Coating of L-Arginine Modified Silica on Magnetite through Two Different Sol-Gel Routes

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ABSTRACT

In this research, magnetite coated with L-arginine modified silica (Fe_3O_4/SiO_2-GPTMS-Arg) has been synthesized through a sol-gel process at a room temperature in two Routes. In Route 1, a precursor of sodium silicate solution (source of SiO_2), 3-glycidoxypropyltrimethoxysilane (GPTMS) as a coupling agent and L-arginine (Arg) as the source of functional groups were added sequentially to magnetite nanoparticles (Fe_3O_4). Gelling was carried out by adding HCl solution dropwise to the mixture to reach pH of 7.0. The product was washed with water and ethanol and then dried at 65 °C for 1 day. In Route 2, sodium silicate solution was added to a mixture of GPTMS and L-arginine, and then the sol obtained was added into magnetite nanoparticles. The results were characterized with FTIR spectroscopy, X-ray diffraction, atomic absorption spectroscopy and volumetric method to identify functional groups, crystal size, iron ions released and amino groups content, respectively. The results showed that Fe_3O_4/SiO_2-GPTMS-Arg has been successfully synthesized through both two routes. Route 1, however, gave product of Fe_3O_4/SiO_2-GPTMS-Arg more stable and more content of amino groups than Route 2. The presence of amino groups leads to the application of the product for metal ion removal from aqueous solution.

Keywords: *L-arginine; magnetite; silica; sol-gel; coating*

ABSTRAK

Pada penelitian ini, magnetit terlapis dengan silika termodifikasi L-arginin (Fe_3O_4/SiO_2-GPTMS-Arg) telah disintesis melalui proses sol-gel pada suhu kamar dalam dua rute. Pada Rute 1, prekursor larutan natrium silikat (sumber SiO_2), 3-glisidoksipropiltrimetoksisilan (GPTMS) sebagai senyawa penghubung dan L-arginin sebagai gugus fungsional permukaan, ditambahkan secara berurutan ke dalam nanopartikel magnetit (Fe_3O_4). Pembentukan gel dilakukan dengan penambahan larutan HCl tetes demi tetes untuk mencapai pH 7. Produk dicuci dengan air dan etanol, kemudian dikeringkan pada 65 °C selama 1 hari. Pada Rute 2, larutan natrium silikat ditambahkan ke dalam campuran GPTMS dan L-arginin, kemudian sol yang terbentuk dimasukkan ke dalam magnetit. Hasil-hasil yang didapat dikarakterisasi dengan spektroskopi FTIR, diffraksi sinar-X, spektroskopi serapan atom, dan metode volumetri, masing-masing untuk mengidentifikasi gugus fungsional, ukuran kristal, kadar ion besi yang terlarut, dan kadar gugus amino. Hasil penelitian menunjukkan bahwa Fe_3O_4/SiO_2-GPTMS-Arg telah berhasil disintesis melalui kedua rute, namun Rute 1 menghasilkan Fe_3O_4/SiO_2-GPTMS-Arg lebih stabil dan kadar gugus aminonya lebih besar daripada Rute 2. Adanya gugus amino memberikan aplikasi produk untuk penghilangan ion logam dari larutan.

Kata Kunci: *L-arginin; magnetit; silika; sol-gel; pelapisan*

INTRODUCTION

In the last few years, the magnetic material has been very interesting, because of the nature and its potential, which is very profitable. Magnetite (Fe_3O_4), one of magnetic iron oxides, has favorable magnetic characteristics. It is one of the most studied materials, due to the highly potential application in many fields, not only in industrial fields (ceramics, catalyst, energy storage, magnetic storage of data), but also in water treatment for removal of toxic metal ions and water disinfection [1-2]. Magnetite nanoparticles become very important for being developed and studied extensively, because of small particle size (less than 40 nm), a high surface area and superparamagnetism [3-4]. Besides, magnetite nanoparticles have a low toxicity, good chemical resistance and excellent biocompatibility [5]. Unfortunately, magnetite nanoparticles are very

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unstable and easily being oxidized by oxygen or dissolved in acidic medium. Therefore, before being used in various fields it is very important to stabilize the magnetite nanoparticles.

