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SYNTHESIS AND CHARACTERIZATION OF NANOSCALE FE$_3$O$_4$ BY IN SITU SONOCHEMICAL ASSISTED CHEMICAL CO-PRECIPITATION

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Abstract. The research of Fe_3O_4 nanoparticles using sonochemical-assisted chemical co-precipitation has been carried out. Synthesis had precursors ferric and ferrous at room temperature is the highlight for this research . The study aimed to improve the conventional co-precipitation method with the help of ultrasound technology. It reached the formation of small spherical and reduction of particle agglomeration by using sonochemical assisted chemical co-precipitation. This nanoparticle was characterized using X-ray Diffraction (XRD) and Fourier Transform Infrared Spectroscopy (FTIR). The magnetic nanoscale synthesized by sonochemical-assisted chemical coprecipitation, sonicated at 800 W 20 kHz for 30 min, had small spherical nanoparticles whose size range was 8 nm. And, the sample synthesized by conventional co-precipitation was 12 nm.

INTRODUCTION

Forms of iron oxide in nature include magnetite (Fe_3O_4), maghemite (g-Fe_2O_3), and hematite (a-Fe_2O_3). Magnetite is known as black iron oxide, with the most potent magnet properties[1]. Its characteristics are easy to prepare[2,3,4,5,6], non-toxic[7], biocompatible[8], superparamagnetic[9] at the nanoscale, and so forth. Magnetite (Fe_3O_4) is an exciting study material because of its vast application opportunities, especially in the industrial sector[10]. Nanotechnology is growing because the material properties, including physical, chemical, and biological, will change when the dimensions of the material become nanometer scale. The magnetic nanoparticles in their formation can be 1 nm to 300 nm[11].

The co-precipitation method is probably the simplest and most effective method of synthesizing magnetic particles. In Fe_3O_4 synthesis, co-precipitation below 60°C will form amorphous Fe_2O_3[12], and the pH that will form Fe_3O_4 is the addition of alkaline conditions[13]. Coprecipitation can be carried out at temperature and reaction times that are relatively short compared to thermal and hydrothermal decomposition. Researchers use many methods to obtain Fe_3O_4 nanoscale. Recently, ultrasonic waves during the synthesis process have attracted significant attention because the process is cheap and simple and can control particle size[14].

It is known that small size, good dispersion, and solid magnetic response are needed in industrial applications of Fe_3O_4 nanoparticles. So it is essential to prepare Fe_3O_4 nanoparticles with nanoscale and good distribution as a catalyst to form more minor compounds. In this work, we studied sonochemical-assisted chemical co-precipitation for the synthesis of Fe_3O_4 nanoparticles. The effect of ultrasonic waves on the crystal structure, morphology, size distribution of Fe_3O_4 was reported in detail.

EXPERIMENTAL

The chemical reagents used in this study were $FeCl_2.4H_2O$, $FeCl_3.6H_2O$, NaOH 3 M, and deionized water. All of the reagents were used without further purification. The Fe_3O_4 magnetic nanoparticles were prepared by conventional coprecipitation and sonochemical-assisted chemical co-precipitation. The schematic flow chart showed precursor preparation, method synthesis (Figure 1 and 2), and post-treatment of nanoparticles. At first, deionized water was heated at 75°C. A solution of 4 g of $FeCl_3.6H_2O$ and 8 g of $FeCl_2.4H_2O$ were added into 60 mL of deionized water. Then the mixture got a sonochemical treatment for 30 min. Next, aqueous solution NaOH 3 M was added into the solution mentioned above dropwise under constant mechanical stirring until it reached the final pH of 11[15]. The precipitate was stirred at 80°C for one hour and cooled at room temperature. As described in Figure 3, during

this process, the temperature and pH were kept constant at 80°C and 7, respectively. The precipitate was filtered and washed three times with deionized water. The Fe_3O_4 nanoparticles were dried at 60°C in a vacuum for six hours. The magnetic nanoparticles were black precipitates, which can be separated from the solution using a permanent magnet.

