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## Synthesis and characterization of Fe<sub>3</sub>O<sub>4</sub> nanoparticles by electrodeposition and reduction methods

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### ABSTRACT

Magnetite (Fe<sub>3</sub>O<sub>4</sub>) 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, Fe<sub>3</sub>O<sub>4</sub> 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 Fe<sub>3</sub>O<sub>4</sub> nanoparticles were prepared by reduction of ferric oxide (Fe<sub>2</sub>O<sub>3</sub>) precursor at 598 K for 10, 20, 30 and 40 min. While, ferric oxide (Fe<sub>2</sub>O<sub>3</sub>) 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 Fe<sub>2</sub>O<sub>3</sub> was carried out with an isothermal heating at 598 K under hydrogen atmosphere. Fe<sub>2</sub>O<sub>3</sub> and Fe<sub>3</sub>O<sub>4</sub> were characterized with XRD, BET Surface area, FTIR, FESEM-EDX and TEM. The surface area of both Fe<sub>2</sub>O<sub>3</sub> and Fe<sub>3</sub>O<sub>4</sub> was 38 - 45 m<sup>2</sup>/g with the average particle size was 40 - 60 nm. The XRD result showed that the crystallinity of Fe<sub>3</sub>O<sub>4</sub> increased with reduction time. The activity of Fe<sub>2</sub>O<sub>3</sub> and Fe<sub>3</sub>O<sub>4</sub> nanoparticles were tested on the adsorption of chromium (VI) at room temperature in which 30-40 % of Cr(VI) ion was adsorbed on the Fe<sub>2</sub>O<sub>3</sub> and Fe<sub>3</sub>O<sub>4</sub> nanoparticles.

| Fe<sub>2</sub>O<sub>3</sub> | Fe<sub>3</sub>O<sub>4</sub> | 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 (Fe<sub>3</sub>O<sub>4</sub>) 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. Fe<sub>3</sub>O<sub>4</sub> 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 Fe<sup>2+</sup> and Fe<sup>3+</sup> ions in the octahedral sites at room temperature, rendering magnetite an important class of half-metallic materials. Fe<sub>3</sub>O<sub>4</sub> 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, Fe<sub>3</sub>O<sub>4</sub> 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, Fe<sub>3</sub>O<sub>4</sub> 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 Fe<sup>2+</sup> and Fe<sup>3+</sup> 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

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behavior at room temperature. The nanoparticles then was characterized by XRD, BET surface area, FTIR, FESEM-EDX and TEM. The activity of  $\text{Fe}_2\text{O}_3$  and  $\text{Fe}_3\text{O}_4$  nanoparticle was tested on batch type of Cr(VI) ion adsorption at room temperature.

## 2. EXPERIMENTAL

### 2.1 Synthesis of $\text{Fe}_2\text{O}_3$ 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  $\text{Fe}_2\text{O}_3$  nanoparticle

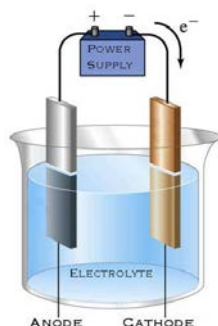
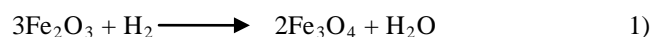


Fig. 1 Schematic diagram of electrodeposition apparatus.

### 2.2 Synthesis of $\text{Fe}_3\text{O}_4$ Nanoparticles

Magnetite ( $\text{Fe}_3\text{O}_4$ ) nanoparticles was prepared by reduction of  $\text{Fe}_2\text{O}_3$  nanoparticles.  $\text{Fe}_2\text{O}_3$  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  $\text{Fe}_3\text{O}_4$  nanoparticles. The reaction proceeds to form  $\text{Fe}_3\text{O}_4$  according to the Eq. (1),



