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# SORPTION OF Au (III) AND Ag (I) ON AMINO- AND MERCAPTO-SILICA HYBRID COLUMNS

## (Jerapan Au (III) dan Ag (I) pada Turus Hibrid Amino- dan Merkapto-silika)

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**Abstract**

Adsorption-desorption of Au(III) and Ag(I) ion on amino-silica hybrid (ASH) and mercapto-silica hybrid (MSH) in a column system has been studied. Adsorption was conducted in a 0.5-g adsorbent packed column passing through 30 mL solution of Au(III)/Ag(I)/Cu(II) ions 10 mg/L for MSH and Au(III)/Ag(I)/Ni(II) for ASH with three repetitions. Desorption used eluent of thiourea in HCl solution with volume of 10 mL each. Concentration of metal ions in the eluent was analyzed with flame atomic absorption spectroscopy and the amount of metal ions desorbed was calculated. The results showed that metal ions loaded in the columns were adsorbed completely in both adsorbents. However, the amount of metal ions desorbed for first three fractions is depended on the concentration of eluent. Thiourea 1M in 1M HCl solution eluted 96.7% and 59.1% of Au(III) ion from MSH and ASH, respectively; and Ag(I) was desorbed 79.2% from MSH and 97.6% from ASH. Metal ions of Cu(II) and Ni(II) are not easily eluted with that eluent; only 45.8% of Cu(II) was eluted from MSH and 5.0% of Ni(II) from ASH. Repetition of process in three-time use indicates the highly stability of the adsorbents; hence those are potential for solid phase extraction application.

**Keywords**: sorption, gold, silver, silica, rice hull ash

**Abstrak**

Dalam kajian ini, jerapan dan nyahjerapan ion Au (III) dan Ag (I) pada hibrid amino-silika (ASH) dan hibrid merkapto-silika (MSH) telah dikaji dalam sistem turus. Jerapan dilakukan dalam turus padat 0,5 g penjerap dengan mengalirkan 30 mL larutan ion Au(III)/Ag(I)/Cu(II) masing-masing 10 mg/L untuk MSH dan Au (III)/Ag(I)/Ni(II) untuk ASH dengan tiga kali ulangan. Nyahjerapan dilakukan dengan menggunakan eluen tiourea dalam larutan HCl dan setiap 10 mL. Kepekatan ion logam dianalisis mengunakan spektroskopi serapan atom nyalaan dan jumlah ion logam yang ternyahjerap dihitung. Hasil penelitian menunjukkan bahawa semua ion logam yang melalui turus akan terjerap sempurna pada kedua adsorben. Namun, jumlah ion logam yang ternyahjerap untuk tiga bahagian pertama bergantung pada kepekatan eluen yang digunakan. Tiourea 1M dalam larutan HCl 1M mengelusi 96.7% dan 59.1% ion Au(III) dan Ag(I) ternyahjerap 79.2% dan 97.6% masing-masing dari MSH dan ASH. Ion logam Cu(II) dan Ni(II) tidak mudah dielusi dengan eluen, hanya 45.8% Cu(II) dielusi dari MSH dan 5.0% Ni(II) dari ASH. Pengulangan proses di dalam tiga kali penggunaan menunjukkan kestabilan penjerap adalah sangat tinggi, sehingga berpotensi untuk diaplikasikan pada pengekstrakan fasa pepejal.

**Kata kunci**: sorpsi, emas, perak, silika, abu sekam padi

## Introduction

Precious metals such as gold, silver, platinum and palladium are widely used in many fields like catalysts in various chemical processes, in electrical and electronic industries, in medicine and in jewelry [1]. The increasing demand for the precious metals is of great economical interest to the recovery of these metals from aqueous and waste

solutions since mineral stocks have started to decline. There are several methods, such as liquid–liquid extraction, membrane filtration and solid phase extraction (SPE), available in the literature for the removal of precious metals from aqueous solutions. Comparatively, SPE seems to be the most suitable method for the recovery of those metals in the case of low concentration due to low cost and high efficiency. Due to the technical and economical point of view, now much attention has been focused on lost cost adsorbents for the removal and recovery of precious metal ions.

In comparison with liquid-liquid extraction of metal ions, the solid phase extractions have two major advantages. First, they are more ecofriendly and second, it is easier to reuse them [2]. Ion-exchangers and chelating resin are the two most important classes of solid phase extractors (adsorbents). However, the later ones are attractive due to their selectivity. Several ligand immobilized organic polymeric matrices have been studied as chelating resins in the recent past [3]. The modified silica gel generally exhibits sorption capacities higher than those of organic polymer based resins. On silica gel reactive sites exist in large number, and therefore, the number of organic molecules immobilized is high, which results in good sorption capacity for metal ions.

Silica gel functionalized with 8-hydroxyquinoline [4], salicyldoxime [5], 1-(2-thiazolylazo)-2-naphthol [6], dithizone [7], acidred-88 [8], acid alizarin violet-N [9], didecylami-noethyl-b-tridecylammonium [10], 3-methyl-1-phenyl-4-stearoyl-5-pyrazolone [11], formylsalicylic acid [12], thiourea [13], 2-mercaptoben-zothiazole [14], dithiocarbamate [15], salicyldehyde [16], o-vanillin [17] and 2-hydroxy-5-nonylacetopheneoxime [18] is reported as a chelating collector for heavy metal ions. Separation and preconcentration methods for gold have been reported, in which the common adsorbents of gold were silica gel modified with mercaptobenzothiazole [19], nanometer titanium dioxide [20], thioethericsites [21], benzoylthiourea [22] and aminopropyltrimethoxysilane [23].

