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ABSTRACT

Synthesis of Fe$_3$O$_4$/SiO$_2$ modified with N-(2-aminoethyl)-3-aminopropyl group (Fe$_3$O$_4$/SiO$_2$/ED) via coating method and its application for adsorption-desorption of anionic gold in aqueous solution have been conducted. The synthesized product was characterized with an X-ray diffractometer (XRD), a Fourier transform infrared (FT-IR) spectrophotometer and a transmission electron microscopy (TEM). Adsorption of Au(III) was conducted in a batch system and the variables included pH, contact time, and initial concentration were investigated. Results showed that magnetite/silica has been successfully functionalized with N-(2-aminoethyl)-3-aminopropyl in a homogeneous system. Kinetics study showed that adsorption of Au(III) followed the pseudo-second order model with rate constant of 0.710 g mmol L$^{-1}$ min$^{-1}$. Furthermore, the experimental data fitted well with the Langmuir isotherm model with the maximum adsorption capacity for Au(III) of 142.9 mg g$^{-1}$ and the energy of 25.0 kJ mol$^{-1}$. Gold loaded on the Fe$_3$O$_4$/SiO$_2$/ED could be easily desorbed with 0.2 mol L$^{-1}$ HCl containing 2 wt.% of thiourea with recovery of 99.8%. Fe$_3$O$_4$/SiO$_2$/ED was reusable and stable in 5 cycles of adsorption-desorption with recovery more than 90%. Fe$_3$O$_4$/SiO$_2$/ED showed high selectivity towards Au(III) in the multimetal system Au(III)/Cu(II)/Cr(VI) with the coefficient selectivity for $\alpha_{\text{Au-Cu}}$ of 227.5 and for $\alpha_{\text{Au-Cr}}$ of 12.3.

Keywords: adsorption; gold; magnetite; silica

INTRODUCTION

Gold is one commodity of the precious metals that has relatively high economic value and interested to be explored [1]. In nature, gold has founded on metal form either in the rock cracks or in mineral quartz. The relative abundance of gold in the earth’s crust is 0.004 g tonne$^{-1}$ which includes 0.001 g tonne$^{-1}$ in seawater [2]. The presence of gold is often used as a mixture for the manufacture of coin, jewelry, or coating material. Gold has a better conductivity than conventional conductors such as aluminium or copper, so it is widely used in electronic manufacturing. Gold has been extracted from nature in a pure state. One of the processes is
purification process using cyanide [3] and amalgamation with mercury [4]. Cyanide is widely used because it is relatively cheap and the isolation process is relatively short and simple.

Even though, there are several methods of gold recovery, such as ion exchange, liquid-liquid extraction, membrane filtration and adsorption, available in the literature for the removal of precious metals from aqueous solutions, comparatively, adsorption seems to be the most suitable method for the recovery of precious metals in the case of low concentration due to low cost and high efficiency [5]. The gold adsorption methods was developed with solid inorganic adsorbent of silica gel [6,7]. This adsorbent has a large surface area and is easy to be modified, but its adsorption capacity is relatively low so further modification with certain functional groups such as –NH₂ [7], –SH [8] and -SO₃H [9] is needed groups.

The surface modification of mesoporous silica with amino group (-NH₂) has performed in order to increase the performance of adsorption of precious metals [8]. At pH < 4.7 that functional group is protonated to form cation –NH₃⁺. On the other hand gold ions in solution of chloride form anion of [AuCl₄]⁻; hence both ions may interact electrostatically and adsorption occurs [10]. Attempt to improve the adsorption performance multifunctional groups has been introduced. Introducing ethylenediamine on the surface of the adsorbent is predicted to increase the capability in adsorbing gold ion.

Recently, in order to simplify the separation of adsorbate and adsorbent from the solution, magnetic material such ash magnetite (Fe₃O₄) has been introduced to adsorbent; hence the adsorbent could be attracted with an external magnet and separated from the solutions easily. After reaching the equilibrium stage, the gold(III) on the surface of adsorbent is desorbed by contacting with a leaching agent such as cyanide solution. However it’s low desorption rate and toxicity made cyanide less favorable as a leaching agent [11]. Based on the environmental problems, environmentally friendly solvents is required for desorption of gold from the adsorbent.