### 2.3 Characterization of $\text{Fe}_2\text{O}_3$ and $\text{Fe}_3\text{O}_4$ Nanoparticles

$\text{Fe}_2\text{O}_3$  and  $\text{Fe}_3\text{O}_4$  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  $\text{Fe}_2\text{O}_3$  and  $\text{Fe}_3\text{O}_4$  nanoparticles was carried out in a batch reactor at room temperature and pH 2 with the initial concentration of Cr(VI) ion was  $10 \text{ mg L}^{-1}$  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  $\text{Fe}_2\text{O}_3$  which the peaks were observed at  $2\theta = 24, 33, 36, 49, 54, 62$  and  $64^\circ$ . 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  $\text{Fe}_3\text{O}_4$  which the diffraction peaks were observed at  $2\theta = 18, 30, 35, 37, 43, 57$  and  $62^\circ$ . This XRD pattern matched with Ref: 86-1338 which indicated the presence of magnetite,  $\text{Fe}_3\text{O}_4$ .

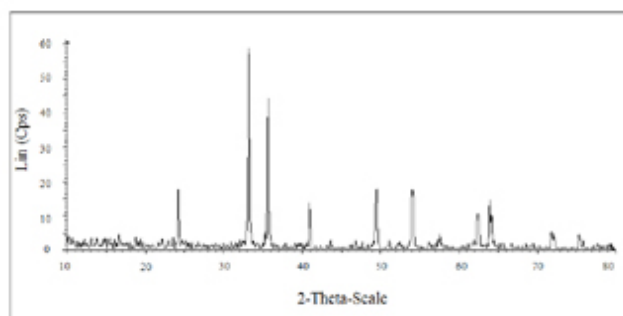


Fig. 2 XRD pattern of  $\text{Fe}_2\text{O}_3$ .

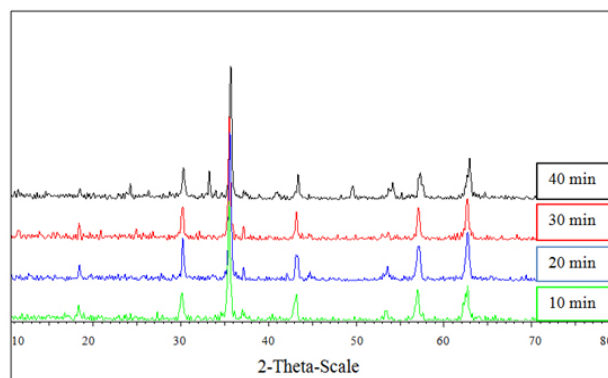


Fig. 3 XRD pattern of  $\text{Fe}_3\text{O}_4$  at 598 K in 10-40 minutes.

The crystallinity of  $\text{Fe}_3\text{O}_4$  nanoparticle increased slightly with the reduction time. However, the  $\text{Fe}_3\text{O}_4$  nanoparticle reduced for 40 min showed small peaks corresponding to  $\text{Fe}_2\text{O}_3$  at  $2\theta = 33$  and  $49^\circ$ . This peak may be due to the incomplete conversion of  $\text{Fe}_2\text{O}_3$  to  $\text{Fe}_3\text{O}_4$  during the reduction of  $\text{Fe}_2\text{O}_3$ .

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  $569.74\text{ cm}^{-1}$  for  $\text{Fe}_3\text{O}_4$  reduced at  $598\text{ K}$  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  $\text{Fe}_3\text{O}_4$  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).

