

New Silica Magnetite Sorbent: The Influence of Variations of Sodium Silicate Concentrations on Silica Magnetite Character

C Azmiyawati¹, P I Pratiwi¹, and A Darmawan¹

¹University of Diponegoro, Indonesia

Email: choiril.azmiyawati@live.undip.ac.id

Abstract. The adsorption capacity of an adsorbent is determined by the adsorbent and the adsorbate properties. The character of the adsorbent will play a major role in its ability to adsorb the corresponding adsorbate. Therefore, in this study we looked at the effects of variations of sodium silicate concentrations on the resulting magnetite silica adsorbent properties. The application of silica coating on the magnetite was carried out through a sol-gel process with sodium silicate and HCl precursors. Based on the characterization data obtained, it was found that the silica coating on magnetite can increase the resistance to acid leaching, increase the particle size, but decrease the magnetic properties of the magnetite. Based on Gas Sorption Analyzer (GSA) and X-ray Diffraction (XRD) data it can successively be determined that increase in concentration of sodium silicate will increase the surface area and amorphous structure of the Silica Magnetite.

1 Introduction

Magnetite is a particle that has super paramagnetic properties often used in a variety of applications; one of which is as an adsorbent support material [1]. Magnetite can be pulled strongly by a magnetic field [2], thereby facilitating the separation process between adsorbent and adsorbate by utilizing the help of external magnetic field. Unfortunately, the main composition of magnetite is iron which is highly vulnerable to oxidation. The silica coating on the magnetite in addition to preventing corrosion also generates the active side of the silanol and siloxane groups in the resulting silica magnetite. It is known that silica containing silanol and siloxane groups can bind metal ions. In addition, the silica coating on magnetite provides inert, non-toxic, and biocompatible properties to the human body thus its application is often used in biotech and biomedical practices.

Studies of modified silica magnetics have previously been conducted. A study previously conducted by Mao et al. [3] analysed the synthesis of Fe_xO_y @ silica-pillared clay (SPC) by sol-gel method to control drug release and release. Another study was also conducted by Merdekani [4] concerning the synthesization of Fe_3O_4 / SiO_2 nanocomposite particles using coprecipitation methods. According to Merdekani, the nature of Fe_3O_4 / SiO_2 nanocomposite particles will decrease as heating and increase time increases. Other studies were also performed by incorporating triethylenetetramine on the surface of nanomagnetic iron oxide by using nanosilicon oxide and sorbent yields with covalent triethylenetetramine bonds.

One of the most popular methods used to coat magnetite with silica is the sol-gel method [6]. The sol-gel method is chosen because it has several advantages: better homogeneity, high purity,



relatively low temperature, no reaction with residual compound, and minimal evaporation loss. [7] Silica gel can be synthesized via a sol-gel process through condensation using a solution of sodium silicate in an acidic atmosphere. The thickness of the coating and the number of functional groups present on the magnetite surface will affect the adsorption ability of an adsorbent. Therefore, this study will discuss the effect of sodium silicate on the silica layer of the magnetite. Subsequently, with the information gained each character of the silica magnetite formed and the optimum sodium silica concentration can be determined and used as a reference for further researches.

2 Experimental

2.1 Chemicals and reagent.

Magnetite particles used as the core material in the synthesis of magnetic silica were obtained from the shores of Marina beaches. The magnetite particle size used is 100-170 mesh. Other ingredients used were HCl and Na₂SiO₃ from Merck.

2.2 Instrumentation

The tools used in the extraction of magnetite from natural sand were permanent rod magnets and Vibrational Ball Mill (VBM), Fourier transform infrared spectroscopy (FT-IR) Prestige-21 Shimadzu, powder X-Ray Diffractometer (XRD) Shimadzu XRD-6000, and Gas Sorption Analyzer Quantachrome Instruments versions 2.2 .

2.3 Synthesis of adsorbent

In order to create a solid shell on the surface of the magnetite particles (Fe₃O₄), 5 g Fe₃O₄ were mixed with 400.0 mL of sodium silicate 5% (v/v). Next, HCl 1 M was added dropwise as the mixture was stirred until pH = 7 at room temperature. The gel was aged for further 24 h, and dried in an oven for 2 h at 80°C. The gel was thoroughly washed with distilled water. The particles were separated with a magnet and was air dried. The same steps were applied for each sodium silicate concentrations of 6.7%, 10%, and 20% (v/v). The varying sodium silicate concentrated particles formed and the blank were then coded according to the concentration of sodium silicate, i.e., MS 5%, MS 6.7%, MS 10%, MS 20%, and blank as S. Determination of the characteristics of each products was carried out using FTIR, XRD and GSA to determine the functional group, crystallinity, surface area and pore size contained in the product.

