Coating of mercapto modified silica on iron sand magnetic material for Au(III) adsorption in aqueous solution

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Abstract. The functionalized silica coating mercapto on iron sand magnetic material (MM/SiO2/MBI) has been done through sol-gel process. The successfully synthesized material is used as adsorbent (MM/SiO2/MBI) in the Adsorpti Au (III) process. Material characterization is carried out with an adsorbent stability test against acids. Adsorption is performed in a batch system and the unadsorbed Au (III) ion is analyzed with the Atomic Absorption Spectrophotometer (AAS). Characterization results indicate the synthesis of PB/SiO2-MBI adsorbent has been successfully performed. The coating of iron sand magnetic material enhances stability to acid. Adsorbent (MM/SiO2/MBI) is capable of adjudisorate ion Au (III) with the highest adsorption occurring at pH 1. Kinetics review indicates that the adsorption of the ion (III) is following the second-order pseudo kinetics with a value of k $3.57 \times 10^{-3}$ g/mg. Minute and adsorption isotherm follows the isotherm pattern of Langmuir with an adsorption capacity of 125 mg/g.

1. Introduction
The surface of the silica gel containing silanol functional groups (=Si-OH) and siloxane (=Si- O-Si=) that has been widely used as adsorbent heavy metal ions [1]. However, silica gel has drawbacks when applied as an adsorbent for soft metal. The weak interaction is caused by the low capacity of the oxygen atom in the silanol and siloxane in donating electrons to the soft metal ions [2,3,4].

Gold is one type of metal ion growing software utilization in various fields, especially the use of gold in electronic devices. This should be a concern for electronic waste produced continues to rise and the electronic waste is precious metals that they can be utilized such as Au, Ag, Pd and Pt as well as basic metals constituent electronic devices such as Cu, Al, Ni, Sn, Zn and Fe [5,6,7]. Gold in electronic waste is mixed with other metals that we need a method to process the collected (recovery) of gold from e-waste that is by adsorption methods. Selection of adsorption method is used because the equipment is simple, economical, easy to operate and high efficiency of metals with low concentrations. silica is used as an adsorbent to absorb ions of gold metal by modifying the surface using specific functional groups. Modification of the silica surface adsorption determines the selectivity of the gold metal ions. Generally, modifier compounds having functional groups such as -OH, -NH, -SH and -COOH (Takeuchi et al., 2007). Based on the theory of hard-soft acid-base (HSAB), gold is classified as soft acids and tends to form strong bonds with functional groups such as -NH soft alkaline, -CN and
- SH. Based on the theory HSAB the silica surface modified with compounds containing basic groups to become more malleable gold is selectively adsorbed soft acid. Modified silica functional groups proved to be selective for the adsorption soft gold [4,5,8,9]. Modifications of adsorbents have been carried out to produce adsorbents that are selective and specific in absorbing gold. Some researchers, use the -NH group as a modifier in the adsorbent to absorb gold. More and more - NH groups are expected to get more gold metal ions absorbed. Some modifiers used include the use of chitosan which has many -NH groups, the use of aminobenzimidazol with two -NH groups and tolylbiguanide with three -NH groups [3,4,15]. Modification of the adsorbent with mercaptobenzimidazole has one -SH group. This research was conducted to determine the effectiveness of the -SH group in adsorption gold.

However, the adsorption method has drawbacks in the separation process for the separation of the adsorbent from the adsorbate performed with conventional filtering techniques, decantation or can also utilize the instrument via centrifugation. It will be very difficult if applied in the neighborhood so attractive to develop the silica material that has magnetic properties to facilitate the separation process only with the help of an external magnet. Easily oxidized magnetite but with their coating with silica and magnetite functional groups are protected from the acidic or alkaline [10,11,12]. The commonly used magnetic source is a synthesis FeCl₂·6H₂O and FeCl₂·4H₂O to produce magnetite (Fe₃O₄). The use of magnetic materials can also be used from natural iron sand. The sand iron content of magnetite (Fe₃O₄) in nature has a fairly high [13,14]. The advantage of this research is to use magnetite from natural sand to produce adsorbent materials that have magnetic properties. Thereby reducing the use of chemicals for magnetite synthesis. Also, the adsorbent produced is an adsorbent that has been modified with the thiol (-SH) functional group which is expected to have the ability of adsorption with gold metal ions according to the principle of HSAB.

