L-ARGININE-MODIFIED SILICA FOR ADSORPTION OF GOLD(III)

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Received December 1, 2014; Accepted March 17, 2015

ABSTRACT

In this research, L-arginine-modified silica (SiO_2-Arg) with 3-glycidoxypropyl-trimethoxysilane (GPTMS) as the linking agent has been synthesized through sol gel process for adsorption of Au(III) in aqueous solution. Tetraethyl orthosilicate (TEOS) as the silica source precursor, L-arginine solution 0.9 M with various volume ratios and the linking agent were mixed together to form a gel. SiO₂-Arg was characterized using Fourier transform infrared (FTIR) spectrophotometer, thermogravimetric analysis (TGA), and an elemental analysis. Adsorption was carried out in a batch system under various experimental conditions including contact time and initial concentration of metal Au(III). The selectivity of adsorbent toward Au(III) was examined in the presence of Cu(II), Fe(III), and Zn(II) ion at various pHs. Results of characterization showed that silica has been successfully modified with L-arginine. The optimum adsorption of Au(III) on SiO₂-Arg was obtained at pH of 3.0 and the adsorption isotherm of Au(III) on SiO₂-Arg gives the adsorption capacity of 52.79 mg/g. The kinetic study demonstrates that the adsorption of Au(III) ion follows pseudo-second order with the rate constant of 53197 g mol⁻¹ min⁻¹. The selectivity order of Au-Zn = Au-Cu > Au-Fe. This sol-gel preparation is simple and provides prospective application of SiO₂-Arg material as an effective adsorbent for metal ions particularly gold(III).

Keywords: silica; modification; L-arginine; adsorption; gold(III)

ABSTRAK

Dalam penelitian ini, silika termodifikasi L-arginin (SiO₂-Arg) dengan 3-glisidoksipropil-trimetoksisilan (GPTMS) sebagai penggandeng telah disintesis melalui proses sol gel untuk adsorpsi Au(III) dalam larutan air. Tetraetil ortosilikat (TEOS) sebagai prekursor sumber silika, larutan L-arginin 0,9 M dengan berbagai perbandingan volume dan zat penggandeng dicampur bersama-sama untuk membentuk gel. SiO₂-Arg dikarakterisasi menggunakan spektropotometer Infra Merah, analisis termogravimetri, dan analisis unsur. Adsorpsi dilakukan dalam sistem batch pada berbagai kondisi termasuk waktu kontak dan konsentrasi awal ion logam Au(III). Selektivitas adsorben terhadap Au(III) diuji dengan hadirnya ion logam Cu(II), Fe(III), dan Zn(II) pada berbagai pH. Hasil karakterisasi menunjukkan bahwa silika telah berhasil dimodifikasi dengan L-arginin. Adsorpsi optimum Au(III) pada SiO₂-Arg diperoleh pada pH 3,0 dan isoterm adsorpsi Au(III) mengikuti pseudo orde dua dengan konstanta laju 53197 g mol⁻¹. Urutan selektivitas Au-Zn = Au-Cu > Au-Fe. Preparasi sol-gel ini sederhana dan memberikan aplikasi yang prospektif dari material SiO₂-Arg sebagai adsorben yang efektif terutama untuk ion logam emas(III).

Kata Kunci: silica; modifikasi; L-arginin; adsorpsi; emas(III)

INTRODUCTION

Recovery of gold from waste water is more interesting than that of most other metals [1]. Moreover gold recovery from aqueous solutions has received significant attention because gold is present in appreciable amounts in electronic parts and plating materials [2]. The content of gold in electronic waste is greater than the gold content of the ore. For example, gold concentrations in mobile phone handsets and

* Corresponding author. Tel/Fax : +62-85725590941 Email address : hastuti.uns@gmail.com computer circuit boards are about 300-350 and 200-250 g/t, respectively [3] while the ore contains gold in a range of 5-30 g/t [4].

