

Synthesis of silica coated on iron sand magnetic materials modified with 2-mercaptobenzimidazole through sol-gel

Martasiana Karbeka^{a*}, Nuryono^b, Suyanta^b

^aDepartment of Chemistry, Tribuana Kalabahi University, Alor, 85812 Indonesia

^bDepartment of Chemistry, Gadjah Mada University, Yogyakarta, 55284 Indonesia

Abstract

Synthesis of silica coated on iron sand magnetic materials modified with mercapto was carried out through a sol-gel method. This study aims to obtain adsorbent material that has magnetic properties. The purpose of this research are gift magnetic proprties of adsorbent. It was easy access to the separation of the adsorbent after the adsorption process in aqueous system. Modified silica surface with mercapto group provides spesific and selective for soft metals according to hard soft acid base (HSAB) principle. Solution of Na_2SiO_3 as a silica precursor were coated on the surface of iron sand magnetic materials (MM) that has been activated by acid. Silica which have been coated on MM then modified with compound 2- mercaptobenzimidazole as a functional group of mercapto (-SH). The compound 2- mercaptobenzimidazole does not have a functional group of silanol (Si-OH) and siloxane (Si-O-Si) to bind to the functional group on silica surface. Therefore, chloropropyltrimethoxysilane (CPTMS) was added as a link between silica and 2-mercaptobenzimidazole. Chloropropyltrimethoxysilane (CPTMS) was reacted with 2-mercaptobenzimidazole as mixture I then mixed into silica which has coated MM as mixture II by sol-gel process. Material characterization was carried out by Fourier Transform Infrared (FTIR) spectrophotometer, X- ray diffractometer (XRD) and Vibrating Sample Magnetometer (VSM), and the stability of coated magnetite against acid. The characterization results showed that synthesized adsorbent of MM/ SiO_2 /SH was successful. Coating of iron sand magnetic material with silica modified mercapto increases the stability of the acid and decreases the magnetic properties.

* Corresponding author:

martasianakarbeka@untribkalabahi.ac.id

Received 22 Dec 2019,

Revised 02 Jan 2020,

Accepted 09 Jan 2020

Keywords: Chloropropyltrimethoxysilane; magnetic adsorbent; mercapto group; sodium silicate

1. Introduction

Silica gel is a supporting solid that is widely used in the adsorption process because it is stable in acidic, non-swelling conditions has specific porosity and surface area and has a high resistance to heat. It has been widely used as an adsorbent for the adsorption of heavy metal ions. However, silica gel has a weakness if applied as an adsorbent for soft metal ions such as Hg (II), Pd (II), Au (III). This was due to the interaction of oxygen atoms on the surface of the silica gel containing the functional groups silanol ($\equiv\text{Si-OH}$) and siloxane ($\equiv\text{Si-O-Si}\equiv$) which have a low ability to donate electrons to soft metal ions [1]. Atom O in Silanol and Siloxane group on silica surfaces are hard acids so the ability to be a donor atom against soft metals becomes ineffective. This is in accordance with the principle of hard soft acid base which states that hard atoms interact strongly with hard atoms and soft atoms interact with soft atoms [2,3]. The presence of silanol ($\equiv\text{Si-OH}$) and siloxane ($\equiv\text{Si-O-Si}\equiv$) functional groups make it possible to modified silica surface with various functions such as amino ($-\text{NH}_2$), cyano ($-\text{CN}$), carboxyl ($-\text{COO}$) and mercapto ($-\text{SH}$) to produce silica hybrids. In this research was used mercapto group ($-\text{SH}$) from 2- mercaptobenzimidazole aims to adsorb soft metal ions more specific and selective [1,4]. Modified silica function groups have higher adsorption capability than without modification. Modified silica is very specific and selective to certain heavy metals. The investigation indicate that silica 2-aminothiazole (S2A) is characterized by a relatively higher sorption capacity than that of SG. It is found that S2A can be used for separating Hg(II) and Co(II) ions from the Ni(II), Pb(II), Cu(II), Cd(II) ions an acidic medium [3]. Modifiers of mercapto group wasn't silane reagents, link agent was needed to connected mercapto group on the material magnetic coated silica. Chloropropyltrimethoxysilan (CPTMS) compounds were have silane groups to be used as link agent. Methoxy groups of CPTMS are hydrolyzed to produce silanol, which then condenses to form the silica network. However, the adsorption method has a weakness in the separation process. Adsorbent separation from the adsorbate was carried out conventionally by screening techniques, decantation or can also use the instrument through centrifugation. It was difficult if applied in the environment. The problem becomes interesting to develop adsorbent has magnetic properties begins were facilitate the separation process with the help of external magnets. The silanol ($\equiv\text{Si-OH}$) and siloxane ($\equiv\text{Si-O-Si}\equiv$) functional group on the silica surface makes it easy to coated silica with magnetite (Fe_3O_4) through the formation of Fe-O-Si bonds. Generally, the magnetic source used is the synthesis of $\text{FeCl}_2 \cdot 6\text{H}_2\text{O}$ and $\text{FeCl}_3 \cdot 4\text{H}_2\text{O}$ to produce magnetite (Fe_3O_4) [5–7]. In the present study, utilizing natural iron sand as a giver of magnetic properties in silica modified mercapto adsorbents. Weaknesses of magnetic material are very unstable and easily oxidized by oxygen, can agglomerate and dissolved in acidic medium. The magnetite/silica composite particles present a unique system that enables studying the interactions between magnetic nanoparticles in confined dimensions since the rigid silica layer prevents direct contact between the magnetite particles quite effectively [8]. Coating of 2-mercaptobenzimidazole on silica surface coated magnetic material become a layer to protect magnetic material against oxidation, agglomeration and dissolution in acidic medium. Coating process can reaches up size of silica composite. The agglomerate size of the magnetite (M) is 205.7 nm reaches up to 1029.5 nm the sodium metasilicate magnetite (MS-M); this result is due to the increase in the particle size that this sample suffered during its coating process [9]. In this work, modified of mercapto on silica coated material magnetic was carried out through sol-gel method. This technique is simple and faster because the binding reaction takes place simultaneously with the solid formation process. In addition, the immobilization technique through the sol-gel was easier to do in the laboratory because reactions can be carried out at room temperature so that simpler tools can be used. In the future, this adsorbent could be applied to adsorption soft metal ions such as gold and other precious metals. It was be predicted based on Pearson's Hard-Soft Acid-Based (HSAB) concepts, soft bases strongly interact with soft acids and vice-versa. Mercapto group ($-\text{SH}$) clasified as soft base and gold clasified as soft acid.

