Synthesis and Properties of Fe_3O_4 Nanoparticles by Co-precipitation Method to Removal Procion Dye

Poedji Loekitowati Hariani, Muhammad Faizal, Ridwan, Marsi, and Dedi Setiabudidaya

***Abstract*—Fe_3O_4 (magnetite) nanoparticles were synthesized by chemical co-precipitation method. The structure, morphology and magnetic properties of as-prepared were characterized by X Ray Diffraction (XRD), Scanning Electron Microscope-Energy Dispersive X Ray Spectrometry (SEM-EDS), Transmission Electron Microscope (TEM) and Vibrating Sample Magnetometer (VSM). The result of XRD characterization was indicated Fe_3O_4 as the product. SEM and TEM image of the Fe_3O_4 showed nanoparticles Fe_3O_4 have the mean diameter 5-20 nm. The EDS spectra showed strong peaks of Fe and O. Magnetic characteristic of Fe_3O_4 nanoparticles was indicated super paramagnetic properties. The saturation magnetic was 89.46 emu g^{-1}. Therefore, the nanoparticles Fe_3O_4 is suitable to remove dye in the water by a simple magnetic separation process. The optimum adsorption occurred at initial concentration of procion dye 100 mg L^{-1}, pH solution 6, dosage of Fe_3O_4 0.8 g L^{-1} and contact time 30 minutes under room temperature with color removal 24.40 % and adsorption capacity was 30.503 mg g^{-1}.**

***Index Terms*—Fe_3O_4 nanoparticles, co-precipitation, adsorption, dye**

I. Introduction

The magnetic nanoparticles have many uses such as magnetic drug target, magnetic resonance imaging forclinical diagnosis, recording material and catalyst, environment, etc [1]-[3]. Iron oxides nanoparticles play a major role in many areas of chemistry, physics and materials science. Fe_3O_4 (magnetite) is one of the magnetic nanoparticles. There are many various ways to prepare Fe_3O_4 nanoparticles, which have been reported in other papers, such as energy milling [3], reducing [4], ultrasonic assisted impregnation [5], and using Tridax procumbens leaf extract [6]. Co-precipitation method is a method of synthesis of Fe_3O_4 which is easy to do with the success rate from 96 to 99.9% [7]. In this method, ferrous and ferric ions at the ratio of 1 to 2 in alkaline medium. Chemical co-precipitation can produced fine, stoichiometry particles of single and multi component metal oxides [8].

The application of magnetic technology to solve environmental problems has received considerable attention in recent years. Many of papers have been published demonstrating that magnetic Fe_3O_4 can be used for wastewater purification, such as to adsorb arsenite, arsenate, crom, cadmium, nickel [9],[10]. Fe_3O_4 also can be used to alkalinity and hardness removal, desalination, decolorisation of pulp mill effluent and removal of natural organic compounds [3]. After adsorption, Fe_3O_4 can be separated from the medium by a simple magnetic process. Thus, an efficient, economic, scalable, and non toxic. Synthesis of Fe_3O_4 nanoparticles is highly preferred for potential application and fundamental research [11],[12].

In current study, Fe_3O_4 will be used to adsorb dye. Removal of dyes from wastewater is a major environmental problem because dyes are visible even at low concentration. The existence of highly colored waste is not only aesthetically disturbance, but it also impedes light penetration, thus up setting biological process within a stream, some dyes also being toxic or carcinogenic [13]. It is estimated that 10-50 % of the dye is lost in the effluent [14]. Therefore, the treatment of effluent containing such a dye is a interest due to its harmful impacts on receiving waters [15].

The objective of this study were to synthesis Fe_3O_4 by co-precipitation methods and assess the ability of Fe_3O_4 to remove procion dye. The procion dye including azo dyes which have -N=N- bond. Additionally procion dyes have two of aromatic group and one atom sodium. These dye are used in the textile industrial for dyeing process. Various techniques for removing dyes from effluents have been developed, including electrochemical treatment, sonochemical treatment, photo catalytic oxidation and adsorption. Adsorption method is a promising and attractive alternative for treatment of azo containing effluents if adsorbents used are inexpensive and readily available [12], [14], [15].

