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Coating of Sulfonic Silica onto Magnetite from Marina Beach Iron sand, Semarang, Indonesia

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Abstract. The mineral iron oxide is the main component of sand iron that are abundant in nature. Mineral iron oxide not yet widely applied into more useful products. The main component of iron ore is magnetite. Magnetite can be used as a basic ingredient in the manufacture of magnetite-modified silica adsorbent sulfonate. In this research, the adsorbent made from sulfonic functionalized silica-coated magnetic particle has been successfully produced, with the magnetite was obtained from iron sand at Marina Beach, Semarang Indonesia. This adsorbent was then used as a metal ion preconcentration media. From the research that it was found that the sulfonic has been bound to the silica marked by the emergence of element S on EDX. Whilst, the evidence that silica has coated on the magnetite could be seen from the SEM images which showed the morphology of sulfonic functionalized silica-coated magnetic particles were larger than the sulfonic functionalized silica without magnetite. From the DSC results showed that the addition of magnetite on sulfonic functionalized silica did not change the heat resistance of the sulfonic functionalized silica. Based on the XRD patterns show that magnetite sulfonate silica was formed.

1. Introduction

Indonesia is the largest archipelago in the world because it has 13 466 large and small islands with a fourth longest coastline in the world, which is 95.161 km [1]. The sand beaches in Indonesia with an iron content which is quite large and has not been used optimally. The main content of iron ore is iron oxide, one of which is magnetite. A magnetite nanoparticles are superparamagnetic [2] so that it can be used as a solid adsorbent support. The presence of magnetite in the adsorbent is expected to facilitate the desorption of the metal ions. However, magnetite has a poor stability so that the necessary modifications to the surface of the magnetite, one of which is the coating. Wang et al. [3] have done a magnetite coating with tetraethoxyisilane (TEOS) by sol-gel method at 50° C and pH 9. Magnetite coated silica has a better resistance to oxidation than magnetite without coating. Another source of silica as magnetite coating is sodium silicate (Na₂SiO₃). Sodium silicate can prevent the occurrence of corrosion reported that the magnetite coating using sodium silicate sol-gel method could improve resistance to thermal.

Research conducted Huang and Hu [4] using Mercaptopropyltrimethoxysilane (MPTMS) as a coating of silica coated magnetite by grafting generate magnetic with two layers, the first layer in the form of silica and a second layer MPTMS. Two of these layers increases the size of magnetite particles coated. The larger the size of the coated magnetite particles, the nature of magnetism is



reduced so that it will complicate the process of separation of the adsorbent from the matrix. Efforts to overcome these problems can be done by changing the structure of the coated magnetite which has two layers into one layer, namely through the sol-gel process that is expected to form a single layer on the surface of magnetite. In general, this binding reaction depends on the ability of substitution between molecular modifier with the active side are distributed on the surface of a solid inorganic support. Of the few studies ever conducted showed that the metal adsorption by modified silica increases with increasing active group. Azmiyawati et al. [5] has studied the thermodynamics of adsorption of Mg (II), Cd (II), and Ni (II) on silica gel modified sulfonate to determine the type of bonding that occurs between the silica sulfonate with Mg (II), Cd (II), and Ni (II). Provided that the bond between the silica sulfonate with the metal ion is a chemical bond indicated by the value of metal ion adsorption adsorbent with greater than 20.9 kJ / mol. Other research is the use of modified silica sulfonate group as an adsorbent metal ions Ca (II), Cd (II), and Cu (II) which results from adsorption Ca (II) was better than Cd (II) and Cu (II) [6] In this research, sulfonate silica was coated on magnetite. The presence of silica sulfonate will increase against metal ion adsorption process. While the presence of magnetite as a support material of the compound will increase the metal ion desorption process. So expect the recovery of metal ions already desorption better.

2. Experimental

2.1. The Chemicals

Magnetite was collected 12 m Marina Beach iron sand, Semarang, Indonesia. Chemicals for synthesis of MSS included 4-amino-5-hydroxy-naphthalene-2,7-disulfonic acid monosodium salt ($C_{10}H_8NNaO_7S_2$) (AHNSNa) as the sulfonate source, 3-chloropropyltrimethoxysilane (CPTS), triethylamine ($C_6H_{15}N$), and hydrochloric acid. Sodium bicarbonate solution was used for the solvent of AHNSNa, diethyl ether and acetone for washing solvents. All chemicals were of analytical reagent grade (Merck) and used as received.