The stabilization of magnetite with an inorganic material, such as silica [6-9] may produce magnetite nanoparticle surface coated with silica and enhance the performance of magnetite. Methods for preparation of silica coated magnetite have been reported by various methods, such as direct silanation [10], sol-gel [11-12] dense-liquid and two-step coating of silica [13]. However, aminopropyltriethoxysilane film silanized on maghemite with direct silanation method shows less stable after leaching test with acid solution [10]. The sol-gel process is a method commonly applied to coat mild particles using a precursor, such as tetraethoxy-orthosilicate (TEOS) in an organic solvent, to produce porous material. The presence of Si-OEt terminal groups of TEOS is reported to be responsible for the porous nature of the coated film [13]. Synthesis of mesoporous silica using a mixture of sodium silicate (Na_2SiO_3) solution and TEOS reported by Liu et al. [14] shows that addition of TEOS can induce larger pore diameter. Higher the content of TEOS more porous particles and the higher the content of sodium silicate gets smaller pore diameter.

The presence of silanol groups on the silica surface can be modified with various functional groups. The addition of basic organic compounds such as L-arginine stabilized magnetite nanoparticles [15-16]. To attach organic functional groups on the magnetite coated silica, a coupling agent is needed. A coupling agent of 3-glycidoxypropyltrimethoxysilane (GPTMS) reported by Davis et al. [17] forms a network of silica and organic epoxy. Methoxy groups of GPTMS are hydrolyzed to produce silanol, which then condenses to form the silica network [18]. The opening of the epoxy ring may occur at room temperature and an organic network may be formed using amine containing compounds [17-19]. Each active hydrogen in the amino group can open and bind to one epoxy group.

In this work, we synthesized L-arginine modified silica coated on magnetite nanoparticle surface using linker of GPTMS through a sol-gel process. Since the synthesis involved some precursors namely magnetite, sodium silicate solution, L-arginine, and GPTMS, the sequence of mixing precursors (mixing Route) may affect the characters of the product. Therefore, this paper also reports the synthesis of magnetite coated with L-arginine modified silica conducted through two different Routes. On Route 1, an interaction of precursors (magnetite, sodium silicate, GPTMS, L-arginine) was carried out sequentially. On Route 2, mixing of precursors was conducted in two stages. GPTMS and L-arginine were mixed firstly and then incorporated into sodium silicate solution and suspension of magnetite. We demonstrate the differences of both types of Route in term of the crystal size, chemical stability, and the elements composition.

EXPERIMENTAL SECTION

Materials

Magnetite (Iron (II)(III)) oxide powder, GPTMS (≥ 98%) were purchased from Sigma-Aldrich. Sodium silicate solution (25.5-28.5% SiO_2), L-arginine powder, ethanol absolute (99.5%), hydrochloric acid (HCl 37%), sodium hydroxide (NaOH) were purchased from Merck and used as received.

