Extraction of Pb^{2+} using Silica from Rice Husks Ash (RHA) – Chitosan as Solid Phase

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ABSTRACT

The existence of lead (Pb) compounds in waters can be caused of waste pollution from industrial activities such as dye and battery industries. Lead is toxic and able to cause some deseases. The aim of this study is to create solid phase from natural material as an alternative method for determination of lead in water samples. The solid phase is silica prepared from rice husks ash (RHA), was prepared and modified using chitosan. To achieve that aim, the optimization of silica : chitosan composition was performed. The influence of Pb^{2+} concentration and citric acid concentration was studied to obtain optimum recovery of Pb^{2+}. Interaction between Pb^{2+} ion and solid phase silica – chitosan could be estimated based on the result. This showed the optimum composition of silica : chitosan was 65% silica : 35% chitosan with Cation Exchange Capacity (CEC) 0.00455 mek/g. Mass adsorbed Pb^{2+}for 1 g silica : chitosan 65% was 9.715 mg/g. Optimum recovery of Pb^{2+} on solid phase extraction was reached at concentration of Pb^{2+} 10 ppm and citric acid concentration 0.05 M (88.25 % and 81.18 %). This result indicated that solid phase extraction prepared from silica – chitosan can be applied as an alternative method for Pb^{2+} determination in water.

Key word: Solid phase silica – chitosan, Pb^{2+} ion, solid phase extraction, recovery

INTRODUCTION

Lead (Pb) in the waters mostly is caused the discharge of industrial waste. Lead has a high toxicity and this is indicated by the LD$_{50}$ values (500 mg/kg). Pb^{2+} accumulation can cause liver damage, kidney failure, brain damage, muscle damage, irritation, and disorders of the nerves system [1]. Indonesian Government Regulation No. 82 at 2001 limits the permitted maximum concentration of Pb^{2+} in the waters is 0.03 ppm. Therefore, the presence of Pb^{2+} in water needs to be controlled so that the amount of water pollution can be reduced.

Several methods have been used to reduce Pb^{2+} in water by electroplating, oxidation, reduction, using membrane separation and adsorption. Adsorption is a good choice because this is the most economical method [2]. Adsorption of metal ions has been developed by utilizing a lot of adsorbents. One of the most commonly used adsorbent is activated carbon. Activated carbon from cashew nut shells can be used to adsorb Pb^{2+} and Cd^{2+}, with efficiency until 98.87% [3]. Another potential natural source can be used as adsorbent is silica from rice husk ash. This ash contains 86.9% - 97.3% silica, has a large surface area (50-430 m^2/g), large pore volume (0.7 to 1.2 mL/g), and sufficient diameter [4]. Silica has been used in solid phase extraction for adsorption of Pb^{2+}, Cu^{2+}, Cd^{2+}, and Ni^{2+} in which the silica is modified

using gallic acid as the solid phase. Immobilization using organic ligand has been widely used in metal separation and concentration. Gallic acid is multidentate ligand with high affinity for metal ions so that have a high ability to form a chelate. Elution process in this research used HCl, H_3PO_4, EDTA, and thiourea as eluents. The extraction result was measured using AAS. The results showed that the optimum conditions for recovery of Pb^{2+} were in the pH 3-7; elution using 10 mL of 0.05 M HCl, and percent recovery was 98.2% [5].

Silica is less able to interact with heavy metal ions because most of the active silanol groups form hydrogen bonds with each other so that each cover and less than the maximum adsorption process [6]. However, this limitation can be improved by surface modification using the chitosan active site for the adsorption of the desired metal. Chitosan is a natural polymer that is abundant and widely used for adsorption of heavy metals. Chitosan has been used for the adsorption and desorption of ions Cu^{2+}, Cd^{2+}, and Pb^{2+}. Chitosan were crosslinked with epichlorohydrin-triphosphate. The results reported the adsorption of Pb^{2+} appropriate to the Langmuir equation with a pH optimum 5 and adsorption capacity 166.94 mg/g. HNO_3 and HCl gave good desorption results, and Pb^{2+} can be separated from the crosslinked chitosan [7]. Modification of chitosan is expected to increase the adsorption of Pb^{2+}. Adsorbate in this study contains Pb^{2+}, so silica-chitosan adsorbent is expected to serve as a cation exchanger because the free silanol groups (SiOH) on silica surfaces easily release H^+ at pH > 4 and stabilized in - Si – O^- form [8]. Therefore, optimization of silica-chitosan should be done by determining cation exchange capacity (CEC) of silica-chitosan and how its exchange capacity for Pb^{2+} ions. In this paper, silica-chitosan which has been optimized to be applied as a cation exchange solid phase extraction using a column. Solid phase extraction is done because the method can be done to overcome the difficulty of measuring the concentration of Pb^{2+} concentration due to the small concentration of these ions in the water. Extract Pb^{2+} ion is eluted using citric acid ($C_6H_8O_7$) because these compounds can form complexes with metal ions. Citric acid has a group - carboxyl groups that can form a chelate with divalent metal [9]. The process of extraction is carried out at pH 5 due to silanol groups on silica can be transformed into -Si - O^- above pH> 4 and the existence of -OH groups from chitosan so that they can interact with Pb^{2+} ions.