There are several methods for the removal of gold(III) from aqueous solutions, such as solvent extraction [5-6] and adsorption [1]. The last method seems to be the most suitable for the recovery of gold(III) in the case of low concentration due to low cost and high efficiency. In development of adsorbent, silica gel is very important material because it can be

used as a support material possesses some advantages such as high mechanical and chemical properties, high porosity, large surface, no swelling, resistant in microbial attack, resistant in decay radiation and heat-stable [7-10]. In addition, chelating agents can be easily bonded chemically to the support, that affording a higher stability [7]. Chemically, silica contains functional groups of silanol (-Si-OH) and siloxane (-Si-O-Si-) on the surface, allowing to be modified with active groups specific to certain targets [11-13].

One way to improve the ability of silica as an adsorbent is by surface modification with organic functional groups. Modification may be chemically conducted by using organosilane compound as a linker, which then is followed by attachment of the active group to the linker. The various linker has been used for the modification of silica, such as 3-aminopropyltriethoxy silane (APTES) [14], 3-chloropropyltrimethoxysilane (CPTMS) [15], 3-aminopropyltrimethoxysilane (APTMS) [16-17]. 3-glycidoxypropyltrimethoxysilane (GPTMS) [18]. Donor atoms commonly used as the active group include nitrogen (e.g. amine, azo, amide and nitrile), hydroxyl, carbonyl oxygen (e.g carboxyl, and phosphoryl), and sulfur (e.g. thiocarbamate, thioethers, and mercapto) [8]. The selectivity of the immobilized surface towards Au(III) depends on various factors such as kind of complexing agent and characteristic of the hard-soft acid-base [19-20]. Chelating agents with N and S groups are highly efficient for the selective sorption of Au(III). The investigator reported that the modified silica may improve the capacity and selectivity for Au(III) [19].

Amino acids are organic compounds containing carboxylic (-COOH) and amine (-NH₂) groups that can act as ligands. Study on utilizing of amino acids (e.g. glycine, valine, leucine and serine) as active sites to modify chitosan has performed by Oshita et al. for adsorption cationic and anionic species [21]. Glycine [22] and lysine [20] as active sites to modify chitosan was used for adsorption Au(III), Pt(IV) and Pd(II). The aim of the present work is modification of silica with L-arginine through sol-gel process by using a linker of GPTMS, and the precursor of TEOS. L-arginine was chosen as the modifier because it contains four amine groups per molecule available as chelating agents. Amine groups on L-arginine causes a high efficiency for the selectivity of adsorption of Au(III). The synthesized material was then used as an adsorbent for Au(III) ion in aqueous solution. The adsorption kinetics of Au(III), the adsorption isotherm and the selectivity toward Au(III) are evaluated, as well.

EXPERIMENTAL SECTION

Materials

Materials used for preparation of adsorbent were TEOS (Merck), L-arginine (Merck), GPTMS (Merck), and ethanol 99.5% (v/v) (Univar). A solution of Au(III) 500 ppm was prepared in our laboratory by dissolving gold in an aquaregia solution. Sodium hydroxide (NaOH), hydrochloric acid (HCl), copper chloride dihydrate (CuCl₃·2H₂O), ferric chloride hexahydrate (FeCl₃·6H₂O) and zinc nitrate tetrahydrate (Zn(NO₃)₂·4H₂O) in analytical reagent grade were purchased from Merck, Germany without prior treatment.

Instrumentation

The functional group of materials was identified with FTIR spectrophotometer (Shimadzu IR prestige 21). Thermogravimetric method was used to calculate the thermal weight loss of adsorbent at the temperature range of 27-800 °C with heating rate of 10 °C/min (stapt-1600 TG-DSC/DTA linseis thermal analyzer). The determination of metal ion concentrations was performed with flame atomic absorption а spectrophotometer (FAAS, Shimadzu AA 6650). The content of elements was determined with a Yanaco CHN CORDER MT-6 Elemental Analyzer.

