Synthesis and characterization of L-Arginine modified silica by sol-gel method prepared rice hull ash

Sri Hastuti1,*, Nuryono2, Agus Kuncaka2

1 Department of Chemistry, Faculty of Mathematics and Natural Sciences, Sebelas Maret University, Surakarta, Indonesia
2 Department of Chemistry, Faculty of Mathematics and Natural Sciences, Gadjah Mada University, Yogyakarta, Indonesia
* Corresponding author: hastuti.uns@gmail.com

Abstract. The synthesis of L-arginine modified silica using 3-glycidoxypropyl-trimethoxysilane (GPTMS) as linking agent has been done through sol-gel process. Sodium silicate (Na2SiO3) from rice hull ash (RHA) as the silica source precursor, L-arginine solution 0.9 M with various volume ratios and the linking agent were mixed to form a gel labelled SiO2(RHA)-Arg. The synthesis was successfully carried out in the form of bone white solids. Furthermore, SiO2(RHA)-Arg were characterized using Fourier transform infrared (FTIR) spectrophotometer, elemental analyser, thermogravimetric analyser (TGA) and 29Si-NMR. FTIR spectra of SiO2(RHA)-Arg shows two new peaks at 1672 and 1583 cm⁻¹ confirming NH₂ and C=O groups, respectively. Elemental analysis indicates that the mol ratio of GPTMS: L-arginine is 5:1. TGA analysis explains that the ratio of SiO2: GPTMS: Arg is 5:5:1. The analysis of 29Si-NMR indicate that the silica binds two molecules of GPTMS. The results of SiO2(RHA)-Arg characterization show that silica atom binds two molecules of GPTMS, and every molecule of GPTMS binds five L-arginine molecules.

Keywords: Synthesis, L-Arginine, Modified, Silica, Rice Hull Ash

1. Introduction

Rice husk is a waste product of the process results in agricultural commodities produced about 75 million tons per year worldwide [1]. Rice husk ash contains very high concentrations of silica, more than 60% [1-4]. Moreover, husk ash is a very potential material as a source of silica (Na₂SiO₃) to produce new silica-based materials [5].

As an adsorbent, silica is a very important support solid. The advantage of silica is that it has high porosity, large surface, no swelling, resistance to microbial attack, radiation decay and thermal [6-9]. Chemically, silica contains silanol (-Si-OH) and siloxane (-Si-O-Si) group, which can be modified with active groups [10-12]. On the other hand, silica also has weaknesses such as low selectivity and low adsorption to metal ions. It is because silica contains only oxygen atoms as electron donors. The investigator reported that the modified silica may improve the capacity and selectivity for Au(III) [5, 13, 14]. Therefore, modification of the silica is a way to improve its ability as adsorbent.

Chemical surface modification of silica can be done in two ways. First, it is immobilized active group of organosilane the silica surface directly. Second, it is immobilized organosilane as linker then followed by conversion of strategic groups into active groups having better properties such as high capacity and selectivity to certain metal ions [11, 15-18].
Sol-gel method is a homogeneous pathway. This method has some advantages such as simple and fast. This is because the binding takes place along with the formation of solids and more active compounds bound to the surface. Pavan et al. [19] modified silica with aniline by sol-gel method. Aniline is immobilized on the silica surface using chloropropyltrimethoxysilane (CPTMS) as linker. Hastuti et al. [14] studied about L-arginine-modified silica (SiO$_2$-Arg) with 3-glycidoxypropyltrimethoxysilane (GPTMS) as the linking agent. It has been synthesized through sol gel process with tetraethyl orthosilicate (TEOS) as the silica source precursor for adsorption of Au(III) in aqueous solution. Sakti and Siswanta [5] make ionic imprinted amino-silica hybrid (Im-ASH). Synthesis was carried out by sol gel with Na$_2$SiO$_3$ from rice husk ash mixed with 3-aminopropyltrimethoxysilane and Au(III) ion as the template. In this study, modification of silica with L-arginine was carried out on a sol gel with Na$_2$SiO$_3$(RHA) as the silica source a precursor, GPTMS as a linker. Compared with 3-aminopropyltrimethoxysilane, L-arginine contains four amine groups thus increasing adsorption capacity.

2. Materials and methods
The materials used were L-arginine (Arg), 3-glycidoxypropyltrimethoxysilane (GPTMS) and HCl from Merck. As the source of silica was used sodium silicate from rice husk ash (Na$_2$SiO$_3$ (RHA)).

