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Synthesis and characterization of Fe₃O₄ nanoparticles by electrodeposition and reduction methods

Nurrulhidayah Salamun¹, How Xin Ni¹, Sugeng Triwahyono^{1*}, Aishah Abdul Jalil², Ainul Hakimah Karim¹

¹Ibnu Sina Institute, Faculty of Science, Universiti Teknologi Malaysia, 81310 UTM Johor Bahru, Johor, Malaysia.

²Department of Chemical Eng., Faculty of Chemical Eng., Universiti Teknologi Malaysia, 81310 UTM Johor Bahru, Johor, Malaysia.

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ABSTRACT

Magnetite (Fe₃O₄) nanoparticles have been studied extensively due to their good magnetic, optic and electric properties which offer a great potential of applications in many field especially in removal of heavy metals such as the adsorption of poisonous Cr(VI) ion in water. In addition, Fe₃O₄ is the only material that has up to now been use in human because it is the only material which is known to be biocompatible, without relevant toxicity in the applied dosage. In this study Fe₃O₄ nanoparticles were prepared by reduction of ferric oxide (Fe₂O₃) precursor at 598 K for 10, 20, 30 and 40 min. While, ferric oxide (Fe₂O₃) precursor was prepared by electrodeposition of iron plate in the *N,N*-dimethylformamide solvent and tetraethylammonium perchlorate and naphthalene as mediators at 263 K. Reduction of Fe₂O₃ was carried out with an isothermal heating at 598 K under hydrogen atmosphere. Fe₂O₃ and Fe₃O₄ were characterized with XRD, BET Surface area, FTIR, FESEM-EDX and TEM. The surface area of both Fe₂O₃ and Fe₃O₄ was 38 - 45 m²/g with the average particle size was 40 - 60 nm. The XRD result showed that the crystallinity of Fe₃O₄ increased with reduction time. The activity of Fe₂O₃ and Fe₃O₄ nanoparticles were tested on the adsorption of chromium (VI) at room temperature in which 30-40 % of Cr(VI) ion was adsorbed on the Fe₂O₃ and Fe₃O₄ nanoparticles.

| Fe₂O₃ | Fe₃O₄ | Nanoparticles | Electrodeposition | Reduction | Cr(VI) adsorption |

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1. INTRODUCTION

In recent years, nanotechnology is shaping the world atom by atom. 'Nano' comes from the Greek word which means 'Dwarf'. A nanoparticle (or nanopowder or nanocluster or nanocrystal) is a microscopic particle with at least one dimension less than 100 nm that exhibit new or enhanced size-dependent properties compared with larger particles of the same material.

Magnetic (Fe₃O₄) nanoparticles due to their size, exhibit electrical, chemical, magnetic and optical properties different from those presented in bulk size. These particles show superior properties than traditional micrometer sized particles. Fe₃O₄ is a common magnetic iron oxide that has a cubic inverse spinel structure with oxygen forming a face-centered cubic (fcc) closed packing and Fe cations occupying interstitial tetrahedral sites and octahedral sites [1,2]. The electrons can hop between Fe²⁺ and Fe³⁺ ions in the octahedral sites at room temperature, rendering magnetite an important class of half-metallic materials. Fe₃O₄ nanoparticle is widely used in electrical-electronic devices such as pigments magnetite carrier passivation coatings, recording materials, ferrofluid technology and magnetocaloric refrigeration.

Whereas for medical application, Fe₃O₄ nanoparticles are used for biomolecule separation, drug delivery agents, DNA detection, magnetic resonance imaging (MRI), biolabeling, and contrast agents for NMR imaging. In chemical industry, Fe₃O₄ nanoparticles are used for absorbent, catalysis, photocatalysis and metal separation from wastewater [1,3,4].

