Article

Adsorption of Au(III), Cu(II) and Ni(II) on Magnetite Coated with Mercapto Groups Modified Rice Hull Ash Silica

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Abstract

Adsorption of Au(III) in multi-metal systems Au/Cu/Ni on mercapto modified silica coated on magnetite ($\text{Fe}_3\text{O}_4/\text{SiO}_2\text{-SH}$) has been studied. $\text{Fe}_3\text{O}_4/\text{SiO}_2\text{-SH}$ was synthesized via sol-gel process by using magnetite obtained through co-precipitation of $\text{Fe}^{2+}/\text{Fe}^{3+}$ salt mixture with NH_4OH as the precipitating solution, sodium silicate solution extracted from rice hull ash and 3-mercaptopropyltrimethoxysilane (MPTMS) as the mercapto group source. $\text{Fe}_3\text{O}_4/\text{SiO}_2\text{-SH}$ was characterized with Fourier transform infrared (FTIR) spectrophotometer, X-ray diffraction (XRD) and ion chromatography for sulfur analysis. Optimization of Au(III) adsorption in a batch system was carried out as function of pH, contact time and ion concentration. Adsorption kinetics was evaluated with pseudo-first order and pseudo-second order models based on the data of contact time variation, while the adsorption isotherm was studied based on Langmuir and Freundlich models. The adsorbed metal ions Au(III), Cu(II) and Ni(II) quantitatively were calculated based on the difference of metal concentrations before and after adsorption analyzed with flame atomic absorbance spectrophotometer (FAAS). Results of characterization showed that $\text{Fe}_3\text{O}_4/\text{SiO}_2\text{-SH}$ has been successfully synthesized. Adsorption of Au(III) on $\text{Fe}_3\text{O}_4/\text{SiO}_2\text{-SH}$ slightly decreased with increasing the pH in a range of 2.0-6.0 and fits to pseudo-second order model with the rate constant of $1.37 \times 10^{-3} \text{ g mg}^{-1} \text{ min}^{-1}$. $\text{Fe}_3\text{O}_4/\text{SiO}_2\text{-SH}$ shows a linear plot of Langmuir isotherm model with adsorption the capacity for Au(III) of 125 mg/g. Adsorption on multimetal systems shows that capacity of Au(III) on $\text{Fe}_3\text{O}_4/\text{SiO}_2\text{-SH}$ is higher than that of Cu(II) and Ni(II), and high selectivity for Au(III) toward Cu(II) and Ni(II) ions.

Keywords: Adsorption, gold, magnetite, rice, silica, mercapto

1. Introduction

Recent years the demand for precious metals such as gold has shown an increasing trend. Hence, development of techniques to recover gold from industrial wastewater due to its vast applications, high market prices, and limited resource is still an interesting topic to be investigated¹⁾. Several methods including adsorption, solvent extraction, ion exchange, cementation, have been utilized more often than pyrometallurgical method.^{2,3)} Among those methods, adsorption is considered as a promising technology because this method uses a simple equipment, and shows low cost, ease operation, and high efficiency even at low metal-ion concentration^{4,5,6)}.

An effective and selective adsorbent should consist of a stable and insoluble porous matrix having suitable active groups (typically organic groups) that interact effectively with gold ion. Silica gel is an ideal support for organic groups because it is an

inorganic material, stable under acidic conditions and no swelling, and has satisfactory mass exchange characteristics and very high thermal resistance.⁷⁾ This material is commonly synthesized via sol-gel method based on the hydrolysis of tetraethoxyorthosilane (TEOS). Depending on the purpose of the application of the final material the preparation conditions can be changed to adjust the desired reaction. Besides TEOS, sodium silicate solution that may be produced from rice hull ash (RHA) has been reported as precursor. RHA with high content of silica (87-97 %) is well known as a by-product of agriculture solid waste that may be used economically to prepare silica gel.^{8,9)}

In comparison to a column system, adsorption in a batch system shows more efficient due to effectiveness of contact between adsorbent and metal ions. However, the weakness in practical application of the batch system is the difficulty to separate

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adsorbents from the solution. Therefore, adsorbents with magnetic property have recently gained much attention in applications for removal of heavy metal ions as well as precious metal ions from wastewater.¹⁰⁻¹³⁾ Magnetic material such as magnetite

(Fe_3O_4) can be separated from solution by using an external magnetic field due to their paramagnetism.