The equipment used was infrared spectrophotometer (FTIR, Shimadzu IR Prestige 21) for functional group analysis. Elemental analyser (CHN Corder MT-Yanaco 6 Elemental Analyser) was used to determine the elemental composition of the compound. Thermogravimetric (sta-PT-1600 TG-DSC/DTA Linseis Thermal Analyser) was used to calculate the weight percent lost during heating. Nuclear magnetic resonance spectrometer (NMR 29Si, Agilent 600 MHz NMR) was used to determine the position modifier bound by silica atoms.

The synthesis was carried out by mixing 6 mL of Na$_2$SiO$_3$(RHA), 1 mL GPTMS 4.5 M, and 0.9 M in variation in volume (1, 2, 3 and 4 mL). The mixture was stirred with a magnetic stirrer for 2 hours. Then it was added with HCl 6.0 M to form a gel. The gel formed was left for 24 hours. The product was neutralized with 1.0 M HCl, then washed with distilled water and dried at 60°C. The solids obtained was L-arginine modified silica (SiO$_2$(RHA)-Arg). The next, SiO$_2$(RHA)-Arg) were characterized using FTIR spectrophotometer, element analyser, thermogravimeter and $^{29}$Si NMR spectrometer.

3. Result and Discussion

3.1. Synthesis of L-arginine modified silica (SiO$_2$(RHA)-Arg)
The ability of adsorbent was influenced by active site of L-arginine. More L-arginine to be added, the adsorption capacity of SiO$_2$(RHA)-Arg increase. In this research, the addition of L-arginine did not change the weight of L-arginine modified silica (Table 1). This is possible because the amount of L-arginine is bound to the maximum GPTMS. Thus the mol L-arginine chosen in this study was 0.9. The mol ratio of GPTMS: L-arginine is 4.5:0.9 = 5:1.

| L-arginine (mmole) | SiO$_2$(RHA)-Arg (g) |
|-------------------|----------------------|
| 0.9               | 1.887                |
| 1.8               | 1.865                |
| 2.7               | 1.755                |
| 3.6               | 1.807                |
3.2. Characteristics of L-Arginine Modified Silica

3.2.1. Functional groups. The synthesized material was analysed by FTIR to study changes in functional groups. The analysis was performed using KBr pellets technique at wave number of 400 to 4000 cm\(^{-1}\). FTIR analysis results can be seen in Fig. 1 and the peak changes are listed in Table 2.

![Figure 1. FTIR spectra: (A) SiO\(_2\)(RHA), (B) SiO\(_2\)(GPTMS), (C) SiO\(_2\)(RHA)-Arg.](image)

**Table 2. Characteristics of IR absorption** (A) SiO\(_2\)(RHA), (B) SiO\(_2\)(GPTMS), (C) SiO\(_2\)(RHA)-Arg.

| Characteristics adsorption | Wave Numbers (cm\(^{-1}\)) | A     | B     | C     |
|----------------------------|-----------------------------|-------|-------|-------|
| Si-OH                      | 3050                        | 3414  | 3414  |
| Si-O-Si                    | 1087                        | 1105  | 1085  |
| C-H (Aliphatic)            | -                           | 2939  | 2943  |
| C=O                        | -                           | -     | 1583  |
| O-H (H\(_2\)O)             | 1631                        | 1631  | 1631  |
| N-H                        | -                           | -     | 1672  |

FTIR spectra of SiO\(_2\)(RHA)-Arg shows two new peaks at 1672 and 1583 cm\(^{-1}\) confirming NH\(_2\) out of plane bending and stretching vibration of C = O, respectively (Kumar and Rai, 2010). This shows that L-arginine is bound to the GPTMS.

3.2.2. The element composition. Elemental analysis was performed using elemental analyser (Elemental Analyser) to determine the content of C, H and N. The result of elemental analysis of SiO\(_2\)(RHA) and SiO\(_2\)(RHA)-Arg were shown in Table 3. Table 3 shows that SiO\(_2\)(RHA)-Arg contains of 2.70% nitrogen. Meanwhile there is no nitrogen atom in SiO\(_2\)(RHA). The presence of nitrogen in SiO\(_2\)(RHA)-Arg indicates that the modification of silica with L-arginine has been successfully performed.
Table 3. Data elemental composition (% w/w).

| Types         | weight (mg) | C(%) | H(%) | N(%) | (N/C) |
|---------------|-------------|------|------|------|-------|
| SiO$_2$(RHA)  | 2.736       | 1.55 | 1.43 | 0.00 | 0.000 |
| SiO$_2$(RHA)-Arg | 2.611      | 19.06| 4.54 | 2.70 | 0.141 |

