Synthesis and characterization of Fe$_3$O$_4$/SiO$_2$ Nanocomposite from Kaolin Bangka Island

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Abstract. Magnetite is widely used in various fields of separation and adsorbent. Various studies have also reported that magnetite without modification have low thermal stability, low water solubility and may undergo reactions forming a FeOOH intermediate phase. The use of silica templates is done in such a way that the magnetite produced is not easily agglomerated. The source of silica can easily be found in nature, one of which is kaolin. Synthesis of Fe$_3$O$_4$/SiO$_2$ nanocomposites from Kaolin Bangka Island was carried out. The source of silica used is sodium silicate which is made from kaolin. The parameter observed in this study is the effect of silica concentration on the formation of Fe$_3$O$_4$/SiO$_2$ nanocomposites. The SiO$_2$ concentrations used were 5%, 15% and 30%. Based on the XRD analysis results, it appears that the three samples have typical diffraction peaks from Fe$_3$O$_4$/SiO$_2$ nanocomposites at 2θ 24°, 26° and 35°. The average particle size of each composite for 5%, 15% and 30% SiO$_2$ concentrations is 50.05 nm, 43.21 nm and 41.68 nm. It can be concluded that nanocomposite with SiO$_2$ concentration of 30% has the potential to be applied further as a heavy metal adsorbent. FTIR analysis showed an absorption peak indicating the silica has coated the magnetite material from Fe$_3$O$_4$.

1. Introduction
Nanotechnology research has recently seen a large increase, one of which is the synthesis of nanoparticles. Various forms of nanoparticles, including nanoparticles of iron oxide, have been successfully synthesized. Synthesis and study of iron oxide nanoparticles, in particular magnetite (Fe$_3$O$_4$), attracted the attention of researchers as magnetite is widely used in various fields of separation, biochemistry and adsorbent [1],[2]. It is well known that the magnetic properties are strongly influenced by the size of the magnetic material granules, especially on the nanometer scale [3]. Magnetic iron oxide nanoparticles are proved to be an efficient, cost effective and non-hazardous candidate for adsorption research [4],[5]. However, the large surface energy of the magnetic nanoparticles may cause aggregation during catalytic reactions. This drawback revealed the need for nanoparticle stabilizers to be used or supported. The main function of these media is to control the particle size, morphology and dispersion of nanoparticles [6–8]. To optimize the size and structure of the magnetic pores, the surface must be modified by adding a silica template (SiO$_2$) so that the size and pore can be more controlled. Various
studies have also reported that magnetite nanoparticles without modification have low thermal stability, low water solubility and may undergo reactions forming a FeOOH intermediate phase [9]. The use of silica templates is done in such a way that the magnetite produced is not easily agglomerated or clotted. The source of silica can easily be found in nature, one of which is kaolin.

Kaolin is a silica mineral that has the potential to be used as an alternative raw material for silica templates in the synthesis of nanocomposites. Kaolin is easily found in Bangka Belitung, the Kaolin reserve in Bangka reaches 205,487.50 tons [10]. This figure makes Bangka Belitung one of the provinces with the largest reserves of kaolin in Indonesia. Various methods have been used to synthesize these magnetic composites as impregnation, ball milling, single-pot method [11],[12] and chemical co-precipitation [13-15]. Because no special chemicals or procedures are needed and because of its simplicity, chemical co-precipitation is the most frequently used method. In this research, the synthesis and characterization of nanocomposite Fe$_3$O$_4$/SiO$_2$ from kaolin Bangka will be performed using a co-precipitation method through variations in the composition of SiO$_2$ and will be characterized using XRD and FTIR analysis.

2. Materials and Methods

2.1 Material

The material in this study is commercial Fe$_3$O$_4$, distilled water, sodium hydroxide were produced by Merck and Kaolin obtained from Bangka Island.