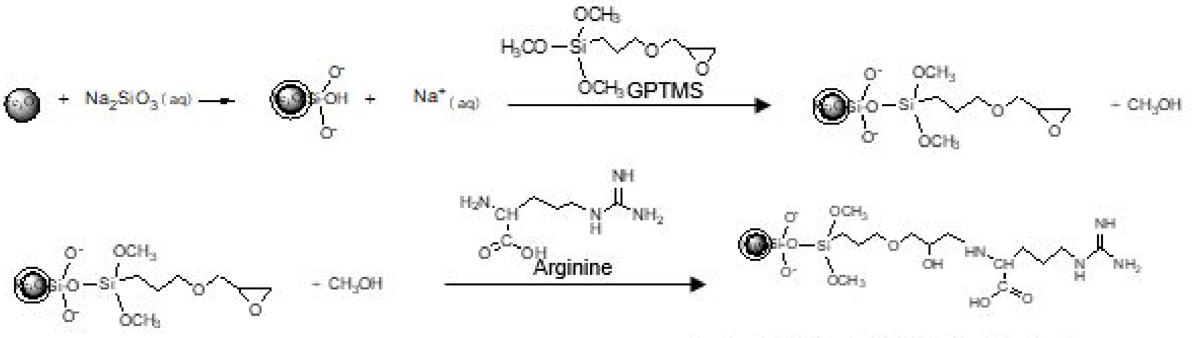
Instrumentation

FTIR spectrophotometer (Shimadzu FTIR 8400S) was used to identify functional groups of materials, diffractometer X-ray (XRD Bruker D8 Advance 206276) was used for determination of material phase and the crystal size. The concentration of iron ion in solution was determined by absorption atomic spectrophotometer (AAS, Analyst 100 Perkin Elmer). The element composition of materials was measured with energy dispersive X-ray (EDX Carl Zeiss 9 EVO MA 10 series 1454). The measurement of pH solution was conducted with a pH meter (pH/ion 510 Eutech Oacton). A set of equipment for acid-base titration was used to analyze the content of amino groups. The magnetic value of coated magnetite samples was measured with vibrating sample magnetometer (VSM) type OXFORD YSMI.2H

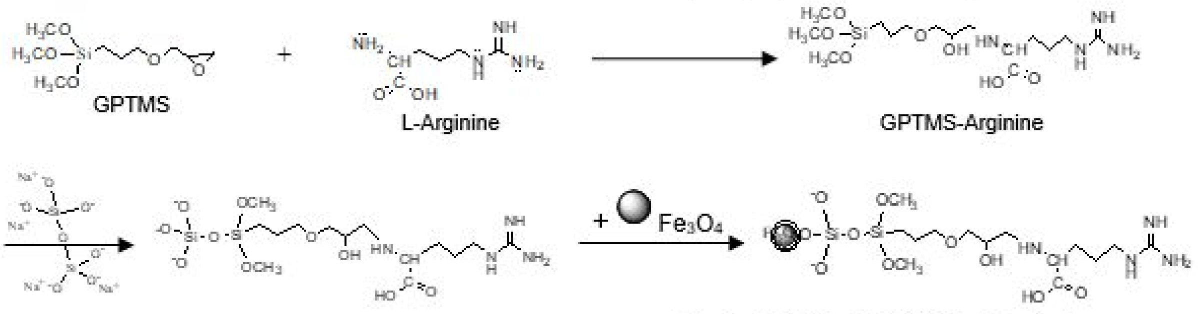
Procedure

Coating of L-Arginine modified silica on magnetite through Route 1 (Fe_3O_4/SiO_2-GPTMS-Arg Route-1)

Magnetite sample 0.2 g, was suspended in 5 mL of distilled water and sonicated for 5 min. Then the magnetite suspension was added with 6 mL sodium silicate solution (1:1) and sonicated for 15 min and followed by mechanical stirring for 30 min. After that, the mixture was added with 1 mL GPTMS and stirred for 30 min, and finally 1 mL of 1 M arginine was added and stirred mechanically for 1 h. The mixture was added with 2 M HCl drop wise up to pH 7 (Adapted from Hastuti et al. [20]). The gel formed was aged and kept overnight at a room temperature, washed with distilled water and ethanol 3 times, and dried in an oven at 65 °C to constant weight.



a) Fe_3O_4/SiO_2-GPTMS-Arg-Route 1



b) Fe_3O_4/SiO_2-GPTMS-Arg-Route 2

Fig 1. The reaction model of coating L-arginine modified silica on magnetite through a) Route1 and b) Route-2

Coating of L-Arginine modified silica on magnetite through Route-2 (Fe_3O_4/SiO_2-GPTMS-Arg Route-2)

Route 2 consisted of two mixtures, namely mixture of GPTMS-arginine-silicate sol and magnetite suspension using the same amount of composition as Route 1. The first mixture was prepared by mixing GPTMS, L-arginine and stirring for 15 min and then was added with sodium silicate solution and stirred for 2 h. The second mixture was prepared by suspending magnetite in 5 mL of distilled water and sonicated for 5 min. The GPTMS-Arginine-silicate sol then was incorporated into the magnetite suspension, sonicated for 15 min and stirred mechanically. Lastly, the similar treatment was carried out to Route 1. The difference of reaction steps of both Routes was modeled in Fig. 1.

Characterization

Samples of Fe_3O_4/SiO_2-GPTMS-Arg obtained were characterized by identification of crystal structure and size with X-ray diffraction. X-ray diffractograms were recorded at a 2θ range of 5-80° in scan speed 5°/min from X-ray diffractometer. The energy source used Cu-Kα radiation (λ 0.154 nm) at voltage 40 kV and current of 30 mA. Identification of functional group was conducted with FTIR spectrophotometer Shimadzu 8400S at a wave number 400-4000 by KBr pellet technique. The element composition of the coated magnetic synthesized was analyzed with Energy Dispersive X-ray Spectroscopy (EDX).