3 Results and discussions

Not only does the silica layer on the magnetite increases its magnetic stability, but it also increases the absorption and desorption ability of the magnetic silica against metal ions. The silica layer on the surface serves as a shield against detrimental environmental effects. Thus, the magnetite becomes more stable and the conversion to FeOOH is curbed. Silica can block magnetic polarization attraction between particles, produce particles dispersed in a liquid medium and protect from damage due to acidic atmosphere. In addition, the presence of silanol groups on the silica coating helps in the adsorption process, especially for metal cations. Aside from being a cation-bonding medium, the silanol group is also a binding site for other functional groups such as sulphonates, thiazols, and surfactants, for instance cetyltrimethylammonium bromide, to facilitate the application of magnetite as an adsorbent.

Visually, the magnetite-silica sorbent produced takes is in a form of grey powder. Figure 1 shows samples of magnetite powder (Figure 1a), silica gel (Figure 1b) and magnetic silica (Fe₃O₄ / mSiO₂) (Fig. 1c). The colour change that occur indicate the presence of magnetite in silica. The black magnetite and the white silica gel subsequently produce magnetite-silica that is grey. The weight of the obtained magnetic silica produced is shown in Table 1.

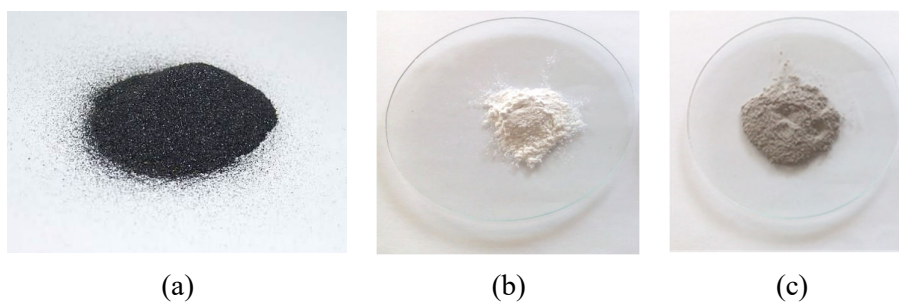


Figure 1 Powder image of magnetite (a), silica gel (b), and magnetite-silica (c)

Based on the data acquired, the greater the concentration of sodium silicate used, the greater is the weight of the resulting silica magnetic particles. Due to the increased concentration of Sodium silicate, silicic anion is more present in the solution. The silicate anion will condense and form a silicate polymer so that more gel is formed. Figure 2 shows the overall reaction of the silica incorporated magnetite layer.

Table 1. Product yield

| Sample | Yield (gram) |
|----------|--------------|
| S | 10.153 |
| MS 20% | 20.0303 |
| MS 10% | 11.285 |
| MS 6.67% | 8.978 |
| MS 5% | 7.524 |

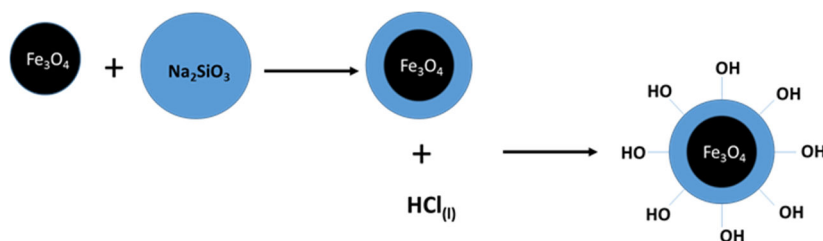


Figure 2 Overall reaction of the silica incorporated magnetite layer

3.1 Functional Groups of the Silica Magnetite

The presence of functional groups on the silica magnetite was determined by FTIR spectra analysis shown in Figure 3. The absorption capacity for silica without magnetite appears at $3400\text{--}3450\text{ cm}^{-1}$ wave number, indicating the presence of vibrations of the free -OH group. The wide and sharp absorption of the wave number $1072\text{--}1126\text{ cm}^{-1}$ shows the asymmetric Si-O group of Si-O-Si . The $1620\text{--}1640\text{ cm}^{-1}$ wave number denotes the vibrations of the -OH group of water molecules, while the wave number $950\text{--}960\text{ cm}^{-1}$ shows the movements of the Si-O group of Si-OH . The absorption at $787\text{--}802\text{ cm}^{-1}$ shows the symmetric Si-O group of Si-O-Si and the uptake at $450\text{--}470\text{ cm}^{-1}$ indicates the bending vibration of the Si-O-Si group.