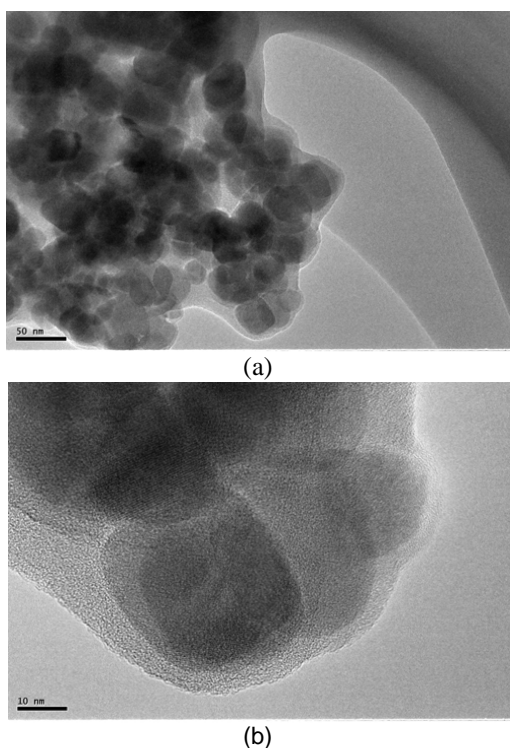


Fig.4 TEM images of  $\text{Fe}_3\text{O}_4$  reduced at  $598\text{ K}$  for 40 min. (a) agglomeration and (b) single particle.

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

Sample	Surface Area ( $\text{m}^2/\text{g}$ )	Average Particle Size (nm)	Fe-O vibration ( $\text{cm}^{-1}$ )
$\text{Fe}_2\text{O}_3$	38	60	
$\text{Fe}_3\text{O}_4$ -10 min	39	50	570.70
$\text{Fe}_3\text{O}_4$ -20 min	40	50	576.19
$\text{Fe}_3\text{O}_4$ -30 min	45	40	559.73
$\text{Fe}_3\text{O}_4$ -40 min	39	55	567.96

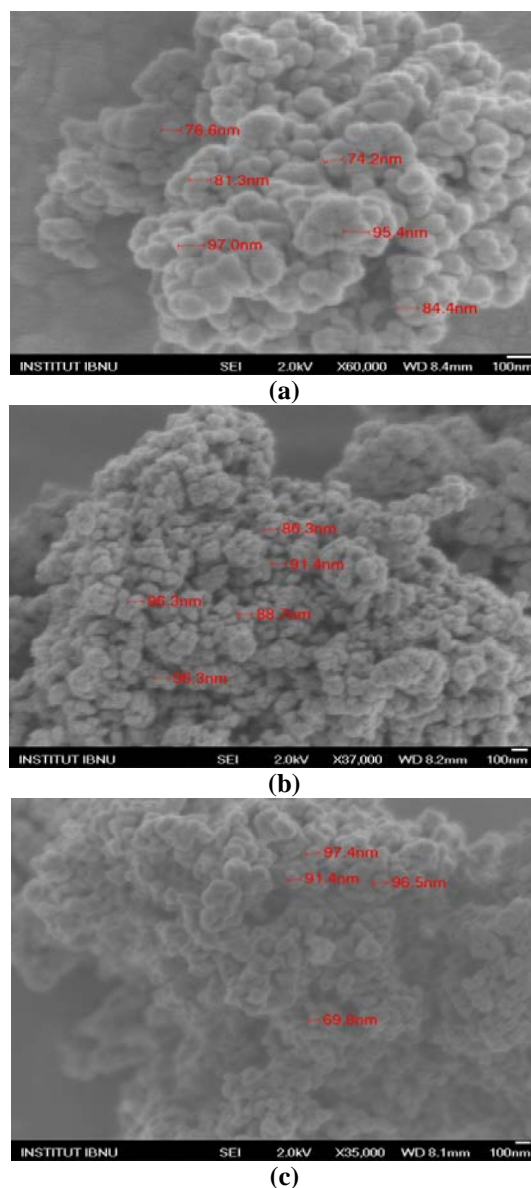


Fig. 5 FESEM micrographs of (a)  $\text{Fe}_2\text{O}_3$ , (b)  $\text{Fe}_3\text{O}_4$  (20 min) and (c)  $\text{Fe}_3\text{O}_4$  (40 min).

Energy Dispersive X-Ray (EDX) results confirmed the present of elements and weight composition in  $\text{Fe}_2\text{O}_3$  and  $\text{Fe}_3\text{O}_4$  nanoparticles, Fig. 6. The results clearly showed that only Fe and O present on the sample to form both  $\text{Fe}_2\text{O}_3$  and  $\text{Fe}_3\text{O}_4$  nanoparticles.