Estimation of amino group content. The content of arginine in the product was estimated based on the number of amino groups analyzed with volumetric analysis [21]. Twenty-five milliliters of 0.05 M HCl solution was added to the 0.05 g of the coated magnetite sample and shaken for 15 h. HCl concentration found in the residue was measured by titration with 0.05 M NaOH solution using phenolphthalein as the indicator. The number of HCl mmol g^{-1}) interacting with amino groups was calculated using Equation 1.

$$\text{Concentration of amino groups} = \frac{(M_1 - M_2)\times 25}{0.05}\,\text{mmol/g} \quad (1)$$

where M_1 and M_2 are the initial and final concentration of HCl, respectively.

Stability toward acidic medium. The chemical stability of coated magnetite was examined by dipping the sample (25 mg) in a solution of hydrochloric acid 1 M. The mixture was shaken for 3 h and stored for a night at a room temperature. The filtrate then was separated from the coated magnetite using an external magnetic field and measured the content of dissolved iron with AAS [22-23]. The magnetic property (magnetization values) of the coated magnetite was measured with vibrating sample magnetometer (VSM) at the maximum field strength of 1 Tesla.

RESULT AND DISCUSSION

The characteristics of L-arginine modified-silica coated magnetite identified with methods described previously are presented and evaluated in the following sections.

Functional Groups of Fe_3O_4/SiO_2-GPTMS-Arg

The success in coating magnetite with L-arginine modified silica is showed by comparing the FTIR spectra of precursor and the products. FTIR spectra of magnetite, L-arginine, GPTMS and silica precursors are presented in Fig. 2a-d and FTIR spectra of Fe_3O_4/SiO_2-GPTMS-Arg Route1 and 2 are presented in Fig. 2e and 2f. In Fig. 2a, 2e, and 2f are observed absorption peaks corresponding to the Fe-O vibration from magnetite phase at 585, 569, and 563 cm^{-1}, respectively [24]. It indicates that the magnetite is coated with arginine-silica. The phenomenon can be explained by the formation of Fe-O-Si bond. Hydrogen atoms of Fe-O-H on the surface have been replaced with Si atom to form Fe-O-Si. Si atom is larger than H, so the bond is longer and weaker, therefore the absorption bands shift to lower wave numbers [25].

In Fig. 2d is observed absorption at 3474, 1092, 800, 469 cm^{-1}, corresponding to stretching vibration of O-H (Si-OH), asymmetric and symmetric stretching vibration and bending vibration of Si-O(Si-O-Si), respectively. Spectra Fig. 2e from Fe_3O_4/SiO_2-GPTMS-Arg Route 1 shows that magnetite has been coated by silica, based on specific absorption at 3441, 1086, 795, and 459 cm^{-1}. Moreover, FTIR spectra of Fe_3O_4/SiO_2-GPTMS-Arg Route 2 (Fig. 2f) shows specific bands of silica at 3402, 1090, 795, and 451 cm^{-1}, assigned to –OH (Si-OH silanol) groups stretching vibration, asymmetric and symmetric stretching and bending vibration of siloxane Si-O(Si-O-Si), respectively [20,26].

The absorption peak associated with GPTMS and L-arginine can be seen at 2940 and 2839 cm^{-1} corresponding to asymmetric and symmetric stretching vibration of C-H, respectively (Fig. 2b and 2c) [26], and also appears in Fig. 2e with wave number at 2943, 2881 cm^{-1} and in Fig. 2f at 2937 and 2878 cm^{-1}. Characteristic absorption bands related to guanidine functional groups of arginine are seen at 1560 and 1684 cm^{-1} (Fig. 2b) assigning to bending vibration of N-H and stretching vibration of C=N [26-28]. In this study, FTIR spectra of Fe_3O_4/SiO_2-GPTMS-Arg Route 1 and 2 (Fig. 2e and 2f) show the bands at 1565, 1664 and 1574, 1668 cm^{-1}, respectively. In addition, the bands at 1256 and 908 cm^{-1} are ascribed to symmetric and asymmetric stretching vibration of the C-O-C the epoxy ring of GPTMS [29], which appears in Fig. 2c at 1196 and 910 cm^{-1}. FTIR spectra of Fe_3O_4/SiO_2-GPTMS-Arg Route 1 (Fig. 2e) shows the peak completely disappears. It indicates that epoxy ring has been opened and covalently bound to N atom of L-arginine. The FTIR spectra of Fe_3O_4/SiO_2-GPTMS-Arg Route 2 shows the peaks are almost completely disappeared. It appears at 1200 cm^{-1} in a weak intensity, nevertheless formed -OH functional group of the C-OH is seen at wave numbers 1063 cm^{-1} [26]. The bands at 1668, and 1574 cm^{-1} related to stretching vibration of C=N and bending vibration of N-H of guanidine group from L-arginine [28]. Other supports of the presence of the amino group from L-arginine on the coated magnetite were confirmed by analysis elemental composition determined from EDX and volumetric data.