Compared to silica without magnetite, magnetic silica has a pattern similarity, followed by a decrease in the intensity of multiple bands, multiple band shifts and the appearance of new bands in

absorption around 300 cm^{-1} wavenumbers indicating the presence of Fe metals. The presence of magnetite particles is shown by the peak of the Fe-O group vibration absorption derived from the bonds in Fe_3O_4 molecules at 1000-1200 cm^{-1} wavelengths and Si-O groups at 970 cm^{-1} . [8] In addition, the silica magnetite coating is shown by the emergence of vibrations corresponding to the Si-O-Si bonds in the 1000-1200 wave numbers and the Si-O groups at 970 cm^{-1} [8].

Clearly observed from the peak level of absorption in the infrared spectrum, a sample of magnetic silica with 20% Na-silicate is the best sample of magnetic silica used as a heavy metal ion adsorbent. This is because the absorption peak of -OH of Si-OH at wave number 3448 cm^{-1} has the largest area. This shows that there are a number of -OH terminal groups in the magnetic silica structure. The -OH terminal group will then bind heavy metal chemically (chemisorption).

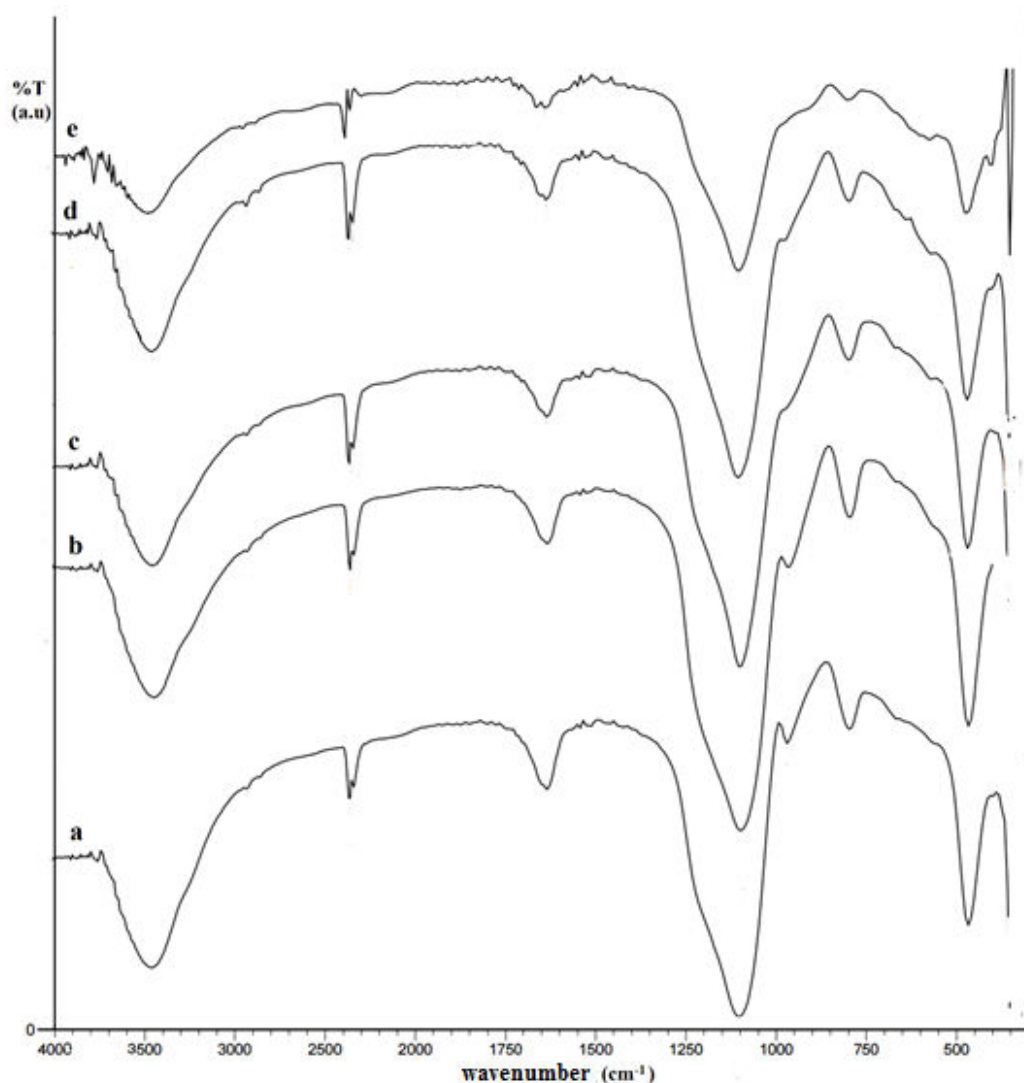


Figure 3 IR spectra of silica gel (S) a), b) MS 20%, c) MS 10%, d) MS 6.67%, and e) MS 5%

3.2 Character of Silica Magnetite