2. Experimental

2.1. Material

Iron sand as magnetic material (MM) from Bugel beach, Yogyakarta, aquades. Solution of Na_2SiO_3 as a source of silica is used for coating magnetic materials, 2- mercaptobenzimidazole (MBI) as functional group of mercapto (-SH), 3- chloropropyltrimethoxysilane or CPTMS, triethylamine, 1 M HCl prepared from 37% HCl, dimethylformide or DMF, pH meters. All chemicals were of analytical reagent grade (Merck).

2.2. Synthesis of mercapto silica hybrid coated magnetic material

The AMOUNT of 0.5 g Iron sand magnetic materials was acidified with 1 mL of 1 M HCl then separated by the help of an external magnet. Solution of Na_2SiO_3 1 mL mixed on magnetic material while stirring (Mixture I). Subsequently dissolved 1.44 g of 2- mercaptobenzimidazole in 2.5 ml of dimethylformide and reacted with 1.8 mL 3- chloropropyltrimethoxysilane while continuing to stir and drip triethylamine 1 mL (mixture II). Reacted mixture II into the mixture I while stirring and continuously adding 1 M HCl until it forms a gel. The gel was measured pH (pH meters) and dried overnight by the oven (Memmert), at 80 °C. Solids of the adsorbent were then neutralized by washing distilled water and then dried at 80 °C and characterized using FTIR (Shimadzu FTIR - PRESTIGE 21), XRD (Rigaku Multiflex) and VSM (VSM Oxford 1.2 T) and acid stability test (pH meter).

2.3. Acid stability test

The amount of 10 mg of the adsorbent was placed in a plastic bottle and put into buffer pH 1-6 in each container and then shaken using a 200 VRN shaker (130 rpm) for 90 minutes. The solution was then separated from the adsorbent using an external magnet (Neodymium, N35 grade, size 40 mm x 30 mm x 10 mm) and then the solution was analyzed by atomic absorption spectrophotometer using FAAS, Analytic Jena contraAA 300.

