

SYNTHESIS OF ADSORBENT MAGNETITE SILICA FUNCTIONALIZED CETYLTRIMETHYLAMMONIUM BROMIDE (CTAB) FROM IRON SAND KLAYAR BEACH PACITAN

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Abstract

Synthesis of Magnetite Silica cetyltrimethylammonium bromide (magsil-CTAB) had been successfully performed using iron sand Klayar beach as a source of natural magnetite, sodium silicate, HCl, and cetyltrimethylammonium bromide (CTAB). Addition of CTAB on silica magnetite was expected to improve the ability of the adsorbent to adsorb polar compounds such as phenols. Synthesis began with the separation of the magnetite from iron sands by separation magnetically done using permanent magnets. Silica coating on magnetite done via sol-gel method with a ratio 1:20 of magnetite and sodium silicate followed by addition of HCl to form a gel. Gel was dried at a temperature of 80 °C and 350 °C for calcination. Results obtained soaked with CTAB solution with a concentration of 0.5 mM; 1 mM; 2 mM and stirred for 24 hours. Binding of silica and magnetite above the CTAB tested by Fourier Transform Infra Red (FTIR). The presence of silica in magnetite indicated by the appearance of spectra at wave number 900 and 3500-3200 cm⁻¹ indicating the presence of a hydroxyl group of silanol and water molecules. Besides the presence of two strong peaks observed around 1100 and 800 cm⁻¹, respectively show the Si-O-Si asymmetric stretching and bending. From the results of spectra could be seen further there were difference intensity of the main peaks for different samples used, especially on the area around 2300 cm⁻¹ to be a group of nitrile (C-N) and about 3700-3500 cm⁻¹ due to the amide (N-H) of the CTAB as expected.

Keywords: magnetite, silica, sol-gel, coating, CTAB

Introduction

Magnetite known as black iron oxide (black iron oxide) or ferrous ferrite has the most powerful magnetic properties [1] that nowadays consider as a valuable candidates for the development of next-generation of adsorbents with great potential for the efficient treatment of large volume of wastewater and fast separation using an external magnetic field [2]. A commonly used method to prepare magnetite particles are chemical co-precipitation [3], sol gel [4,5], electrochemical [6], hydrothermal [7], etc. But these methods use lot of chemicals potentially harmful to the environment which lead us in using natural magnetite.

Natural magnetite is a common oxide mineral in igneous, metamorphic, and sedimentary rocks widely found in iron ore sand [8] which is Indonesia rich of this mineral especially around west coast of Java (Magnetik n.d.). To obtain the quality of iron oxides from iron sand, it is needed to increase iron content by magnetic separation.

Magnetic separation is one purification technique that has been adapted from ore mining

industries to seeding magnetic flocculent [9]. Magnetic separation takes advantage of differences in the magnetic properties of minerals. Minerals fall into one of three magnetic properties: ferromagnetic, paramagnetic and diamagnetic. Ferromagnetic minerals are themselves magnetic (i.e., magnetite and pyrrhotite) and can be easily separated from other minerals with a magnet since they will stick to the poles of the magnet. Magnetic separator can separate iron from ores with nearly 100% efficiency (depending on the particulate sizes, magnetic field and flow rate) according to Yavuz [10]. The magnetic separation technique offers new perspectives to prepare magnetite, generating more efficient and cost-effective remediation approaches as compared with conventional technologies [11].

In order to develop application of magnetite, coating magnetic is important. Among inorganic compounds, silica provides considerable properties such as high chemical and thermal stability and most importantly its easy modification by a wide range of functional groups make it an ideal candidate to protect the surface of magnetic [12-

14]. The surface modification with suitable functional groups can possess a huge potential to enhance the adsorption capacity to specific contaminant type [15]. Sol-gel process has been adopted more widely for preparation of silica-coated magnetic nanoparticles for its advantages compared with the other methods, i.e. relatively mild reaction condition and low cost [13].

Herein, we reported the Synthesis of Magnetite Silica cetyltrimethylammonium bromide (Magsil-CTAB) using iron sand Klayar beach as a source of magnetite. Silica coating on magnetite done via sol-gel method. Addition of CTAB as a cationic surfactant on silica magnetite was expected to improve the ability of the adsorbent to adsorb polar compounds such as phenols. Binding of silica and magnetite above the CTAB tested by Fourier Transform Infra Red (FTIR).