In this paper we report synthesis of magnetite coated with N-(2-Aminoethyl)-3-aminopropyl (ethylene diaminopropyl) modified silica and evaluation of adsorption characteristics towards gold(III). Due to the presence of magnetite particle, the adsorbent could be separated easily from the mixture. Additionally, desorption of Au(III) from magnetic adsorbent using thiourea in HCl solution as a leaching agent has been investigated, as well as the possibility of adsorbent for pre-concentration of Au(III) in very low concentration solution.

**EXPERIMENTAL SECTION**

**Materials**

Iron chloride (FeCl₃·6H₂O and FeCl₂·4H₂O), thiourea, standard solution of HAuCl₄ 1000 mg L⁻¹ were supplied from Merck-Millipore. Sodium silicate (Na₂SiO₃) solution with the concentration of SiO₂ 13 wt.% as precursor was produced from rice husk. N-(2-aminoethyl)-3-aminopropyltrimethoxy-silane (EDS) from Aldrich was used without previous treatment. The solution of HAuCl₄ 500 mg L⁻¹ from Analytical chemistry Lab was used as stock Au(III) solution. Several chemicals such as NH₂OH 25 vol.%, oleic acid, C₂H₅OH, CH₃COONa, the solution of HCl were purchased from Merck were in analytical grade and used without any pre-treatment.

**Instrumentation**

The particle sizes of magnetite (Fe₃O₄) and magnetite coated with ethylenediaminopropyl modified silica (Fe₃O₄/SiO₂/ED) were characterized using a X-Ray Diffractometer (XRD Shimadzu 6000) and a Transmission Electron Microscope (TEM JEM 1400 JEOL/EO). The Fourier Transform Infrared (FTIR) spectra were collected in KBr disc on SHIMADZU IR 8210 PC. The amount of adsorbed Au(III) on Fe₃O₄/SiO₂/ED was measured with an Atomic Absorption Spectrophotometer (Aspect CS contrAA Analytic Jena 300). The existence of Au(III) was characterized with XRD.

**Procedure**

**Synthesis of magnetite Fe₃O₄**

Magnetic material Fe₃O₄ was prepared by co-precipitation as reported by Hou et al. [12]. FeCl₃·6H₂O (5.406 g), FeCl₂·4H₂O (2.780 g), 1.0 g oleic acid, and 25 vol.% NH₂OH solution 15 mL were mixed under nitrogen gas with sonication for 60 min. After 60 min the solution was aged for 24 h. The precipitated magnetite was washed with aquadest until pH 7 and rinsed with Et-OH. After that, the magnetite was dried in an oven at 75 °C.

**Synthesis of Fe₃O₄/SiO₂/ED by one step process**

The Fe₃O₄/SiO₂/ED was prepared by one step sol gel process [13]. Magnetite (Fe₃O₄) 0.5 g was acidized with 5 mL of HCl 1.0 mol L⁻¹. Then, the magnetite was mixed with 2 mL Na₂SiO₃ solution under sonication for 5 min. The mixture was moved to a crucible cub and then 3 mL of N-(2-aminoethyl)-3-aminopropyl trimethoxy-silane (EDS) was added. The pH of mixture was adjusted to 7.0 by adding HCl solution. The
magnetic material was kept for 24 h and then dried in oven at 75 °C.