Procedure

Synthesis of L-arginine modified silica (SiO₂-Arg)

Synthesis of silica modified with L-arginine was performed by mixing 2 mL TEOS 4.5 M (9 mmol), 1 mL ethanol, 1 mL GPTMS 4.5 M (4.5 mmol) and 0.9 M L-arginine (1.568 g in 10 mL solution) at variation of volume (1, 2, 3 and 4 mL). The mixture was stirred with a magnetic stirrer for 2 h, and then allowed for 24 h. The product was washed with 20 mL of distilled water, and heated to a temperature of 60 °C for 6 h.

Adsorption

Adsorption was carried out in a batch system by adding 10 mg of adsorbent in 10 mL solution of Au(III) 15 mg L^{-1} by varying contact time (from 5 to 120 min) at pH 3.0. The mixture was stirred for 2 h and filtered. Au(III) in supernatant was analyzed by FAAS and the percentage of Au(III) adsorbed was calculated using Eq. 1.

$$P = 100x \left(\frac{C_0 - C_e}{C_0}\right) \tag{1}$$

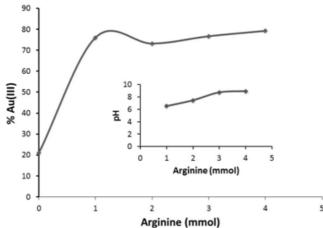


Fig 1. The relation between percentage of absorbed Au(III) and mol of L-arginine in synthesis of SiO₂-Arg at constant volume of TEOS (9 mmol) and GPTMS (4.5 mmol). Adsorption condition: 10 mL Au(III)15 ppm and 10 mg of adsorbent, pH 3.0. The inset shows the relation between mol of L-arginine and pH filtrate

where *P* represents the amount of the metal ion adsorbed (%); C_0 and C_e are the initial and the final concentration of the metal ions (mg L⁻¹), respectively.

Several models of the kinetics (first order, second order, pseudo-first order, and pseudo-second order) were examined and the rate constants were calculated to study the kinetics of the adsorption. Additionally, adsorption in various concentrations of Au(III), in a range of 5–40 mg L⁻¹ at constant pH and contact time was conducted, as well. The data was evaluated using Langmuir [23] and Freundlich [24] equations to calculate the adsorption capacity. The selectivity of the adsorbent in adsorbing Au(III) ion was evaluated in the presence of Cu(II), Fe(III) and Zn(II) ions at various pHs.

RESULT AND DISCUSSION

Effect of the Arginine Addition in SiO₂-Arg Synthesis on Au(III) Absorption

Active sites of L-arginine would affect the ability of the adsorbent. The more number of L-arginine, the greater adsorbent ability (SiO₂-Arg) to absorb Au(III). Fig. 1 shows that the absence of L-arginine on the silica, the amount of Au(III) adsorbed metal ions is very low, while the addition of L-arginine, the amount of absorbed Au(III) is significantly increased. At the addition of Larginine more than 1 mL (0.9 mmol), the amount of the absorbed Au(III) tends to be constant (76%), indicating the maximum amount of L-arginine that can be bonded on the silica through the linker. Excess of L-arginine added in the sol-gel process dissolves during the leaching, resulting in the increase of the solution pH. The

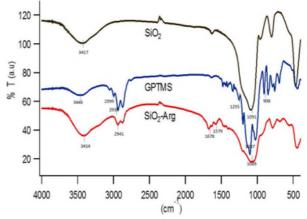


Fig 2. FTIR analysis spectra of SiO₂, GPTMS, SiO₂-Arg

Table 1. The composition of elements in SiO_2 and SiO_2 -Arg

Туре	Weight (mg)	C (%)	H (%)	N (%)	N/C
SiO ₂	2.819	0.38	1.01	0	0
SiO ₂ -Arg	2.617	22.35	4.80	2.81	0.13

inset in Fig. 1 shows the more L-arginine is added, the higher the pH of the solution (mol L-arginine inset). Therefore, the composition to prepare SiO_2 -Arg is optimum at the mole ratio of GTPMS to Arg of 5:1 and this proportion was used at the further experiment.