Experiment

Reagents and Equipments. Magnetite taken from the iron sand beach Klayar Pacitan separated by a permanent magnet diameter 15 cm and thickness 4 cm. Sodium silicate, hydrochloric acid and CTAB reagents, using Merck brand Damstat Jerman dan dissolution was done with aquadest. Size reduction of magnetite done by Retsch PM400 Ball mill, dried with Memmert oven. Magnetite silica-CTAB characterized by FTIR.

Preparation Magnetite Iron Sand. Preparation of magnetite from iron sand refers to the method used by Henny Dwi Bhakti, Mashur (Ku-band n.d.), done by magnetic separation. Iron sand was induced with a permanent magnet to attract magnetite. This method was repeated 7 times. Between the magnet and iron sand given a paper with a thickness of 0.1 cm. After magnetite separated then it was crushed with a ball mill for 4 hours to reduce size done in wet process use alcohol 70% with ratio magnetite : alcohol was 1: 1. The ballmill used was zirconia ball dia. 3 cm and miling speed 400 rpm. After miling, magnetite powder was dried using an oven with a temperature of 80 °C for 4 hours then sieved with a mesh sieve.

Synthesis of Magnetite Silica. Magnetite silica were synthesized according to previous reported method as performed by Zhao [12] with a minor modification as follows:

Sodium silicate 10% was added dropwise into magnetite and the pH value of the mixture was adjusted to 7.0 by addition of 3M HCl within 2 h. The mixture was stirred for 3 h after the addition. During the whole process, temperature was

maintained at 80°C. The mass ratio of magnetite to Na_2SiO_3 10% was 1:20. Finally, the formed magnetite silica were then thoroughly washed with deionized water until free of chloride ion and neutral. The product then was calcined at a temperature of 80°C with oven for 24 hours (MSA) and at 350°C in a furnace for 3 hours (MSB).

Functionalizing The Surface of The Magnetite Silica with CTAB. Functionalization magnetite silica with CTAB can improve the adsorption capacity. A monolayer rod like will be formed when the surfactant concentration is equal to or less than its critical micelle concentration (CMC). The CTAB molecules will form a bilayer of surfactant on the surface of magnetite silica if the surfactant concentration in a solution exceeds the CMC [16]. The CMC of CTAB is 1.0 mmol/L [17]. To determine the effect of CTAB concentration on the adsorption of phenol, three initial concentrations of CTAB (0.5, 1.0 and 2.0 mmol/L) were selected which were in lesser, equal, and higher concentrations than the CMC of the surfactant for modification. For the preparation of functionalized magnetite silica, 10 g of prepared MS was put into a 200 mL conical flask containing 100 mL of different concentration of CTAB (0.5, 1.0 and 2.0 mmol/L). Then, the flasks were shaken in on magnetite for 24 hours. The solid was washed with distilled water repeatedly until no Br^- was detected by AgNO_3 solution; then, it was dried in an oven at 50 °C for 24 hours [18]. The magnetite silica with 0.5, 1.0 and 20 mmol/L of CTAB solutions were named as MSA_1 , MSA_2 and MSA_3 for Magnetite silica-CTAB dried at temperature of 80 °C and MSB_1 , MSB_2 and MSB_3 for Magnetite silica-CTAB dried at temperature of 350 °C, respectively.

Characterization Fourier-Transform Infrared. All samples were characterized by Fourier-transform infrared (FT-IR) spectroscopy and prior to compacting as pellets all samples and KBr were dried at 95 °C for 48 h. Each sample (5 mg) was thoroughly mixed and crushed with 500mg of KBr using a mortar and pestle. The mixture (80 mg) was placed in a pellet former and 10 tons of pressure was applied for 2 min to form the KBr pellet. The FTIR spectrum was in the region between 600 and 4000 cm^{-1} .