II. Material and Methods

A. Materials

All the reagents used for the synthesis Fe_3O_4 were analytical grade and used without further purification. Ferric chloride [$FeCl_3$], ferrous chloride [$FeCl_2$], sodium hydroxide [NaOH] were purchased from Merck, Germany.

B. Synthesis Fe_3O_4

Synthesis of Fe_3O_4 magnetics nanoparticles were prepared by co-precipitation of ferric and ferrous salts under the presence of N_2 gas. 16.25 $FeCl_3$ and 6.35 g of $FeCl_2$ were dissolve into 200 mL of deoxygenated distilled water. After stirring for 60 minutes, chemical precipitation was achieved at 30^0C under vigorous stirring by adding of 2 M NaOH solution under presence of N_2 gas. The reaction system keep

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at 70^0C for 5 h and pH solution ± 12. Completed precipitation of Fe_3O_4 expected at pH between 8 and 14 [16]. After the system was cooled to room temperature, the precipitates were separated by a permanent magnet and washed with deoxygenated distilled water until pH neutral. Finally Fe_3O_4 washed with acetone and dried in oven at 60-70^0C. The relevant chemical reaction can be expressed as follows eq.1:

$$Fe^{2+} + 2Fe^{3+} + 8OH^- \rightarrow Fe_3O_4 + 4H_2O \quad (1)$$

C. Characterizations of Materials.

The crystal structure of the products was characterized by X-ray Diffraction (XRD) Shimadzu XD-610. The patterns with the Cu Kα radiation (λ = 1,54051 Å) were recorded in the region of 2θ range 10 to 80^0. The morphology of the Fe_3O_4 materials were examined by Scanning Electron Microscope-Energy Dispersive X Ray Spectrometry (SEM-EDS) JEOL-JSM-6510 LV. Transmission Electron Microscope (TEM) JEOL JEM 1400 was used for characterizing the size of nanoparticles. The magnetic properties of the Fe_3O_4 materials measurement by Vibrating Sample Magnetometers (VSM) Lakeshore 74004 at room temperature. Uv-Vis Spectrometry by Shimadzu 2550 used to measurement procion dye concentration.

D. Adsorption Experiment.

The studies of procion dye adsorption were performed by batch adsorption method. The adsorption experiments were conducted by varying initial concentration of procion dye from 25 to 150 mg L^{-1}, pH solution was adjusted over the range pH 5-9 using HCl and NaOH 1 M, dosage of Fe_3O_4 from 0,5; 0,6; 0,7; 0,8; 0,9 and 1 g L^{-1} and contact time at 15, 30, 45, 60 and 75 minutes. Adsorption experiments were carried out with a thermostatic shaker at 120 rpm.

Adsorption data analysis. The concentration retained in color removal color (η,%) and adsorption capacity for Fe_3O_4, q_e (mg g^{-1}), was determined by analyzing procion dye before and after the treatment and calculated by using the eq.2. and eq.3

$$\eta\ (\%) = \frac{(C_0 - C_e)\ x\ 100}{C_0} \quad (2)$$

$$q_e = \frac{(C_0 - C_e)V}{m} \quad (3)$$

where C_0 and C_e are initial and equilibrium dye concentration in the solution (mg L^{-1}), m is the adsorbent dosage (mg), and V is the volume of the solution (mL).

III. Result and Discussion

A. Characteristic of the Fe_3O_4.

Fig. 1. shown XRD patterns of the Fe_3O_4. Six characteristic peaks at 30,205^0, 35,515^0, 43,325^0, 53,711^0, 57,215^0 and 62,945^0 were corresponding to the (220), (311), (400), (422), (511) and (440) crystal planes of a pure Fe_3O_4 with a spinal structure (JCPDS file PDF no.65-3107) [17]. The peaks indicating that Fe_3O_4 with a spinal structure and no characteristic peak of impurities are detected in the XRD pattern.