The immobilization of functional groups mostly onto the silica surface was performed through heterogeneous process, in which silica gel was reacted with the compounds containing the desired active groups in toluene medium or other water free mediums^{14,15)}. Zhang et al.¹⁶⁾ developed a magnetite coated with mercapto modified silica for gold ion adsorption. Fe_3O_4 was prepared by co-precipitation method, and SiO_2 was coated on Fe_3O_4 nanoparticles by hydrolysis of Na_2SiO_3 for protecting the core from being oxidized or dissolved under acid solution, and then thiol groups were modified on the $\text{Fe}_3\text{O}_4/\text{SiO}_2$ through silanization reaction.

Modification of silica through silanization requires a complicated apparatus such as a reflux set, heating and long time, leading to a less green process. Sol-gel process for modification of silica with organo groups has been reported by several researchers.¹⁷⁻¹⁹⁾ Kim and Todino¹⁸⁾ used TEOS as the silica source and 3-mercaptopropyltriethoxysilane (MPTES) as the mercapto source to prepare mercapto modified silica. In the experiment, a mixture of MPTES and TEOS in molar to molar percentages of 20% (m/m) was added to the CTAB (cetyl trimethylammonium bromide) and ammonia solution slowly and under continuous agitation. Then, it was agitated during 2 h at 25 °C. The solid was refluxed with HCl 1 mol L⁻¹ in ethanol at 75 °C for 24 h to extract surfactant (CTAB). The adsorbent then was used to preconcentration of Au(III), Cu and Ag(I) in analysis with continuous systems coupled on-line to an atomic absorption spectrometry. Sakti et al.¹⁹⁾ reported the use of sodium silicate solution and 3-aminopropyl-trimethoxysilane (APTMS) to prepare amino modified silica. In the preparation, HCl solution 3 M was added drop wise in a mixture of silicate solution produced from RHA and APTMS with constant stirring until pH reached 7. The resulted gel was aged for 3 d, washed with demineralized water, and dried in an oven at 70 °C for 2 h. The adsorbent then was used to absorb Au(III) and Cu(II) in aqueous solution.

In this study, mercapto modified silica sodium silicate solution extracted from RHA as the silica source has been coated on magnetite through sol-gel process (a one-pot process) and its application for adsorption of Au(III) from aqueous solution. Additionally, adsorption isotherm and kinetic models used to calculate capacity and rate constant, respectively, were discussed based on the adsorption experimental data. The effect of presence of Cu(II) and Ni(II) on adsorption of Au(III) presented in term of selectivity were examined, as well.

2. Experimental

2.1 Chemicals

Chemicals used in this research included $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ (Merck), $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ (Merck), HCl 1M prepared from HCl 37% (Merck), NH_4OH 1M from NH_3 25% (Merck) for synthesis of magnetite (Fe_3O_4). For coating the magnetite, silicate solution extracted from rice hull ash (RHA) containing SiO_2 13 % (w/w) and 3-mercaptopropyltrimethoxysilane (MPTMS) (Merck) were used. The extraction of silica from RHA was performed using a procedure reported by Sakti et al.¹⁹⁾

For adsorption in a batch system, solution of HAuCl_4 containing 500 mg/L of Au(III) prepared by dissolution of gold in aquaregia, Ni(II) 1000 mg/L and Cu(II) 1000 mg/L resulted from dissolution of 4.048 g NiCl_2 (Merck) and 2.682 g $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ (Merck), respectively, with demineralized water to get the volume of 1 L.

2.2 Instruments

X-ray diffraction (XRD) (Shimadzu 6000) and Fourier Transformed-infrared (FTIR) spectrophotometric (Shimadzu FTIR-PRESTIGE 21) instruments were used to identify the structure and presence of functional groups of product. Analysis of metal ions investigated used flame atomic absorbance spectrophotometry (FAAS) (Analytic Jena contraAA 300).

2.3 Procedures

2.3.1 Preparation of mercapto-silica hybrid coated magnetite $\text{Fe}_3\text{O}_4/\text{SiO}_2\text{-SH}$

Magnetite.

It was prepared with a co-precipitation method according to a procedure reported everywhere. $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ 5.2 g and 2 g $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ were mixed, 1 mL HCl 37% was added and dissolved with 200 mL demineralized water. The mixture was sonicated for one hour in nitrogen condition and in a drop wise 15 mL NH_3 25% was added. The suspension then was allowed for 1 hour and the precipitate was separated with external magnet and was washed with 200 mL demineralized water. The product was dried at 70-80 °C for two hours to find magnetite and to be characterized.