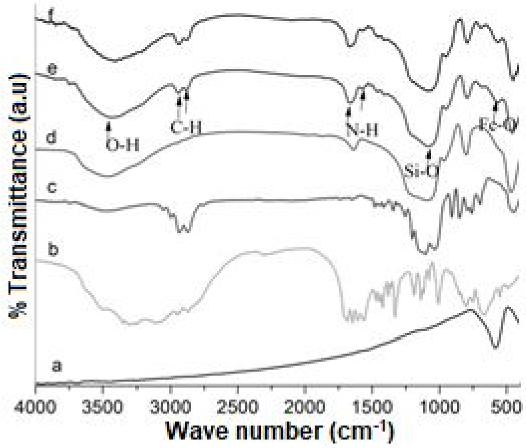


Fig 2. FTIR spectra: a) magnetite, b) L-arginine, c) GPTMS, d) silica e) Fe_3O_4/SiO_2–GPTMS-Arg-Route 1 and f) Fe_3O_4/SiO_2-GPTMS-Arg-Route 2

Structure and Crystal Size

X-ray diffraction method was performed to analyze crystal structure of coated and uncoated magnetite, and the XRD pattern is presented in Fig. 3. The structure of magnetite does not change with presence of silica and L-arginine. From XRD patterns of L-arginine-modified silica-coated magnetite through Route 1 and 2 can be seen a decrease of peak intensity on the index field (220), (311), (400), (511), (440) and (533) (JCPDS card no. 19-0629) in comparison to uncoated magnetite. In addition, it is observed amorphous phase of SiO_2 in 2θ 20-26 degrees (Fig. 3b and c) confirmed with JCPDS No.46-1045, for SiO_2. In Fig. 3b, coated magnetite Route 1 can be seen a phase change, namely maghemite (Fe_2O_3) [30]. This may be attributed to the effect of stirring process and the reaction of magnetite surface with sodium silicate, GPTMS, and L-arginine in Route 1 is longer than that in Route 2.

Table 1. Structural properties of L-arginine modified silica-coated magnetite

Sample	2θ(°)	d_{311}(Å)	D(nm)
Fe_3O_4 uncoated	35.346	2.54	36.00
Fe_3O_4/SiO_2-GPTMS-Arg route 1	35.498	2.53	37.16
Fe_3O_4/SiO_2-GPTMS-Arg route 2	35.506	2.53	45.32

Table 2. Chemical stability of coated magnetite presented in dissolved Fe

Sample	$Fe_{dissolved}$ (mol g^{-1})	Condition	Ref
Fe_3O_4/SiO_2-SH (50/50)	1.88	HCl 1 M	23
Fe_3O_4-D	2678.60	HCl pH 2.5	33
Magnetic-APTES	607.00	HCl 0.01 M	10
Fe_3O_4	10.95×10^{-5}	HCl 1 M	This work
Fe_3O_4/SiO_2-GPTMS-Arg-route 1	0.86×10^{-5}	HCl 1 M	This work
Fe_3O_4/SiO_2-GPTMS-Arg-route 2	3.01×10^{-5}	HCl 1 M	This work

Table 3. Elemental composition of L-arginine modified silica-coated magnetite nanoparticles Route 1 and 2 based on Energy Dispersive X-ray Spectroscopy (EDX) data