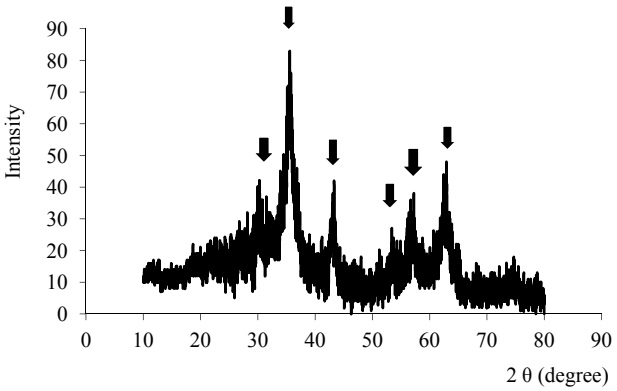

Fig. 1. XRD pattern for Fe_3O_4

In order to investigate the morphology of obtained materials by SEM and TEM images. Fig. 2. shown SEM image of Fe_3O_4, in the picture appears that Fe_3O_4 particles composed of small particle. Fig. 3. shown the TEM image of Fe_3O_4, from which we can know that the diameter size 5-20 nm. Fe_3O_4 synthesized by co-precipitation with different reagen ($FeCl_3.6H_2O$, $FeCl_2.4H_2O$, propylene glycol and ammonium hydroxide) indicated the mean size of particles was 8 nm [18]. The control of the monodisperse size is very important because the properties of nano crystal strongly depend upon the dimension of nanoparticles [16].

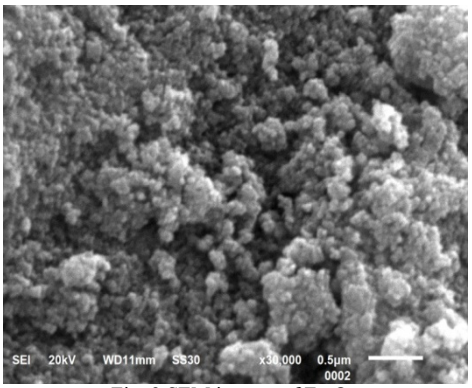

Fig. 2.SEM images of Fe_3O_4

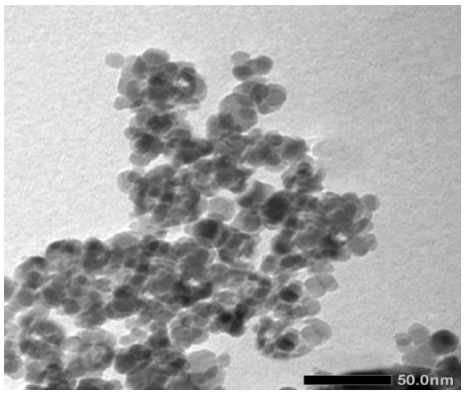

Fig. 3. TEM images of Fe_3O_4

Characterization of Fe_3O_4 using EDS in Fig. 4. The EDS spectra showed the strong peaks of Fe and O. The composition components of Fe_3O_4 formed by co-precipitation synthesis Fe was 73.36% and O was 21.02%. These results demonstrate the purity of the synthesis results.