2.2. Procedure

Magnetite samples obtained by extracting magnetite from iron sand. The first step magnetic sample was grounded to obtain a powder with the particle size of 106 μm . The powder then was mixing and stirring with sodium silicate solution for two h. The second step of synthesis was the attachment of sulfonate groups on the CPTS by mixing 50 mL solutions of AHNSNa (4.08 %, w/v) in sodium carbonate solution 0.05 M, 4.85 mL triethylamine and six mL CPTS added dropwise and constantly stirring for 5 hours. The solution then was added to 100 mL magnetic sodium silicate solution and 3 M of HCl solution dropwise, and the suspension was then constantly stirred for 24 h at a room temperature (25 °C) until the gel was formed. This gel was aged for 2 h at 70 °C, and dried in a vacuum for 24 h. The gel was filtered, and the residue was washed with distilled water till free of acid. The gel was dried at 70 °C for 2 h to obtain magnetite silica sulfonate (MSS). The functional group of the MSS was evaluated from FTIR spectra. The surface topology was identified with SEM-EDX. The heat resistance of MSS was evaluated from DSC.

3. Result and discussion

3.1. Magnetite Precursor from Iron sand

Iron sand is one of the abundant natural resource in Indonesia that haven't been used well. The main content of the iron sand is iron oxide, which is magnetite. Magnetite is an iron oxide that has the strongest magnetic properties so that it can be use as solid support for adsorbent. However, magnetite has a poor stability, so it's necessary to modify the surface of the magnetite by synthesis of magnetite-modified silica.

3.2. Chemical Structure of SS and MSS

The existence of functional groups of the Si-O-Si, Si-OH, Fe-O and S-O can be shown through FT IR spectra. Compared with silica sulfonate without magnetite, magnetite-silica resemblance pattern, followed by a decrease in the intensity of several bands, shifting some of the peak and the emergence of new bands in the absorption wavelength around 300 cm^{-1} which indicate the presence of iron oxide. The presence of magnetite particles indicated by the vibration absorption peak of Fe-O from bonding in the molecule Fe_3O_4 at wavelength $324\text{-}354$ and $550\text{-}586\text{ cm}^{-1}$ are attributed to the formation of the ferrite phase. Different from magnetite, FT-IR spectra of silica coated magnetite there are pronounced changes, particularly at a region of $1300\text{-}700\text{ cm}^{-1}$, indicating the presence of silica coating. The first change is the decrease of absorbance intensity that is probable due to the magnetite coverage of magnetite by silica as well as AHNSNa. The presence of silica coated on magnetite is shown by a characteristic band at $450\text{-}470\text{ cm}^{-1}$ from bending vibration of Si-O-Si and. Asymmetry bending vibration corresponding to Si-O-Si bonding is revealed with absorbance band at $787\text{-}802\text{ cm}^{-1}$ and $1072\text{-}1126\text{ cm}^{-1}$. Absorbance bands in coated magnetite IR spectra around $1620\text{-}1640\text{ cm}^{-1}$ and $3400\text{-}3450\text{ cm}^{-1}$ come from bending and stretching vibration, respectively, of -OH groups from both Fe-OH and Si-OH. Stretching vibration of Si-O-H bonding results in absorbance band at $950\text{-}960\text{ cm}^{-1}$. In IR spectra of magnetite coated only with silica, the absorbance of Si-OH vibration does not appear clearly due to overlap with the broad band of stretching vibration from Si-O-Si. In comparison to magnetite and silica coated magnetite, IR spectra of mercaptosilica coated magnetite gives the characteristic absorbance of propyl and mercapto groups from ATR-FTIR. The presence of propyl groups can be indicated by bands at $1040\text{-}1050\text{ cm}^{-1}$ and $1400\text{-}1480\text{ cm}^{-1}$ assigned to stretching vibration of -C-C- chain, bending of CH_2 , respectively. Additionally, C-H bonding in propyl groups results in absorbance at 1240 cm^{-1} and $2920\text{-}2940\text{ cm}^{-1}$ corresponding to bending and asymmetric vibration of C-H. The increase of AHNSNa added during the coating process results in inclining the band intensity characteristics for propyl and sulfonate groups. In addition, a silica coating of magnetite indicated by the appearance of vibration corresponding to bond Si-O-Si at a wavelength of $1000\text{-}1200$ and Si-O at 970 cm^{-1} . The FT-IR spectra of MSS compared to that of SS are shown in Fig. 1.

