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Continuous preparation of Fe_3O_4 nanoparticles using a rotating packed bed: Dependence of size and magnetic property on temperature

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ABSTRACT

Fe_3O_4 nanoparticles were prepared by continuously pumping aqueous solutions of $FeCl_3/FeCl_2$ and NaOH into a rotating packed bed (RPB), co-precipitating 0.019 mol/L of $FeCl_2 \cdot 4H_2O$, 0.037 mol/L of $FeCl_3 \cdot 6H_2O$, and 0.222 mol/L of NaOH. A rotating speed of 1800 rpm and liquid flow rates of 0.5 L/min were used. The mean size of Fe_3O_4 nanoparticles obtained declined as the temperature was increased. The smallest Fe_3O_4 nanoparticles (5.7 nm in diameter, as determined by TEM) were obtained at 60 °C. Fe_3O_4 nanoparticles prepared at all temperatures were superparamagnetic. The saturation magnetizations of Fe_3O_4 nanoparticles that were prepared at 25 °C, 40 °C, and 60 °C were 45, 50, and 50 emu/g, respectively.

1. Introduction

Recently, much attention has been paid to magnetic Fe_3O_4 nanoparticles, owing to their potential applications, including magnetic resonance imaging [1,2], drug delivery [1,2], bioseparation [1], hyperthermia [1,2], magnetofection [2], and catalytic degradation [3–5]. Medical applications require that Fe_3O_4 nanoparticles are superparamagnetic, smaller than 20 nm and with a narrow size distribution to ensure that they have uniform properties [6]. Therefore, the preparation of superparamagnetic Fe_3O_4 nanoparticles with a narrow size distribution has long been of scientific and technological interest. Among various methods of preparation [7], co-precipitation is regarded as the simplest, most efficient and most economic [1,7,8]. However, the conventional co-precipitation method has several drawbacks, such as difficulty of mass-production, wide distribution of sizes, and poor dispersion [9]. To overcome these drawbacks, some researchers have developed modified co-precipitation methods, including ultrasonic co-precipitation [5], interfacial co-precipitation [9], mechanochemical co-precipitation [10], microwave co-precipitation [11], and co-precipitation with rapid stirring [12]. These modified co-precipitation methods cannot produce Fe_3O_4 nanoparticles on a large scale. Therefore, the need to develop a novel method for the continuous preparation of Fe_3O_4 nanoparticles is urgent.

In our previous work, Fe_3O_4 nanoparticles were continuously prepared using the rotating packed bed (RPB). This process was the first to be published that can be utilized for the mass-production of Fe_3O_4 nanoparticles [13,14]. In the RPB, a high centrifugal acceleration effectively generates high-gravity conditions, which spread or split reactant solutions into tiny droplets and thin films. Therefore, uniform supersaturation and homogeneous nucleation occur, yielding relatively small particles with a narrow size distribution. Based on our results [13,14], the RPB can be utilized to prepare Fe_3O_4 nanoparticles with a mean diameter of 6.4 nm. However, those studies did not elucidate the effect of temperature on the size of Fe_3O_4 nanoparticles. Indeed, the effect of temperature on prepared Fe_3O_4 nanoparticles has rarely been investigated. The exact mechanism by which temperature influences the size of Fe_3O_4 nanoparticles that are prepared by a co-precipitation method in the RPB must be examined to develop the RPB for use on an industrial scale. Therefore, this study elucidates the effect of temperature on the size and magnetic properties of Fe_3O_4 nanoparticles that are prepared by a co-precipitation method in the RPB.

2. Experimental

2.1. Chemicals

$FeCl_3 \cdot 6H_2O$ (98.0%) was purchased from Sigma-Aldrich. $FeCl_2 \cdot 4H_2O$ (98.0%) was supplied by Alfa-Aesar. NaOH (99.0%) was obtained from Mallinckrodt. All reagents were used without further purification. All stock and working solutions were prepared in deionized water with a resistivity of 18.2 MΩ·cm, obtained using a Direct-Q 3 UV-R Tap to Pure & Ultrapure water purification system (Merck Millipore).

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2.2. Preparation of Fe_3O_4 nanoparticles

The RPB was utilized to prepare Fe_3O_4 nanoparticles by a co-precipitation method using the following equation:

$$Fe^{2+} + 2Fe^{3+} + 8OH^- \rightarrow Fe_3O_4 + 4H_2O. \tag{1}$$

Fig. 1 schematically depicts the experimental setup for the preparation of Fe_3O_4 nanoparticles in the RPB according to the above chemical reaction. The packing in the RPB had an inner radius of 2.1 cm, an outer radius of 3.9 cm, and an axial height of 2.2 cm. Therefore, the depth (radial length) of the packing was 1.8 cm, and its total volume was 75 cm^3. The packing was stainless steel wire mesh, which comprised interconnected filaments with a mean diameter of 0.22 mm. The packing had a specific surface area of 790 m^2/m^3 and a voidage of 0.95.