Various preparation methods of magnetite nanoparticles including sonochemical, co-precipitation sol-gel or hydrolysis [1,3,5], microwave hydrothermal method, thermal decomposition of organic metals, microemulsion method, electrochemical synthesis, pyrolysis, impregnation, a special precipitation technique (Massart's process) and mechanical crushing of powder have been developed [5-8]. Most of the methods have some problems so that only a few of them could be used in mass production. Moreover producing magnetite particles with the desired size and acceptable size distribution has consistently been a problem. The characteristics of the formed particles are greatly affected by the synthesis parameters. For example, they involve difficulties in preventing flocculation and controlling proportion of Fe²⁺ and Fe³⁺ in co-precipitation, and in the removal of surfactants in micro-emulsion [9,10].

In this study, the direct synthesis of magnetite nanoparticles by electrodeposition and reduction methods focused to form magnetite nanoparticles with the average size particle between 20 to 100 nm which has ferromagnetic

Corresponding author at: Ibnu Sina Institute, Faculty of Science, Universiti Teknologi Malaysia, 81310 UTM Johor Bahru, Johor, Malaysia
E-mail addresses: sugengtw@ibnusina.utm.my (S. Triwahyono)

behavior at room temperature. The nanoparticles then was characterized by XRD, BET surface area, FTIR, FESEM-EDX and TEM. The activity of Fe_2O_3 and Fe_3O_4 nanoparticle was tested on batch type of Cr(VI) ion adsorption at room temperature.

2. EXPERIMENTAL

2.1 Synthesis of Fe_2O_3 Nanoparticles

Electrodeposition involves passing an electric current through an electrolyte; the result is a movement of charged ions from one electrode to the other. In this process, platinum plate acts as cathode and iron plate acts as anode, Fig. 1. The electrolyte consisted of N,N-dimethylformamide, naphthalene and tetraethylammonium perchlorate. Constant current of 1.35 A at 263 K was applied and electrodeposition was being carried out until the saturated condition. At the end of the electrodeposition, the black solution was purified by centrifugation at 20,000 rpm for 120 minutes. After that, the product was dried at 383 K overnight in air to eliminate the water content. Then, the product was calcined at 823 K for 3 hours to obtain Fe_2O_3 nanoparticle

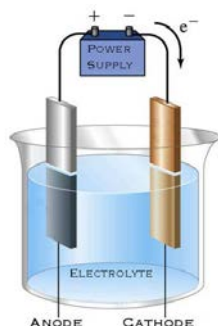
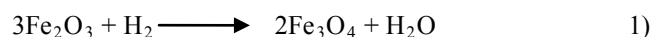


Fig. 1 Schematic diagram of electrodeposition apparatus.

2.2 Synthesis of Fe_3O_4 Nanoparticles

Magnetite (Fe_3O_4) nanoparticles was prepared by reduction of Fe_2O_3 nanoparticles. Fe_2O_3 precursor was placed in a glass tube reactor which connected to hydrogen gas (993.999%) line. Isothermal heating (598 K) was applied with 100 ml/min hydrogen gas stream to provide a uniform and consistent heat to the sample. Four different reduction times (10, 20, 30 and 40 min) were chosen to investigate the effect on the crystallinity, surface area and magnetic properties of Fe_3O_4 nanoparticles. The reaction proceeds to form Fe_3O_4 according to the Eq. (1),



2.3 Characterization of Fe_2O_3 and Fe_3O_4 Nanoparticles

Fe_2O_3 and Fe_3O_4 nanoparticles were characterized with X-ray diffraction (XRD), BET Surface area, Field Emission Scanning Electron Microscope (FESEM), Energy Dispersive X-Ray Spectroscopy (EDX), Fourier Transform Infrared Spectrometry (FTIR) and Transmission Electron Microscope (TEM).

2.4 Adsorption of Cr(VI)

Adsorption of Cr(VI) ion in simulated water over Fe_2O_3 and Fe_3O_4 nanoparticles was carried out in a batch reactor at room temperature and pH 2 with the initial concentration of Cr(VI) ion was 10 mg L^{-1} and mass dosage of nanoparticles was 0.4 g. The data was taken after 12 h of adsorption (equilibrium condition). The Cr(VI) ion content was detected with AAS Spectrometer.

