Co (II) desorption from silica gel and mercapto-silica hybrid

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Abstract. This paper aims to study Co (II) desorption from silica gel (SG) and mercapto-silica hybrids (MSH) by many desorbing agents. SG was prepared from sodium silicate from rice husk ash, whereas MSH was modified by organic compounds 3- (trimethoxysilyl) -1-propanthiol. The characterization of adsorbents covered by an X-ray diffractometer and an FTIR spectrophotometer. Optimization of contact time for adsorption of Co (II) on HMS and the procedure of desorption agents (H2O, HCl, Na2EDTA.2H2O) at different contact times and concentrations via batch methods. The results showed that the optimum contact time for Co (II) adsorption on MSH was 120 minutes. The most appropriate desorbing agents for SG and MSH were HCl and Na2EDTA.2H2O. The optimum contact times for Co (II) desorption on SG and MSH were 90 and 120 minutes, respectively. The optimum concentration of HCl for desorbing Co (II) on SG was 0.025 M. While, the optimum concentration of Na2EDTA.2H2O for Co (II) desorption on MSH was 0.1 M.

1. Introduction
Abundant rice husk from the rice mills had been used as a fuel for combustion of red brick, cooking, media hydroponic plants, or burned away. Another application, waste rice husk ash (ASP) has a great potential as the source of silica-based adsorbent because numerous studies showed that the ASP contains sufficiently high points of silica, equivalent to 98% (w/w) [1]. Mujiyanti, et al. [2] reported that the silica content in the rice husk ash from the peat, Banjar Regency, South Kalimantan extended 95.6% (w/w).

Expenditure of the adsorbent adsorbs heavy metals, became a smaller amount of consideration. The adsorbent can be reused through recovery. Natalia [3] has investigated for desorption studies hybrid silica on metal sulfonate with Ca (II) and Cd (II) ions via technique column. The results showed that the result of desorption was Cd (II) ion, 98% with 0.1 M HCl and 100% with 0.05 and 0.1 M Na2EDTA.2H2O. On the other side, Ca (II) ion desorbed on HCl 0.5 M, amounting to 78.13% and for Na2EDTA.2H2O, Ca (II) ion desorbed amounting to 88.66%.

Furthermore to adsorbent recovery, desorption can be carried out for the recovery of adsorbed metals. Through desorption studies, we can also find out the adsorption mechanism between the metal and the adsorbent. Mujiyanti (2007) conducted a study of the multi-metal adsorption-desorption of Ag (I), Pb (II), Cr (III), Cu (II), and Ni (II) through a column system in mercapto-silica hybrids (MSH) using three types of eluents, HCl, H2O, and Na2EDTA.2H2O. The desorption with H2O % was variety 0.8-31.0% for monometallic solutions and 0.3-24.4% for multi-metal solutions. Meanwhile, the contribution of the adsorption mechanism for the formation of complex bonds with Na2EDTA.2H2O in
monometallic solutions alternated from 0.3-29.4% and multi-metal solutions reached from 0.2-14.3%. The desorption process indicated that the adsorption mechanism tends to the formation of hydrogen bonds. This is maintained by the formation of an octahedral aqua complex from the five metal ions in water.

Mujiyanti, et.al [4], stated that Co (II) adsorption on silica gel (SG) optimum at pH 5 and contact time of 75 minutes, while the MSH takes place optimally at pH 3, but the optimum time on MSH could not be determined. The contact time of adsorption was only until 90 minutes in a 50 mL solution of Co (II) 100 mg/L at pH 3 and the amount of adsorbed metal showed a tendency to rise. Therefore, one of the initial steps in this paper was to study the effect of the optimum contact time for Co (II) adsorption by MSH. Furthermore, this paper will observe some aspects of Co (II) desorption from SG and MSH.

2. Materials and methods

2.1. Materials
The material used was rice husk ash from peat area, South Kalimantan as a source of silica, NaOH (pa Merck), HCl 37% (pa Merck), 3- (trimethoxysilyl) -1-prophantiol (pa Merck), the stock solution of Co (II) 10000 ppm (pa Merck), Na2EDTA•2H2O (pa Merck).

2.2 Determining optimum contact time of Co(II) adsorption
The procedure of determining optimum contact time of Co (II) adsorption on the MSH referred to research that had been conducted by Mujiyanti, et.al [4]. A total of 100 mg of MSH interacted with 50 mL solution of Co (II) 100 mg / L at pH 3. The solution was stirred with a variation of the contact time 30, 60, 90, 120, and 150 minutes, and strained with filter paper. The filtrate was analyzed by Atomic Absorption Spectrophotometry (AAS).