**Adsorption of Au(III) by Fe₃O₄/SiO₂/ED**

Adsorption was carried out in a batch system by mixing 10 mg of the adsorbent with 10 mL of CH₃COONa-HCl buffer solution (pH 3.0) containing Au(III) 100 mg L⁻¹. The mixture was shaken for 1 h and the adsorbent was separated with an external magnet. The concentration of Au(III) ion in supernatant was analyzed with an atomic absorption spectrophotometer (AAS). The amount of Au(III) ion adsorbed was calculated using Eq. 1.

\[
Q = \frac{(C_0 - C_e)V}{W}
\]

where \(Q\) represents the amount of the metal ion adsorbed (mg g⁻¹); \(C_0\) and \(C_e\) are the initial and the final concentration 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 CH₃COONa-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 kinetics models (pseudo-first order, and pseudo-second order), were applied 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 experimental data were evaluated using Langmuir and Freundlich isotherm models to calculate the adsorption capacity.

**Desorption of Au(III) from Fe₃O₄/SiO₂/ED**

Gold(III) adsorption experiments were performed from Fe₃O₄/SiO₂/ED to the solution of 50 mg L⁻¹ HAuCl₄ in buffered solution (pH = 3) and equilibrated with a shaker at room temperature for 50 min. The adsorbent was then leached with solution of thiourea 2% in HCl buffer during 10 min to desorb the Au(III) ion. After leaching, the amount of Au(III) desorbed was determined with AAS.

**Preconcentration of Au(III) with Fe₃O₄/SiO₂/ED**

Fe₃O₄/SiO₂/ED (10 mg) was added to the solution of 10 mg L⁻¹ HAuCl₄ in a buffered solution (pH = 3) at various volumes (20, 40, 60, 80, 100, and 120 mL) and equilibrated with a shaker at a room temperature for 50 min. The adsorbent was separated from the solution using an external magnet and contacted with 10 mL of 9 wt.% thiourea in 0.1 mol L⁻¹ HCl for 50 min in order to desorb the Au(III) ion. After desorption, the recovered Au(III) was calculated and the preconcentration factor for Au(III) on Fe₃O₄/SiO₂/ED was obtained.

**Reusability of Fe₃O₄/SiO₂/ED**

Repeated adsorption-desorption steps were conducted to examine the reusability of Fe₃O₄/SiO₂/ED. The Fe₃O₄/SiO₂/ED (10 mg) was equilibrated with 10 mL of 50 mg L⁻¹ HAuCl₄ solution (pH = 3) under sonication at room temperature for 50 min. The Fe₃O₄/SiO₂/ED was separated from solution using an external magnet and contacted with 10 mL of 3 wt.% thiourea in 0.1 mol L⁻¹ HCl during 10 min to desorb Au(III). The desorption was carried out twice to obtain the final solution of 20 mL of 3 wt.% thiourea in 0.1 mol L⁻¹ HCl.

**Selectivity of Fe₃O₄/SiO₂/ED**

The selectivity of Fe₃O₄/SiO₂/ED towards Au(III) ion was evaluated in the presence of Cu(II) and Cr(VI) ions with various concentrations. The selectivity coefficient and the relative selectivity coefficient were calculated using Eq. 2.

\[
D = \frac{D_M}{D_N} = \frac{D_M}{D_N} = \frac{\alpha}{C_M/C_N}
\]

where \(D\) represents distribution ratio, \(D_M\) and \(D_N\) is distribution ratio of M ion and N ion, \(\alpha\) is selectivity coefficient.

**RESULT AND DISCUSSION**

**Characteristics of Fe₃O₄/SiO₂/ED**

Effect of silica coating on crystallinity of magnetite can be evaluated based on the XRD pattern presented in Fig. 1. In Fig. 1 XRD pattern of Fe₃O₄ can be observed five specific peaks at 2θ = 30.08°; 35.43°; 43.08°; 56.97°; and 62.57° which the specific peaks from magnetite. It was indicated that magnetite Fe₃O₄ has been synthesized successfully. Fig. 1 also showed the intensity of XRD pattern of Fe₃O₄/SiO₂/ED indicating compatibility with XRD pattern of bare Fe₃O₄, and it supports result reported by Lin et al. [14] that coating does not change the structure of magnetite. Furthermore, the particle size with a certain phase can be determined from the data of XRD. The result of the particle size calculations are presented in Table 1.