Characteristic of SiO₂-Arg

Elemental analysis

Elemental analysis was conducted by a Yanaco CHN CORDER MT-6 Elemental Analyzer to determine the concentration of elements exist in the material. The data of elemental analysis of SiO_2 and SiO_2 -Arg are presented in Table 1.

Table 1 shows that the SiO₂-Arg containing 2.81% nitrogen, whereas silica (SiO₂) does not contain nitrogen. The presence of nitrogen suggests that arginine has been bound by silica through GPTMS linker. The structure of SiO₂-Arg can be predicted by comparing the mass ratio of nitrogen to carbon (N/C) of the theoretical and analysis. Ratio of the elemental composition N/C analysis is closer to the theoretical yield of 0.129. This condition suggests that the arginine molecule binds five molecules of GPTMS. This is also supported by the data of influences the amount of arginine for adsorption of Au(III) that the mole ratio of GTPMS:Arg is 5:1. The proposed structure of interaction between GPTMS and arginine on silica can be seen Fig. 3.

Functional group of SiO₂-Arg

The presence of the functional group in (GPTMS), and L-arginine-modified silica (SiO₂-Arg) are shown in

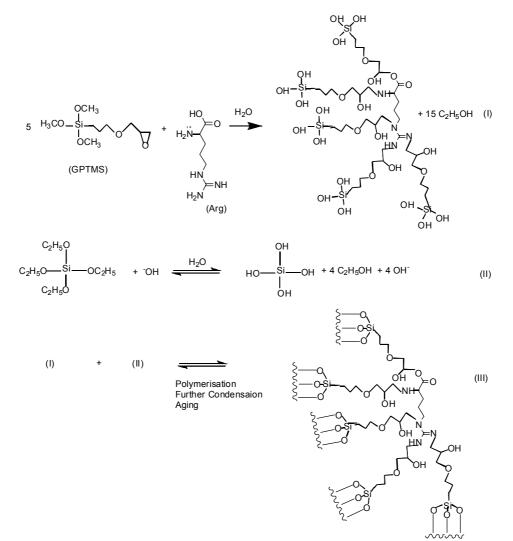


Fig 3. Proposed reaction mechanism of L-arginine-modified silica synthesis

Fig. 2. Silica is characterized by the presence of two peaks at 3417 and 1091 cm⁻¹ from Si-OH and Si-O-Si stretching vibration, respectively [25-26]. Similar to silica, FTIR spectra of GPTMS also shows two peaks from Si-OH and Si-O-Si stretching vibration at 3446 and 1105 cm⁻¹, respectively. The peak at 2939 cm⁻¹ is the aliphatic C-H stretching vibration and the peak at 999 cm⁻¹ is the C-H stretching vibration of epoxy ring. Furthermore the other evidence of epoxide groups was indicated by peaks of C-C asymmetric and symmetric at 908 and 1255 cm⁻¹, ring stretching vibration respectively [25]. The formation of SiO₂-Arg was evidenced by the appearance of two new peaks at 1678 and 1579 cm⁻¹ from asymmetric NH₂ out-of-plane bending vibration and C=O stretching vibration, respectively [27]. Moreover the disappearance of the peaks of the epoxide ring C-C asymmetric and symmetric stretching vibration at 908 and 1255 cm⁻¹, respectively, confirms that the L-arginine molecule is successfully attached on the silica surface by covalent bond.

The formation model of L-arginine-modified silica (SiO_2-Arg) is described as a multi-step of hydrolysis and condensation reactions (Fig. 3). The first stage is an attack on the epoxide group by the amine followed by hydrolysis illustrated in Fig. 3 reaction I. At the same time TEOS also undergoes hydrolysis to form orthosilicic acid $(Si(OH)_4)$ in Fig. 3 reaction II. The second stage is the condensation reaction of GPTMS-Arg and $(Si(OH)_4)$ as shown in Fig. 3 reaction III.