Coating magnetite with mercapto modified silica.

Coating was carried out through sol-gel process. Magnetite resulted (0.5 g) in HCl acidic condition was mixed with 2.3654 mL of silicate solution extracted from RHA, sonicated for 5 min. MPTMS 0.6348 mL was then added to the mixture and the pH was adjusted to be 7.0 with HCl 1M or NH_4OH 1M drop wise. The formed gel was kept overnight and then was washed with demineralized water, dried in an oven at 70 °C, and grounded to pass through a sieve 200 mesh. The mercapto-silica hybrid coated magnetite produced was characterized with FTIR spectrophotometry, sulfur analyzer and XRD. Coating was carried out without addition of MPTMS to produce silica coated magnetite ($\text{Fe}_3\text{O}_4/\text{SiO}_2$).

2.3.2 Adsorption of metal ions

Adsorption was carried out in a batch system by adding 10 mg of the adsorbent in 10 mL of buffer solution containing Au(III) 100 mg/L. The mixture was stirred for 1 h and the adsorbent was separated with an external magnet. The concentration of Au(III) ion in supernatant was analyzed with a flame atomic absorption spectrophotometer (FAAS). The amount of Au(III) ion adsorbed was calculated based on the FAAS data using Eq. (1).

$$Q = \frac{(C_0 - C_e)V}{W} \quad (1)$$

where Q represents the amount of the metal ion adsorbed (mg g^{-1}); C_0 and C_e are the initial and the final concentrations of the metal ions (mmol L^{-1}), respectively; W is the mass of the adsorbent (g), and V is the volume of the metal ion solution (L). The pH was adjusted and varied from 1.0 to 6.0 with $\text{CH}_3\text{COONa-HCl}$ buffer solution. An analogue work of the adsorption was carried out by varying contact time (from 5 to 60 min) at constant pH to study the kinetics of the adsorption. Two models of the kinetics (pseudo-first order, and pseudo-second order), common models used, were examined and the rate constants were calculated.

Additionally, adsorption in various concentrations of Au(III), in a range of 25–300 mg L^{-1} at constant pH and contact time was conducted, as well. The resulting data were evaluated using Langmuir²⁰⁾ and Freundlich²¹⁾ equations to calculate the adsorption capacity. The selectivity of the adsorbent in adsorbing Au(III) ion was evaluated in the presence of Cu(II) and Ni(II) ions with different concentration. The selectivity coefficient and the relative selectivity coefficient were calculated using Eq. 2.

$$D = \frac{Q}{C_e}; \alpha = \frac{D_M}{D_N} \quad (2)$$

where D represents distribution ratio, D_M and D_N is distribution ratio of M and N, α is selectivity coefficient.

3. Results and Discussion

3.1 Characteristics of $\text{Fe}_3\text{O}_4/\text{SiO}_2\text{-SH}$

3.1.1 Functional groups

The presence of functional groups of the product may be interpreted based on the infrared spectra that can be seen in **Fig. 1**. As can be seen in Fig. 1(a) and 1(b)), IR spectra of commercial and synthetic magnetites do not give significant different absorbance bands. The bands at 324–354 and 550–586 cm^{-1} correspond bending vibration of Fe-O bond and are attributed to formation of ferrite phase²²⁾. The absorbance difference of synthesized magnetite from commercial one is observed at 1635 and 3448 cm^{-1} indicating bending vibration of O-H bonding remaining at the magnetite surface²³⁾. Different from magnetite, FT-IR spectra of silica coated magnetite (Fig. 1(c)) there are pronounce changes, particularly at region of 1300 – 700 cm^{-1} , indicating the presence of silica coating. The first change is the decrease of

Fig. 1 Infrared spectra of commercial Fe_3O_4 (a), synthetic Fe_3O_4 (b), $\text{Fe}_3\text{O}_4/\text{SiO}_2$ (c) and $\text{Fe}_3\text{O}_4/\text{SiO}_2\text{-SH}$ (d)

the absorbance intensity that is probable due to the coverage of magnetite by silica. The second change is the presence of characteristic band at 450–470 cm^{-1} from bending vibration of Si-O-Si. Asymmetric bending vibration corresponding to Si-O-Si bonding is revealed with absorbance band at 787–802 cm^{-1} and 1072–1126 cm^{-1} . Absorbance bands in IR spectra of the silica coated magnetite around 1620–1640 cm^{-1} and 3400–3450 cm^{-1} come from bending and stretching vibration, respectively, of –OH groups from both Fe-OH and Si-OH. Stretching vibration of Si-O-H bonding results in an absorbance band at 950–960 cm^{-1} .