As shown in Table 1, the particle size of Fe₃O₄/SiO₂/ED is relatively bigger than that of bare Fe₃O₄ which is agreed with the result reported by Nuryono et al. that coating of magnetite with thiol modified silica increases the particle size from 14.2 to 27.5 nm [13]. Furthermore, to ensure the increase of the particle size, the characterization was carried out using TEM and presented in Fig. 2. As shown in Fig. 2a, TEM micrograph of bare Fe₃O₄ indicates that some particles of magnetite were separated each other. Transparent layer was estimated to be oleic acid, so the magnetite particles seem to be separated with the
Table 1. The result of the particle size calculations

<table>
<thead>
<tr>
<th>Material</th>
<th>2θ (°)</th>
<th>cos θ</th>
<th>FWHM (rad)</th>
<th>D_XRD (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bare Fe₃O₄</td>
<td>35.3975</td>
<td>0.9527</td>
<td>0.0120</td>
<td>10.4586 ± 1.14</td>
</tr>
<tr>
<td>Fe₃O₄/SiO₂/ED</td>
<td>35.2800</td>
<td>0.9530</td>
<td>0.0091</td>
<td>14.2897 ± 2.82</td>
</tr>
</tbody>
</table>

particles size at 9.0-12.0 nm. TEM micrograph of Fe₃O₄/SiO₂/ED (Fig. 2b) shown that the particles are more clustered with the particles size at 17.0–19.0 nm. The presence of silica and functional groups on magnetite may form some new bonds, which can be characterized using a FT-IR spectroscopy and the result is expressed in Fig. 3. As can be seen in Fig. 3 IR spectra of bare Fe₃O₄ gives a characteristic band at around 586.36 cm⁻¹ from Fe-O stretching [15]. Additionally, a band at around 2924.09 cm⁻¹ that indicates -CH₂- stretching from oleic acid is also observed [16]. FT-IR spectra of Fe₃O₄/SiO₂/ED gives broad strong bands at 1072 and 3449 cm⁻¹ which indicates stretching mode for Si-O-Si [15, 17] and O-H/N-H [18], respectively. The presence of ED groups is indicated from strong bands at 1087.85 and 2939.52 cm⁻¹, which are characteristic for Si-O, and –CH₂- stretching mode, respectively [18].

Adsorption Au(III) on Fe₃O₄/SiO₂/ED

Adsorption isotherm
As shown in Fig. 4, the adsorption of Au(III) on Fe₃O₄/SiO₂/ED increase as the initial concentration increase and reaches the equilibrium stage at initial Au(III) concentration of 250 mg L⁻¹. Based on the correlation of Au(III) at equilibrium with adsorbed Au(III), two isotherm models (Langmuir and Freundlich) are used to evaluate the adsorption capacity and the adsorption energy of Au(III) on Fe₃O₄/SiO₂/ED. The results of calculation of these parameters are presented in Table 2. Based on Table 2, the R² value showed that the experimental data of adsorption Au(III) are fit well with the Langmuir isotherm model. The energy of adsorption is 25 kJ mol⁻¹ which is categorized as chemisorption [19].

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 0-180 min which expressed in Fig. 5. Fig. 5 shows that adsorption of Au(III) is very fast and reaches equilibrium within 50 min. Models used to evaluated the kinetics include first-order (Eq.4) and second-order (Eq.5) applied by Huang et al. [20], pseudo-first-order and pseudo-second-order reactions applied by Ramesh et al. [5] which the formulas are expressed in Eq.5 and Eq.6., respectively [21].