NANOPARTICLE CHARACTERIZATION TECHNIQUES

X-ray diffraction (XRD) analysis was performed using a Bruker D2 phaser with a Cu Ka radiation source (0.154056 nm). The crystallography of samples was investigated at a scanning angle (2q) of 5 - 80°. The phase identification was made with comparison to Joint Committee on Powder Diffractions Standards (JCPDSs). Surface functional groups of the nanoparticles were investigated using Fourier Transform Infrared Spectroscopy (FTIR, Nicolet Avatar 360 IR) in the range of 500 – 4000 cm^{-1} wave number.

FIGURE 1. Conventional co-precipitation synthesis of Fe_3O_4 nanoparticle
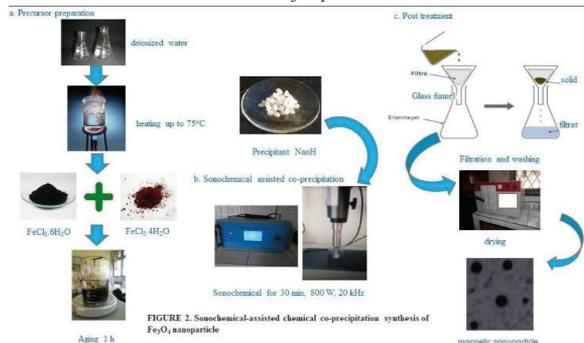
FIGURE 2. Sonochemical-Assisted Chemical Co-Precipitation Synthesis of Fe_3O_4 Nanoparticles

FIGURE 3. Experimental Setup for Sonochemical Co-Precipitation Synthesis of Fe_3O_4 Nanoparticles

RESULTS AND DISCUSSIONS

XRD and FTIR analyzed the sonochemical precipitated magnetic nanoparticle to identify their physicochemical properties. The nanoparticle fabricated by conventional co-precipitation and sonochemical assisted chemical coprecipitation were characterized to investigate their structural and physicochemical properties. For this purpose, the crystallography morphology and particle size analysis, functional group dictation.
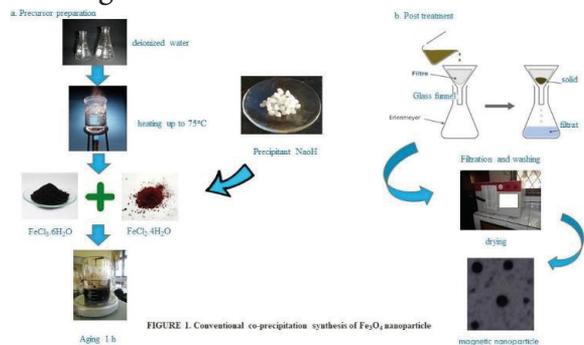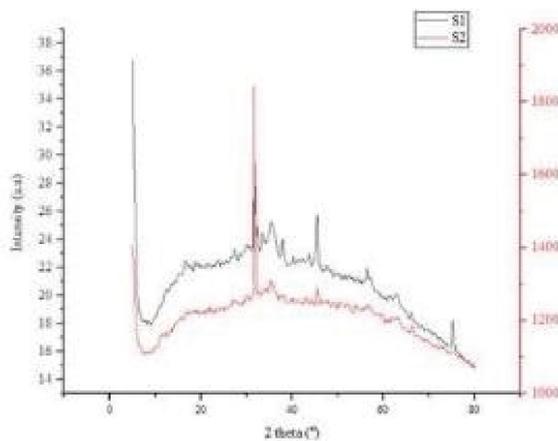

FIGURE 4. XRD pattern of sonochemical assisted co-precipitation (S1) and conventional co-precipitation (S2) magnetite nanoparticles

The XRD patterns of powders of sonochemical assisted co-precipitation (S1) and conventional co-precipitation (S2) magnetite nanoparticles are shown in figure

4. The product has an orthorhombic crystal related to JCPDS 210-7249[16]. Using the Scherrer formula can estimate the average size of crystals of nanoparticles. It was found that S1 crystal size is smaller than S2. The crystallize size is estimated at 8 nm (S1) and 12 nm (S2). The sample S2, synthesized by conventional co-precipitation, has sharper diffraction peaks and higher crystallinity than another sample.