In comparison to magnetite and silica coated magnetite, IR spectra of mercapto-silica coated magnetite (Fig. 1(d)) gives characteristic absorbance of propyl and mercapto groups from MPTMS. The presence of propyl groups is indicated by bands at 1040–1050 cm^{-1} and 1400–1480 cm^{-1} assigned to stretching vibration of –C-C- chain, bending of CH_2 -, respectively. Additionally, C-H bonding in propyl groups results in absorbance at 1240 cm^{-1} and 2920–2940 cm^{-1} corresponding to bending and asymmetric vibration of C-H.¹⁹⁾ The presence of mercapto groups is identified by the appearance of bands at 694 cm^{-1} and 879 cm^{-1} that can be assigned to asymmetric stretching of C-S and bending vibration of S-H. Band at 2450–2600 cm^{-1} expected is not appeared in the IR spectra probable due very low content of mercapto groups and weak absorbance²⁴⁾. The evidence of thiol presence on the product is showed from the elemental analysis with an ion chromatography method obtaining the sulfur content of 4.2 % (w/w).

Coating reaction is predicted through two processes, namely polymerization of silica from silicate anions and bonding MPTMS to the silica polymers.⁹⁾ Modification of silica with mercapto groups occurs simultaneously. Polymerization of silica from silicate solution is followed with attachment of mercapto

Fig. 2 XRD patterns of commercial Fe_3O_4 (a), synthetic Fe_3O_4 (b), $\text{Fe}_3\text{O}_4/\text{SiO}_2$ (c) and $\text{Fe}_3\text{O}_4/\text{SiO}_2\text{-SH}$ (d); M= magnetite, G= goethite

groups through siloxane (O-Si-O) bonding. Atom O in silicate anion, SiO_3^- , may attack atom Si in mercaptopropyl-trimethoxysilane followed with the release of methoxy, CH_3O^- that forms methanol by interacting with H^+ .

3.1.2 Crystallinity

The structure of magnetite and coated magnetite produced was analyzed with XRD method and the result is expressed in Fig. 2 showing five dominant diffraction peaks (220, 311, 400, 511 and 440) characteristic for spinal structure of magnetite (M) phase and two characteristic peaks of goethite (G) commonly presents as impurity in magnetite.^{25,26} The XRD pattern of coated magnetite shows similarity of diffraction peaks suggesting that the magnetic core was unchanged within the silica matrix. Coating process does not change the peak position but the intensity, particularly for index plane [311], decreases with the presence of silica and mercapto groups. The decrease of peak intensity of [311] after coating was also observed by previous researcher.²⁷ It means that coating process does not lead to change the presence of the crystalline. Addition of silica and MPTMS as an amorphous material may result in the peak intensity lower.

3.2 Adsorption

3.2.1 Individual Au(III)

Effect of pH.

The data of the amount of Au(III) adsorbed at various pHs is presented in Fig. 3.

It can be seen that the amount of Au(III) adsorbed on $\text{Fe}_3\text{O}_4/\text{SiO}_2\text{-SH}$ gives a trend to decrease slightly with increasing the pH. Zhang et al.¹⁶ reported that the increase of pH led to the decrease of zeta-potential of the adsorbent; and the consequence is that the interaction between anion Au(III) and the adsorbent surface decreases. Among adsorbents investigated,

Fig. 3 Correlation curve of Au(III) adsorption on magnetite material at various pHs. Condition: adsorbent mass 10 mg, solution volume 10 mL, initial concentration of Au(III) 100 mg/L, contact time 1 h, temperature 25 °C

