The helical module was immersed in 60°C water bath to provide a stable crystallization temperature for MIONPs, where the residence time of stream was less than 1.3 min, demonstrating a faster preparation, compared with that in the SR. Finally, the MIONPs in suspension were collected from the outlet of the helical tube and separated by a 0.6 T magnet after being washed five times with deionized water.

2.3. Recovery of MIONPs

The recovery of MIONPs after magnetic separation was calculated based on the mass balance of element Fe in MIONPs. During a run, 100 ml suspension with 0.02 g MIONPs was static set in a magnetic field with a given external magnetic strength for 30 min. The supernatant was collected and tuned its pH value to 1.0 by adding 1 mmol/L HCl , which dissolves all unrecovered and insoluble Fe_2O_3 or Fe_3O_4 into soluble Fe^{2+} or Fe^{3+} . The concentration of Fe ions (c_1) in supernatant was detected by ICP-AES. As control, 100 ml suspension with 0.02 g MIONPs without magnetic separation was also treated by adding 1 mmol/L HCl to the final pH value of 1.0. The concentration of Fe ions (c_0) was also detected by ICP-AES. Then, the MIONPs recovery η_r is obtained from Eq. (1):

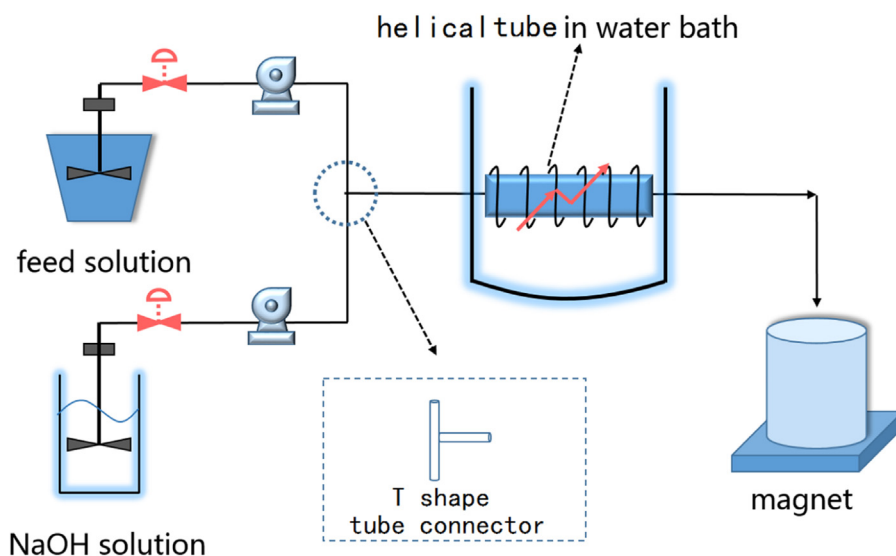
$$\eta_r = (c_0 - c_1)/c_0 \times 100\% \quad (1)$$

2.4. Conversion of Fe

The suspension with MIONPs was collected from the MR outlet for a given time and diluted with deionized water in a volumetric flask to detect the Fe concentration, after using HCl to dissolve all MIONPs in suspension. The conversion of Fe (η_c) in raw solution is thus obtained from Eq. (2):

$$\eta_c = (c_0V - c_1V')/c_0V \times 100\% \quad (2)$$

where c_0 and c_1 are the Fe ion concentrations (mg/L) of feed solution and suspension after dilution, respectively. V' is the solution volume after dilution (L), and V is the volume of feed solution (L).



Scheme 1. The flow-process diagram of preparing MIONPs by co-precipitation in MR.

Download English Version:

<https://daneshyari.com/en/article/6477340>

Download Persian Version:

<https://daneshyari.com/article/6477340>

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