The structure of SiO$_2$(RHA)-Arg can be predicted by comparing the weight percent of nitrogen with carbon (N/C). Based on the elemental analysis, the value (N/C) for SiO$_2$(RHA)-Arg is 0.141. Theoretically, the mole ratio of GPTMS to L-arginine is presented in Table 4. The weight of the nitrogen atom in one L-arginine molecule is 56 g/mol. N to C ratio of SiO$_2$(RHA)-Arg in Table 3 close to the results of theoretical calculations as listed in Table 4 for 0.129. It confirms the mol ratio of GPTMS: L-arginine is 5: 1.

Table 4. Data (N/C) theoretically.

| GPTMS: Arg | Atomic weight of C$_{Tot}$ (g/mol) | N/C theoretical |
|------------|-----------------------------------|-----------------|
| 1: 1       | 144                               | 0.388           |
| 2: 1       | 216                               | 0.259           |
| 3: 1       | 288                               | 0.194           |
| 4: 1       | 369                               | 0.155           |
| 5: 1       | 432                               | 0.129           |

3.2.3. The thermal properties. The thermal properties of SiO$_2$(RHA), SiO$_2$(RHA)-Arg and SiO$_2$(GPTMS)-Arg were studied through thermogravimetric analysis (TGA). The analysis was carried out from at 27-800°C with a heating rate of 10°C/min. The result of thermogravimetric analysis was shown in Fig. 2.

![Figure 2](image_url)

Figure 2. The curve of thermogravimetry analysis: (A) SiO$_2$(RHA), (B) SiO$_2$(RHA)-Arg, (C) SiO$_2$(GPTMS)-Arg.

SiO$_2$(RHA) thermogram shows two-stages process during heat treatment. The first stage is releasing of bound water at 70-140°C characterized by mass loss of 9.32% (-1.172 mg). The second stage is
condensation of silanol to form siloxane groups by releasing water molecules characterized by a mass loss of 2.74% (-0.345 mg) at 140-200°C [20].

The SiO$_2$(RHA)-Arg thermogram shows three stages of the process. The release of water molecules is characterized by a loss of mass of 11.23% (-1.481 mg) at 70-125°C and 3.51% (-0.464 mg) is silanol condensation at 125-270°C. The third stage is the degradation of GPTMS and L-arginine 270-700°C with a mass loss of 30.35% (-4.006 mg).

On the SiO$_2$(GPTMS)-Arg thermogram shows two stages. The first stage is the release of water bound 60 -140°C characterized by a mass loss of 13.50% (-3.026 mg). The second stage is the degradation of GPTMS and L-arginine 140 -700°C with a mass loss of 61.72% (-21.351 mg). Based thermogram patterns indicate that SiO$_2$(RHA)-Arg and SiO$_2$(GPTMS)-Arg have binding L-arginine while SiO$_2$(RHA). This confirms that the synthesis of L-arginine modified silica has been formed. Detailed degradation can be seen in Table 5.

**Table 5.** molecules produced in the process of analysis by TGA.

| Molecules          | SiO$_2$(RHA) | SiO$_2$(RHA)-Arg | SiO$_2$(GPTMS)-Arg |
|--------------------|--------------|-----------------|-------------------|
| H$_2$O adsorbed    | 9.32         | 12.22           | 13.50             |
| H$_2$O condensation| 2.74         | 3.51            | -                 |
| R-Arg              | -            | 30.36           | 61.72             |
| SiO$_2$            | 87.94        | 53.91           | 24.78             |

TGA analysis results on SiO$_2$(GPTMS)-Arg (Table 5) can then be used to predict the structure of L-arginine modified silica. SiO$_2$(GPTMS)-Arg is a reaction between GPTMS and L-arginine without Na$_2$SiO$_3$(RHA). Each one molecule of SiO$_2$(GPTMS)-Arg consists of one Si atom (SiO$_2$) which binds to the alkyl chain (R) in the GPTMS. Whereas L-arginine will bind to alkyl (R) in the GPTMS. When heated at a temperature of around 700°C, the organic group from GPTMS and L-arginine (R-Arg) will be released. Theoretically, the molecular weight of R-Arg can be calculated by comparison of GPTMS: Arg = 1:1, 2:1, 3:1, 4:1, 5:1.