The success of the silica layer on the magnetite can be seen from the seven diffractograms in Figure 4. It can be seen that the presence of silica in magnetite is indicated by the larger peak of

amorphous magnetic silica having a greater silica concentration. Therefore, it can be said that the addition of sodium silicate concentration increases the amorphous properties of the adsorbent. That is, the formed silica layer gets bigger with the addition of sodium silicate.

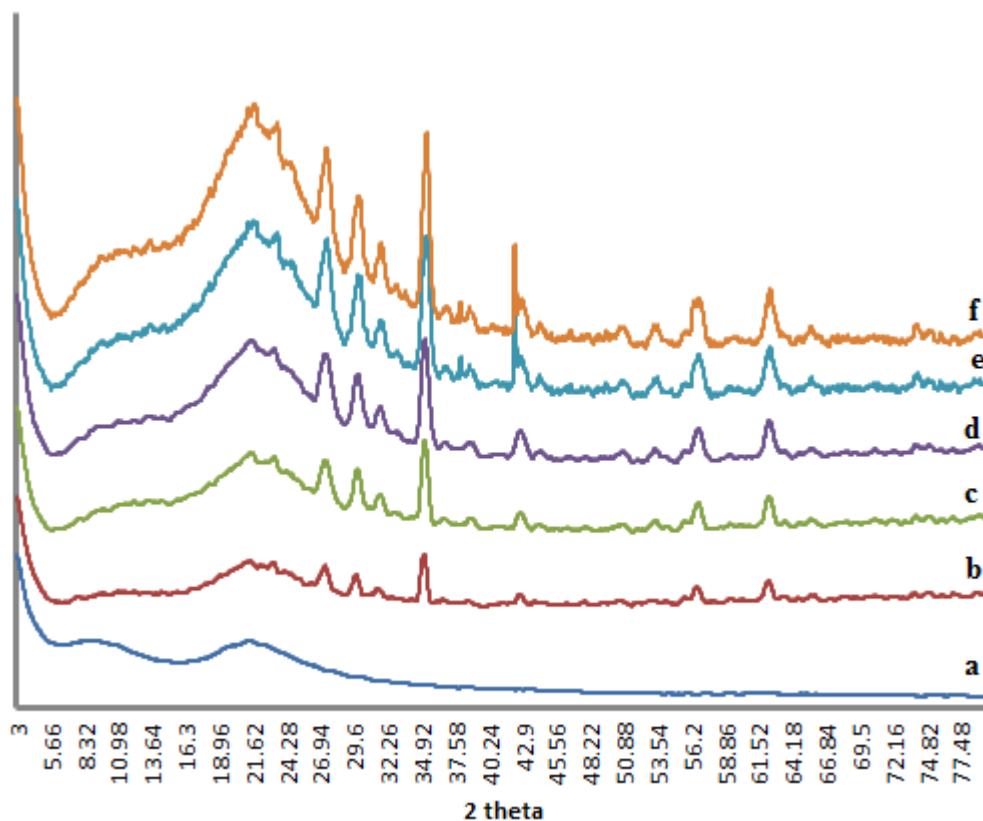


Figure 4 Diffractogram of a) Silica, b) Natural magnetite, c) MS 5%, d) MS 6.67%, e) MS 10%, and f) MS 20%

This silica-coated magnetite is expected to be used in the process of desorption of metal ions by retracting the adsorbent using an external magnetic field so that the adsorbent can be separated from the adsorbed and reusable metal ions. Increasing the amount of silica present in the magnetite layer will forge the active side of the adsorbent in the form of a silanol group thus the adsorbent is expected to bind more metal ions. The addition of the silanol active group can be seen from the results of the FTIR spectra for each of the adsorbents. As can be seen, MS 20% has the sharpest and widest band of about 960 cm^{-1} which shows more silanol groups than the same absorption bands on other spectrums.