Elements	Fe_3O_4/SiO_2-GPTMS-Arg-Route 1		Fe_3O_4/SiO_2-GPTMS-Arg -Route 2	
	wt%	at%	wt%	at%
O	46.88	49.25	47.03	51.25
Si	25.87	15.48	28.50	17.69
C	20.89	29.23	17.48	25.38
N	4.58	5.49	3.76	4.68
Fe	1.78	0.54	3.23	1.01

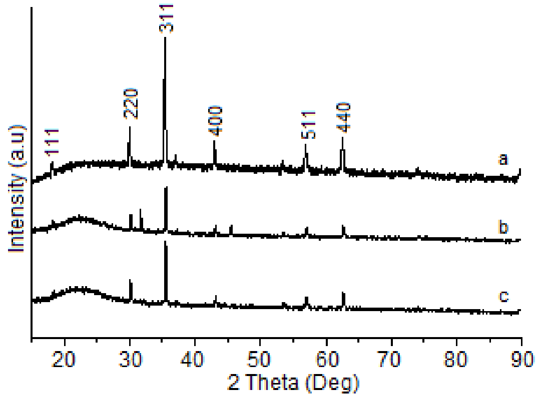


Fig 3. XRD patterns of a) magnetite, b) Fe_3O_4/SiO_2-GPTMS-Arg Route 1 and c) Fe_3O_4/SiO_2-GPTMS-Arg Route 2

Analysis of the index plane peaks of the samples Route 1 and 2 based on XRD pattern, d_{311} spacing and the crystal size are obtained and presented in Table 1. In general, coating increases crystal size and slightly decreases d_{311} spacing. From Table 1 can be seen that crystals size of L-arginine modified silica-coated magnetite is greater than that of uncoated magnetite. The crystal size is calculated using Scherer equation (2).

$$D = \frac{K\lambda}{\beta \cos\theta} \qquad (2)$$

K is a constant of 0.9, λ is the wavelength of light diffraction (1.54 Å), β is a diffraction peak full-width half maximum (FWHM) in radian and cos θ is the angle of diffraction peaks [30-31]. The crystals size of Fe_3O_4/SiO_2-GPTMS-Arg Route 2 (45.32 nm) is greater than that of Route 1 (37.16 nm). This can be explained, that in Route 2 the epoxy group of GPTMS react with nitrogen atom of L-arginine to form covalent bond of C-N and to produce crystals [32] greater size than in Route 1.

The value of spacing basal in Table 1 shows a slight decrease in magnetite nanoparticles coated with L-arginine-modified silica (2.53 Å) compared to uncoated magnetite (2.54 Å). It is possible that the presence of arginine-modified silica in the magnetite surface leads to result in the distance between the molecules of magnetite decrease.

Chemical Stability

The chemical stability of Fe_3O_4/SiO_2-GPTMS-Arg Route 1 and 2 was examined in acid solution (hydrochloric acid 1 M for 1 day). The chemical stability of Fe_3O_4/SiO_2-GPTMS-Arg sample was based on the quantity of iron dissolved. The quantity of iron dissolved from Fe_3O_4/SiO_2-GPTMS-Arg was measured by atomic absorption spectroscopy and results were expressed in Table 2. The quantity of iron dissolved for Fe_3O_4/SiO_2-GPTMS-Arg Route 1 (0.859×10^{-5}mol g^{-1}) is smaller than that of Route 2 (3.01×10^{-5}mol g^{-1}). In hydrochloric acid solution, Fe_3O_4 are dissolved to produce $Fe^{2+}$and Fe^{3+} ions, according to Equation (3)

$$Fe_3O_{4(s)} + 8HCl_{(aq)} \rightarrow 2FeCl_{3(aq)} + FeCl_{(aq)} + 4H_2O_{(l)} \qquad (3)$$

It is necessary to point out that the product of Fe_3O_4/SiO_2–GPTMS-Arg Route 1 is more stable in the