Diffraction peaks became broader and gradually disappeared as the ultrasonic irradiation power increased. This treatment is because of the role of sonication to prevent the growth of the crystals after nucleation. Fast kinetics of formation and collapse of the bubbles postponed the increase of the crystallites[17]. The power of ultrasound irradiation would produce smaller crystals in the sonochemical co-precipitation. It is expected that sonochemical-assisted coprecipitation can synthesize smaller crystals and have a good performance.
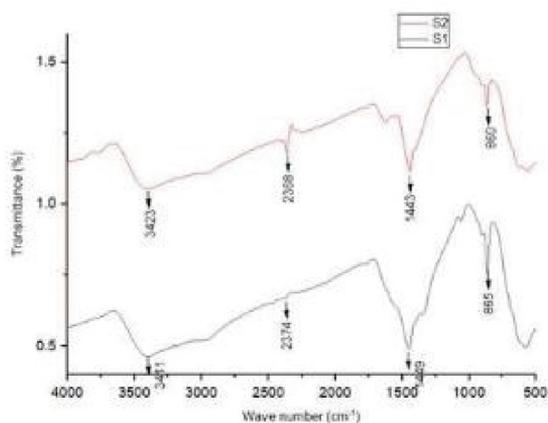

FIGURE 5. FTIR Spectra of sonochemical assisted co-precipitation (S1) and conventional co-precipitation (S2) magnetite nanoparticles

Figure 5 indicates the FTIR spectrum for sonochemical assisted co-precipitation (S1) and conventional co-precipitation (S2) magnetite nanoparticles in the wavenumber range of 500 – 4000 cm^{-1}. There are slight differences between FTIR spectrums of all samples, so it can be concluded that ultrasound irradiation has no effect on functional groups on the surface. Generally, the peaks in the range of 500 – 900 cm^{-1} are related to metal oxide bonds. The Small peaks in the range of 1000 – 3000 cm^{-1} can be allocated to the adsorption of CO_2 and H_2O from the environment or water in the structure of the catalyst. The characteristic peak is also showed stretching vibration and bending vibration of C-H in – CH_2. The peak led the absorption band of O-H groups from the absorbed H_2O into materials. The peaks that appeared at 3000 – 3500 cm^{-1} indicate the bending vibrations of O-H.

The valence of the iron salt used in the synthesis appears to play an essential role in determining the size of the Fe_3O_4 nanoparticle. In this case, synthesis with solution ferrous and ferric, a black iron was formed. Ultrasound irradiation generates many local hot spots within the solution. The desirable local area is beneficial to the rapid loss of organic residue and water. This further causes the formation of many seed nuclei, which leads to smaller grain size. Compared to conventional technology, sonochemical-assisted co-precipitation has proven to stimulate the speed of the reaction in liquid. The experiments showed the iron solution was amorphous in the absence of sonication. Thus, high-intensity ultrasound can accelerate the crystallization of Fe_3O_4 nanoparticles.

CONCLUSION

Fe_3O_4 nanoparticles from the material used in this study were successfully synthesized using sonochemical-assisted chemical co-precipitation at room temperature. The size and quality of Fe_3O_4 crystals are strongly influenced by the ultrasonic frequency and stirring time.

From the XRD results, it can be concluded that the ultrasonic frequency (99%, 800 W) and stirring time (30 min) are optimal parameters for the synthesis of Fe_3O_4. The particle size requires to achieve superparamagnetism in Fe_3O_4 nanoparticles is widely estimated to be below 20 nm[18]. From the morphology and structure characterized by XRD and FTIR, the Fe_3O_4 nanoparticle showed an excellent magnetic property. It could be added to other materials for photocatalyst, separation, purification process, and bio-sensing[19].

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