Selectivity of adsorption for the target metal ions may be improved by imprinting the target metal ion in the modified silica. Imprinting of silica with Au nanoparticles using aminosilanes was achieved at high loadings [24, 25] and phenyl-functionalized silica gels with embedded gold particles were also prepared in a basic medium, albeit with particle sizes larger than 10 nm [26]. Sakti et al. [23] reported synthesis of ionic imprinting amino-silica hybrid (Im-ASH) for adsorption of gold ion in a batch system. The result shows that Im-ASH increases selectivity in absorbing Au (III) but reduces the capacity. The selectivity of this hybrid silica-based materials mainly depends on the structure of the immobilized organic compound, the nature of the incorporated donor atoms (O, N, S and P), the positioning of the functional groups along the surface of the silica support and the steric requirements of the complex formed after uptake of the desired metal ion. In the present paper, we report sorption characteristic of two active sites namely mercapto (-SH) and amino (-$NH_2$) immobilized on silica toward multimetal ions Au(III)/Ag(I)/Cu(II) and Au(III)/Ag(I)/Ni(II), respectively, in a dynamic (column) system. In addition, reusability of the adsorbents loaded column is examined as well.

## Materials and Methods

### Chemicals

Sodium silicate solution, as the source of silica, from rice husk ash was prepared using a procedure reported by Sakti et al.[23]. As site active sources two precursors namely 3-aminopropyltrimethoxysilane (APTMS) and 3-mercaptopropyltrimethoxysilane (MPTMS) were supplied from Merck. Standard Au(III) solution 1000 mg/L in HCl solution was purchased from Merck and solution of Ag(I), Ni(II) and Cu(II) were prepared by dissolving salts of metal nitrate (Merck). Eluent for desorption of metal ions was prepared by dissolving thiourea (Merck) in HCl solution. All above chemicals were used without further purification.

### Apparatus

A solid phase extraction set consisting of a chamber for fitting the bottom side of the SPE polyethylene column and reaction tubes below the column for collecting the eluat and a vacuum pump was used in this research. A flame atomic absorbance spectrophotometer (FAAS) (Perkin Elmer 3110) was used analysis of metal ions and Fourier transform infrared (FTIR) spectrophotometer (Shimadzu FTIR-8210 PC) were used for identification of functional group present in the adsorbents.

**Procedures**

***Synthesis of adsorbent with sol-gel process***

A mixture of 40 mL sodium silicate solution and 10 mL APTMS was added with 3 M HCl solution dropwise with constant stirring until pH of the mixture reached 7.0. The resulting gel was aged for one night, washed with demineralized water, and dried in an oven at 70 °C for 2 h. The resulting dry gel was ground and sieved 200 mesh in size. The product then used for further experiment was called adsorbent of amino-silica hybrid (ASH). The similar work was carried out to obtain mercapto-silica hybrid (MSH) by replacing APTMS with MPTMS. The hybrids were characterized with FTIR spectrophotometer dan XRD.

***Packing of solid phase extraction (SPE) column***

A SPE column (100 mm long x 5 mm inlet diameter) completed with a 20-µm polyethylene frit in the bottom was washed with water and ethanol prior use. Adsorbent 0.5 g suspended in 5 mL ethanol was homogenized in an ultrasonic bath for 5 min. The suspension then was poured into the column with help of a vacuum pump at a flow rate of 0.6 mL/min and the second frit was put above the adsorbent in the column.

***Adsorption-desorption of metal ions in SPE column***

A 10-mL aliquot of Au(III)/Ag(I)/Cu(II) solution (10 mg/mL, each) was passed through the column at a flow rate of 0.5 mL/min. The loading was repeated three times. Metal ions in the filtrate were analyzed with FAAS to calculate the amount of metal ions un-adsorbed. The adsorbed ion was eluted with 1.0 M thiourea solution in 0.5 M HCl at an elution rate of 1.0 mL/min. The metal ion in each fraction (10 mL) of elution was determined with FAAS and the recovery percentage was calculated. The cycle of adsorption-desorption was repeated 3 times using the same column to evaluate stability and reusability of the adsorbent.

## Results and Discussion

**Characteristics of adsorbent**

The presence of amine ($-NH_2$) groups in ASH and thiol (-SH) in MSH was confirmed with FTIR spectra (Figure 1). In Figure 1(a) (silica gel, SG) bands observed at 3426, 1636, and 957 $cm^{-1}$ indicate vibration of O–H from silanol group (Si–OH), and at 1088 and 463 $cm^{-1}$ come from Si–O–Si vibration of the siloxane groups. Those bands are also observed in spectra of ASH and MSH. The characteristic spectra of ASH (Figure 1(b)) are seen at 1528 $cm^{-1}$ from N–H and at 2940 $cm^{-1}$ from C–H band. Similar spectra were also observed for MSH in Fig. 1(c). A sharp band at 2931.8 $cm^{-1}$ was originated from C-H vibration and a weak band of S-H is observed at 2553.75 $cm^{-1}$.