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**Fig 4.** Influence of Au(III) initial concentration on Au(III) adsorption onto Fe₃O₄/SiO₂/ED (Conditions: adsorbent dose: 1.0 g L⁻¹; pH: 3 and contact time: 50 min)

**Fig 5.** Effect of contact time on adsorption of Au(III) by Fe₃O₄/SiO₂/ED (Conditions: adsorbent dose: 1.0 g L⁻¹; pH: 3 and initial Au(III) concentration: 100 mg L⁻¹)

<table>
<thead>
<tr>
<th>Isotherm</th>
<th>Langmuir</th>
<th>Freundlich</th>
</tr>
</thead>
<tbody>
<tr>
<td>Q_max (mg g⁻¹)</td>
<td>K_L (L mg⁻¹)</td>
<td>R²</td>
</tr>
<tr>
<td>142.857</td>
<td>0.125</td>
<td>0.996</td>
</tr>
</tbody>
</table>

**Table 2.** The Langmuir and Freundlich isotherm models parameter for adsorption of Au(III) adsorption by Fe₃O₄/SiO₂/ED

<table>
<thead>
<tr>
<th>Kinetics model</th>
<th>Adsorption rate constant (k)</th>
<th>R²</th>
</tr>
</thead>
<tbody>
<tr>
<td>Order 1</td>
<td>0.001 min⁻¹</td>
<td>0.567</td>
</tr>
<tr>
<td>Order 2</td>
<td>0.066 mM⁻¹ min⁻¹</td>
<td>0.692</td>
</tr>
<tr>
<td>Pseudo order-1</td>
<td>0.028 min⁻¹</td>
<td>0.954</td>
</tr>
<tr>
<td>Pseudo order-2</td>
<td>0.710 g mM⁻¹ min⁻¹</td>
<td>0.996</td>
</tr>
</tbody>
</table>

\[
\begin{align*}
\ln C_e &= -k_1 t + \ln C_0 \\
\frac{1}{C_e} &= k_2 t + \frac{1}{C_0} \\
\log(q_e - q_t) &= \log q_e - k_p t / 2.303 \\
1/ q_t &= 1/k_p q_e^2 + t / q_e \\
\end{align*}
\]

where \(C_e\) and \(C_0\) are the concentration of Au(III) at equilibrium and initial time, \(q_e\) and \(q_t\) are the amounts of Au(III) adsorbed at equilibrium and time \(t\), respectively; and \(k_1, k_2, k_p\) and \(k_{p2}\) are adsorption rate constants for first-order, second order, pseudo-first-order and pseudo-second-order kinetics, respectively. The adsorption rate constant and linearity of each model are shown in Table 3.

From four selected models in Table 3 is observed that adsorption of Au(III) on investigated adsorbents tends to follow pseudo-second-order kinetic model. The presence of high concentration of chloride ions in the solution gives a chance of either proton or anion from the solution to involve in the adsorption. Another possibility is that the number of the active sites on adsorbent after and before adsorption is not significantly different since the concentration of metal ions is considered very low.

**Desorption of Au(III) for Fe₃O₄/SiO₂/ED**

As shown in Fig. 6a, the desorption of Au(III) from Fe₃O₄/SiO₂/ED slightly increases as the concentration of HCl increase. The increase of the amount of Au(III) desorbed from Fe₃O₄/SiO₂/ED is due to the existence of ion H⁺ in solution that can stabilize thiourea and prevent the degradation leadings to decrease the consumption of thiourea [22]. Additionally, Cl⁻ ion from HCl has a function as competitor for the Au(III) complexes [23]. As shown in Fig. 6b, amount of degraded Fe₃O₄/SiO₂/ED increases as the concentration of HCl increases. However not more than
Fig 6. Desorption of Au(III) from Fe₃O₄/SiO₂/ED (a) and degraded Fe₃O₄/SiO₂/ED in 2 wt.% thiourea with different concentration of HCl (b)

5% of Fe₃O₄/SiO₂/ED is degraded. This result indicates that the Fe₃O₄/SiO₂/ED is relatively stable during desorption processes.

Preconcentration of Au(III) Using Fe₃O₄/SiO₂/ED

As shown in Fig. 7, Au(III) on Fe₃O₄/SiO₂/ED can be quantitatively recovered when the sample volume was less than 400 mL. When the sample volume is more than 400 mL, the recovery decreases. Consequently, by considering the final elution volume of 1.0 mL of 9 wt.% thiourea in 0.1 mol L⁻¹ HCl, a preconcentration factor of 40 was easily achieved.