$\text{Fe}_3\text{O}_4/\text{SiO}_2\text{-SH}$ is the most effective in adsorbing Au(III). It is probable that adsorption is not caused by ionic interaction between anion $[\text{AuCl}_4]^-$ and positive sites on the adsorbent surface resulted in protonation. Atom S with low electronegativity may not be readily to interact with proton at low pH. It is different from the adsorption of Au(III) on silica modified with amino ($-\text{NH}_2$) group, in which pH of 3.0 is the optimum condition for maximum adsorption.¹⁹ At that pH, $-\text{NH}_2$ is protonated into $-\text{NH}_3^+$ resulting in ionic bonding with anion $[\text{AuCl}_4]^-$. This explanation is agreed with result reported by Lam *et al.*²⁸ that adsorption of Au(III) on silica modified with mercapto is predicted via coordination covalent bonding between Au(III) and S atom as a ligand. Complexation of Au(III) with S atom of mercapto groups is not influenced significantly by acidity but depends on the high capability of S as a soft base to interact Au(III) soft acid.²⁹ As being observed in the figure that coating magnetite with mercapto modified silica increases dramatically the capability in adsorbing Au(III). This significant increase is probable due to the presence of those groups on the surface that are assessable for interaction with metal ions.

Adsorption of Au(III) on $\text{Fe}_3\text{O}_4/\text{SiO}_2\text{-SH}$, however, may also be considered as ion exchange of proton from thiol groups with Au(III) ion in anion complex $[\text{AuCl}_4]^-$.³⁰ In solution, Au(III) of $[\text{AuCl}_4]^-$ attacks atom S followed with the release of parts of chloride ions and proton from thiol. Possible ion exchange of Au(III) on adsorbent may be presented in Eq. 3.

For $\text{Fe}_3\text{O}_4/\text{SiO}_2$, the adsorption of Au(III) increases lightly with increasing pH. At pH higher than 2.0, the species of

Table 1 Adsorption kinetics parameter of Au(III) on adsorbents

Adsorbent	Pseudo first-order			Pseudo second-order		
	k_3 (min ⁻¹)	q_e (mg/g)	R^2	k_4 (g mg ⁻¹ min ⁻¹)	q_e (mg/g)	R^2
Fe ₃ O ₄	4.34×10^{-2}	8.58	0.9569	1.52×10^{-2}	24.69	0.9986
Fe ₃ O ₄ /SiO ₂	5.00×10^{-3}	0.90	0.2323	8.76×10^{-2}	2.04	0.9572
Fe ₃ O ₄ /SiO ₂ -SH	4.46×10^{-2}	42.01	0.9604	1.37×10^{-3}	95.23	0.9958

Fig. 4 Curve of correlation between Au(III) adsorbed on magnetite material versus contact time; Condition: adsorbent mass 10 mg, solution volume 10 mL, initial concentration of Au(III) 100 mg/L, pH 3.0, temperature 25 °C

$[\text{AuCl}_4]^-$ gradually changes into $[\text{AuCl}_3\text{OH}]^-$. The presence of OH⁻ groups in Au(III) gives a chance to form hydrogen bonding with silanol groups on the surface of Fe₃O₄/SiO₂.

Covalent bonding between Au(III) and thiol groups results in difficulty to release Au(III) from the adsorbent and common eluents such as strong acid solution are not capable to leach the absorbed metal ion. However, the presence of thiourea in HCl solution is able to desorb almost completely Au(III) from thiol group containing adsorbent. Solution of 1 mol/L thiourea in 1 mol/L HCl were reported to desorb about 85% of Au(III) from 3-MPTMS modified magnetic cobalt ferrite nanoparticles adsorbents¹²⁾. The desorption efficiency of 0.5 mg Au(III) on 5 mg of thiol modified silica coated magnetite was 98.5% with 2 mol/L HCl containing 2% of thiourea.¹⁶⁾ It is due to the liability of Au(III) to form complex with thiourea.³¹⁾

Adsorption kinetics.

Evaluation of adsorption kinetics is evaluated based on the adsorption data of Au(III) at variation of contact time in a time range of 0-120 min and expressed in **Fig. 4**. Fig. 4 shows that adsorption of Au(III) is very fast and reaches equilibrium within 50 min. Models used to evaluate the kinetics include pseudo-first-order and pseudo-second-order reactions suggested by Lagergren and applied by Ramesh *et. al.*⁴⁾, which the formulas are expressed in Eq.4 and Eq.5., respectively.

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

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

where q_e and q_t are the amounts of Au(III) adsorbed at equilibrium and time t , respectively; and k_3 and k_4 are adsorption rate constants for pseudo-first-order and pseudo-second-order kinetics, respectively. By plotting curves of $\log(q_e - q_t)$ versus t and t/q_t versus t , k_3 and k_4 can be calculated and are summarized in **Table 1**.