The structure of materials was identified with XRD. The patterns resulted (not presented) show that there is a broad peak at $2\theta = 21\text{-}22^{o}$ for all three materials (SG, ASH and MSH) indicating the amorphous structure [27]. These results reveal that the modification with the silane reagent does not alter the nature of amorphous silica.

**Adsorption of multimetal ion in column**

In this study, the adsorption was carried out three repetitions in separated columns. The adsorption result was presented in Table 1.

**Adsorption metal ions on ASH**

Table 1(a) shows that the total metal ions adsorbed on ASH reaches 100 %. It is consistent with the capacity of ASH in adsorbing those metal ions in a batch system reported by previous researchers. Sakti et al. [23] found that ASH is able to adsorb 132 mg/g of Au(III) and Nuryono et al. [28] reported that the capacity of adsorption for Ni(II) and Ag(II) are 21 and 154 mg/g, respectively. In this study, the pH of the solution multilogam used for the adsorption process is 4.0. This is consistent with previous studies reporting that the maximum adsorption capacity of Au(III) on amino silica hybrids occur between pH 3-5 [23]. At this pH range, amino ($-NH_2$) groups on the ASH surface are protonated to form ammonium ($-NH_3^+$) groups and interact with Au(III) in $AuCl_4^-$ form.

Possible interactions between the metal Au(III) with amino silica hybrid is through ionic interactions presented in Figure 2. This leads to Au(III) to be adsorbed more than Ag(I) and Ni(II). In this study, multimetal adsorption of Au(III), Ag(I) and Ni(II) was conducted in the medium of water leading to tendency metal ions to form octahedral

complexes. Ion Au(III) dissolved in HCl solution forms complex anion of $[AuCl_4]^-$ while Ni(II) and Ag(I) complexes form $[Ni(H_2O)_6]^{2+}$, $[Ag(H_2O)_6]^+$ [29].

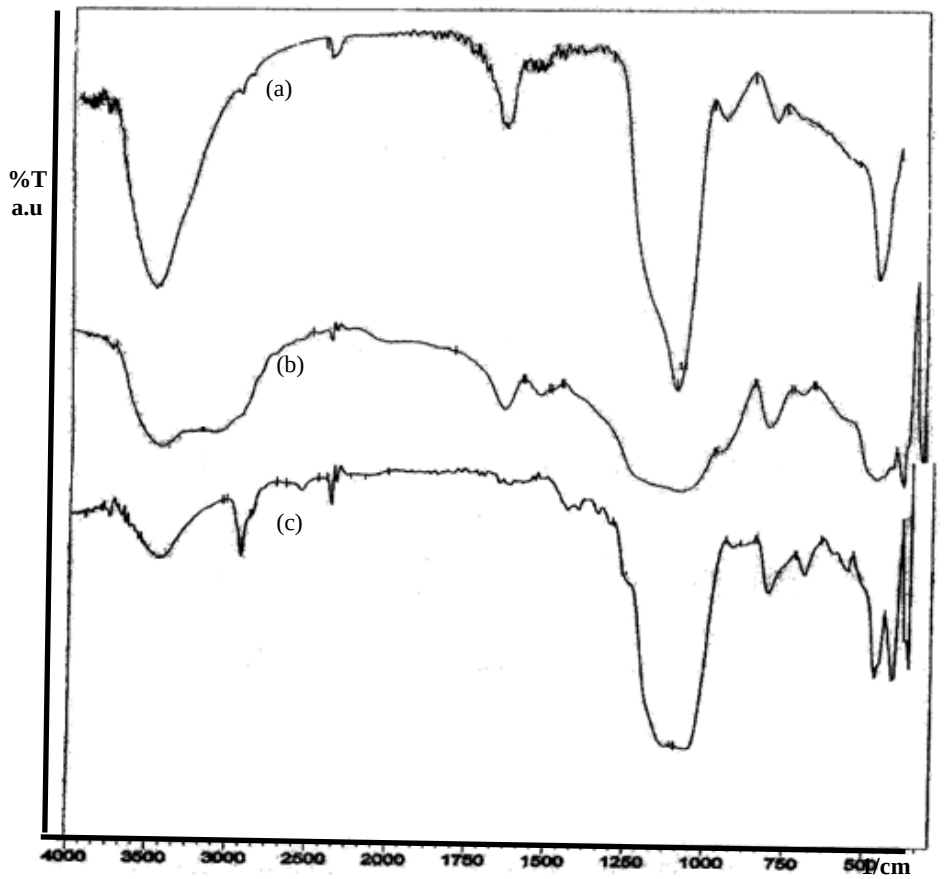


Figure 1. Infrared spectra of SG (a), ASH (b) and MSH (c)

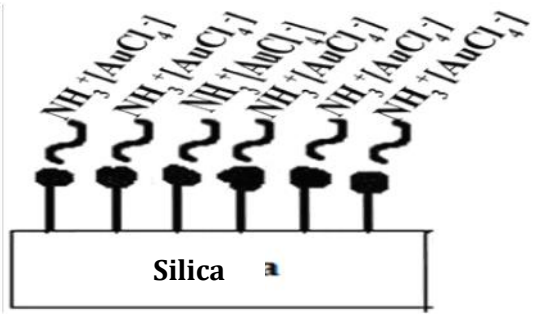


Figure 2. Model of ionic interaction between ammonium groups and anion of Au(III)

Ni(II) and Ag(I) cations with the ammonium groups are expected to repel each other and adsorption would not occur. However, Table 1 shows that Ag(I) and Ni(II) are adsorbed in high percentage (90 %). This is probably due to substitution of proton on ammonium groups by metal cation to form metal ion-amine complexes followed by removal of water molecule hydrated on the metal ions. Another possibility is that adsorption occurs through hydrogen bonding between silanol groups remaining on silica and water molecule hydrated on the metal ions.