Fig 7. Recovery of Au(III) by Fe₃O₄/SiO₂/ED (Condition: adsorbent: 10 mg, Initial Au(III) concentration: 10 mg L⁻¹, adsorption and desorption time: 50 min)

Fig 8. Reusability of Fe₃O₄/SiO₂/ED for Au(III) adsorption

Reusability of Fe₃O₄/SiO₂/ED for Sorption of Au(III)

As shown in Fig. 8, almost all of Au(III) in the solution was removed and could be recovered quantitatively. Besides, almost all of Fe₃O₄/SiO₂/ED could be recollected easily using an external magnet which indicates that Fe₃O₄/SiO₂/ED can be used for adsorption of Au(III) repeatedly without any significant loss on its performance.

The slightly increasing on adsorption performance after the first cycle might be resulted from the mercapto groups which has binding Au(III) are still able to binding other Au(III). The remainder of mercapto groups were bonded onto silica surfaces tightly and were not readily to be destroyed by desorption process, so the adsorption capacity is stable in the following reuse [15].
Table 4. Selectivity of Fe₃O₄/SiO₂/ED for Au(III) adsorption toward Cu(II) and Cr(VI)

<table>
<thead>
<tr>
<th>Co (mM)</th>
<th>D (L g⁻¹)</th>
<th>αAu-Cu</th>
</tr>
</thead>
<tbody>
<tr>
<td>Au (mM)</td>
<td>Cu</td>
<td></td>
</tr>
<tr>
<td>0.5</td>
<td>0.5</td>
<td>0.599</td>
</tr>
<tr>
<td>0.5</td>
<td>1</td>
<td>0.626</td>
</tr>
<tr>
<td>0.5</td>
<td>2</td>
<td>0.806</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Co (mM)</th>
<th>D (L g⁻¹)</th>
<th>αAu-Cr</th>
</tr>
</thead>
<tbody>
<tr>
<td>Au (mM)</td>
<td>Cr</td>
<td></td>
</tr>
<tr>
<td>0.5</td>
<td>0.5</td>
<td>0.599</td>
</tr>
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<td>0.5</td>
<td>1</td>
<td>0.626</td>
</tr>
<tr>
<td>0.5</td>
<td>2</td>
<td>0.806</td>
</tr>
</tbody>
</table>

Adsorption Selectivity

Selectivity of Fe₃O₄/SiO₂/ED towards Au(III) in from multimetal ion system was evaluated by adsorbing Au(III) in multimetal ion system at constant concentration of Au(III) and various concentrations of other metal ions. Selectivity was presented as a ratio of coefficient distribution calculated using Eq. (2) and the result can be seen in Table 4. Based on Table 4, selectivity coefficient of Au(III) toward Cu(II) and Cr(VI) is high which indicates that Fe₃O₄/SiO₂/ED has a high selectivity towards Au(III) in the presence of Cu(III) and Cr(VI).

CONCLUSION

Functionalization of Fe₃O₄/SiO₂ with N-(2-Aminoethyl)-3-aminopropyl to obtain Fe₃O₄/SiO₂/ED has been successfully conducted. The performance of Fe₃O₄/SiO₂/ED as an adsorbent for Au(III) in aqueous solution has been studied. The experimental data showed that the adsorption of Au(III) by the Fe₃O₄/SiO₂/ED followed the Langmuir isotherm model. The pseudo-second order kinetics model was the best model to describe the experimental data. The Fe₃O₄/SiO₂/ED could be recollected easily by a magnet due to the presence of Fe₃O₄. Adsorbed Au(III) on the surface of Fe₃O₄/SiO₂/ED could be desorbed with thiourea in HCl solution and the Fe₃O₄/SiO₂/ED was ready for the next cycle. The regeneration data showed that Fe₃O₄/SiO₂/ED could be used until 5 times without any significant loss on its performance.

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