From two selected models in Table 1 is observed that adsorption of Au(III) on investigated adsorbents tends to follows kinetic model of pseudo-second-order. The adsorption rate constant (k_4) of Au(III) on Fe₃O₄/SiO₂ is higher than that on Fe₃O₄ and Fe₃O₄/SiO₂-SH. Those represent quantitatively the rate in the curves; as the unit of constant is gram of adsorbent / mg of Au(III) adsorbed in time unit (min), higher value of k_4 shows a little amount of Au(III) adsorbed on constant mass of adsorbent at the time unit. In other words, the k_4 value is inversely proportional to adsorption rate. The pseudo-second order may indicate that the rate limiting step might be chemical adsorption involving covalent forces through sharing of electrons between thiol group of adsorbent surface and Au(III)³²⁾, as being stated in the hard-soft acid-base (HSAB) theory. This result supported kinetics models reported by previous researchers revealing that adsorption of Au(III) on solid adsorbents follows pseudo-second order with k_4 in order of 10^{-3} g/mg min.^{17-19, 33)}

Adsorption isotherm.

Adsorption isotherm is a thermodynamics approach to calculate capacity and constant of adsorption. Two models namely Langmuir and Freundlich are mostly used to interpret the adsorption experimental data⁴⁾. This evaluation is based on the adsorption data by varying initial concentration of Au(III) as presented in **Fig.5**.

Langmuir adsorption isotherm assumes that the surface of adsorbent contains a number of adsorption sites proportional with surface area and the adsorption occurs in monolayer. The adsorption does not happen on the adsorbate occupied sites. When active sites of adsorption are not fully occupied by adsorbates, the amount of adsorbates adsorbed inclines with increasing concentration and this proportion is ended if the adsorption reaches saturated condition.³⁴⁾ Adsorption isotherm model can be written as Eq (6).

$$\frac{C_e}{q_e} = \frac{1}{bK_L} + \frac{C_e}{b} \quad (6)$$

Fig. 5 Curve of correlation between Au(III) adsorbed on magnetite material versus equilibrium concentration. Condition: adsorbent mass 10 mg, solution volume 10 mL, pH 3.0, contact time 1 h, temperature 25 °C

Table 3 Adsorption capacity of Au(III) on several reported adsorbents

Adsorbent	Capacity (mg/g)
2-Mercaptobenzothiazol silica gel	4.5 ⁽³⁷⁾
Modified thiol cotton fiber	68.0 ⁽³⁸⁾
N,N'-Bis-(2-hydroxybenzylidene)-2,2'-(aminophenylthio)ethane carbon nano-tube	75.00 ⁽³⁹⁾
MPTS-modified cobalt ferrite	120.2 ⁽³²⁾
Thiol-modified Fe ₃ O ₄ @SiO ₂	84.75 ⁽¹⁶⁾
Amino-silica hybrid	131.97 ⁽¹⁹⁾
Ionic imprinted amino-silica hybrid	76.14 ⁽¹⁹⁾
Fe ₃ O ₄ /SiO ₂ -SH	125 ^(this work)

Table 2 Adsorption isotherm parameters of Au(III) on adsorbent

Adsorbent	Langmuir			Freundlich		
	<i>b</i> (mg/g)	<i>K_L</i> (L/mg)	<i>R</i> ²	<i>K_F</i> (mg/g)	<i>n</i>	<i>R</i> ²
Fe ₃ O ₄	36.36	0.0543	0.9954	1.35	1.22	0.6774
Fe ₃ O ₄ /SiO ₂	0.054	1.1008	0.9580	1.00	1.45	0.4513
Fe ₃ O ₄ /SiO ₂ -SH	125.0	1.1429	0.9967	69.02	8.99	0.7178

where q_e and C_e are the amount adsorbed and concentration of Au(III) at equilibrium, respectively, b is adsorption capacity and K_L is Langmuir constant relating to affinity of binding sites. The values of b and K_L can be calculated from the curve of C_e/q_e versus C_e .