Table 1. Amount of metal ions adsorbed on column loaded with adsorbent.

**a. Adsorbent ASH**

| Ion | Column | Total metal Ion | | |
|---|---|---|---|---|
| | | Loaded | Adsorbed | |
| | | (mg) | (mg) | (%) |
| | I | 0.42 | 0.41 | 98.7 |
| **Au(III)** | II | 0.41 | 0.40 | 97.6 |
| | III | 0.39 | 0.39 | 100 |
| | I | 0,42 | 0.38 | 90.5 |
| **Ag(I)** | II | 0.42 | 0.40 | 95.2 |
| | III | 0.48 | 0.48 | 100 |
| | I | 0.38 | 0.37 | 98 |
| **Ni(II)** | II | 0.38 | 0.37 | 98 |
| | III | 0.39 | 0.39 | 100 |

**b. Adsorbent MSH**

| Ion | Column | Total metal Ion | | |
|---|---|---|---|---|
| | | Loaded | Adsorbed | |
| | | (mg) | (mg) | (%) |
| | I | 0.30 | 0.30 | 100 |
| **Au(III)** | II | 0.30 | 0.30 | 100 |
| | III | 0.30 | 0.27 | 90 |
| | I | 0.36 | 0.29 | 81 |
| **Ag(I)** | II | 0.35 | 0.34 | 97 |
| | III | 0.35 | 0.35 | 100 |
| | I | 0.35 | 0.35 | 100 |
| **Cu(II)** | II | 0.35 | 0.35 | 100 |
| | III | 0.35 | 0.35 | 100 |

**Adsorption of metal ions on MSH**

Similar result is also observed for adsorption of Au(III)/Ag(I)/Cu(II) on MSH (Table 1(b)) that all metal ions are adsorbed. It is also consistent with data resulted for the batch system. In that system, adsorption capacity of MSH for Au(III) is 203.4 mg/g [29] and for Ag (I) and Cu (II) is 359.54 mg/g and 48.83 mg/g, respectively [30]. Probably interaction between Au(III) and adsporbent MSH is expressed in Figure 3. It seems that Au(III) is adsorbed through complex formation between S as electron donor atom and Au(III) as acceptor.

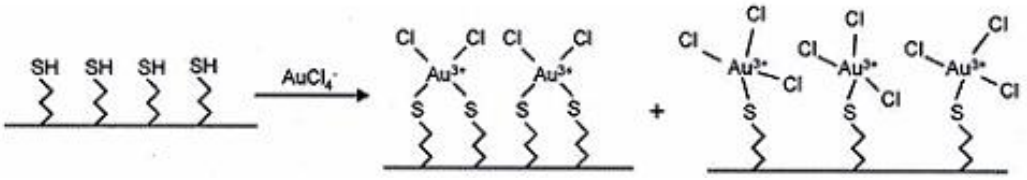


Figure 3. Model of complex formation between anion of Au(III) and MSH

Based on the HSAB concept, the active groups thiol (-SH) present on the surface of the MSH is a soft base, so it may adsorb the soft metal, Au(III). Theoretically, adsorption HMS multilogam system will only adsorb Au(III) ions and will not adsorb Cu(II) and Ni(II), which are intermediate acid. However, based on Table 1(b) shows that Cu(II) and Ni(II) adsorbed on HMS is much lower than that of Au(III). This is possible because according to FTIR spectra the surface of HMS is covered not only by thiol groups but also silanol, -OH. The atom O in the silanol groups may act as harder electron donor than S atom on the HMS. Therefore silanol groups are be able to bind metal ions Cu(II) and Ni(II), intermediate acids. According to Lam [31] the adsorbed Au(III) on the surface of the adsorbent at acidic conditions (pH ~ 2-3) provides a partial negative charge on the surface of the adsorbent, since at that pH range Au(III) ions present in $AuCl_4^-$. Partial negative charge on the surface of the adsorbent allow to interact with Cu(II) and Ni(II) ions, which is positively charged in water medium.

**Desorption**

To study performance of the SPE column in separating/extracting Au(III) ion from the adsorbent, in this research elution with 1M thiourea in different concentration of HCl (0.5 and 1 M) was conducted. Thiourea solution has a low toxicity and desorption runs faster compared to conventional cyanide solution [32]. The addition of thiourea led to Au (III) is unstable then reduced to Au(I). Metal ion Au(I) is then used to react with thiourea to form a stable complex by the reaction:

$$Au^+ + 2\ SC(NH_2)_2 \rightarrow [Au(SC(NH_2)_2)_2]^+ \quad (1)$$

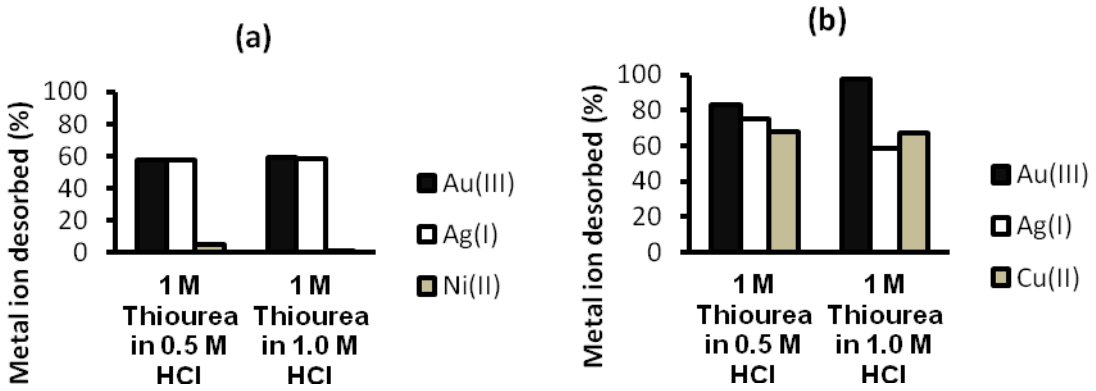


Figure 4. Diagram of metal ions desorbed from adsorbent ASH (a) dan MSH (b) using eluent of 1 M thiourea in 0.5 M HCl and in 1.0 M HCl

Desorption also aims to evaluate the selectivity of thiourea in HCl solution in eluting the metal ions from the column. The total percentage of metal ions desorbed from the adsorbent with both eluents in the first three fractions can be seen in Figure 4.

**Desorption of metal ions from ASH**

Figure 4(a) shows that Au(III) and Ag(I) are desorbed in similar amount and Ni(II) is practically not desorbed from the ASH column. As mentioned previously, S atom acting as desorbing agent is categorized into soft base so that soft metal ions i.e. Au(III) and Ag(I) form complexes with thiol groups much more stable than Ni(II) categorized as a borderline acid. In addition, a ligand with large donor atom such as S is not readily to form strong interaction with small metal ion. Complexes formed by small metal ions lead to low coordination since those metal ions should provide large space to accommodate the ligand large atom [33]. Based on the size of the ion, the order is Au (III)>Ag (I)>Ni (II); hence Au (III) forms a complex with thiourea more stable than Ag (I). However, both ions Au (III) and Ag (I) in the system multimetal Au (III)/Ag (I)/Ni (II) are desorbed only about 50%. This is probably due

to slow rate of complex formation and competition of multimetal ions present in the solution to form complexes with thiourea.

**Desorption of metal ions from MSH**

From Figure 4(b) can be seen that 84.61% of Au (III) in multimetal Au (III)/ Ag (I)/Cu (II) can be eluted using a solution of 1 M thiourea in 0.5 M HCl and almost complete amount (96.00%) of Au (III) is desorbed with 1 M thiourea in 1.0 M HCl. Metal ion of Cu (II) 68.12% is eluted with the first eluent and 66.67% with the second eluent. A similar trend is also seen for Ag (I), in which 74.28% is eluted with 1M thiourea in 0.5 M HCl and only 57.14% with 1M thiourea solution in 1M HCl.

From the results of desorption the increase of the HCl concentration did not significantly improve the percentage of Cu (II) and Ag (I) desorbed. The eluent of 1 M thiourea in 1 M HCl solution desorbs Au(III) in the highest amount among the investigated metal ions for the multilmetal system of Au (III)/Ag (I)/Cu (II). Based on the HSAB concept the softness of S atom in thiourea may act as good desorbing groups for soft metal ions. Hence, thiourea forms more stable complex with Au (III) than with Cu (II) and Ag (I). Also in the solution, the ligands with large donor atoms such as S may limit their ability to form stable complexes with smaller metal ions.

According to Lacoste-Boucet [34] addition of acid may stabilize and prevent thiourea degraded, thereby reducing the consumption of thiourea. Chloride ions ($Cl^-$) derived from the addition of HCl serves as a competing agent (competitors) for Au-Cl complexes on the surface so that Au(III) may be desorbed from HMS [35]. Higher concentration of HCl increases the amount of chloride ions as competitor. These results give similar trend to that done in a batch system [29]. Elution process in three fractions yield percentage of metal ions desorbed as presented in Figure 5.

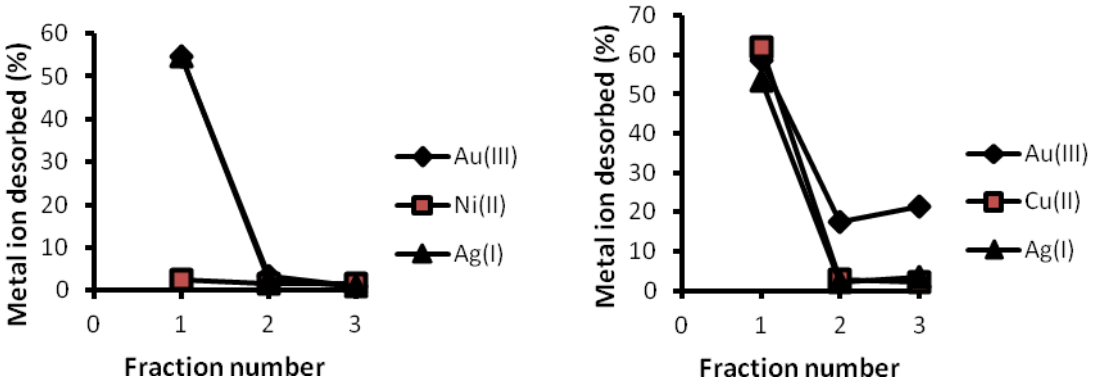


Figure 5. Curves of metal ions desorbed from adsorbent ASH (a) and MSH (b) versus fraction number of elution using 1 M thiourea in 1 M HCl