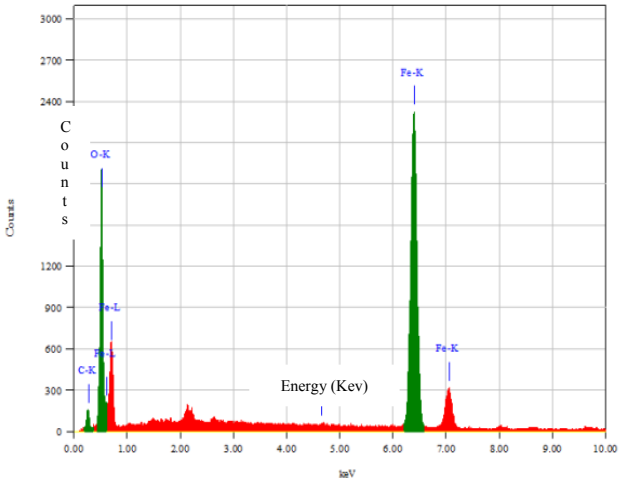

Fig. 4. EDS images of Fe_3O_4

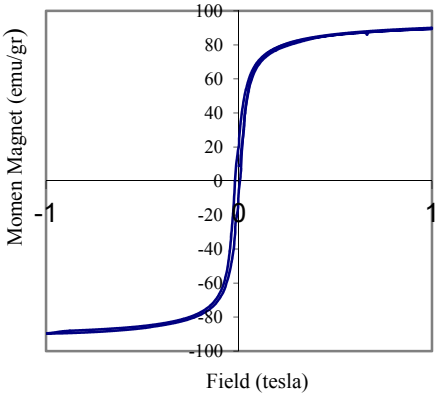

Fig. 5. Saturation Magnetization of Fe_3O_4

Fig. 5 shows the magnetization curve of Fe_3O_4 obtained by VSM at 25^0C. The saturation magnetization of Fe_3O_4 nanoparticles was 89.46 emu g^{-1}. The magnetization of Fe_3O_4 is not far from the actual magnetization of the Fe_3O_4 is 92 emu g^{-1} [19]. The excellent magnetic responsivity was necessary for magnetic separation from dye-containing effluents in the future.

B. Optimum Condition Adsorption

The effect of initial concentration of procion dye on the adsorption properties shows in Fig. 6. The increase of color removal has positive comparison with the increase of initial concentration of procion dye. It was clear that the adsorption process dependent on initial procion dye concentration. The large number of vacant surface sites were available for adsorption during initial stage. Initial concentration of procion dye on the adsorption process is then used at a concentration of 100 mg L^{-1}

The pH of dye solution plays an important role in the whole adsorption process and particularly on the color removal. The most color removal was 25.19 % at pH solution 5. The dye with two sulfonic groups ionized easily even in acidic media and became a soluble anion dye. Anion dye and neutral solutions were easily adsorbed to Fe_3O_4 with positive surface charge [20]. All the adsorption was highly pH dependent. The optimal pH for the removal of Cr(VI), Cu(II) and Ni(II) were 2.5, 6.5 and 8.5 by maghemite nanoparticles. Under the optimal pH , their uptakes mainly resulted from electrostatic attraction [21]. The color removal of procion dye at pH 6 which is 24.40 %, no thighly different from th pH 5 shown in Fig. 7. Thus, in the adsorption process used at pH 6 because it closer to neutral pH solution.

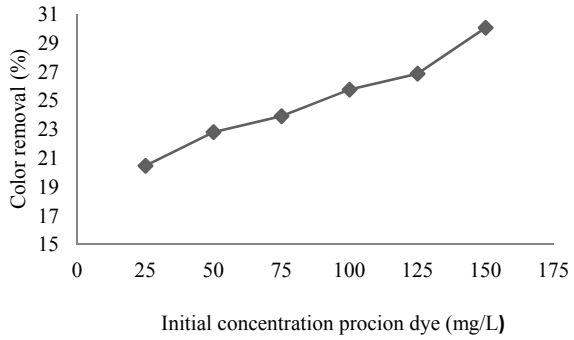

Fig. 6. Effect initial concentration of procion dye

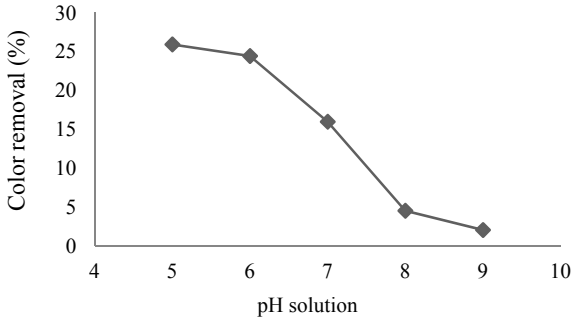

Fig. 7. Effect pH solution procion dye

Fig. 8 shows effect of dosage Fe_3O_4 and contact time to adsorb procion dye. The corresponding result showed that an increased in adsorbent dosage could increase adsorption capacity. With increasing adsorbent dosage, more surface area was available for adsorption due to the increase in active site on the surface Fe_3O_4 and thus making easier penetration of adsorbate to adsorption. The dosage Fe_3O_4 to adsorb procion dye at a fixed of 0.8 g L^{-1}.