Based on the adsorption isotherm curve in Fig. 5, the higher the concentration of sodium silicate, the bigger is the surface area of the magnetite-silica. Overall, the magnitude of surface area, pore size and pore volume are shown in Table 2.

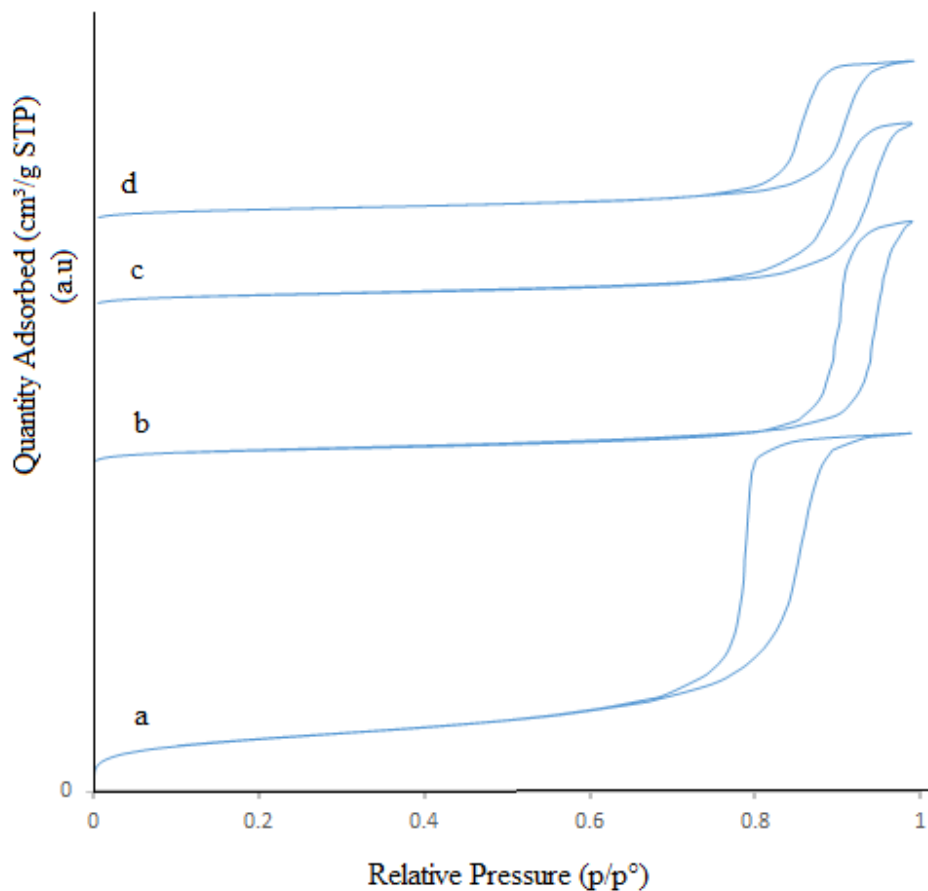


Figure 5 Isotherm adsorption of a) silica, b) MS 20%, c) MS 10%, d) MS 5%

Table 2: Surface area, pore volume and pore size of adsorbent

| Adsorbent | Surface Area (m ² /g) | Pore Volume (cm ³ /g) | Pore size (nm) |
|-----------|----------------------------------|----------------------------------|----------------|
| S | 266.5461 | 0.822 | 12.092 |
| MS 20% | 102.3459 | 0.509 | 19.511 |
| MS 10% | 88.3644 | 0.414 | 18.410 |
| MS 5% | 86.6157 | 0.380 | 17.265 |

Without magnetite, silica has a larger surface area and the volume than magnetite-silica. On the other hand, the pore size of silica is smaller than silica magnetite. The addition of silica to magnetite will create a product with substantial surface area of the as well as the pore volume. Increase in the surface area of the magnetite signifies the increasing amount of silica gel that lines the magnetite. With the addition of sodium silicate concentration, the amount of silica gel coating will increase.

4 Conclusion

Magnetite modified silica was successfully prepared as proven by diffractogram results. The magnetite already exists in magnetic silica compounds. Increased concentrations of sodium silicate affect the number of Si-OH groups and the surface area of magnetite-silica produced. The results explain

that the increase in the number of Si-OH group and the surface area will affect the adsorption capacity of the product.

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