3. Results and discussion

3.1. Functional group of MM/ SiO_2 /MBI

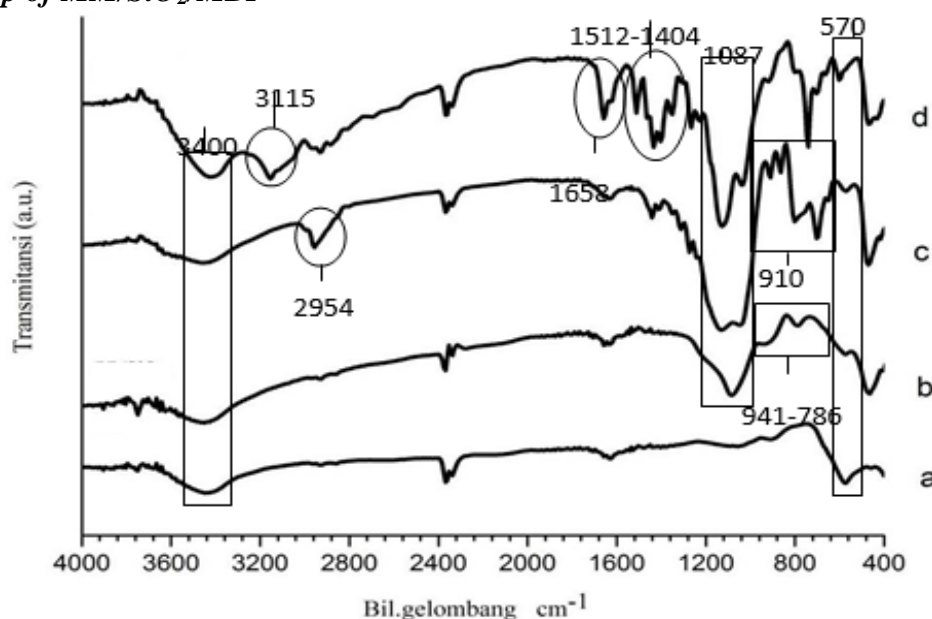
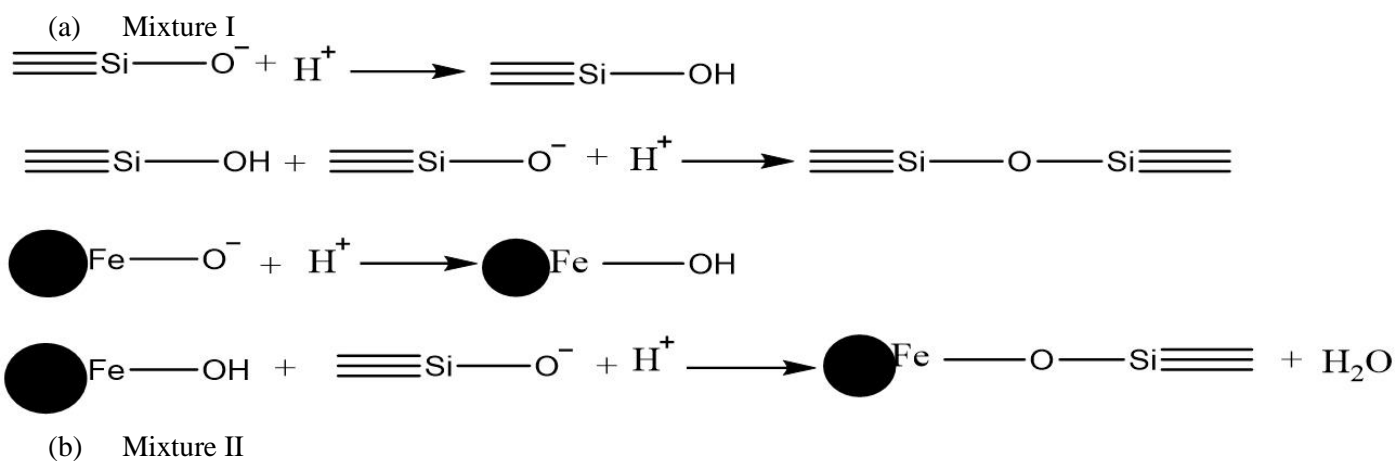
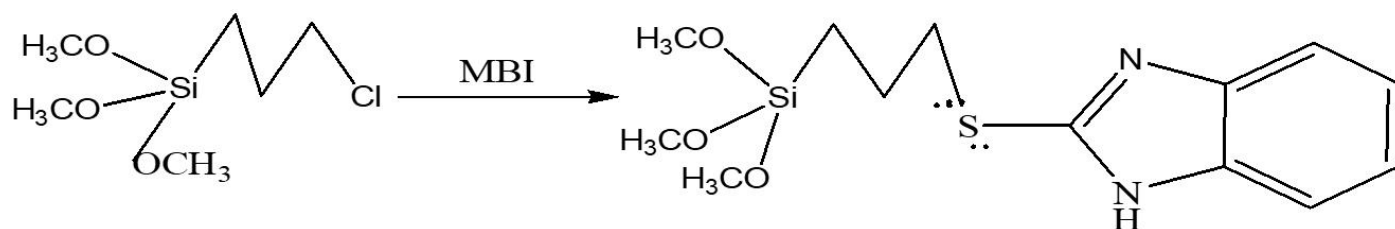