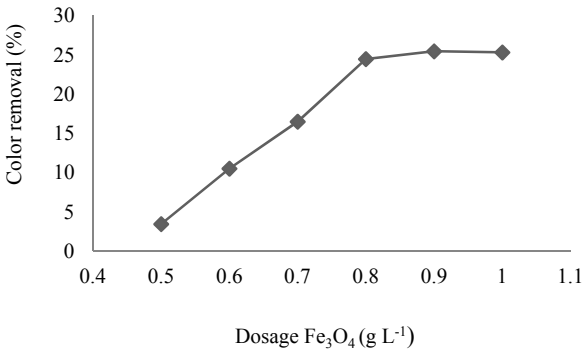

Fig. 8. Effect dosage Fe_3O_4

Effect contact time, color removal also increased with increasing contact time shown in Fig. 9. The equilibrium time at 30 minutes and after equilibrium time the color removal was stable. In the optimum condition adsorption has color removal was 24.40 % . This condition color removal is optimum so that extra time does not increase the color removal.

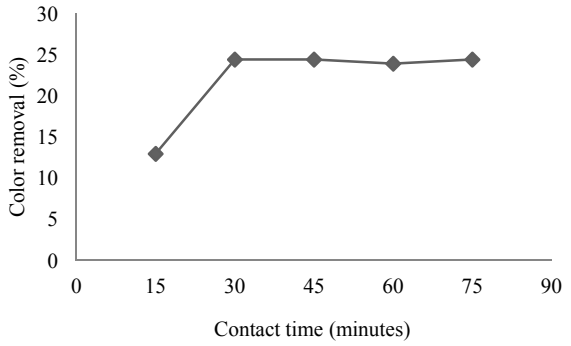

Fig. 9. Effect contact time

The adsorption capacity at the equilibrium time was 30.503 mg g^{-1}. The adsorption capacity of Fe_3O_4 nanoparticles is greater than adsorption capacity of iron oxide/carbon nanotube nanocomposite for removal methylene blue. It was reported 20 mg g^{-1} at the equilibrium time 20 minutes [22].

IV. Conclusions

Fe_3O_4 nanoparticles were synthesized by chemical co-precipitation method have the diameter 5-20 nm and the saturation magnetic was 89.46 emu g^{-1}, which indicated super paramagnetic properties. The nanoparticles Fe_3O_4 is suitable to remove dye in the water by a simple magnetic separation process. The optimum adsorption occurred at initial concentration of procion dye 100 mg L^{-1}, pH solution was 6, dosage of Fe_3O_4 0.8 g L^{-1} and contact time 30 minutes adsorption capacity was 30.503 mg g^{-1}.