2.3 The adsorption of Co (II) on silica gel and mercapto-silica hybrid
The adsorption process referred to research by Mujiyanti, et.al [4] in optimum conditions, pH = 5 and contact time 75 minutes for SG. For MSH accomplished at pH 3 and contact time obtained in determining the optimum contact time adsorption Co (II) at MSH. A total of 1 g of MSH contacted with 50 mL solution of metal ions Co (II) 100 mg/L at the optimum condition. The mixture was filtered then the filtrate was analyzed by AAS. The same treatment was also examined for SG.

2.4 The desorption of Co(II) Ion by silica gel and mercapto-silica hybrid

2.4.1 Determining desorption agent of Co(II) desorption. The desorption agent used in this study were H2O, HCl 0.1 M and 0.1 M Na2EDTA• 2H2O. Total of 25 mL desorption agent contained in erlenmeyer and MSH residues that have adsorbed metal ions Co (II), then solution shaken by contact time for 120 minutes. The mixture strained then the filtrate was analyzed by AAS. The same treatment was also examined for SG.

2.4.2 Determining optimum contact time of Co (II) desorption. Desorption was done as in the determination of desorption agent in variation of 30, 60, 90, 120, and 150 minutes.

2.4.3 Determining optimum concentration of desorption agent for Co (II) desorption. Desorption was done as in the determination of desorption agent and contact time, but consuming the suitable agent with a concentration of 0.025; 0.05; 1; 1.5; and 2 M for optimum contact time.

3. Results and discussion

3.1 Determining optimum contact time of Co(II) adsorption
Interaction time between adsorbent and the metal ion was one of the factors that play a role in determining the optimum conditions for interaction of metal ions and the equilibrium state of the adsorbent [5]. Figure 1, showed that the number of ions Co (II) adsorbed MSH on contact time 30, 60, 90, 120, and 150 minutes, respectively.

![Figure 1](image_url)  
**Figure 1.** The chart of % ion Co(II) adsorbed with the various contact time.

The quantity of Co (II) ions adsorbed was enlarged with an accumulative interval of stirring (30-120 minutes). The extended contact time of MSH and metal ion approved diffusion and annealing process taken more immaculate adsorbate molecules and the amount of Co (II) ions that absorbed increasingly. Adsorption was assessed by the maximum point when the contact time of 120 minutes, in which the percentage of adsorption MSH compared to Co (II) ion was 24.21%. Adsorption equilibrium was characterized by the lack of the concentration of metal ion alterations both on the surface of the adsorbent and metal ion in solution [6], in which the rate of adsorption was equal to the rate of desorption [7]. After passing through 120 minutes of the percentage of Co (II) ions adsorbed tended constantly, even declining. This trend suggested that the active sites on the surface of the adsorbent had been saturated by metal adsorbates and MSH no longer able to adsorb Co (II) ions. Metal ions that had been adsorbed could be desorbed from the surface of the adsorbent. This could occur if the interaction between Co (II) metal ions with the active site on MSH was fragile.

3.2 The desorption of Co(II) ion by silica gel and mercapto-silica hybrid

3.2.1 Determining desorption agent of Co(II) desorption. Desorption is the opposite of the adsorption process. Desorption is the process of releasing the adsorbate from the adsorbent into a solution [8]. The desorption process can provide information about the adsorption mechanism that plays a role in the adsorption of Co (II) by SG and MSH adsorbents. Co (II) metal ion, which had been adsorbed by the adsorbent, desorbed by the eluents; H₂O, 0.1 M HCl and 0.1 M Na₂EDTA•2H₂O by batch method. The relationship between percent Co²⁺ which was desorbed with desorption agent types is showed in figure 2.

Distilled water (H₂O) as a solvent metal ion was attached to the surface of the adsorbent. Desorption result with distilled water did not have a significant effect to release ions Co (II), just 0.76 and 1.47% for SG and MSH. Co(II) metal ion desorbed on surface SG and MSH by HCl solution was successively as much as 103.46 and 54.53%. HCl was a strong acid group that releases H⁺ ions to replace metal ions adsorbed by ion exchange process or through hydrogen bonding interactions. Desorption percentage by HCl on SG exceed 100% due to the addition of HCl was expected to dissolve some of the SG, so that Co(II) less reacted with SG. Desorption with Na₂EDTA•2H₂O solution indicated that as many as 93.84 and 67.40% of ions Co(II) previously adsorbed by SG and MSH desorbed. The results showed that the adsorption of Co (II) in the adsorbent occurred such as through the formation of a complex between Co(II) with active sites, mercapto (-SH) in the adsorbent.
EDTA is a strong ligand, so when the ability of the ligand adsorbent active group is weaker than the EDTA then the metal ions on the adsorbent will be adsorbed by the formation of a stable complex [3].