EXPERIMENT
Reagents
Silica source was from rice husk ash, was burned at 900 ^{o}C and destructed using HCl 6 M, chitosan (DD 65%), $Pb(NO_3)_2$, CH_3COOH 95% $\rho = 1,05$ g/mL, NaOH, HNO_3 conc., $C_6H_8O_7.H_2O$, and glutaraldehyde 25%. All solutions were prepared using distilled water. The stock solution of Pb^{2+} was prepared by dissolving 0.799 g $Pb(NO_3)_2$ in HNO_3 pH 5 at 500 mL conical flask. The working solutions were conditioned at pH 5.

Construction of Silica – Chitosan (SC)
SC was prepared by dissolving 0.5, 1.5, 2.5, and 3.5 g of chitosan in 80 mL of CH_3COOH 2% (v/v). Silica that already prepared was added to this solutions with variation of weight 9.5, 8.5, 7.5, and 6.5 g. Then this solution was stirred for 12 hours. This mixture was neutralized with 30 mL NaOH 1 M, and left for a while. The mixture was decanted and soaked into 40 ml glutaraldehyde 0.5% (v/v) for 24 hours, and was filtered and heated at 105 ^{o}C until a constant weight. The adsorbent was crached using mortar and filtered (120 mesh).

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Determination of SC's Adsorption Capacity

SC's adsorbent with silica content 100%, 95%, 85%, 75%, and 65% was weigh 0.2 g each. These adsorbents were added into 20 mL Pb^{2+} solutions pH 5 then mixture for 2 hours with 100 rpm speed. The mixture was filtered then measured the absorbance using AAS.

The adsorbents that already used for adsorption were dried at temperature 105°C until we got the constant weight. HNO_3 20 mL, 0.01 M was added into each adsorbents then mixture for 2 hours with 100 rpm speed. The mixture was filtered then measured the absorbance using AAS.

Preparation of Extraction Column

A dry and clean of SPE column and filters was prepared, and a solid phase (0.1 g) was conditioned using HNO_3 pH 5 for 5 minutes. Adsorbent that already homogenous was placed into SPE column.

Effect of Pb^{2+} Concentration in Solid Phase Extraction

SC with optimum composition (0.1 g) was inserted into the column. Then, Pb^{2+} solution (0.02; 0.5; 1.0; 10; 15 ppm) was added into SC. Volume of each Pb^{2+} solutions was 10 mL and column was washed with 5 mL distilled water, and flowed with 3 mL of 0.01 M citric acid (flow rate 1 mL/min). The filtrate afforded was measured using AAS.

Effect of $H_3C_6H_5O_7$ Concentration in Solid Phase Extraction

SC with optimum composition (0.1 g) was inserted into the column. Then, 10 mL of Pb^{2+} solution at optimum concentration was added into SC (flow rate was 1 mL/min). The resulting filtrate was collected and measured using AAS. The column was washed with 5 mL distilled water, and flowed with 3 mL of 0.01, 0.05, and 0.1 M citric acid solution with flow rate 1 mL/min. The filtrate resulted was measured using AAS.

RESULT AND DISCUSSION

Effect of SC's Composition for Pb^{2+} Adsorption

Pb^{2+} adsorption processes using SC with 100%, 95%, 85%, 75%, and 65% silica (w/w). Table 1 showed the % adsorption of Pb^{2+} based on changes in the SC's composition. Adsorption of Pb^{2+} increased when chitosan's mass were also increased. Adsorption of Pb^{2+} using SC 65% gave the best adsorption. These results are in accordance with the CEC of adsorbent (Figure 1) which shows that the cation exchange process is most pronounced in SC 65%. Figure 1 showed the CEC of SC 65% was 0.00455 mek/g. The CEC increased proportionally with the increasing addition of chitosan. CEC of SC 100%, 95%, 85%, 75%, and 65% were 0.0009, 0.0023, 0.0039, 0.0044, 0.0045 mek/g.