Figure 5(a) shows that two metal ions namely Au (III) and Ag (I) are eluted together with large amount in the first fraction. However, Ni (II) is not easily desorbed from the column. Based on HSAB, Ni (II) is categorized into hard acid, as well as donor atom N is hard base. Therefore, those acid and base may interact strongly, and difficult to be broken by soft base such as S atom in thiourea. In contrary, interaction between soft acid Ag (I) and hard base N atom is very weak; hence this metal ion is eluted fast. Ionic interaction between ammonium cation and Au (III) anion is ready to be broken by S atom due to complex bonding formation.

From Figure 5(b) can be seen that in the first fraction the amount of ions desorbed for all metals shows the same percentage. It is probable desorption occurs for metal ions adsorbed on the MSH through trapping interaction. In this case, the amount of Au (III) bounded on MSH is not difference from other metal ions. However, in the second and third fractions, percentage of Ag (I) and Cu (II) eluted drops drastically in comparison to that of Au (III). This is

probable due to the un-effective contact between the adsorbent and metal ions in the column. Low stability constant of Cu-thiourea complexes (log $\beta = 2.3 \pm 0.1$) causes Cu (II) not easily to be eluted with this eluent and this also happens for Ag (I). In contrary, the stability constant of gold-thiourea complex is log $\beta \approx 24$ [36].

Table 2. Amount of metal ions desorbed from column in three repetitions.

**a. ASH**

| Ion | Cycle | Total metal ions | | |
|---|---|---|---|---|
| | | Adsorbed | Desorbed | |
| | | (mg) | (mg) | (%) |
| Au (III) | 1 | 0.41 | 0.29 | 96.7 |
| | 2 | 0.37 | 0.36 | 96.8 |
| | 3 | 0.39 | 0.38 | 98.6 |
| Ag (I) | 1 | 0.38 | 037 | 96.6 |
| | 2 | 0.38 | 0.36 | 94.4 |
| | 3 | 0.36 | 0.35 | 98.1 |
| Ni (II) | 1 | 0.48 | 0.06 | 0.37 |
| | 2 | 0.42* | 0.05 | 12.2 |
| | 3 | 0.37* | 0.04 | 9.50 |

**b. MSH**

| Ion | Cycle | Total metal ions | | |
|---|---|---|---|---|
| | | Adsorbed | Desorbed | |
| | | (mg) | (mg) | (%) |
| Au (III) | 1 | 0.30 | 0.29 | 96. 7 |
| | 2 | 0.30 | 0.29 | 96.7 |
| | 3 | 0.27 | 0.27 | 100 |
| Ag (I) | 1 | 0.29 | 0.23 | 79.3 |
| | 2 | 0.34 | 0.27 | 79.0 |
| | 3 | 0.35 | 0.26 | 74.3 |
| Cu (II) | 1 | 0.35 | 0.16 | 45.7 |
| | 2 | 0.19* | 0.04 | 21.1 |
| | 3 | 0.15* | 0.01 | 6.70 |

* The column was not reloaded with the ion logam since not all metal ion was eluted in the previous elution

**Reusability of Adsorbent**

Regeneration of the adsorbent for reuse is a key in the improvement of the economic process. Additionally, study on reusability of adsorbent in the column is used to evaluate the stability of the adsorbent during the adsorption-desorption process. To determine the reusability adsorbent in SPE columns was used for adsorption-desorption process (cycle) in several times. Elution was performed in ten fractions (10 mL each) and the adsorption-desorption cycle was repeated 3 (three) times. The results can be seen in Table 2. From the data in Table 2 can be seen that in three repetitions the metal ions are desorbed in the similar amount for the both adsorbents. It indicates the higher chemical stability, and within three months from the first usage performance of columns does not change significantly. Similar to the previous result, three metal ions (Au (III)/Ag (I)/Cu (II)) absorbed on ASH column are eluted in different amount (Table 2(a)). Au (III) and Ag (I) are desorbed completely but Ni (II) is difficult to be desorbed from the ASH column. It can be stated that ASH column and eluent of thiourea in HCl solution give highly selectivity for the separation of Au (III) from Ni (II) but not from Ag (I).

Different from ASH, three metal ions adsorbed on MSH are eluted with the order of desorbed percentage Au (III)>Ag (I)>Cu (II). This result is different from the data of the first three fractions (Figure 2(b), in which the order is Au (III)>Cu (II)>Ag (I). Ion Cu (II) is eluted faster than Ag (I); in the first three fractions elution of Cu (II) has reached maximum amount and Ag (I) may be eluted up to ten fractions. Competition between S atom from –SH in adsorbent and from thiourea makes removal of Ag (I) from adsorbent occurs slowly and need a lot amount of eluent/fraction. Similar to ASH, MSH selective for Au (III) toward Cu (II) but not toward Ag (I), even though Au (III) and Ag (I) can still be separated since Au (III) is easier eluted than Ag (I).