Figure 1: Spectra FTIR of: (a) MM, (b) MM/ SiO_2 , (c) MM/ SiO_2 /CPTMS, (d) MM/ SiO_2 /CPTMS/MBI

Based on Fig. 1(a), shows the spectra at the area of 570 cm^{-1} which indicates the presence of vibrations of Fe-O bonds from Fe_3O_4 found in natural iron sand magnetic material (MM). The absorption peak in the area of 3417 cm^{-1} is the stretching vibration of the -OH group of SiOH and FeOH [4]. In Fig. 1(b), Silica coated magnetic material with the appearance of additional peaks with strong and sharp absorption at the area of 1087 cm^{-1} which is a stretching vibration of Si-O asymmetry from siloxane (Si-O-Si) groups [1]. The absorption peak produced is increasingly sharp because addition of Si-O groups through the formation of siloxane groups (Si-O-Si). This indicated reinforced by the vibration stretching Si-O-Si shown at wave number 941 cm^{-1} . The bands appeared at 786 cm^{-1} is belong to symmetrical stretching vibration of Si-O-Si [10]. Spectra were process of added a link CPTMS shows the characteristic absorption peak at region 2954 cm^{-1} and 2800 cm^{-1} which is C-H stretching vibration of chain alkyl of CPTMS [11]. Fig. 1(c), shows the process of adding CPTMS, there is a shift in the wavelength in the area of 1087 cm^{-1} to 1126 cm^{-1} and the area of 786 cm^{-1} to 702 cm^{-1} . This shift was caused by an environmental change. The siloxane (Si-O-Si) group resulting from the condensation between silicate anions and silanol groups on surface silica with silane groups in CPTMS through a sol-gel process. The formation of siloxane groups is evidenced by the emergence of an increasingly sharp absorption peak at the area of 1126 cm^{-1} [4]. Fig. 1(d), shows spectra with the presence of MBI containing mercapto group (-SH). The mercapto groups in spectra are expected to appear in regions $2600\text{--}2450\text{ cm}^{-1}$ but the absorption peaks in the area are not observed. The active group -SH produces a weak absorption in the infrared spectra. Generally, this band was absent spectra, or had a very low intensity S-H stretches were found at 2509.93 cm^{-1} , which are typically very weak and convoluted by contamination of the CO_2 stretching bands from the background [12]. The vibrations that are active in Raman can be inactive in infrared, and vice versa. Raman spectra recorded of the mercapto groups. It could be observed that all spectra contained lines attributed to C-S and S-S stretching vibrations at 640 and 2575 cm^{-1} [13]. However, to determine the presence of MBI in organosilica material, the aromatic group and the amine group were observed in MBI. The NH group vibration is observed in the area of 3155 cm^{-1} and overlaps with the OH group at 3448 cm^{-1} [1]. The emergence of a new absorption peak at the area of 1512 cm^{-1} is a bending vibration of the N=H of imidazole ring [4]. Stretching vibration $\text{C}=\text{C}$ aromatic is seen in 1658 cm^{-1} and 1404 cm^{-1} of imidazole ring [14]. The results of the analysis by FTIR indicated that the magnetic material was successfully coated with mercapto silica hybrids. Prediction of possible interactions between the surface of magnetite and silica as a coating material through the formation of Fe-O-Si and the addition of a mercapto functional group on the silica surface with the sol-gel method shown in Fig. 2.