3. RESULTS & DISCUSSION

Fig. 2 shows the XRD pattern of Fe_2O_3 which the peaks were observed at $2\theta = 24, 33, 36, 49, 54, 62$ and 64° . These peaks correspond to syn-hematite (Ref: 80-2377-XRD Bruker D8 Advance) which verified the presence of $\alpha\text{-Fe}_2\text{O}_3$. Whereas the Fig. 3 shows the XRD pattern of Fe_3O_4 which the diffraction peaks were observed at $2\theta = 18, 30, 35, 37, 43, 57$ and 62° . This XRD pattern matched with Ref: 86-1338 which indicated the presence of magnetite, Fe_3O_4 .

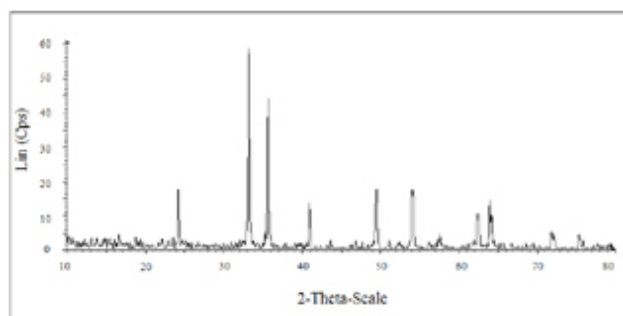


Fig. 2 XRD pattern of Fe_2O_3 .

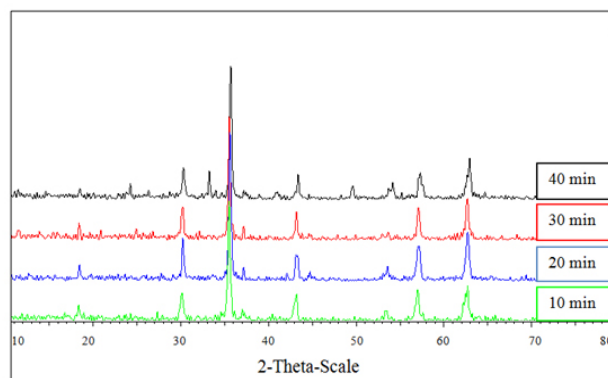


Fig. 3 XRD pattern of Fe_3O_4 at 598 K in 10-40 minutes.

The crystallinity of Fe_3O_4 nanoparticle increased slightly with the reduction time. However, the Fe_3O_4 nanoparticle reduced for 40 min showed small peaks corresponding to Fe_2O_3 at $2\theta = 33$ and 49° . This peak may be due to the incomplete conversion of Fe_2O_3 to Fe_3O_4 during the reduction of Fe_2O_3 .

The FTIR study was carried in order to identify the functional groups present in a sample. In this study, Fe-O vibration exists in 'fingerprint' region ($500\text{-}1400\text{ cm}^{-1}$). Although the FTIR spectra of samples were not shown here, the Fe-O peaks were observed at 570.70 , 576.19 , 559.73 and 569.74 cm^{-1} for Fe_3O_4 reduced at 598 K for 10, 20, 30 and 40 min respectively (Table 1). Increase in the reduction time also changed slightly the specific surface area and average particle size of Fe_3O_4 nanoparticles. The specific surface area increased to $45\text{ m}^2/\text{g}$ and based on the TEM results the average particle size decreased from 60 to 40 nm (Fig. 4). Whereas the FESEM images showed the agglomeration of nanoparticles which have an average 'agglomeration' size of 60 - 100 nm (Fig. 5).