## Conclusion

Adsorption of metal ions investigated from multimetal ion solution on the adsorbents ASH and HMS in a column technique shows almost the same results, in which three metal ions in solution are adsorbed completely on the adsorbents if the metal ions loaded are less than capacity calculated in a batch system. The process of separation of Au(III) through the desorption of gold metal ion in the multimetal system Au(III)/Ag(I)/ Cu(II) from MSH surfaces using a solution of thiourea-HCl shows high selectivity (97% desorbed) toward Ag(I) and Cu(II). However, desorption of Au (III) from the adsorbent ASH gives low selectivity toward Ag (I) but excellent to Ni (II). Adsorbents developed in the separation of metal Au (III) from multimetal system in column technique with three adsorption-desorption cycles show no decrease in performance of adsorption-desorption characteristic indicating high stability of the adsorbents. Therefore, those adsorbents may be reusable and potential for solid phase extraction application in the future.

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## References

1. Goswami A., & Singh, A. K., (2002).1,8-Dihydroxyanthraquinone anchored on silica gel: synthesis and application as solid phase extractant for lead(II), zinc(II) and cadmium(II) prior to their determination by flame atomic absorption spectrometry, *Talanta*, 58, 669 - 678.
2. Ramesh, A., Hasegawa, H., Sugimoto, W., Maki, T. & Ueda, K. (2008). Adsorption of gold(III), platinum(IV) and palladium(II) ontoglycine modified crosslinked chitosan resin, *Bioresource Technology*, 99: 3801 – 3809.
3. Zih-Pere ´nyi, K., Lasztity, A., Horvath, Z., Levai, A. (1998). Use of a new type of 8-hydroxyquinoline-5-sulphonic acid cellulose (sulphoxine cellulose) for the preconcentration of trace metals from highly mineralised water prior their GFAAS determination, *Talanta*, 47: 673 - 679.
4. Kasahara, I., Willie, S. N., Sturgeon, R. E., Berman, S. S., Taguchi, S., Goto, K. (1993). Preparation of 8-quinolinol immobilized adsorbents with minimum contamination for the preconcentration of trace metals in water, *Bunseki Kagaku*, 42: 107-110.
5. Sarkar, A. R., Datta, P. K. & Sarkar, M. (1996). Sorption recovery of metal ions using silica gel modified with salicylaldoxime, *Talanta*, 43: 1857-1862.
6. Zaporozhets, O. A., Nadzhafova, O. Y., Zubenko, A. I. & Sukhan, V. V. (1994). Analytical Application of Silica Gel Modified with Didecylaminoethyl-β-Tridecylammonium Iodide, *Talanta*, 41, 2067 - 2071.
7. Zaporozhets, O., Petruniock, N. and Sukhan, V. (1999). Determination of Ag(I), Hg(II) and Pb(II) by using silica gel loaded with dithizone and zinc dithizonate, *Talanta*, 50: 865 - 872.
8. Kocjan, R. (1999). Retention of Some Metal Ions and Their Separation on Silica Gel Modified with Acid Red 88, *Microchim. Acta*, 131: 153-158.
9. Ferreira, S. L. C., & de Brito, C. F. (1999). Separation and Preconcentration of Cobalt after Sorption onto Amberlite XAD-2 Loaded with 2-(2-Thiazolylazo)-*p*-cresol, *Anal. Sci.*, 15: 189 - 192.
10. Zaporozhets, O., Petruniock, N., Bessarabova, O., Sukhan, V. (1999). Determination of Cu(II) and Zn(II) using silica gel loaded with 1-(2-thiasolylazo)-2-naphthol, *Talanta*, 49: 899 - 906.
11. Tong, A., Akama, Y. & Tanaka, S. (1990). Pre-concentration of copper, cobalt and nickel with 3-methyl-1-phenyl-4-stearoyl-5-pyrazolone loaded on silica gel, *Analyst*, 115: 947 - 949.
12. Mahmoud, M. E. & Soliman , E. M. (1997). Silica-immobilized formylsalicylic acid as a selective phase for the