2. Objects and Methods

2.1. Adsorption of metal ions Au (III)

2.1.1 Variations in pH. The solution of Au (III) 1000 ppm was diluted to 100 ppm in a 100 mL flask. The solution of Au (III) of 100 ppm was diluted to 50 ppm in a 10 ml flask. 1-6 pH adjustment is done by adding 1 M NaOH and 1 M HCl and then diluted with a buffer of pH 1-6. Solution with a variety of pH placed in a plastic bottle and put 10 mg of adsorbent MM/SiO₂/MBI after it was shaken for 60 minutes using a 200 VRN shaker (130 rpm). The next stage is separated from the solution adsorbent using an external magnet (Neodymium, N35 grade, size 40 mm x 30 mm x 10 mm) then the solution was analyzed using FAAS, Analytic Jena contrAA 300 to determine the optimum pH solution of Au (III) adsorbed on the adsorbent MM/SiO₂/MBI.

2.1.2 Variation of contact time. Adsorption was done by varying the contact time of 15, 30, 45, 60, 90, 120 and 150 minutes at optimum pH. Adsorbent MM/SiO₂/MBI has added as much as 10 mg and shaken on every variation of a predetermined time using a 200 VRN shaker (130 rpm). Adsorbent MM/SiO₂/MBI separated from the solution of Au (III) using external magnetic assistance. The solution that has been separately analyzed using FAAS, Analytic Jena contrAA 300.

2.1.3 Variations in the concentration of metal ions Au (III). Solution of Au (III) to be varied concentration of 10 ppm, 20 ppm, 50 ppm, 100 ppm, 150 ppm, 200 ppm and 300 ppm at optimum pH and dissolved in 10 mL flask using optimum pH buffer (pH meters). Further included 10 mg of adsorbent MM/SiO₂/MBI on every variation of the concentration and shaken for 90 minute using a 200 VRN shaker (130 rpm) then adsorbent MM/SiO₂/MBI separated from the solution of Au (III) using an external magnetic assistance. The solution that has been separately analyzed using FAAS, Analytic Jena contrAA 300.
3. Results and Discussion

3.1. Effect of pH

pH plays an important role in determining the ability of the adsorbent to adsorb metal ions due to changes in pH affects the surface of the adsorbent and is followed by changes in metal ion species. Therefore, to determine the effect of pH on the adsorption of Au (III) by MM/SiO$_2$/MBI must perform variations of pH 1-6. The effect of pH changes on the number of ions Au (III) adsorbed can be seen in Figure 1.

Based on Figure 1 is known that the higher the pH, the number of ions Au (III) adsorbed decline. MBI group has a pKa value of 2.38 and a pH $<$pKa associated with the formation of the pair RNH$_3^+$/RNH$_2$. The decrease in pKa increases the number of protonated amines. Protonated at pH 1-2 occurs quickly because the value of pH $<$pKa, making it possible to pH 1 occurs perfect protonated amine groups on MBI. Thus despite the anion Cl competition with [AuCl$_4$]$^-$ to be bound by the -SH group but the presence of the anion Cl no effect because [AuCl$_4$]$^-$ in addition to interacting with the -SH group may also interact electrostatically with the amine group via the Cl atom in the [AuCl$_4$]$^+$. The more the amine groups are protonated at low pH led to the increasing number of electrostatic forces formed by the anion [AuCl$_4$] so that at pH 1 provides the highest adsorption amount. Therefore, at low pH (pH 1), the amine group (-NH) and mercapto group (-SH) play a role in the process of adsorption of Au (III) so that the number of metal ions Au (III) adsorbed to be very high.