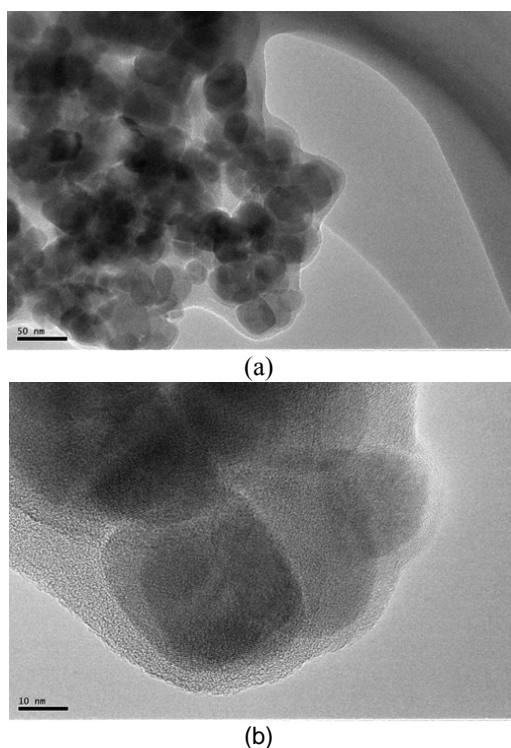


Fig.4 TEM images of Fe_3O_4 reduced at 598 K for 40 min. (a) agglomeration and (b) single particle.

Table 1 Surface area, average particle size and vibration of Fe-O fingerprint

Sample	Surface Area (m^2/g)	Average Particle Size (nm)	Fe-O vibration (cm^{-1})
Fe_2O_3	38	60	
Fe_3O_4 -10 min	39	50	570.70
Fe_3O_4 -20 min	40	50	576.19
Fe_3O_4 -30 min	45	40	559.73
Fe_3O_4 -40 min	39	55	567.96

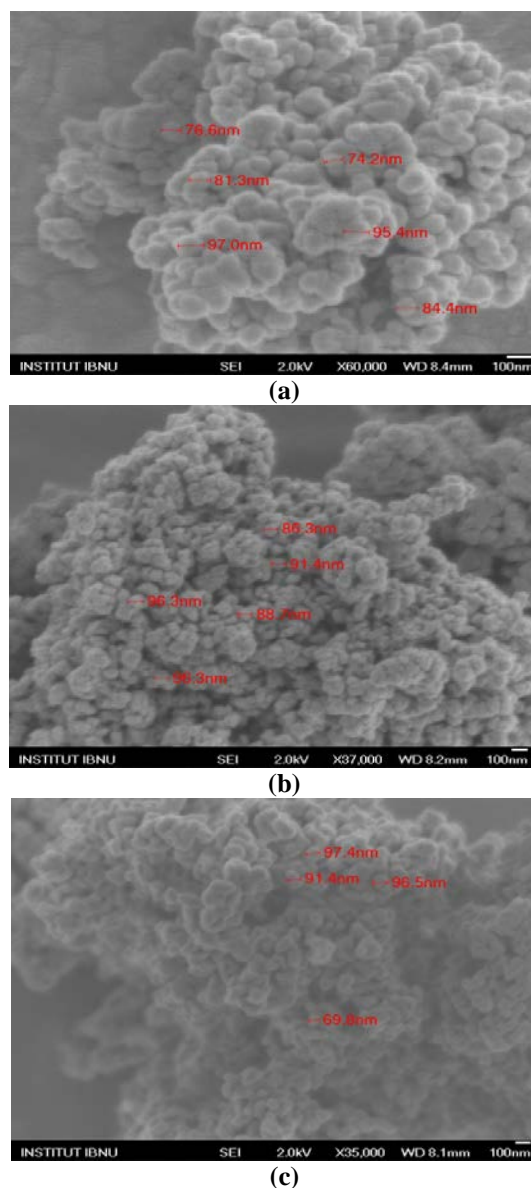


Fig. 5 FESEM micrographs of (a) Fe_2O_3 , (b) Fe_3O_4 (20 min) and (c) Fe_3O_4 (40 min).

Energy Dispersive X-Ray (EDX) results confirmed the present of elements and weight composition in Fe_2O_3 and Fe_3O_4 nanoparticles, Fig. 6. The results clearly showed that only Fe and O present on the sample to form both Fe_2O_3 and Fe_3O_4 nanoparticles.