(c) Reaction of mixture I and mixture II

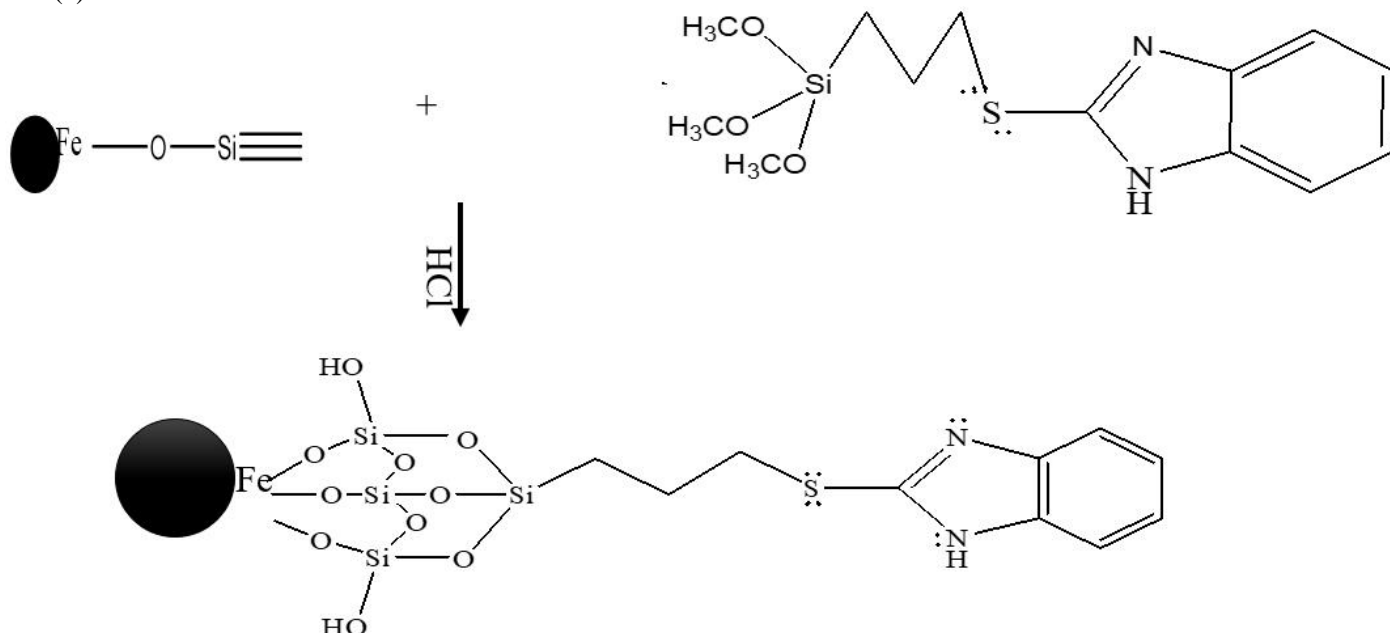


Figure 2: Predicted reaction of synthesized MM/SiO₂/MBI by sol-gel process (a). Acidified of material magnetic (MM) and mix with Na₂SiO₃ formation Si-O-Si and Fe-O-Si; (b). Reaction of CPTMS dan MBI; (c). Reaction of mix.I and mix.II in acidic solution

3.2. The crystallinity of MM/SiO₂/MBI

The presence of magnetite in iron sand magnetic material (MM) and MM/SiO₂/MBI can be identified based on characteristic diffraction angles according to the crystal lattice. The results of X-ray diffraction comparing the diffractogram of MM and MM/SiO₂/MBI are present in Figure 3.