At pH 2-3 decrease the number of ions Au (III) is adsorbed. This indicates that not only the S atom that plays a role in the process of adsorption of Au (III), but it is possible that a reduced number of protonated N atom caused a decrease in adsorption capacity. Ion absorption Au (III) at pH 4 slightly increased and then remained constant at pH $>$ 4. In the area of pH 4-6 speciation occurred metal hydroxide ions Au (III) to [AuCl$_3$(OH)]$^-$, [AuCl$_2$(OH)$_2$]$^-$ and [AuCl(OH)$_3$]$^-$]. The existence of OH- ligands with O atoms which are rich in pairs of free electrons and a large electronegativity and also the presence of Cl-rich electrons lead to increased repulsion between the metal ion complexes Au (III) with the MBI group. Speciation of metal ions to hydroxide causes an increased number of hydroxide ions resulting in a decrease in the adsorption of Au (III) by the adsorbent MM/SiO$_2$/MBI. N atoms in the pH range 4-6 MBI have not experienced so protonated N atoms still has a free electron pair causing electrostatic repulsion. The repulsion leads to a decrease in the number of ions Au (III) adsorbed. The existence of OH- ligands with O atoms which are rich in pairs of free electrons and a large electronegativity and also the presence of Cl-rich electrons lead to increased repulsion between the metal
ion complexes Au (III) with the MBI group. Speciation of metal ions to hydroxide causes an increased number of hydroxide ions resulting in a decrease in the adsorption of Au (III) by the adsorbent MM/SiO$_2$/MBI.

3.2. Metal ion adsorption kinetics Au (III)
The adsorption kinetics explain the rate of absorption of solute by the contact time of the reaction is an essential characteristic absorption efficiency. The longer the contact time Au (III) will also be increased to at a certain time to reach equilibrium. Figure 2 shows the influence of variations in the time on the efficiency of the adsorption of Au (III) by MM/SiO$_2$/MBI.

Figure 2. Graph effect of contact time on the adsorption of Au (III)

Figure 2, the kinetic curve shows that the first 60 minutes happen speed of absorption Au (III) which is fast and the number of ions Au (III) adsorbed increasing. Adsorption speed slows down until it reaches equilibrium at 90 minutes so the addition of interaction time does not give effect to an increase in the number of metal ions Au (III) are adsorbed. Increasing the amount of Au (III) happens quickly because the surface of the MM/SiO$_2$/MBI is -SH group with a high affinity for Au (III) so that when there is contact between the Au (III) with an adsorbent then will quickly -SH group donate electron pairs. Also, there is the amine group (-NH) protonated thus accelerating the process of adsorption of metal ions Au (III), which is in the form of [AuCl$_4$]$^-$.

This interaction occurs electrostatically. When the contact time of the longer visible reaction was slow. In this process the -SH group is estimated to have been used to interact with the ion Au (III) so that the slow phase is due to the interaction of Au (III) with silanol and siloxane contained in the material MM/SiO$_2$/MBI.

This reaction takes place slowly because the ions Au (III) is acidic soft and O atoms in silanol - OH group is alkaline but -SH group more alkaline so that Au (III) more effectively interact with -SH and when interacting with -OH become less effective. Silanol role in the slow reaction because it is located on the relatively inside so that when the interaction of Au (III) with silanol takes longer and silanol is also less effective in donating an electron pair to interact with Au (III). In this process the -SH group is estimated to have been used to interact with the ion Au (III) so that the slow phase is due to the interaction of Au (III) with silanol and siloxane contained in the material MM/SiO$_2$/MBI.