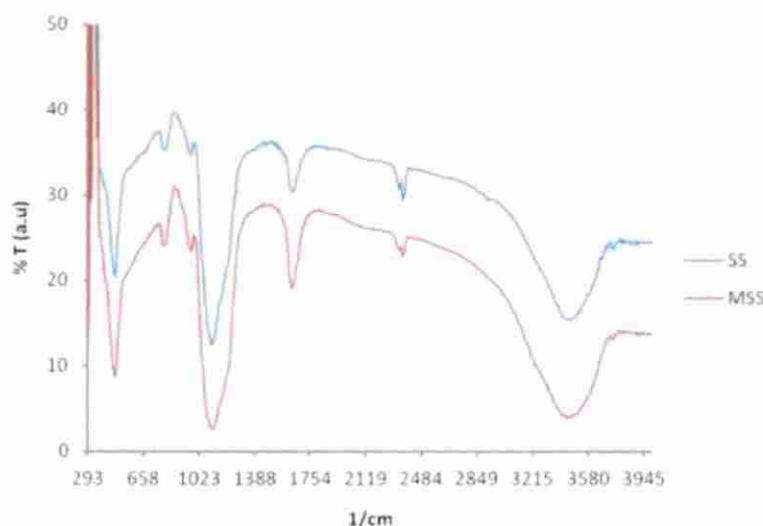


Figure 1. FT-IR spectra of SS and MSS

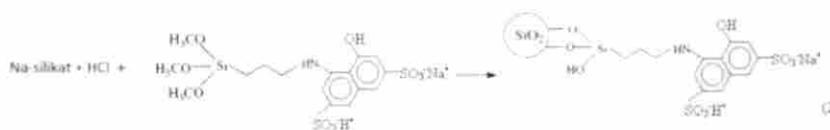
It can be seen from Fig. 1 that absorbance band for MSS at 972.12 cm^{-1} is broader than that of SS (at 956.69 cm^{-1}). It is probable due to overlaps between of Si-O stretching vibration from Si-OH and symmetric stretching of C-S at around $1.095 \sim 1.085\text{ cm}^{-1}$. Also, the two sharp absorbance bands at 2931.80 and 2962.66 cm^{-1} for the SS and MSS indicate the presence of stretching vibration of C-H from methyl and methylene groups, respectively [7], [8]. Absorption bands for the stretching vibration of S = O characteristic at 1.028 , 1.254 , and 1.084 cm^{-1} can not be seen because those overlap with broad band of Si-O from siloxane (at around 1.072 cm^{-1}) [9], [10]. Broad absorption band from 3.100 to 3.450 cm^{-1} is predicted as an overlapping peak between the characteristic band for the O-H vibration (3.450 cm^{-1}), and symmetry was stretching vibration of N-H (3.270 cm^{-1}) [11].

The success of the MSS synthesis can be observed from the composition of the hybrid material by an EDX analyzer (Table 1). If the material contains sulfur, can be expected to emerge successful synthesis SS and MSS. The presence of Fe in the MSS was indicated by the appearance of the element in EDX analyzer. MSS analysis results. This shows that the right of magnetite has been coated by silica sulfonate. The binding sulfur atom was supported by the emergence of other atoms as a supplement, such as the addition of oxygen.

Table 1. The average mass (in w/w) of the element S and Fe in SS and MSS based on data from EDX

Sample	Element	Average mass (% w/w)
Silika Sulfonat (SS)	sulfur, S	23,44
	Silika Oxide, SiO ₂	76,56
Magnetit Silika Sulfonat (MSS)	Sulphur, S	21,02
	Silika Oxide, SiO ₂	78,40
	iron oxide, (Fe ₂ O ₃)	0,57

The presence of iron oxide indicates that magnetite compounds have been tacked on silica gel. While the presence of sulphur showed, a magnetit silica was attached by sulfonato groups. The above structure elucidation supports the reaction model proposed by Azmiyawati et al. [5] that the attachment of AHNSNa onto silica gel occurs in a sequence of two distinct steps. The first step is consisted of binding CTS onto AHNSNa to form disulfonato-aminopropyltrimethoxysilane (PTMDS), Eq. (1), and the second stage, APTMDS reacts with sodium silicate (from RHA) to produce disulfonato-silica hybrid (DSSH), Eq. (2).



3.3. Morphology of SS and MSS

FT-IR spectra is supported by the data of SEM (Fig. 2) which shows that the surface topology of the SS looks and does not accumulation for globular. Based on Fig. 2 shows differences in the surface topology of the two materials. MSS looks to have larger grains than the SS. This size difference may

be result in the gel formation of those materials. SS formation bonding with a sulfonato compound, formation of siloxane framework stop when Si atom bonds to organic groups. Resulting the growth smaller ball polymer. MSS formation occurs continually and grow produce siloxane bonding, leading to formation of larger ball polymer [12]. Coating silica sulfonat onto magnetite, the larger ball polymer formed.