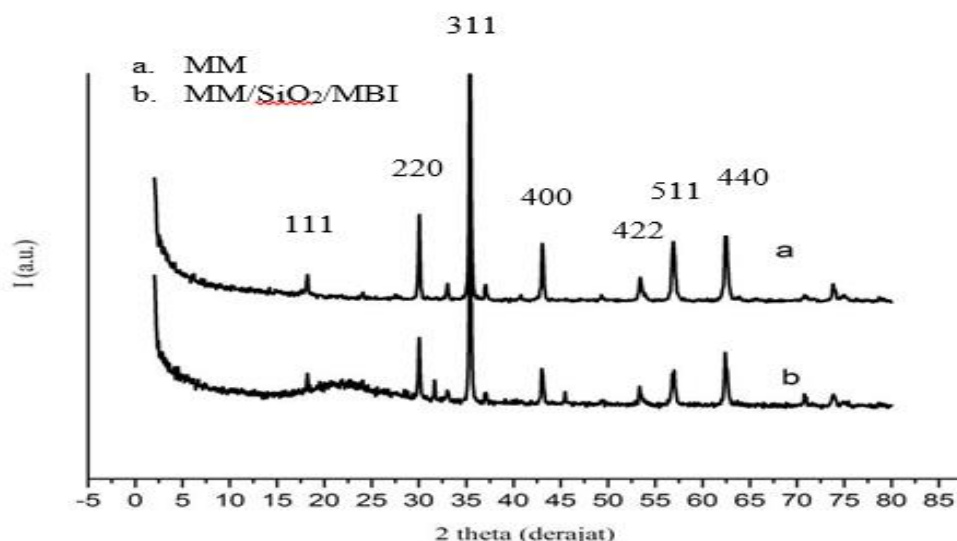


Figure 3: Diffraction of X-rays (a) MM and (b) MM/SiO₂/MBI

Based on Figure 3. shows the peaks that appear in area $2\theta = 30.06^\circ$ [220]; 35.399° [311]; 43.04° [400]; 53.401° [422]; 56.92° [511] and 62.46° [440]. The data corresponds to the magnetite database in the Powder Diffraction File (PDF No.19-0629) which has characteristic peaks with field indices [220], [311], [400], [422] and [511]. The main peaks of 35.50° [311] which are characteristic of magnetite (Fe₃O₄) [15–17]. XRD data in accordance with the results of iron oxide research of the magnetic material Lansilowo iron sand in the form of magnetite iron oxide. To ensure that based on the difraktogram it looks the peaks characteristic of the iron sand magnetic material Lansilowo appeared on $2\theta = 18.74^\circ$; 30.87° ; 36.13° ; 43.78° ; 53.89° ; 57.89° ; and 63.55° . These peaks correspond to the difraktogram of a commercial magnetite with a characteristic crest on $2\theta = 18.29^\circ$; 30.13° ; 35.48° ; 43.13° ; 53.52° ; 57.02° ; and 62.62° [15]. The MM/SiO₂/MBI peak material characteristic of magnetic (Fe₂O₃) not changes after magnetic materials are coated with silica due to silica is a template. Diffractogram of MM with sharp intensity shows that MM has a crystal structure not amorphous showed at Fig. 3(a). Material magnetic (MM) peak intensity is higher than MM/SiO₂/MBI. The decreased in magnetite phase intensity due to the magnetite surface was covered by several coating materials. In this work, the coating of materials such as silica with an amorphous structure undergoing oligomerization and then coated with CPTMS and MBI with considerable molecular weight. the peak widening in the area of $2\theta = 21.8^\circ - 24^\circ$ is characteristic of the amorphous silica structure [5,6,15,18] showed at Fig. 3(b).

Table 1: Crystal size, chrystal lattice and and $d_{hkl}(\text{\AA})$

Material	Dxrd(nm)	a(Å)	dhkl(Å)
MM	28.04	8.4199	2.4733
MM/SiO ₂ /MBI	30.14	8.4069	2.4685

Besed on Table 2. These results indicate that the presence of coating material does not alter the crystal structure of MM. The presence of coating does not affect the structure of magnetite crystals evidenced by obtaining the same value for distances between crystal fields and magnetite crystal lattice parameters in MM and MM/SiO₂/MBI. The MM size increased from 28.04 nm to 30.14 nm after coating. This is possible due to the occurrence of oligomerization of silica

before it is coated on the PB surface and the addition of CPTMS and MBI prevents further oligomeration and this is suspected to affect the occurrence of increased particle size.

3.3. Magnetic properties of MM and MM/SiO₂/MBI

The magnetic properties of the material can be seen in the hysteresis curve in Figure 4.