Freundlich adsorption isotherm model is used to describe non-ideal adsorption on the heterogeneous surface caused by the diversity of the active sites or adsorbate species. Empirically this model can be expressed in Eq. (7).

$$\log q_e = \log K_F + \frac{\log C_e}{n} \quad (7)$$

where K_F is Freundlich constant related to adsorption capacity of adsorbent and n is the Freundlich exponent related to adsorption intensity. The values of K_F and n can be calculated from the slope and intercept of plot of $\log q_e$ versus $\log C_e$ (the curve is not showed). Values of Langmuir and Freundlich parameters and regression coefficient can be seen in **Table 2**.

Table 2 displays the linear regression coefficient (R^2) for Freundlich model (less than 0.7178) lower than that for Langmuir one (more than 0.9580). Those values indicate that adsorption of Au(III) on adsorbents investigated fits with Langmuir model. This phenomenon may be understood because of adsorption site homogeneity on the adsorbent surface. The functional groups dominant in adsorption are Fe-OH, Si-OH and -SH for Fe₃O₄, Fe₃O₄/SiO₂ and Fe₃O₄/SiO₂-SH, respectively. This reason is agreed with the FT-IR spectra indicating presence of those functional groups. Adsorption capacity of Au(III) on Fe₃O₄/SiO₂-SH based on the Langmuir model (125.0 mg/g) is highest among that on other magnetite materials tested, showing effect of coating with mercapto groups. In comparison

to other adsorbents reported (**Table 3**), the capacity resulted is relatively high. Our work, Fe₃O₄/SiO₂-SH containing 4.2 % of sulfur gives capacity of 125.1 mg/g is higher than thiol-modified Fe₃O₄@SiO₂ containing only 2.57 % of sulfur reported before (84.75 mg/g)⁽¹⁷⁾. Therefore, type and quantity of functional groups present on the adsorbent surface seem to be dominant factors for adsorption effectiveness.

3.2.2 Multimetal system

Effect of metal ion competition.

Study on adsorption characteristics of multisystem metal ions was conducted similar to that of single metal ion. In this case, a mixture of two and three metal ions (Au/Cu, Au/Ni, and Au/Cu/Ni) in an aqueous solution with various concentrations (25, 50, 100, 150, 200 and 300 mg.L⁻¹) at the same concentration ratio (1:1) was contacted to adsorbent in a batch system and model is presented in **Table 4**.

From Table 4 can be stated that adsorption of multimetal ion system examined fits well with Langmuir model ($R^2 \sim 0.99$), similar to that of Au(III) single metal ion system. Results also demonstrate difference of capacity of Au(III) from other metal ions (Cu(II) and Ni(II)). Fe₃O₄/SiO₂-SH adsorbs Au(III) in larger amount than does Cu(II) and Ni(II). This phenomenon may be explained with HSAB concept, in which active sites of hard acid tends to strongly interact with hard base and soft acid prefers to soft base.⁽³⁸⁾ Based on the HSAB concept thiol group is categorized into soft; hence strongly interact with Au(III) as softer acid in comparison to Cu(II) and Ni(II). The capability of

Table 4 Langmuir model parameters of adsorption isotherm for multimetal system

Multimetal system	Metal ion	Adsorption capacity (b)		K_L (mg/g)	R^2
		mmol/g	mg/g		
Au(III)/Cu(II)	Au(III)	0.725	142.86	0.069	0.967
	Cu(II)	0.317	62.50	0.017	0.967
Au(III)/Ni(II)	Au(III)	1.015	200.00	0.060	0.981
	Ni(II)	0.212	41.67	0.101	0.951
Au(III)/Cu(II)/Ni(II)	Au(III)	0.846	166.67	0.052	0.983
	Cu(II)	0.242	47.02	0.041	0.914
	Ni(II)	0.137	27.03	0.008	0.924

Table 5 Selectivity of Fe₃O₄/SiO₂-SH for Au(III) adsorption toward Cu(II) and Ni(II)

Multimetal system	Initial concentration (mmol/L)			D(L/g)		α		
Au(III)/Cu(II)	Au(III)	Cu(II)		Au(III)	Cu(II)		Au(III)/Cu(II)	
		0.5	0.5		2.94	0.08	34.01	
		0.5	1.0		2.16	0.24	9.02	
	0.5	2.0		3.11	0.48		6.51	
Au(III)/Ni(II)	Au(III)	Ni(II)		Au(III)	Ni(II)		Au(III)/Ni(II)	
		0.5	0.5		2.47	0.14	17.86	
		0.5	1.0		4.44	0.39	11.34	
	0.5	2.0		3.21	0.29		10.88	
Au(III)/Cu(II)/Ni(II)	Au(III)	Cu(II)	Ni(II)	Au(III)	Cu(II)	Ni(II)	Au(III)/Cu(II)	Au(III)/Ni(II)
		0.5	0.5		0.14	0.42		
		0.5	1.0		0.35	1.12		
	0.5	2.0	2.0	4.15	0.38	0.77	11.05	5.37