2.2 Preparation of sodium silicate from kaolin

The initial stage of kaolin preparation is washing using clean water from impurities, then dried in an oven of 100 °C and calcined at 500 °C for 2 hours. 100 grams of activated kaolin is added to the preparation with 4 M NaOH solution dissolved in 150 mL. The mixture is heated until much of the water has evaporated. The mixture is then put in the oven at 500 °C for 3 hours.

2.3 Synthesis of Fe$_3$O$_4$/SiO$_2$ nanocomposite

Fe$_3$O$_4$ nanoparticles with different concentrations of SiO$_2$. The source used for silica is the Sodium Silicate Solution (Na$_2$SiO$_3$) formed from kaolin. Starting by mixing Na$_2$SiO$_3$ with distilled water for 10 minutes on the stirrer at room temperature after Fe$_3$O$_4$ was placed in the solution for 5 hours, the solution was centrifuged and the precipitate washed with distilled water. The precipitate is dried in a 100 °C oven. Dry samples are then analyzed using X-Ray Diffraction (XRD) and Fourier Transform Infra Red (FTIR). The SiO$_2$ variation parameters can be seen in table 1 as follows:

| Sample | Fe$_3$O$_4$: Sodium silicate solution (SS) |
|--------|-----------------------------------------|
| 1      | 0.800 g : 5% SiO$_2$                     |
|        | 20 ml SS + 20 ml H$_2$O                  |
| 2      | 0.800 g : 15% SiO$_2$                   |
|        | 8 ml SS + 32 ml H$_2$O                   |
| 3      | 0.800 g : 30% SiO$_2$                   |
|        | 4 ml SS + 36 ml H$_2$O                   |

3. Result and Discussion

3.1 X-ray diffraction (XRD) analysis

XRD analysis was carried out on several samples including activated kaolin, Fe$_3$O$_4$, Fe$_3$O$_4$/SiO$_2$ 5%, 15% and 30%. The XRD analysis was carried out to see the crystalline phase formed by the nanocomposite synthesis process and to calculate the crystal size using the Scherrer’s formula.
Figure 1. XRD analysis for activated kaolin, Fe$_3$O$_4$ and Fe$_3$O$_4$/SiO$_2$ nanocomposite

Figure 1 shows that the typical diffraction peaks of kaolin appear at 2θ 12.27°, 20.8° and 26.59° corresponding to the typical diffraction peaks of kaolin (JCPDS No: 01-078-2109), in addition to XRD Fe$_3$O$_4$ data showing the diffraction peaks at 2θ 30.1°, 35.47°, 43.13°, 56.97° and 62.6° which are typical peaks of the magnetite phase (JCPDS No: 01-071-6766). The size of the magnetite particles calculated using the Scherrer formula is 28.29 nm [16]. XRD analysis on the three composite samples, SiO$_2$ of 5%, 15% and 30% showed a diffraction peak at 2θ 24°, 26° and 35° which is the diffraction peak of the Fe$_3$O$_4$/kaolin composite [17].

Based on the Scherrer’s formula, the particle size of the three composites, Fe$_3$O$_4$/SiO$_2$ 5%, 15% and 30% respectively 50.05 nm, 43.21 nm and 41.68 nm, this size is included in the nanometer scale which indicates that the material in this study is nanocomposite. Detailed calculations are presented in Table 2. Increased concentrations of SiO$_2$ cause smaller nanocomposite particle sizes due to the increasing number of SiO$_2$ chains limiting particle growth causing smaller crystalline sizes [18]. It can be concluded that nanocomposite with SiO$_2$ concentration of 30% has the potential to be applied further as a heavy metal adsorbent because with small particle size it has a large surface area so that it is easier to adsorb heavy metals. SiO$_2$ in this case functions as a coating/template that is useful for preventing particles from being aggregated and easily dispersed in liquid media, and silica has a free silanol (Si-OH) group and a siloxane group (Si-O-Si) which is known to be able to adsorb ions heavy metal. In this functionalization process, if there is a large amount of silanol group on the surface of the particle, it will make the particle easily activated with various functional groups. The illustration mechanism can be seen in the Figure 2.