Adsorption kinetics MM/SiO$_2$/MBI on Au (III) was studied with the first-order reaction kinetics model, second-order, pseudo-1 order and pseudo-2 order. Kinetic parameters are shown in Table 1.
Table 1. Parameters of adsorption kinetics of Au (III) in MM/SiO$_2$/MBI

| Material       | Reaction kinetics model | The parameters of reaction kinetics |
|----------------|-------------------------|-----------------------------------|
|                |                         | K       | $q_e$          | $R^2$   |
| MM/SiO$_2$/MBI | Order 1                 |         |               | 0.52    |
|                | Order 2                 |         |               | 0.5     |
|                | Pseudo-1 order          | 0.026 min$^{-1}$ | 0.929 mg$g^{-1}$ | 0.708   |
|                | Pseudo-2 order          | 0.003 g / mg.min | 50 mg$g^{-1}$ | 0.998   |

Selection of kinetic model based on the degree of linearity for any kinetic model used. Based on Table 1 it can be seen that the greatest value of $R^2$ lies in the pseudo second-order kinetic model. Based on the price of $R^2$ can be interpreted that the appropriate kinetic model to describe the adsorption of Au (III) by MM/SiO$_2$/MBI is a Pseudo-2 order kinetic model. Order kinetic model pseudo-2 order based on the assumption that the rate-limiting step is the chemical adsorption involving power valence electron exchange between the metal ions with the adsorbent. The adsorbent is not in excessive quantities to adsorb metal ions. The number of active sites on the adsorbent decreases linearly during the adsorption process takes place. The kinetic data of Au (III) adsorption with MM / SiO$_2$ / MBI were compared with the kinetic data of pseudo-2 order adsorbent of chitosan silica magnetic material (MMSC) of 51.020 mg/g, aminobenzimidazole (MM@SiO$_2$/AB) kinetic data of 9.50 mg/g and tolylbiguimide (MM@SiO$_2$/TB) magnetic material of 6.83 mg/g [3,4,15]. Based on the kinetic parameters it can be seen that the modified adsorbent of the thiol group (-SH) has a higher gold adsorption ability than the -NH group. Judging from the number of groups in the modifier, it can be seen that the -NH groups in chitosan, aminobenzimidazol, and tolylbiguimide are more than the -NH groups in mercaptothenzonizidazole. The results of this study indicate that the -SH group is more effective at adsorption gold metal ions.

3.3 Metal ion adsorption isotherms Au (III)

Total Au (III) adsorbed on MM/SiO$_2$/MBI as a function of concentration is shown in Figure 3. The increased concentration of Au (III) the amount of adsorbed also increased.

![Figure 3. Graph ion concentration influences Au (III)](image_url)

Based on the results of the adsorption of Au (III) in MM/SiO$_2$/MBI with various concentrations obtained by the equilibrium concentration at 200 mg/L. Then contacted the equilibrium concentration of silica without modification. Comparative results are presented in Table 2 adsorption.
Table 2. Adsorption comparison of Au (III) in silica unmodified (MM/SiO$_2$) and silica modified (MM/SiO$_2$/MBI)

| Material       | The initial concentration Au (III) (mg/L) | Total Au (III) adsorbed (mg/g) |
|----------------|------------------------------------------|-------------------------------|
| MM/SiO$_2$     | 200                                      | 45.833                        |
| MM/SiO$_2$/MBI | 200                                      | 156.111                       |

The results proved that the adsorption of Au (III) with modified silica (MM/SiO$_2$/MBI) 3.5 times greater than the silica without modification (MM/SiO$_2$). According to the principle, HSAB - SH group and the amine group can interact better with Au (III) because of the -SH group and amine alkaline than the soft -OH groups on MM/SiO$_2$ alkaline hard. Low ability O atoms in silanol and siloxane as an electron donor is a result of the bond is between the O atoms with atomic Si in the structure of silica (possibility occurs bond partially between O and Si through bonding πd-p) so that the electron density of the O atoms is reduced and effect on the low capacity of O atoms as electron donors. Based on the principle HSAB-OH group is less effective as a donor atom. Therefore, it can be stated that the modification of the silica with the functional groups (MM/SiO$_2$/MBI) was able to increase the adsorption capacity to Au (III). Predictions made possible interaction between Au (III) with MM/SiO$_2$/MBI.