Fe₃O₄/SiO₂-SH in adsorbing hard/border line metal ions such as Cu(II) and Ni(II) probably arises from interaction of those ions with hard acid of silanol (Si-OH) groups present in the surface of Fe₃O₄/SiO₂-SH as identified by IR spectra. Another possibility is interaction of Cu(II) and Ni(II) with negative sites on the surface of Fe₃O₄/SiO₂-SH adsorbing Au(III). As seen in Eq. 3, -SH groups are protonated after bonding with [AuCl₄⁻] to form negative charge on the surface that easily interacts with cation of Cu(II) and Ni(II) from the solution²⁸. In aqueous solution, Cu(II) and Ni(II) form aquo complex of [Cu(H₂O)₆]²⁺ and [Ni(H₂O)₆]²⁺. Molecules of H₂O may act as a bridge between silanol groups on the adsorbent surface and metal ions through hydrogen bonding. However, to prove those hypotheses need further investigation.

If the adsorption capacity of Au(III) from single metal ion system (Table 2) is compared to that of multimetal ion system (Table 4), it seems that based on Langmuir model the values increase with the presence of metal cations. This phenomenon has not been understood but probable due to multilayer formation resulted in the synergism effect of metal cations. In

comparison to other metal ions, Au(III) gives the highest capacity value, demonstrating the high selectivity of adsorbent for Au(III) from Cu(II) and Ni(II) and it seems that there is no competition between Au(III) and other metal ions happens in adsorption process of multimetal ion system. It can be understood that Au(III) is adsorbed in the different active sites from Cu(II) and Ni(II). As mentioned before, adsorption of Au(III) is dominated by interaction with mercapto groups via coordination bonding, while adsorption of Cu(II) and Ni(II) tend to interact with silanol through hydrogen bonding.

Adsorption selectivity.

Selectivity of Au(III) on Fe₃O₄/SiO₂-SH from multimetal ion system was tested by adsorbing metal ions in multimetal ion system at constant concentration of Au(III) and various concentrations of other metal ions. Selectivity presented as selectivity coefficient (ratio of coefficient distribution) calculated using Eq. (2) can be seen in Table 5.

Based on Table 5 seems that selectivity coefficient of Au(III) toward Cu(II) (34.1) is higher and that toward Ni(II) (17.1) and tends to be decreased with the increase of Cu(II) and Ni(II) con-

centrations. It is consistent with Table 2 showing higher differences of adsorption capacity for Au(III) from other metal ions. The selectivity value of Fe₃O₄/SiO₂-SH for Au(III)/Cu(II) resulted in this work is comparable to those of other adsorbents such as chitosan³⁹, thiourea-formaldehyde and ureaformaldehyde resin⁴⁰ with the selectivity coefficient of 12.6, 39.8 and 25.1, respectively. However, the Fe₃O₄/SiO₂-SH shows much lower selectivity than amino modified silica (AMS) and ionic imprinted AMS¹⁹ with selectivity coefficient of 100.5 and 187.5, respectively. Ammonium cation of AMS interacting strongly with anion [AuCl₄]⁻ results in high selectivity for Au(III) toward other metal ions, such as Cu(II) present as cation in the aqueous solution.

4. Conclusions

Adsorbent of mercapto-modified silica coated magnetite using silicate solution extracted from rice hull ash is effective and selective for Au(III) forward Cu(II) and Ni(II). The capacity of adsorption for Au(III) is not interfered by the presence of those other metal ions. The results of kinetic studies demonstrated that adsorption occurs fast and follows pseudo-second order model; however, attempts to find agents easily and quickly desorbing Au(III) from adsorbents are important for the purposes of preconcentration, separation and recovery of Au(III) with a adsorption technique in a batch system. The study of presence effect of similar metal ions such as silver and mercury on the selectivity toward Au(III) is also necessary to see comprehensively adsorption characteristics of mercapto-silica hybrid coated magnetite for metal ions often co-exist in Au(III) ores or in waste water.

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