Adsorption of Cr(VI) was carried out to observe the activity of  $\text{Fe}_2\text{O}_3$  and  $\text{Fe}_3\text{O}_4$  nanoparticles in which average particle size or magnetic properties may affect on the adsorption of Cr(VI). The result showed that  $\text{Fe}_2\text{O}_3$  show a lowest adsorption capacity and increase in the reduction time increased the Cr(VI) adsorption capacity. The increase of the adsorption on  $\text{Fe}_3\text{O}_4$  may be caused by the average particle size become smaller and/or the magnetic properties increase corresponding to the increase in the crystallinity of  $\text{Fe}_3\text{O}_4$ .

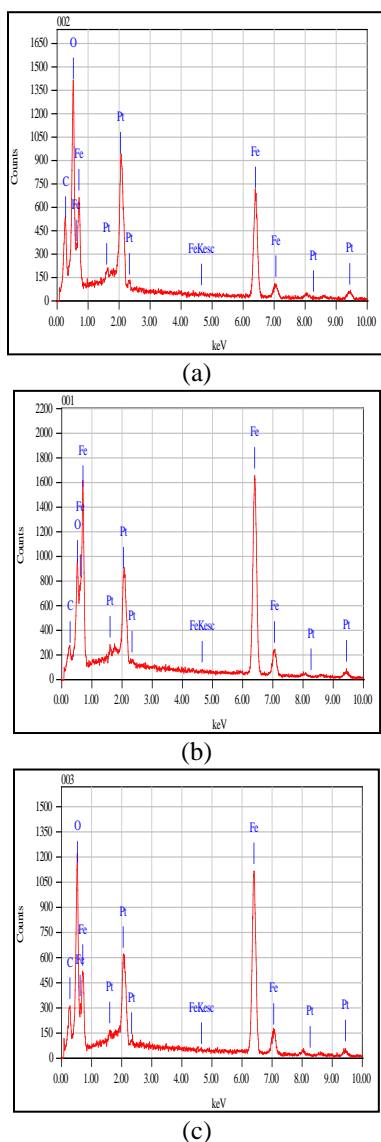


Fig. 6 EDX pattern of (a) Fe<sub>2</sub>O<sub>3</sub>, (b) Fe<sub>3</sub>O<sub>4</sub> at 20 minutes and (c) Fe<sub>3</sub>O<sub>4</sub> at 40

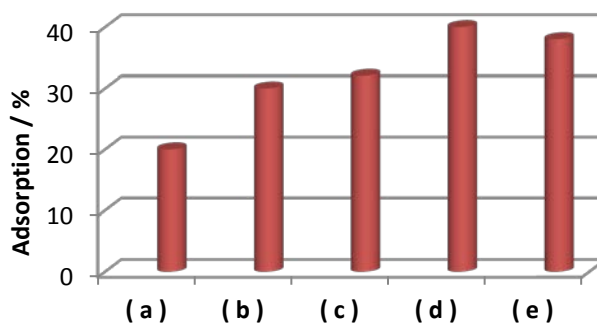


Fig. 7 Adsorption of Cr(VI) on (a) Fe<sub>2</sub>O<sub>3</sub>, (b) Fe<sub>3</sub>O<sub>4</sub> (10 min), (c) Fe<sub>3</sub>O<sub>4</sub> (20 min), (d) Fe<sub>3</sub>O<sub>4</sub> (30 min) and (e) Fe<sub>3</sub>O<sub>4</sub> (40 min).

#### 4. CONCLUSION

Fe<sub>3</sub>O<sub>4</sub> 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 m<sup>2</sup>/g. The XRD, FTIR, FESEM-EDX results confirmed high purity of Fe<sub>3</sub>O<sub>4</sub> nanoparticles. The activity of Fe<sub>2</sub>O<sub>3</sub> and Fe<sub>3</sub>O<sub>4</sub> nanoparticles were tested on the adsorption of chromium (VI) at room temperature in which 30 - 40 % of Cr(VI) was adsorbed on the Fe<sub>2</sub>O<sub>3</sub> and Fe<sub>3</sub>O<sub>4</sub> 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 Fe<sub>3</sub>O<sub>4</sub> nanoparticles.

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