The interaction of Au (III) with MM/SiO$_2$/MBI adsorbents can be hypothesized as shown in Figure 4. The adsorption process is carried out in an acidic atmosphere (pH 2). At pH 2 it is possible to protonate the -NH group in the form of −NH$^+$ which is present in the mercaptobenzimidazol modifier and at pH 2 also the gold metal ions are in the metal ion complexes Au (III). Thus, in an acid solution, the surface of iron sand is coated with silica through and the mercaptobenzimidazol modifier interacts with silica through the CPTMS 'bridge' through the formation of siloxane bonds. The silane group in CPTMS is needed in bond formation because the mercaptobenzimidazole modifier does not have a silane group to be able to interact directly with silica. This hypothesis is supported by research on Coatings of L-Arginine Modified Silica by using GPTMS as a 'bridge' connecting [16]. In contrast to the mercaptopropyltrimethoxysilane modifier (MPTMS) which already has a silane group, it does not need a 'connecting bridge' [17,18]. When there is an interaction of the gold metals with MM/SiO$_2$/MBI adsorbents in an acidic atmosphere, the gold metals in the form of Au (III) interacts with the -SH group by giving electron pairs to form covalent bonds. Another possible interaction is the electrostatic interaction between the group -NH which undergoes protonation to become -NH$^+$ with anion [AuCl$_4$]$^-$ in an acidic solution.

![Figure 4. Predicted interactions Au (III) with MM/SiO$_2$/MBI](image)

The adsorption process with ion concentration variations Au (III) in MM/SiO$_2$/MBI then studied the adsorption isotherm. The equilibrium isotherms are used to explain the nature of the adsorbent surface and affinity MM/SiO$_2$/MBI on Au (III). Two types of isotherm are used to describe the data in Table 3 is the Langmuir isotherm and Freundlich isotherm. The most important part in the adsorption process is a site owned by the adsorbent located on the surface, but the number of these sites will be reduced if
a closed surface is increasing. Freundlich isotherm models suggest that the process of adsorption on the surface is heterogeneous. Freundlich isotherm models show the adsorbate layer formed on the surface of the adsorbent is a multilayer. The relationship between the parameters of Langmuir and Freundlich shown in Table 3.

| Table 3. Langmuir and Freundlich isotherm parameters on the adsorption of Au (III) |
|------------------|------------------|------------------|------------------|
| parameter Langmuir | parameter Freundlich |
| $R^2$   | $q_m$ (mg / g) | $K_L$ (L/mg) | $R^2$ | $K_F$ mg / g | $N$ |
| 0.66   | 333.33        | 0.022         | 0.97   | 2.62          | 1.67 |

Data Table 3 shows the adsorption isotherms patterns Au (III) tends to follow the Freundlich adsorption isotherm. This is an indication that the adsorption of Au (III) in the adsorbent MM/SiO$_2$/MBI is a multilayer. Which follows the pattern adsorption isotherm Freundlich, when the surface is saturated or nearly saturated with adsorbate, there can be two things: the adsorption layer is formed over the second and so on adsorbate that has been bound to the surface, this phenomenon is called multilayer adsorption.

4. Conclusion
Based on the results of the research showed that the maximum adsorption of ions Au(III) adsorbent occurs at pH 1 with an optimum contact time of 60 minutes. Mercapto modified silica has an ability to adsorb ions Au (III) 3.5 times higher than unmodified silica. Adsorption capacity obtained was 333.33 mg/g (based on the Langmuir isotherm models). Kinetics study follows the model Pseudo-2 order with constant adsorption 3x10$^{-3}$g/mg.menit. Further studies can be done by ion desorption and adsorption Au(III) in multi-metal system.

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