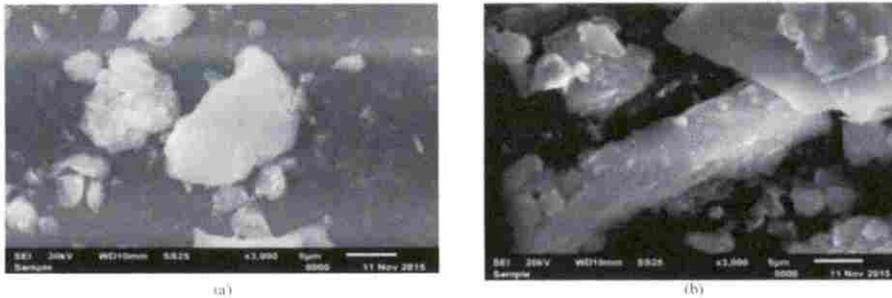


Figure 2. Surface topology of (a) SS and (b) MSS from SEM to 3,000 times magnification.

3.4. Physical Properties of SS and MSS

The effect of magnetite on the formation of magnetite sulfonate silica as shown by their XRD patterns, is illustrated in Fig.3. In the samples obtained by adding the amount of magnetite (b), the characteristic peak of the XRD patterns correspond to the magnetite (JCPDS 19-0629) [13]. And then there is no diffraction peak in the XRD pattern of (b). This shows that magnetite sulfonate silica was formed.

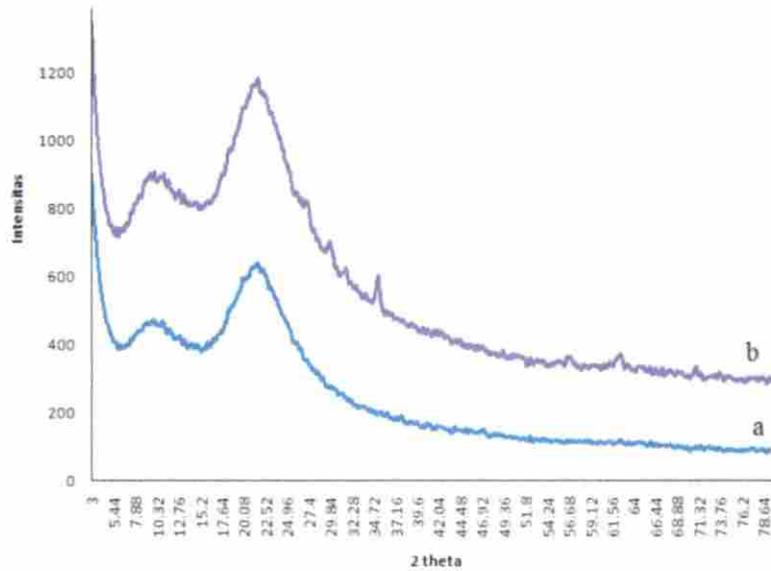


Figure 3. XRD patterns of (a) SS and (b) MSS

The physical properties of a material can be seen one of them through the material resistance to changes in temperature. The heat resistance of a material can be determined via DSC pattern (Fig. 3).

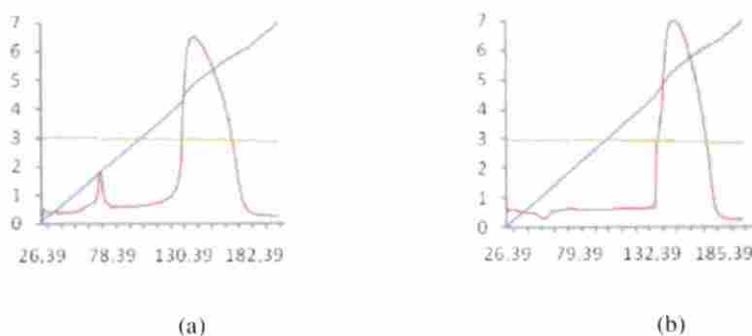


Figure 3. DSC of (a) SS and (b) MSS

4. Conclusion

The iron sand can be used as material for the synthesis of magnetite-based material, such as magnetite silica sulfonate (MSS). The attached of magnetite on silica sulfonate will increase the size of ball polymer in the MSS and the emergence of iron oxide on FTIR spectra was obtained from MSS. In general sulfonate silica coating on magnetite has no effect on the thermal resistance of the MSS

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