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Reference

[1] U. Hafeli, W. Schutt, J. Teller, and M. Zborowski, *Scientific and Clinical Applications of Magnetic Microspheres,* Plenum, New York, pp. 324-326, 1997.
[2] V. S. Zaitsev, D. S. Filimonov, I. A. Presnyakov, R. J. Gambino, and B. Chu, "Physical and Chemical Properties of Magnetite and Magnetite Polymer Nanoparticles and Their Colloidal Dispersions," *Journal Colloid Interface Sci*., vol. 212, pp. 49-57, 1999
[3] B. A. Bolto, "Magnetic Particle Technology for Wastewater Treatment," *Waste Management*, vol. 10, pp. 11-21, 1990
[4] A. B. Fuertes and P. Tartaj, "A Facile Route for the Preparation of Superparamagnetic Porous Carbon," *Chem. Mater*, vol. 18, pp. 1675-1679, 2008.
[5] T. Yang, S. H. Zhu, D. Zhang, and S. H. Xu, "Synthesis and properties of magnetic Fe_3O_4-Activated Carbon Nanocomposite Particles for Dye Removal," *Mater. Lett.*, vol. 62, pp. 645-647, 2008.
[6] M. Senthil and C. Ramesh, "Biogenic Syhthesis of Fe_3O_4 Nanoparticles using Tridax Procumbens leaf Extract and Its Antibacterial Activity on Pseudomonas Aeruginosa," *Journal of Nanomaterials and Biostructures*, vol. 7, no. 3, pp. 1655-1660, 2012.
[7] S. Liong, "A Multifunctional Approach to Development, Fabrications and Characterizations of Fe_3O_4 Composite," Georgia Institut of Technology, North Ave, Atlanta, Georgia, pp. 213-217, 2005.
[8] S. E. Kentish and G. W. Stevens, "Innovation in Separations Technology for the Recycling and Re-use of Liquid Waste Streams," *J. Chem. Eng*., vol. 84, pp. 149-159, 2001.
[9] J. T. Mayo, et al., "The Effect of Nano Crystalline Magnetite Size on Arsenic Removal," *Journal of Science and Technology Materials*, vol. 8, pp. 71-75, 2008
[10] F. Rosada, M. Otero, A. Moran, and A. I. Garcia, "Adsorption of Heavy Metals onto Sewage Sludge-Derived Materials," *Bioresour Technology*, vol. 99, pp. 6332-6338, 2008.
[11] S. H. Sun and H. Zeng, "Size Controlled Synthesis of Magnetite Nanoparticles," *Journal Am.Chem.Soc*., vol. 24, pp. 8204-8205, 2002.
[12] S. R. Wan, J. S. Huang, H. S. Yan, and K. L, Liu, "Size controlled preparation of magnetite nanoparticles in the presence of graft copolymer," *Journal Mater.Chem*., vol. 16, pp. 298-303, 2006.
[13] S. Wang, Y. Boyjoo, A. Choueib, and H. Zhu, "Removal of Dye from Solution using Fly Ash and Red. Mud," *Water Research*, vol. 39, pp. 29-38, 2005.
[14] S. Senthilkumaar, P. Kalaamani, K. P. R. Varadarajan, and S. V. Subburaam, "Adsorption of dissolved reactive red dye from aqueous phase onto activated carbon prepared from agricultural waste," *Bioresour. Technology*, vol. 97, pp. 1618-1625, 2006.
[15] I. A. W. Tan and B. H. Hameed, "Adsorption isotherm, kinetics, thermodynamics and desorption studies of basic dye on activated carbon derived from oil palm empty bunch," *Journal of Applied Science*, vol. 10, no. 21, pp. 2565-2671, 2010.
[16] L. Sophie, F. Delphine, P. Marc, R. Alain, R. Caroline, V. E. Luce, and N. M. Robert, "Magnetic iron oxide nanoparticles: synthesis, stabilization, vectorization, physicochemical characterization, and biological applications," *Chem. Rev*., vol. 108, pp.2064-2110, 2008.
[17] G. L. Li, Y. R. Jiang, K. L. Huang, P. Ding, and I. I. Yao," Kinetics of adsorption of sacharomyces cereviceae mandelated dehydrogenase on magnetic Fe_3O_4-chitosan nanoparticles," *Journal Colloid Interface Sci*., vol. A 320, pp 11-18, 2008.
[18] Y. F. Shen, J. Tang, Z. H. Nie, Y. D. Wang, Y. Ren, and L. Zuo, "Preparation and application of magnetic nanoparticles fe_3o_4 for water purification," *Separation and Purification Technology*, vol. 68, pp. 312-319, 2009.
[19] H. M. Lu, W. T. Zheng, and Q. Jiang, "Saturation magnetization of ferromagnetic and ferrymagnetic nanocrystal at room temperature," *Journal of Phys. D. Appl.Phys.*, vol. 40, pp. 320-325, 2007.
[20] H. Y. Zhu, Y. Q. Fu, R. Jiang, L. Xiao, G. M. Zeng, S. L. Zhao, and Y. Wang, "Adsorption removal of congo red onto magnetic cellulose/Fe_3O_4/activated carbon composite: equilibrium, kinetic, and thermodynamic studies," *Chemical Engineering Journal*, vol. 173, pp 494-502, 2011.
[21] J. Hu, G. H. Chen, and I. M.C. Lo, "Removal and recovery of Cr(VI) from wastewater by maghemite nanoparticles", *Water. Res*., vol. 39, pp. 4528-4538, 2005.
[22] T. Pankay and A. J. Pattayil, "Superparamagnetic nanocompocite of magnetite and activated carbon for removal dyes from wastewater," *Nanoscience and Nanotechnology Letters*, vol. 1, pp. 171-175, 2009.

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