Adsorption of Cr(VI) was carried out to observe the activity of Fe_2O_3 and Fe_3O_4 nanoparticles in which average particle size or magnetic properties may affect on the adsorption of Cr(VI). The result showed that Fe_2O_3 show a lowest adsorption capacity and increase in the reduction time increased the Cr(VI) adsorption capacity. The increase of the adsorption on Fe_3O_4 may be caused by the average particle size become smaller and/or the magnetic properties increase corresponding to the increase in the crystallinity of Fe_3O_4 .

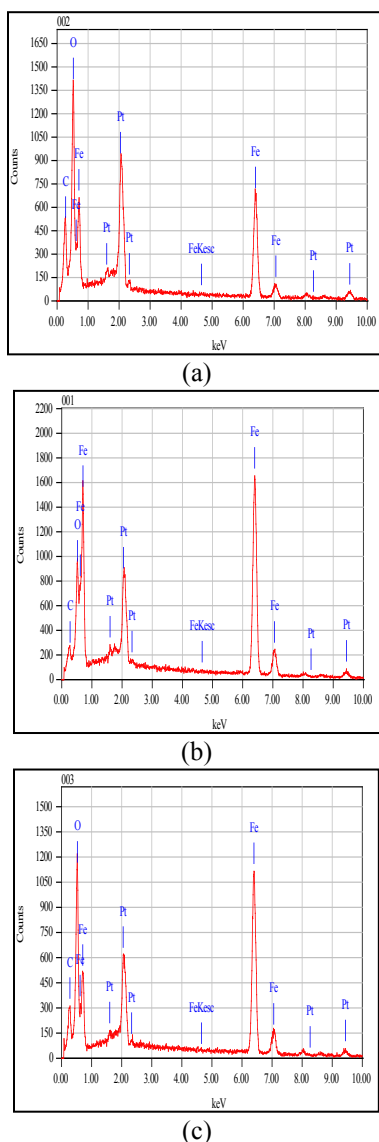


Fig. 6 EDX pattern of (a) Fe₂O₃, (b) Fe₃O₄ at 20 minutes and (c) Fe₃O₄ at 40

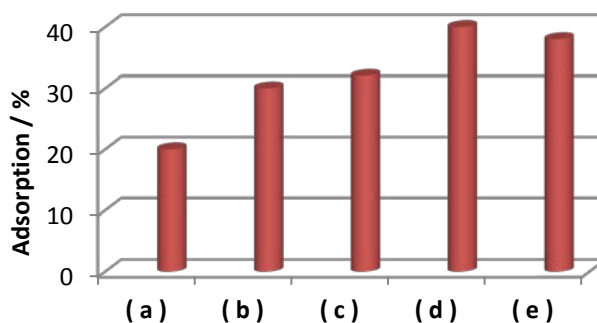


Fig. 7 Adsorption of Cr(VI) on (a) Fe₂O₃, (b) Fe₃O₄ (10 min), (c) Fe₃O₄ (20 min), (d) Fe₃O₄ (30 min) and (e) Fe₃O₄ (40 min).

4. CONCLUSION

Fe₃O₄ nanoparticle was synthesized successfully via electrodeposition and reduction methods. The average particle sizes were in the range of nanoparticles which lies in 40 - 60 nm with the specific surface area was 38 - 45 m²/g. The XRD, FTIR, FESEM-EDX results confirmed high purity of Fe₃O₄ nanoparticles. The activity of Fe₂O₃ and Fe₃O₄ nanoparticles were tested on the adsorption of chromium (VI) at room temperature in which 30 - 40 % of Cr(VI) was adsorbed on the Fe₂O₃ and Fe₃O₄ nanoparticles. Although it is not certain at present, the increase in the adsorption capacity may be caused by increase in surface area and/or magnetic properties of Fe₃O₄ nanoparticles.

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