Results and Discussions

The FTIR spectra of silica coating on magnetite and pure natural magnetite are

shown in Fig. 1. FTIR spectrum for pure magnetite (M) shows the major absorption band appearing at 583 cm^{-1} which is the magnetite finger print; Fe–O bond vibration of Fe_3O_4 [19]. The presence of silica on magnetite indicated by the appearance of spectra at wave number 900 and $3500\text{--}3200\text{ cm}^{-1}$ indicating the presence of a hydroxyl group of silanol and water molecules. Besides the presence of two strong peaks observed around 1100 and 800 cm^{-1} , respectively show the Si–O–Si asymmetric stretching and bending. No peaks related to magnetite were observed after coating with silica in the FTIR spectrum due to complete coating by SiO_2 as [20].

To understand whether the silica coating that forms a layer on magnetite surface, we have performed dissolution experiments in acidic solution. Magnetite is soluble under acid

conditions, while amorphous silica is barely insoluble. Two powder samples of 20 mg each, were digested in 20 mL of 10^{-5} M HCl solution for 3 h. followed by periodically sampling 3 mL aliquots from each of the solutions to examine the dissociation of magnetite into Fe^{+3} and Fe^{+2} ions. The aliquot was then added to 3 drops of 1 M $\text{KFe}(\text{CN})_6$ solution, the dark blue of complex iron cyanide will confirm the dissolution. The result showed the magnetite-silica remained undissolved. Magnetite silica appears to be protected by the silica on the surface, which slows the dissolution rate. These observations confirmed that magnetite silica as identified by the FTIR spectrum forms a layer on the surface of the magnetite particles completely. But these silica could not prevented transformation of magnetite to $\gamma\text{-Fe}_2\text{O}_3$ due to calcination temperature.

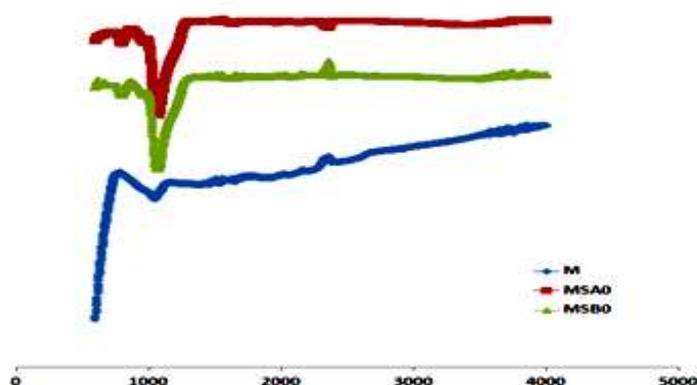


Figure 1. . FTIR spectra of magnetite (M), magnetite silica and at temperature of calcination $350\text{ }^{\circ}\text{C}$ (MSB0) and $80\text{ }^{\circ}\text{C}$ (MSA0)



Figure 2. (a) iron sand, (b) M (magnetite resulted from magnetic separation before coating), (c) MSA (magnetic after silica coating calcined in 80°C), and (d) MSB (magnetic after silica coating calcined in 350°C)