A typical preparation procedure was followed: $FeCl_3 \cdot 6H_2O$ and $FeCl_2 \cdot 4H_2O$ were the initial reactants, and NaOH was the precipitant. NaOH (17.76 g) was dissolved in 2 L of deionized water that did not contain dissolved oxygen. Tank A contained this as-prepared solution whose pH value depended on temperature, as shown in Table 1. $FeCl_2 \cdot 4H_2O$ (7.55 g) and $FeCl_3 \cdot 6H_2O$ (20 g) were dissolved in 2 L of deionized water that did not contain dissolved oxygen. This solution, whose pH value depended on temperature, as shown in Table 1, was then placed in tank B. Solutions from both tanks A and B at the desired temperature were pumped into the packing through the liquid distributors at flow rates of 0.5 L/min, which were maintained using flowmeters. The liquid distributors consisted of two tubes with a diameter of 0.5 cm and a length of 11 cm, as shown in Fig. 2. They were set up parallel to each other and 2 cm apart, and parallel to the inner edge of the packing at a distance of 0.5 cm. Each tube had four 0.1-cm diameter holes with 0.2 cm interval nearby the end. The rotational speed of the RPB was fixed at 1800 rpm. To reduce the oxygen content in the RPB, gaseous nitrogen was made to flow through a heat exchanger, and then moved at a desired temperature from the exterior of the RPB toward the interior of the RPB.

The subsequent suspension that contained the product, Fe_3O_4, which was formed in the rapid co-precipitation reaction (Eq. (1)) in the RPB, was expelled into the collection tank at 4 °C. The pH value of the resulting Fe_3O_4 suspension declined as the temperature was increased, as presented in Table 1, revealing that the pH values at all temperatures exceeded 11. The suspension was centrifuged at 3500 rpm for 30 min to purify the product. The precipitate was rinsed with deionized water and ethanol. This purification process was repeated until the pH value of the filtrate was 7. Then, these wet particles were dried at 60 °C for 12 h in a vacuum. Finally, black Fe_3O_4 nanoparticles were obtained by milling the dry particles using a ceramic mortar. The as-obtained Fe_3O_4 nanoparticles were stored in sealed vials.

Table 1
pH values of reactants, precipitant, and Fe_3O_4 suspension.

Temperature (°C)	Reactants and precipitant				Fe_3O_4 suspension	
	T (°C)		pH		T (°C)	pH
	Fe^{+2}/Fe^{+3}	NaOH	Fe^{+2}/Fe^{+3}	NaOH		
25	25.6	22.3	2.0	12.7	26.0	12.0
40	40.0	40.0	1.9	12.3	40.0	11.6
60	60.2	59.8	1.5	11.8	60.2	11.3

2.3. Characterization of Fe_3O_4 nanoparticles

The crystalline structure of Fe_3O_4 nanoparticles was verified using an X-ray diffractometer (XRD, Siemens, D5005) with Cu K_α radiation and a scanning speed of 4°/min. The shape and size distribution of Fe_3O_4 nanoparticles were determined using a transmission electron microscope (TEM, JEOL, JEM-1200 EXII). The saturation magnetization of Fe_3O_4 nanoparticles was analyzed at 25 °C using a superconducting quantum interference device (SQUID, Quantum Design, MPMS7).

3. Results and discussion

The effect of temperature on the size of Fe_3O_4 nanoparticles was studied. The crystalline structure of Fe_3O_4 nanoparticles was determined by XRD analysis. As displayed in Fig. 3, the XRD peaks from Fe_3O_4 nanoparticles that were prepared at all temperatures were sharp and distinct, revealing excellent crystallinity and homogeneity. In Fig. 3, the reflection peaks at 30.1°, 35.4°, 43.1°, 53.4°, 57.0°, and 62.6° were assigned to the characteristic peaks in the standard pattern of magnetite Fe_3O_4 (JCPDS 11-0614), so all peaks from Fe_3O_4 nanoparticles that were prepared at all temperatures were consistent with pure Fe_3O_4. The results herein also establish the feasibility of preparing Fe_3O_4 nanoparticles by a co-precipitation method in the RPB at any of the temperatures used herein.

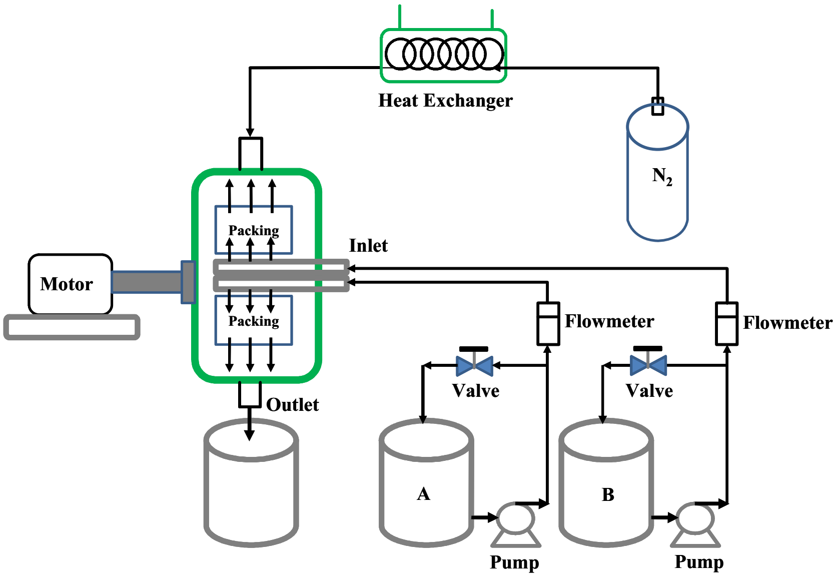

Fig. 1. Experimental setup for preparing Fe_3O_4 nanoparticles in RPB.