From figure 2, showed that the main interaction on SG and MSH was chemisorption. The adsorption mechanism of Co (II) cations on SG adsorbent was the most dominant estimated by ion exchange and/or hydrogen bonding, because the percentage of desorption with HCl equated to other desorbing agents maximum. However, the adsorption mechanism on MSH adsorbent, assumed mostly through the complex formation, an interaction was stronger than ion exchange interactions and the formation of hydrogen bonds.

3.2.2 Determining optimum contact time of Co (II) desorption. Determination of the optimum contact time of desorption aimed to obtain information on how long it takes to achieve optimum Co (II) desorption from the adsorbent. The variation of contact time was from 60 to 180 minutes. This research was using the desorbent agents 25 ml of 0.1 M HCl and 0.1 M Na₂EDTA·2H₂O as. The amount of Co (II) depleted for each variation of contact time is shown in figure 3.

From figure 3 it was shown that the extended contact time of metal ions using 0.1 M HCl and 0.1 M Na₂EDTA·2H₂O in SG and MSH, the number of Co (II) ions were separated greatly. However, at a certain moment the addition of time would decrease the percent desorption Co (II) ion which was separated from the adsorbent. Figure 3(A) indicated that the optimum contact time of desorption achieved after SG interacted with HCl for 90 minutes. This was due to the H⁺ ion from HCl was strong enough to replace metal ions attached to the adsorbent SG [9]. While the pattern of desorption time
relationship with the percentage of Co (II) ions was separated on MSH by Na2EDTA•2H2O showed in figure 3(B). Desorption of MSH continued to rise until it reached a maximum desorption at 120 minutes, which amounted to 98.54%. For the interaction time of 150 and 180 minutes, separate Co (II) ions decreased. According to Khasanah [10] a similar tendency was possible due to a decrease in the surface of the adsorbent that had been saturated by Co-EDTA complex was formed.

3.2.3 Determining the optimum concentration of desorption agent for Co (II) desorption. This research also studied the effect of the concentration of desorption agent compared to Co (II) desorption (variation of the concentration of the agent 0.025 M to 0.2 M). The relationship between the concentration of HCl with Co (II) ions which desorbed on SG can be seen in figure 4(A). by desorption at 97.82%.

Figure 4(A) showed the increasing of concentration of HCl had lower percentage desorption of Co (II) ions. It was possible that the solvent concentration was too high affecting Co (II) which were separated partially settled down as CoCl2. From this research, it was found that the maximum percentage of Co (II) ions was desorbed at a concentration of 0.025 M for HCl as a desorption agent for the Co (II) attached to SG. Figure 4(B) shows that the accumulated concentration of Na2EDTA • 2H2O caused the desorbed Co (II) ion to increase at a certain concentration. At a concentration of 0.1 M, the optimum amount of Co (II) ions was absorbed at 95.68%. The increase in the desorbed Co (II) ion is proportional to the increase in the concentration of Na2EDTA • 2H2O. But after the concentration had exceeded the optimum, a decrease Co (II) ion was desorbed. This phenomenon was possible due to the partial of deprotonitation Na2EDTA•2H2O therefore the acid groups ionized carboxyl was less active and caused the formation of the coordination bonding between EDTA and metal ions was not intensive.

4. Conclusion
Based on the results of the research, adsorption of Co (II) ion on MSH had reached a maximum point at a contact time of 120 minutes as much as 24.21%. The maximum desorption process of Co (II) ions from SG with HCl and in MSH with Na2EDTA•2H2O as a desorbing agent. The contact time used in desorption of Co (II) ions on SG by 0.1 M HCl reached a maximum in 90 minutes, as much as 99.27% and MSH by 0.1 M Na2EDTA•2H2O was 120 minutes, as much as 98.54%. The concentration of 0.025 M HCl as desorbing ion Co (II) in SG which maximally absorbed Co(II) was 97.82% and the concentration of Na2EDTA•2H2O in the desorption of ion Co(II) from MSH was 95.68%.
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