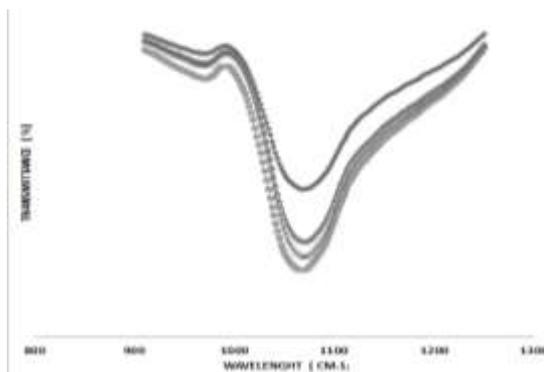


FIGURE 3. FTIR spectra for MSA0 , MSA1, MSA2, MSA3

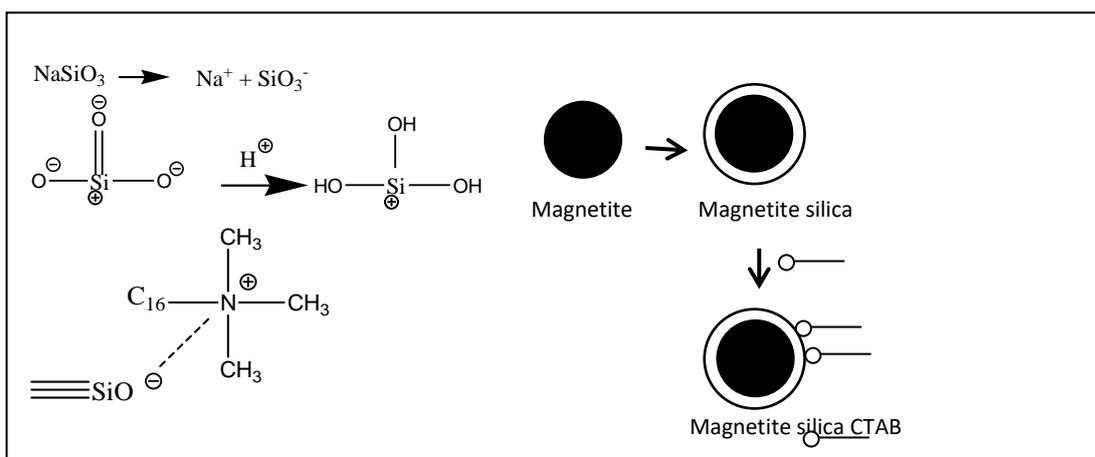


FIGURE 4. Simple mechanisms for the formation Magnetite silica CTAB

Iron oxides can vary quite significantly in colourant this can be used as an aid in their identification. It may also be used as a rule of thumb guide to purity in some cases. Magnetite (Fe_3O_4) is black, maghemite ($\gamma\text{-Fe}_2\text{O}_3$) is reddish brown, while hematite ($\alpha\text{-Fe}_2\text{O}_3$) is red [21]. Magnetite resulted from magnetic separation from iron sand Klayar beach was black jet iron (M) and therefore expected to be pure magnetite. But after calcined at $350\text{ }^\circ\text{C}$ for 3 hour in air, the black magnetite powder transformed to dark red-brown powder (MSB). It didn't happened to MSA which was calcined in $80\text{ }^\circ\text{C}$ as seen in Fig. 2. The composition and structure of iron oxide depend on the preparation conditions, such as the nature of the anions present, the acidity of solution, and other factors. During hydrolysis some of the iron oxide reacted with Cl^- ions, the $\beta\text{-FeOOH}$ structures formed. Annealing in air resulted a transfer of $\beta\text{-FeOOH}$ to $\alpha\text{-Fe}_2\text{O}_3$ [22]. In addition Fe_3O_4 oxidized to $\alpha\text{-Fe}_2\text{O}_3$, and can be

further transformed into $\gamma\text{-Fe}_2\text{O}_3$ by heat treatment at a higher temperature. The results indicated that the synthesized magnetite silica at $350\text{ }^\circ\text{C}$ in air could transformed magnetite to $\gamma\text{-Fe}_2\text{O}_3$. Similar results about the oxidation of Fe_3O_4 to $\gamma\text{-Fe}_2\text{O}_3$ have been reported in literatures [23].

From the results of spectra could be seen further there were difference intensity of the main peaks for different samples used, especially on the area around 1070 cm^{-1} to be a change on intensity of percent transmittance Si-O-Si caused by addition of CTAB as seen in Fig. 3. It could be proposed that the interactions between silica and CTAB act as follows: small quantities of CTAB could firstly act in a monolayer formation that is controlled by electrostatic interaction between positively charged surfactant headgroups and siloxane groups ($-\text{SiO}-$) on the silica surface. Furthermore, it is well known that adsorption of CTAB on silica surface could overcome the micelles formation. From the results of spectra could be seen further there were difference intensity of the main peaks for different

samples used, especially on the area around 2300 cm^{-1} to be a group of nitrile (C-N) and about 3700-3500 cm^{-1} due to the amide (N-H) of the CTAB as expected.

Simple mechanisms for the formation of a silica layer on the surface of the magnetite particles are illustrated schematically in Fig. 4.

Conclusion

Magnetite silica have been synthesised using CTAB as surface modification agent. By variation of the calcination temperature conditions variants with different CTAB adding have been obtained and characterized. Iron sand from Klayar beach can be used as a source of magnetite done by magnetic separation. The silica coating have to be done in low temperature to avoid transformation of magnetite to $\gamma\text{-Fe}_2\text{O}_3$. Our next work are test the performances of these materials as phenol adsorbent. Capacity of adsorption will be tested due to the effect of contact time and pH.

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