| Sample            | 2θ (deg) | θ (rad) | FWHM (rad) | D (nm)   | Average Particle Size (nm) |
|-------------------|----------|---------|------------|----------|-----------------------------|
| Fe$_3$O$_4$/SiO$_2$ 5% | 24.88    | 0.217   | 0.004      | 35.35    | 50.05                       |
|                   | 26.65    | 0.232   | 0.002      | 69.75    |                             |
|                   | 35.46    | 0.309   | 0.003      | 45.06    |                             |
| Fe$_3$O$_4$/SiO$_2$ 15% | 24.85    | 0.216   | 0.003      | 40.65    | 43.21                       |
|                   | 35.50    | 0.309   | 0.003      | 48.19    |                             |
|                   | 26.61    | 0.232   | 0.003      | 40.80    |                             |
| Fe$_3$O$_4$/SiO$_2$ 30% | 26.70    | 0.233   | 0.002      | 62.30    | 41.68                       |
|                   | 35.58    | 0.310   | 0.003      | 41.90    |                             |
|                   | 24.93    | 0.217   | 0.006      | 20.85    |                             |
3.2 X-ray diffraction (XRD) analysis

To identify the functional groups of Fe₃O₄/SiO₂ nanocomposite that has been synthesized, an infrared spectrum analysis was obtained using a Fourier Transform Infrared (FTIR) spectroscopy. Kaolin and Fe₃O₄ spectra were used as a comparison in analyzing the spectrum of Fe₃O₄/SiO₂ composite synthesized. In figure 3, the FTIR data for activated kaolin, there is strong band at 3674 cm⁻¹. This peak indicates the Al-O-H stretching which OH is bound to Al octahedral atom on the surface of the kaolin silicate. But in the Fe₃O₄/SiO₂ composite, that peak becomes very weak almost disappears. This is due to reduction in the amount of water on the surface of kaolin, which can cause changes in the molecular structure of kaolin [17]. The FTIR data for activated kaolin, there is also a peak at 1003 cm⁻¹ corresponds to Si-O stretching in tetrahedral layer. The peak at 1003 and 770 cm⁻¹ is typical absorption of quartz, smectite and muscovite [20,21]. While FTIR data for Fe₃O₄/SiO₂ composite shows that the peaks at 545-565 cm⁻¹ is corresponds to Si-O-Si bending. This peak indicates that the silica has coated the magnetite material from Fe₃O₄ [18].

4. Conclusion

The particle size of the three composites, Fe₃O₄/SiO₂ 5%, 15% and 30% respectively 50.05 nm, 43.21 nm and 41.68 nm, this size is included in the nanometer scale which indicates that the material in this study is nanocomposite. It can be concluded that nanocomposite with SiO₂ concentration of 30% has
the potential to be applied further as a heavy metal adsorbent because with small particle size it has a large surface area so that it is easier to adsorb heavy metals. FTIR analysis showed an absorption peak indicating the silica has coated the magnetite material from Fe$_3$O$_4$.