Thermogravimetry Analysis (TGA)

Thermogravimetry was conducted at temperatures between 27–800 °C with the heating rate of 10 °C/min. The TGA curve of SiO₂ (Fig. 4) presented a mass loss of 9.3100% (1.1720 mg) up to 100 °C, related to adsorbed water, and presented a mass loss of 2.7449% (0.3452 mg) above 200 °C, assigned to lost

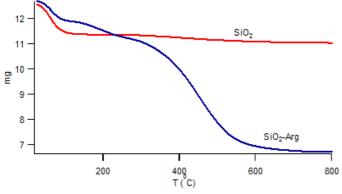


Fig 4. Thermogravimetric analysis curve of SiO_2 and SiO_2 -Arg

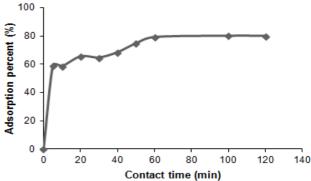


Fig 5. Effect of contact time on adsorption Au(III) onto SiO₂-Arg (initial concentration: 15 mg L⁻¹, mass dosage 0.01 g, pH 3.0)

Table 2. Constant rate of Au(III) adsorption on SiO₂-Arg and linear coefficient in various kinetics models

	<u> </u>	
Kinetic model	Constant rate	R^2
First order	0.0070 min ⁻¹	0.8489
Second order	0.2592 mM ⁻¹ min ⁻¹	0.8653
Pseudo-first order	0.0329 min ⁻¹	0.9012
Pseudo-second order	53197 g mol ⁻¹ min ⁻¹	0.9922

water from condensation of silanol groups to form siloxane groups. The TGA curve of the SiO₂-Arg (Fig. 4) presents a mass loss of 6.2752% (0.7967 mg), assigned to the adsorbed water up to 100 °C. At a temperature of about 190-240°C, the weight of SiO₂-Arg reduced 5.3767% (0.6826 mg) indicates the formation of siloxane by releasing water molecules [27]. The weight of L-arginine-modified silica (SiO₂-Arg) reduced 35.4639% (4.5027 mg) showing the decomposition by releasing L-arginine molecules.

Adsorption of Au(III)

Kinetics of adsorption

Fig. 5 shows that the adsorption increases with increasing of contact time and reached equilibrium within 60 min. Furthermore, the data of contact time variation will be used to determine the kinetics of adsorption. Adsorption kinetics describing the solute uptake rate is one of the important characteristics that determine absorption efficiency. First order (Eq. 2) [28], second order (Eq. 3), pseudo-first order (Eq. 4) [29], and pseudo-second order (Eq. 5) [30] were applied to evaluate the experimental data. Kinetic model and parameters for Au(III) adsorption are presented in Table 2.

$$\ln C_e = -k_1 t + \ln C_0 \tag{2}$$

$$\frac{1}{C_e} = k_2 t + \frac{1}{C_0}$$
(3)

$$\log(q_e - q_t) = \log q_e - \frac{k_3}{2.303}t \tag{4}$$

$$\frac{t}{q_t} = \frac{1}{k_4 q_e^2} + \frac{t}{q_e}$$
(5)

where C_e is concentration of Au(III) at equilibrium (mM), C_0 is initial concentration of Au(III) (mM); q_e and q_t are the amounts of Au(III) adsorbed (mol g⁻¹) at equilibrium and at any time *t* (mol g⁻¹), respectively; k_1 , k_2 , k_3 , and k_4 are adsorption rate constant of first order (min⁻¹), second order (mM⁻¹min⁻¹), pseudo-first order (min⁻¹), and pseudo-second order (g mol⁻¹ min⁻¹), respectively.