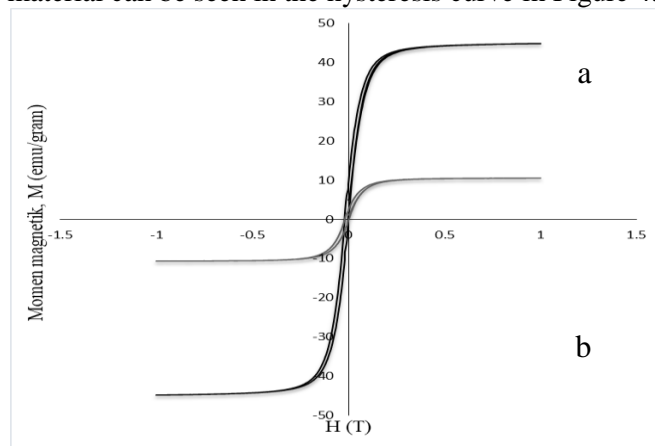


Figure 4: Hysteresis curve (a) MM and (b) MM/SiO₂/MBI

Figure 4 shows narrow curve area, low coercivity, and high saturation. Generally, soft magnets are materials based on Fe as the main material in MM also MM/SiO₂/MBI utilizes magnetite (Fe₃O₄) from iron sand magnetic materials. The hysteresis curve has an almost symmetrical reverse sequence when MM and MM/SiO₂/MBI are subjected to a magnetic field or when the magnetic field is removed. The magnetic properties of MM and MM/SiO₂/MBI show the narrow hysteresis curve area and are classified as soft magnets in Fig. 4 [4–6]. The greater the increase of SiO₂ concentration and the hysterical looped more upright and softmagnetic [19]. Coercivity is used to distinguish hard magnets and soft magnets. The greater coercivity force, the harder of magnetic properties and the magnetic properties are not easily removed. Hysteresis curve area are soft magnets so they require small energy for magnetization and demagnetization according to the small value of H_c (Table 1).

Table 2: Magnetic parameters

Sample	M _s (emu.g ⁻¹)	H _c (Tesla)	M _r (emu.g ⁻¹)
MM	44.9	0.0169	10.9
MM/SiO ₂ /MBI	15.5	0.0161	3.32

Table 2 provides information that MM has greater magnetic properties than MM/SiO₂/MBI which is seen from the M_s value that in MM is greater than MM/SiO₂/MBI. The reduction of magnetic material crystallinity may attributed by coating with amorphous silica which affects magnetite (M_s) saturation magnetization. Silica coating influence on the properties of magnetics is the coercivity of Fe₃O₄ will be proportional to the size of the magnetic nanoparticles are larger. While the value of remanence (M_r) and saturation (M_s) is getting smaller, so when the size of nanoparticles is increasingly predicted to have multi-domain and Barrier energy (Anistropinya energy) is also increasingly greater [20]. This means that more coating material, the more magnetic properties will decrease. The value of M_r is the magnetization remaining after the influence of the outer field of material is removed. Therefore, if the value reaches saturation (M_s) is large then when the external field is reduced then it is possible that remanence or delay (M_r) will also be large.

3.4. Stability of iron sand magnetic materials

Material MM/SiO₂/MBI material which has magnetic properties can be applied in the adsorption process. The adsorption process can be carried out by adding acidic solutions and unstable magnetite in the acid medium. Pure Fe₃O₄ nanoparticles also suffer from its weak chemical stability at low pH.



If the magnetic material has direct contact with acid, it is very possible that dissolved Fe will increase. Therefore, the coating of MM will reduce the amount of dissolved Fe [21]. Magnetic properties of the adsorbent MM/SiO₂/MBI can still be used to process the adsorbate separation from the adsorbent. The stability of the coated magnetic material to the effect of acid addition is presented in Figure 5.