The experimental results show the mole ratio SiO$_2$: R-Arg is 0.401 (24.78%/61.72%) while theoretical results are shown in the table 6. The calculation of experimental corresponds to the theoretical result of 0.398. It indicates that the ratio of SiO$_2$: GPTMS: Arg = 5:5:1.

**Table 6.** Mole ratio (SiO$_2$: GPTMS: L-arginine) theoretically.

| SiO$_2$: GPTMS: Arg | Theoretical molecular weight (g/mol) | Theoretical |
|---------------------|--------------------------------------|-------------|
|                     | SiO$_2$(GPTMS)-Arg | SiO$_2$ | R- Arg | SiO$_2$: R- Arg |
| 1: 1: 1             | 350 | 60 | 290 | 0.207 |
| 2: 2: 1             | 526 | 120 | 406 | 0.296 |
| 3: 3: 1             | 702 | 180 | 522 | 0.345 |
| 4: 4: 1             | 878 | 240 | 638 | 0.376 |
| 5: 5: 1             | 1054 | 300 | 754 | 0.398 |

3.2.4. $^{29}$Si-NMR analysis. The $^{29}$Si-NMR analysis of SiO$_2$(RHA)-Arg shows three peaks (Fig. 3). The peaks are 61.148; 96.717; 105.609 ppm showing T$_2$ (Si(OSi)$_2$R$_2$); Q$_3$ (Si(OSi)$_3$OH and Q$_4$ (Si(OSi)$_4$), respectively [21-23].
Figure 3. $^{29}$Si-NMR Spectra of SiO$_2$(RHA)-Arg.

$T_2$ type in Fig. 4 indicate that the silica bound another compound referred (R). The $^{29}$Si NMR spectra can be used to the structural form of the L-arginine modified silica. The proposed model is described in Fig. 5.

Figure 4. Silicone unit types in silica: $T_2$, $Q_3$, and $Q_4$ type [24].

Figure 5. Proposed model of L-arginine modified silica structure.

Based on the results of the characterization of FTIR, TGA, elemental analysis and $^{29}$Si NMR analysis could be estimated that the scheme of the formation mechanism of L-arginine modified silica SiO$_2$(RHA)-Arg follow stages as depicted in (Fig. 6). The first stage is hydrolysis of GPTMS with water (Fig. 6 reaction I). The second stage is the opening of the epoxide ring and reaction with the amine group of L-
arginine (Fig. 6 reaction II). The third stage is the hydrolysis of Na₂SiO₃(RHA) with HCl 6.0 M (Fig. 6 reaction III). The fourth stage is the condensation reaction (Fig. 6 reaction IV).

**Figure 6.** Proposed mechanism of synthesis reaction SiO₂(RHA)-Arg.

4. Conclusion
The synthesis of modified L-arginine silica can be performed by sol-gel method, with Na₂SiO₃(RHA) as precursor, GPTMS as linker and L-arginine as modifier. The result of the synthesis is a solid bone white. The success of the synthesis can be seen from the results of L-arginine optimization, elemental analysis, FTIR, TGA and ²⁹Si-NMR.

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References
[1] Kalapathy U, Proctor A and Shultz J 2002 An improved method for production of silica from rice hull ash Bioreour. Technol. 85 3 285-9
[2] Mujiyanti D R, Nuryono N and Kunarti E S 2016 Sintesis Dan Karakterisasi Silika Gel Dari Abu Sekam Padi Yang Diimobilisasi Dengan 3-(Trimetoksisilil)-1-Propantiol Jurnal Sains dan
Terapan Kimia 4 2 150-67

[3] Putro A L and Prasetyoko D 2007 Abu sekam padi sebagai sumber silika pada sintesis zeolit ZSM-5 tanpa menggunakan template organik Akta Kimindo 3 1 33-6

[4] Valchev I, Lasheva V, Tzolov T and Josifov N 2009 Silica products from rice hulls J. Univ. Chem. Technol. Metall. 44 3 257-61

[5] Sakti S C W and Siswa D 2012 Adsorption of gold (III) on ionic imprinted amino-silica hybrid prepared from rice hull ash Pure Appl. Chem. 85 1 211-23

[6] Xie F, Lin X, Wu X and Xie Z 2008 Solid phase extraction of lead (II), copper (II), cadmium (II) and nickel (II) using gallic acid-modified silica gel prior to determination by flame atomic absorption spectrometry Talanta 74 4 836-43

[7] Jal P K, Patel S and Mishra B K 2004 Chemical modification of silica surface by immobilization of functional groups for extractive concentration of metal ions Talanta 62 5 1005-28