As shown in Table 2, the correlation coefficient of pseudo-second order higher than that of pseudo-firstorder. In addition, the value of q_e calculated from the pseudo-second order as 5.63 x 10⁻⁶ mol/g is closer to the experimental q_e value as 5.83 x 10⁻⁶ mol/g. In the case of pseudo-first-order model, qe value calculated as 2.26 x 10⁻⁶ mol/g differs significantly from the experimental q_e value [20]. The q_e was calculated by plotting the $log(q_e - q_t)$ vs. t for the pseudo-first-order (Eq. 4). The slope of the linear plot t/q_t vs. t yielded the value of q_e for the pseudo-second order (Eq. 5). The experimental q_e value is q_t at time (60 min). Based on the higher correlation coefficients and the agreement of calculated q_e value with experimental value, the adsorption of Au(III) by SiO₂-Arg tends to follow the pseudo-second-order. This shows that the kinetic model is chemical adsorption and does not involve mass transfer in solution. It is more likely to predict that the adsorption involves probable the use of shared electrons between the noble metal cations and adsorbent [20,22,31-32]

Table 3. Langmuir and Freundlich	parameters for Au(III) adsorption

	Langmuir Parar	neters	F	reundlich Parameters	6
R^2	Q_m	ΔE	R^2	<i>k</i> f	N
0.7853	52.79 mg/g	24.197 kJ/mol	0.9556	0.022678	1.88

No	Adsorben	Q_m (mg/g)	Reference
1	lonic imprinted amino-silica hybrid prepared from rice hull ash	76.14	[19]
2	L-lysine modified cross-linked chitosan resin	70.34	[20]
3	Glycine modified crosslinked chitosan resin	169.98	[22]
4	4-amino-4-nitro azobenzene modified chitosan	69.93	[31]
5	L-arginine-modified silica (SiO ₂ -Arg)	52.79	This work

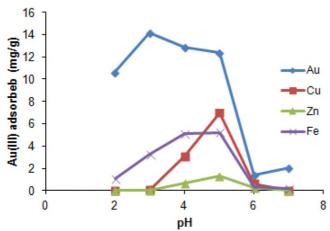


Fig 6. Effect of pH on the adsorption selectivity Au(III) onto SiO_2 -Arg with the presence of Cu(II), Zn(II) and Fe(III) by varying the pH (mass dosage 0.01 g, 1 h)

Adsorption isotherm

Adsorption was conducted at various initial concentrations of Au(III) 10 mL, ranging from 5 to 40 mg/L with adsorbent 10 mg at pH 3.0. Experimental data was evaluated using Langmuir and Freundlich isotherm models. Langmuir isotherm is based on monolayer adsorption on the active sites of the adsorbent. On the other hand, Freundlich isotherm describes the adsorption on heterogeneous (multiple-layer) surface with uniform energy. The relationship between the Langmuir and Freundlich parameters with regression coefficients was shown in Table 3. Correlation coefficient values indicate that the Freundlich model is more suitable than the Langmuir model. The adsorption capacity data of SiO₂-Arg compared to other adsorbents reported can be seen in Table 4.

Table 4 compares the adsorption capacity of various types of adsorbents for the adsorption of Au(III). The difference in the absorption of ions Au(III) at various adsorbent were caused by characteristics (functional groups, surface area, particle size, etc.) of the adsorbent.

Selectivity of adsorption

Effect of pH on the adsorption selectivity Au(III) by SiO_2 -Arg was studied together with the presence of Cu(II), Fe(III) and Zn(II) by varying the pHs. The results are presented in Fig. 6.

The mechanism of adsorption of Au(III) could be through electrostatic force, ion exchange and chelation. The nature of the mechanism depends on several parameters such as pH, metal ions and adsorbent properties. Au(III) reacts with hydrochloric acid to form complex anion, [AuCl₄] [20,22,31-32]. The amine group can contribute to form a chelate with metal ions, but protonation that occurs will significantly reduces its ability to form a chelate. Thus most of the absorption of the metal Au(III) is due to the electrostatic attraction of metal complex anions by protonated amine groups. The mechanism of adsorption in acid solution to Au(III) on the SiO₂-Arg was assumed to occur due to electrostatic force and ion exchange.