References

[1] Guin D and Manorama S V 2008 Room temperature synthesis of monodispersed iron oxide nanoparticles Mater. Lett. 62 3139–42
[2] Deng Y, Qi D, Deng C, Zhang X and Zhao D 2008 Superparamagnetic High-Magnetization Microspheres with an Fe3O4@SiO2 Core and Perpendicularly Aligned Mesoporous SiO 2 Shell for Removal of Microcystins J. Am. Chem. Soc. 130 28–9
[3] Pauzan M, Kato T, Iwata S and Suharyadi E 2013 Pengaruh Ukuran Butir dan Struktur Kristal terhadap Sifat Kemagnetan pada Nanopartikel Magnetit (Fe3O4) Prosiding Pertemuan Ilmiah XXVII HFI Jateng&DIY (Solo) pp 24–8
[4] Shen Y F, Tang J, Nie Z H, Wang Y D, Ren Y and Zuo L 2009 Preparation and application of magnetic Fe3O4 nanoparticles for wastewater purification Sep. Purif. Technol. 68 312–9
[5] Afkhami A, Sayari S S, Moosavi R and Madrakian T 2015 Magnetic nickel zinc ferrite nanocomposite as an efficient adsorbent for the removal of organic dyes from aqueous solutions J. Ind. Eng. Chem. 21 920–4
[6] Saikia P K, Sarmah P P, Borah B J, Saikia L, Saikia K and Dutta D K 2016 Stabilized Fe3O4 magnetic nanoparticles into nanopores of modified montmorillonite clay: a highly efficient catalyst for the Baeyer–Villiger oxidation under solvent free conditions Green Chem. 18 2843
[7] Nourafkan E, Asachi M, Gao H, Raza G and Wen D 2009 Preparation of Water-Soluble Magnetite Nanocrystals from Hydrated Ferric Salts in 2-Pyrrolidone: Mechanism Leading to Fe3O4 Angew. Chemie Int. Ed. 44 123–6
[10] BPPTPM Babel 2015 Sektor Pertambangan Provinsi Bangka Belitung
[11] Mu B, Tang J, Zhang L and Wang A 2016 Preparation , characterization and application on dye adsorption of a well-de fi ned two-dimensional superparamagnetic clay/polyaniline/Fe3O4 nanocomposite Appl. Clay Sci. 132 7
[12] Kumari M, Pittman C U and Mohan D 2015 Heavy Metals [Chromium (VI) and Lead (II)] Removal from Water Using Mesoporous Magnetite (Fe3O4) Nanospheres J. Colloid Interface Sci. 442 120–32
[13] Liu H, Chen W, Liu C, Liu Y and Dong C 2014 Magnetic mesoporous clay adsorbent : Preparation , characterization and adsorption capacity for atrazine Microporous Mesoporous Mater. 194 72–8
[14] Liao M and Chen D 2002 Preparation and characterization of a novel magnetic nano-adsorbent J. Mater. Chem. 12 3654–9
[15] Yap M W, Mubarak N M, Sahu J N and Abdullah E C 2016 Microwave induced synthesis of magnetic biochar from agricultural biomass for removal of lead and cadmium from wastewater J. Ind. Eng. Chem. 45 287–95
[16] Julianti E, Samsiar A, Siregar R N and Fabiani V A 2019 The Adsorption Efficiency of Iron from Post-Tin Mining Water using Nanomagnetic Fe3O4/Chitosan Portunus pelagicus shells The Adsorption Efficiency of Iron from Post-Tin Mining Water using Nanomagnetic Fe3O4/Chitosan Portunus pelagicus shells IOP Conference Series: Earth and Environmental Science 353 (2019) 012018 (IOP Publishing) pp 1–7
[17] Magdy A, Fouad Y O, Abdel-aziz M H and Konsowa A H 2017 Synthesis and characterization of Fe3O4/kaolin magnetic nanocomposite and its application in wastewater treatment J. Ind. Eng. Chem. 56 299–311

[18] Taib S and Suharyadi E 2015 Sintesis Nanopartikel Magnetite (Fe3O4) dengan Template silika (SiO2) dan Karakterisasi Sifat Kemagnetannya Indones. J. Appl. Phys. 5 23–30

[19] Zhang S, Zhang Y, Liu J, Xu Q, Xiao H, Wang X, Xu H and Zhou J 2013 Thiol modified Fe3O4@SiO2 as a robust, high effective, and recycling magnetic sorbent for mercury removal Chem. Eng. J. 226 30–8

[20] Ekosse G E 2015 Fourier Transform Infrared Spectrophotometry and X-ray powder Diffractometry as Complementary Techniques in characterizing Clay size fraction of Kaolin J. Appl. Sci. Environ. Manag. 9 43–8

[21] Nugraha I and Kulsum U 2017 Sintesis dan Karakterisasi Material Komposit Kaolin-ZVI (Zero Valent Iron) serta Uji Aplikasinya sebagai Adsorben Kation Cr (VI) J. Kim. Val. J. Penelit. dan Pengemb. Ilmu Kim. 3 59–70

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