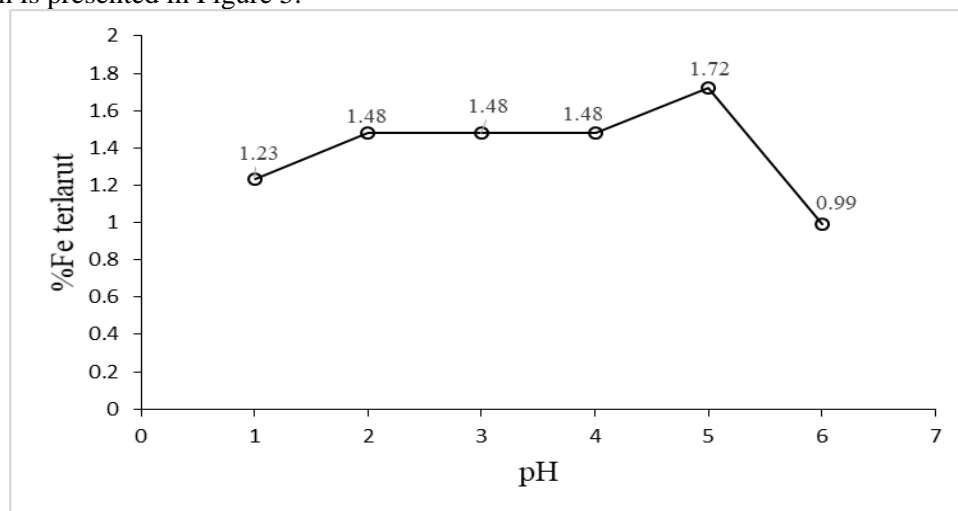


Figure 5: Influence pH of amount dissolved Fe

Figure 5 shows that the amount of dissolved Fe in variations of pH 1-6 is not significant. The stability increased at each step of the support modification thanks to silica- or/and silane- protecting layers and also to the increased hydrophobicity of the silane-containing materials. High stability of the materials at low pH is important for different applications and it is undesirable that the material dissolves while used in the liquid medium with low pH [20]. At extreme pH, the amount of dissolved Fe does not differ greatly from the material at a pH. That it can be said the adsorbent MM/SiO₂/MBI stable against acid. High stability shown by the bound organofunctional group may be caused by an alkyl group - (CH₂)₃- from the CPTMS that binds MBI as connected to the silica surface. The longer the hydrocarbon bridge is more than two methyl groups, the breakdown of the SiC bond does not occur in the acid medium. The coating process causes increased thickness of material MM/SiO₂/MBI due to the presence of oligomerization in silica. Interacts with CPTMS as silane precursors that have carbon chains so that they can prevent acid solutions from being in direct contact with magnetite [7]. In addition, magnetite is not only protected by silica and CPTMS but also on the surface of this material there is MBI. So that the magnetite on the surface of the MM is highly protected from the nature of its instability to acidic solutions.

4. Conclusion

The magnetic material was successfully coated with mercapto silica hybrids with the sol-gel method and adsorbent MM/SiO₂/MBI stable against acid.

References

- [1] C. Azmiyawati, Nuryono, and Narsito, J. Med. Bioeng. 3 (2014) 301–305.
- [2] B. Buhani, N. Narsito, N. Nuryono, E.S. Kunarti, Indones. J. Chem. 9 (2009) 170–176.
- [3] P. Tzvetkova, R. Nickolov, J. Univ. Chem. Technol. Metall. 47 (2012) 498–504.
- [4] A. Amaria, S. Suyanta, N. Nuryono, Indones. J. Chem. 17 (2017) 256–263.
- [5] N. Nuryono, N.M. Rosiati, B. Rusdiarso, S.C.W. Springerplus. 3 (2014) 515.
- [6] M. Muflikhah, B. Rusdiarso, E.G.R. Putra, N. Nuryono, Indones. J. Chem. 17 (2017) 264–273.
- [7] R. Roto, Y. Yusran, A. Kuncaka, Appl. Surf. Sci. 377 (2016) 30–36.
- [8] Y.A. Barnakov, M.H. Yu, Z. Rosenzweig, Langmuir. 21 (2005) 7524–7527.
- [9] S.E. Favela-Camacho, E.J. Samaniego-Benítez, A. Godínez-García, L.M. Avilés-Arellano, J.F. Pérez-Robles, Colloids Surfaces A Physicochem. Eng. Asp. 574 (2019) 29–35.
- [10] H. Setyawan, F. Fajaroh, W. Widiyastuti, S. Winardi, I.W. Lenggoro, N. Mufti, J. Nanoparticle Res. 14 (2012) 807.
- [11] A.P. Tiwari, S.J. Ghosh, S.H. Pawar, Synth. Charact. Funct. Superparamagnetic Nanoparticles Isol. DNA. 5 (2014) 533–542.
- [12] O. Hakami, Y. Zhang, C.J. Banks, Water Res. 46 (2012) 3913–3922.
- [13] I. V Melnyk, R.P. Pogorilyi, Y.L. Zub, M. Vaclavikova, K. Gdula, A. Dąbrowski, G.A. Seisenbaeva, V.G. Kessler, Sci. Rep. 8 (2018) 8592.
- [14] D.L. Pavia, G.M. Lampman, G.S. Kriz, Introduction to Spectroscopy A Guide for student of organic chemistry, London: Brooks/Cole. (2001).
- [15] R. Prasdiantika, S. Susanto, J. Teknosains. 6 (2016) 7–15.
- [16] J. Liu, Y. Yu, S. Zhu, J. Yang, J. Song, W. Fan, H. Yu, D. Bian, M. Huo, PLoS One. 13 (2018) e0191229.
- [17] S. Susanto, R. Prasdiantika, T.C.M. Bolle, J. Teknosains. 6 (2016) 124–129.
- [18] M. Munasir, T. Triwikantoro, M. Zainuri, D. Darminto, J. Penelit. Fis. Dan Apl. 3 (2013) 12–17.
- [19] M. Kuzminska, N. Carlier, R. Backov, E.M. Gaigneaux, Appl. Catal. A Gen. 505 (2015) 200–212.
- [20] S. Taib, E. Suharyadi, Indones. J. Appl. Phys. 1 (2015) 23–30.
- [21] D. Yang, J. Hu, S. Fu, J. Phys. Chem. C. 113 (2009) 7646–7651.