The interaction between the metal ions and protonated sites of SiO_2 -Arg is shown in Eq.(6-8)

 $R - NH_2 + HCI \rightarrow RNH_3^+ + CI^-$ (6)

 $Au(III) + 4HCI \rightarrow AuCl_4^- + 4H^+$ (7)

 $RNH_3^+CI^- + AuCI_4^- \rightarrow RNH_3 + AuCI_4^- + CI^-$ (8)

At pH > 5, the decrease of Au(III) adsorption is likely to occur due to the electrostatic repulsion between the surface sites of the adsorbent and metal ions. In addition, this might occur due to the reduction of anion species Au(III) chloride caused by OH⁻ replacement, subsequently form a precipitate of Au(III) hydroxide as shown in Eq. 9 [19]:

 $\operatorname{AuCl}_{4}^{-} + 4\operatorname{OH}^{-} \rightleftharpoons \operatorname{Au}(\operatorname{OH})_{4}^{-} + 4\operatorname{Cl}^{-} \rightleftharpoons \operatorname{Au}(\operatorname{OH})_{3(S)} + \operatorname{OH}^{-} + 4\operatorname{Cl}^{-}(9)$

At lower pH, the decrease adsorption of Au(III) was caused by reducing of $[AuCl_4]$ species more likely forming HAuCl₄ as shown in Eq.10. Several studies in literatures reported that a highest adsorption of Au(III) on amino based materials was obtained at pH of 2.0-4.0 [20,22, 31].

$$AuCl_{4}^{-} + HCl^{-} \rightleftharpoons HAuCl_{4} + Cl^{-}$$
(10)

The optimum adsorption selectivity is achieved at pH 3.0. At optimum pH 3, amine groups (-NH₂) in the surface SiO₂-Arg are protonated to form ammonium groups $(-NH_3^{T})$. In that condition, Au(III) ions form complexes of [AuCl₄]⁻ anion. The adsorption of Au(III) is due to the electrostatic attraction of metal complex anions by protonated amine groups. On the contrary, Cu(II) and Zn(II) ions may not be adsorbed because the electrostatic repulsion between the surface sites of the adsorbent and metal ions. Thus Au(III) may be adsorbed selectively from solution containing a mixture of Au(III), Cu(II) and Zn(II) on SiO₂-Arg. Whereas Au(III) is less selective towards Fe(III) compared with Cu(II) and Zn(II). At pH 3.0, Fe(III) tend to interact with OH⁻ ions to form hydroxo complex ions $[FeOH]^{2+}$ compared with Zn(II) and Cu(II) ions. This is due to the solubility constants (K_{sp}) of Fe(OH)₃ is smaller than Zn(OH)₂ and Cu(OH)₂. K_{sp} of Zn(OH)₂, Cu(OH)₂ and Fe(OH)₃ are 5.10⁻¹⁷, 2.10⁻¹⁷ and 1.10⁻³⁷, respectively [33]. The amount of [FeOH]²⁺ in solution can form hydrogen bonds between [FeOH]²⁺ with the OH group of silanol of the adsorbent. Thus [FeOH]²⁺ ions are more strongly bound to the SiO₂-Arg compared Cu(II) and Zn(II) ions. The adsorption selectivity for (Au-Zn) and (Au-Cu) were higher than those of (Au-Fe), showing the following order: (Au-Zn) = (Au-Cu) > (Au-Fe) (in Fig. 6).

CONCLUSION

L-arginine-modified silica has been simply prepared through sol gel process with the linker 3glycidoxypropyl-trimethoxysilane using tetraethyl orthosilicate as the precursor and L-arginine solution. The adsorption capacity obtained at optimum pH (3.0) is equal to 52.79 mg/g. The kinetic study indicates that the pseudo-second-order model provides better correlation than the pseudo-first-order one; this suggests that the rate-limiting step may be chemical sorption. SiO₂-Arg was selective for Au(III) adsorption toward Cu(II), and Zn(II) with the selectivity order of (Au-Zn) = (Au-Cu) > (Au-Fe). SiO₂-Arg material provides a prospective application as an effective adsorbent for metal ions as well as gold(III).

ACKNOWLEDGEMENT

The authors are grateful to the Directorate of Higher Education, Ministry of National Education, Republic of Indonesia through Doctoral Scholarships.

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