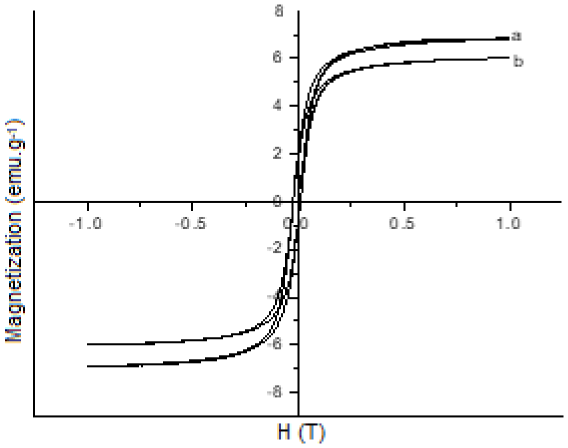


Fig 4. Magnetization curve of Fe_3O_4/SiO_2/GPTMS-Arg (a) Route 1 and (b) Route 2

acid medium than Route 2. When magnetite is added to sodium silicate solution, reaction between silicate monomer with magnetite surface to form complex of ≡Fe-OSi$(OH)_2$OX or $(≡FeO)_2$-Si(OH)OX [34]. While in Route 2, magnetite is added latest after GPTMS, L-arginine and sodium silicate were mixed, it may produce arginine-modified silica-coated magnetite film incompletely.

Elemental Composition and Estimation of Amino Groups Content

Elemental composition analysis was performed with EDX and the result is expressed in Table 3. It is observed that the percentage of Fe is smaller than that of Si due to silica derived from sodium silicate and GPTMS. Based on these data, we performed the semi-quantitative surface analysis by calculating theoretically the weight ratio of silicon to iron (Si/Fe) in the Route 1 and 2 of 14.5 and 8.8, respectively. It is evidence that a number of silica coated on magnetite through Route 1 is higher than that of Route 2. Based on the theoretical calculation of the weight ratio Si/Fe is 12.47. The difference is predicted because there is a small portion of Fe released when the product was washed with water. Carbon content in the product resulted in Route 1 and 2 is 20.89 and 17.48%, and nitrogen content in Route 1 and 2 is 4.58 and 3.76%, respectively. The mole ratio of carbon to nitrogen in Route 1 and 2 is 5.8:1 and 5.44:1, respectively. The observation data is greater than based on the theoretical calculation (C:N = 3.75:1). This is probable due to the polymerization of carbon chains.

These data support the results of stability tests on the acidic medium, in which the quantity of iron dissolved in Fe_3O_4/SiO_2-GPTMS-Arg-Route 1 (0.86×10^{-5} mol g^{-1}) is smaller than that in Route 2 (3.01×10^{-5} mol g^{-1}). In addition, mass percentage of nitrogen in Fe_3O_4/SiO_2-GPTMS-Arg-Route 1 is higher (4.58%) in comparison to Fe_3O_4/SiO_2-GPTMS-Arg-Route 2 (3.76%). Also, the quantity of nitrogen confirmed by the estimation of amino group content of magnetite coated with L-arginine modified silica (Fe_3O_4/SiO_2-GPTMS-Arg) was found to be 0.364 and 0.266 mmol g^{-1} for Route 1 and 2, respectively The presence of amino groups leads to the application of the product Fe_3O_4/SiO_2-GPTMS-Arg for metal ion removal from aqueous solution.

Magnetic Properties

Magnetic property of Fe_3O_4/SiO_2-GPTMS-Arg was examined with a vibrating sample magnetometer (VSM) and the results are shown in Fig. 4. The magnetization of Fe_3O_4/SiO_2-GPTMS-Arg Route 1 and 2 are 6.82 and 6.02 emu.g^{-1}, respectively. The results are agreed with the previous researchers reporting that the coating decreases a value of the magnetization. Nuryono et al. [23] reported that the magnetite coated with thiol-silica decreases the saturation magnetization value from 70.39 to 14.05 emu.g^{-1}. Although the saturation magnetization of the magnetite coated with L-arginine modified silica is smaller than the native magnetite (55-78 emu.g^{-1}) [24], the attractive forces to the external magnetic field is still be proceed. Therefore, the purpose to separate the magnetic product using a magnet can be achieved

CONCLUSION

In this study, L-arginine modified silica-coated magnetite through two different sol-gel routes using GPTMS to link silica and L-arginine has been synthesized successfully. The L-arginine modified silica-coated magnetite through Route 1 (mixing sequentially) is more stable against acidic medium and contains more amino group than that through Route 2 (mixing in two steps). The presence of amino groups in L-arginine-silica coated on magnetite leads to the application of the product for metal ion removal from aqueous solution.

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