extraction of iron(III), *Talanta*, 44: 15 - 22.
13. P. Liu, Q. Pu, Z. Su, (2000), Synthesis of silica gel immobilized thiourea and its application to the on-line preconcentration and separation of silver, gold and palladium, *Analyst*, 125: 147 - 150.
14. Liu, P., Pu, Q. & Su, Z. (1998). Application of 2-mercaptobenzothiazole-modified silica gel to on-line preconcentration and separation of silver for its atomic absorption spectrometric determination, *Analyst*, 123: 239 - 243.
15. Mahmoud, M. E. (1999). Selective solid phase extraction of mercury(II) by silica gel-immobilized-dithiocarbamate derivatives, *Anal. Chim. Acta*, 398: 297 - 302.
16. Kubota, L. T., Moreira, J. C., Gushikem, Y. (1989). Adsorption of metal ions from ethanol on an iminosalicyl-modified silica gel, *Analyst*, 114: 1385 - 1388.
17. Garg, B. S., Sharma, R. K., Bist, J. S., Bhojak, N. & Mittal, S. (1999). Separation and preconcentration of metal ions and their estimation in vitamin, steel and milk samples using *o*-vanillin-immobilized silica, *Talanta*, 48 (1): 49 - 55.
18. Kim, J. S. & Yi, J. (1999). The Removal of Copper Ions from Aqueous Solutions Using Silica Supports Immobilized with 2-Hydroxy-5-nonylacetophenoneoxime, *Sep. Sci. Technol*., 34: 2957 – 2971.
19. Pu, Q. S., Su, Z. X., Hu, Z. H., Chang, X. J. & Yang, M. J. (1998). 2-Mercaptobenzothiazole-bonded silica gel as selective adsorbent for preconcentration of gold, platinum and palladium prior to their simultaneous inductively coupled plasma optical emission spectrometric determination, *Journal of Analytical Atomic Spectrometry*, 13: 249 – 253.
20. Liu, P., Pu, Q. S., & Su, Z. X. (2000) Synthesis of silica gel immobilized thiourea and its application to the on-line preconcentration and separation of silver, gold and palladium, *Analyst (London)*, 125: 147 – 150.
21. Gentscheva, G., Tzvetkova, P., Vassileva, P., Lakov, L., Peshev, O. & Ivanova, E. (2007). Analytical characterization of a silica gel sorbent with thioethericsites, *Mikrochimica Acta*, 156: 303 – 306.
22. Bozkurt, S. S. & Merdivan, M. (2009). Solid phase extraction of gold(III) on silica gel modified with benzoylthiourea prior to its etermination by flame atomic absorption spectrometry, *Environ Monit Assess*, 158: 5 – 21.
23. Sakti, S.C.W., Siswanta, D. & Nuryono (2013), Adsorption of Gold(III) on Ionic Imprinted Amino-Silica Hybrid Prepared from Rice Hull Ash, *Pure Appl. Chem.*, 85 (1): 211 - 223.
24. Bonnemann, H., Endruschat, U., Tesche, B., Rufinska, A., Lehmann, C. W., Wagner, F. E., Filoti, G., Parvulescu, V. and Parvulescu, V. I. (2000) An $SiO_2$-Embedded Nanoscopic Pd/Au Alloy Colloid, *Eur. J. Inorg. Chem*., 5: 819 - 822.
25. Xie, Y. W., Quinlivan S. & Asefa, T. (2008). Tuning Metal Nanostructures in Mesoporous Silica by a Simple Change of Metal Complexes and by Reduction with Grafted Imines and Hemiaminals, *J. Phys. Chem*. 112: 9996 - 10003.
26. Hall, S. R., Davis S. A. & Mann, S. (2000). Cocondensation of Organosilica Hybrid Shells on Nanoparticle Templates: A Direct Synthetic Route to Functionalized Core−Shell Colloids, *Langmuir*, 16: 1454 - 1456.
27. Kalapathy, U., Proctor, A. & Shultz, J. (2000). A simple method for production of pure silica from rice hull ash, *Bioresource Technology*, 73: 257 - 262.
28. Nuryono, Bassir, M., Setyaningsih, A. & Narsito (2007). *Synthesis of Amino-Silica Hybrid from Rice Hull Ash for Heavy Metal Ion Adsorption*, Presented at International Conference of Chemical Sciences (ICCS) Held by Department of Chemistry, Universitas Gadjah Mada and School of Chemistry, University Sains Malaysia on 24-25 May 2007, In Yogyakarta, Indonesia.
29. Hamdiani, S., Nuryono, Rusdiarso, B. & Sakti, S. C. W. (2010). *Kajian Adsorpsi-Desorpsi Au(III) Pada Hibrida Merkapto Silika (HMS)*, Prosiding Seminar Nasional Penelitian, 15 Mei 2010 (Indonesian)
30. Mujiyanti, D. R., Nuryono & Kunarti, E.S. (2007). *Simultaneous Adsorption Of Ag(I), Pb(II), Cu(II), Cr(III), And Ni(II) On Mercapto Immobilized Rice Hull Ash Silica*, Presented at International Conference of Chemical Sciences (ICCS) Held by Department of Chemistry, Universitas Gadjah Mada and School of Chemistry, University Sains Malaysia on 24-25 May 2007, In Yogyakarta, Indonesia.
31. Lam, K. F., Fong, C. M., Yeung, K. L. & Mckay, G. (2008). Selective adsorption of gold from complex mixtures using mesoporous adsorbent, *J. Chem. Eng*., 145: 185 – 195
32. Groenewald, T. (1976). The Solution of Gold in Acidic Solutions Thiourea, *Hydrometallurgy*,1: 277 - 290.
33. Martell, E.A. & Hancock, R.D. (1996). *Metal Complexes in Aqueos Solution*, Plenum Press, New York.
34. Lacoste-Bouchet, P., Deschenes, G. and Ghali E. (1998). Thiourea Leaching of a Copper-Gold Ore Using

Statistical Design, *Hydrometallurgy*, 47: 189 - 203.
35. Ertan, E. & Gulfen, M. (2009). Separation of Gold(III) from Copper(II) and Zinc(II) Ions Using Thiourea-Formaldehyde or Urea-Formaldehyde Chelating Resins. *J. Appl Polym Sci*., 111: 2798 – 2805.
36. Puddephat, R. J., (1978), *The Chemistry of Gold*, Elsevier Scientific Publishing Company, Amsterdam.