[8] Zougagh M, Pavón J C and De Torres A G 2005 Chelating sorbents based on silica gel and their application in atomic spectrometry Anal. Bioanal. Chem. 381 6 1103-13

[9] Mahmoud M E, Masoud M S and Maximous N N 2004 Synthesis, characterization and selective metal binding properties of physically adsorbed 2-thiouracil on the surface of porous silica and alumina Microchim. Acta 147 1-2 111-5

[10] Kunarti E S 2010 Production of metal ion imprinted polymer from mercapto–silica through sol–gel process as selective adsorbent of cadmium Desalination 251 1-3 83-9

[11] Shiraiishi Y, Nishimura G, Hirai T and Komasawa I 2002 Separation of transition metals using inorganic adsorbents modified with chelating ligands Ind. Eng. Chem. Res. 41 20 5065-70

[12] Abou-El-Sherbini K S, Kenawy I, Hamed M A, Issa R and Elmorsi R 2002 Separation and preconcentration in a batch mode of Cd (II), Cr (III, VI), Cu (II), Mn (II, VII) and Pb (II) by solid-phase extraction by using of silica modified with N-propylsalicylaldehyde Talanta 58 2 289-300

[13] Tong A, Akaya Y and Tanaka S 1990 Selective preconcentration of Au (III), Pt (IV) and Pd (II) on silica gel modified with γ-aminopropyltriethoxysilane Anal. Chim. Acta 230 179-81

[14] Hastuti S, Nuryono N and Kuncaka A 2015 L-Arginine-Modified Silica for Adsorption of Gold (III) Indones. J. Chem. 15 2 108-15

[15] Ngeontae W, Aeungmaitepriom W and Tuntulani T 2007 Chemically modified silica gel with aminothioamidoantraquinone for solid phase extraction and preconcentration of Pb (II), Cu (II), Ni (II), Co (II) and Cd (II) Talanta 71 3 1075-82

[16] Budiman H, Sri H and Setiawan A 2009 Preparation of silica modified with 2-mercaptoimidazole and its SorptionProperties of Chromium (III) J. Chem. 6 1 141-50

[17] de Namor A D and Abbas I 2010 Diethyl sulfide modified silica and calix [4] pyrrole chelating resin: Synthesis and mercury (II) cation retention properties Anal. Methods 2 1 63-71

[18] Sipaut C S, Mansa R F, Padavettan V, Rahman I A, Dayou J and Jafarzadeh M 2015 The effect of surface modification of silica nanoparticles on the morphological and mechanical properties of bismaleimide/diamine matrices Adv. Polym. Technol. 34 2

[19] Pavan F A, Leal S, Costa T M, Benvenuti E V and Gushikem Y 2002 A sol-gel synthesis for thermally stable aniline/silica material J. Solgel Sci. Technol. 23 2 129-33

[20] DeOliveira E, Neri C R, Ribeiro A O, Garcia V S, Costa L L, Moura A O, Prado A G, Serra O A and Iamamoto Y 2008 Hexagonal mesoporous silica modified with copper phthalocyanine as a photocatalyst for pesticide 2, 4-dichlorophenoxyacetic acid degradation J Colloid Interface Sci. 323 1 98-104

[21] Castricum H L, Sah A, Geenevasen J A, Kreiter R, Blank D H, Vente J F and Johan E 2008 Structure of hybrid organic–inorganic sols for the preparation of hydrothermally stable membranes J. Solgel Sci. Technol. 48 1-2 11-7

[22] Lelli M, Gajan D, Lesage A, Caporini M A, Vitzthum V, Miéville P, Héroguel F, Rascón F, Roussy A and Thieuleux C 2011 Fast characterization of functionalized silica materials by silicon-29 surface-enhanced NMR spectroscopy using dynamic nuclear polarization J. Am.
Chem. Soc. 133 7 2104-7

[23] Kim S-H, Han O-H, Kim J-K and Lee K-H 2011 Multinuclear solid-state NMR investigation of nanoporous silica prepared by sol-gel polymerization using sodium silicate Bull. Korean Chem. Soc. 32 10 3644-9

[24] Kim K J, Lee M-S, Jo K and Hwang J-K 2011 Piperidine alkaloids from Piperretrofractum Vahl. protect against high-fat diet-induced obesity by regulating lipid metabolism and activating AMP-activated protein kinase Biochem. Biophys. Res. Commun. 411 1 219-25