Table 1. Effect of SC's Composition for Pb^{2+} Adsorption

Composition Silica : Chitosan (SC) (%)	Adsorption Pb^{2+} (%)
100 : 0	30.44
95 : 5	70.02
85 : 15	82.00
75 : 25	73.93
65 : 35	89.18

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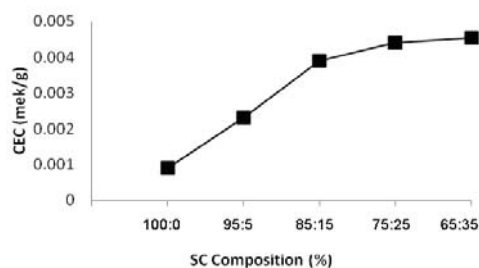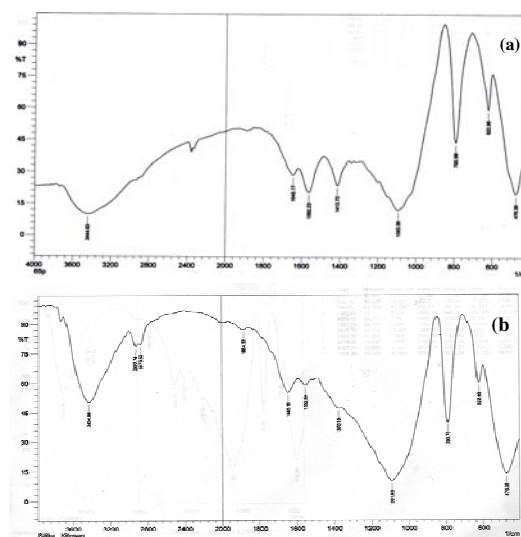
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Figure 1. Effect of SC's composition to CEC (above)

Figure 2. IR Spectra of SC 65% (a) Before used for Pb^{2+} adsorption; (b) After used for Pb^{2+} adsorption (right)

Interaction between Pb^{2+} and SC

Interaction of Pb^{2+} ions with the solid phase silica - chitosan may occur because of the active group in the solid phase has a different charge with Pb^{2+} ions that allows the interaction between the two. SC has several active groups, -OH groups of the - Si - OH and chitosan, - NH_2 active group from chitosan. Figure 2 shows the difference IR spectra of the SC 65% before adsorption and after adsorption of Pb^{2+}.

Figure 2 (a) and (b) showed that the functional groups spectra appear in the wave numbers tend to be similar. However, the – OH wide band that appeared at 3200 - 3600 cm^{-1} (Figure 2 (a)) didn't appear on spectra IR of SC 65% after used for Pb^{2+} adsorption (Figure 2 (b)). It showed that interactions between Pb^{2+} ions and -OH groups of SC could be happened. Figure 2 (b) showed absorption that appeared in 3434.98 cm^{-1}. It was indicated as the existence of the amine group which overlap with the absorption -OH groups that do not appear in the spectra before adsorption (Figure 5.3 (a)). -OH groups can be derived from silica and chitosan. Chitosan also has the-OH group so that when the mass of chitosan increased, it means the amount of – OH groups at SC will also increased.

Effect of Pb^{2+} Concentration to Pb^{2+} Recovery

Effect of Pb^{2+} concentration on the SPE was studied. The Pb^{2+} concentrations were 0.02, 0.5, 1, 10, and 15 ppm with citric acid eluent (0.01 M). The results are shown in Figure 3 which shows the percentage of Pb^{2+} adsorption and recovery of Pb^{2+}. Figure 3 showed that the recovery of Pb^{2+} tended to increase according to the initial concentration of Pb^{2+}. It could be happened because adsorption will be increased due to the concentration of adsorbate was increased. SC would continue to bind Pb^{2+} that passed until it reached the saturation conditions in which SC could no longer to bind Pb^{2+} ions because all active groups have been used. Recovery Pb^{2+} at Pb^{2+} concentration 0.02, 0.5, 1, 10, and 15 ppm were 50, 43.75, 53.25, 75.90, and 69.31 %.
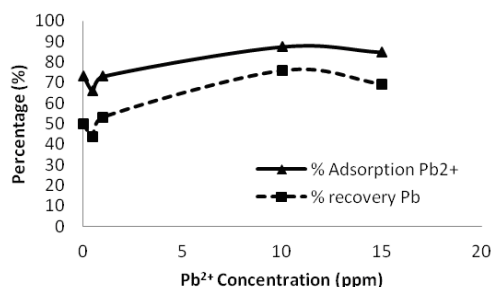
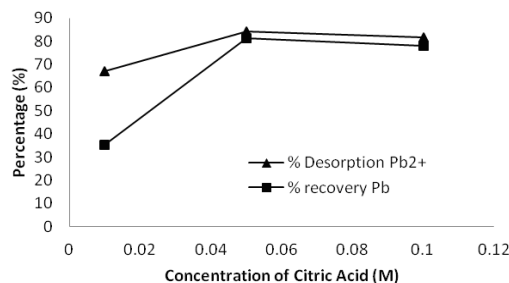**Figure 3.** Effect of Pb^{2+} Concentration in Pb^{2+} Recovery

Figure 4. Effect of $H_3C_6H_5O_7$ to Pb^{2+} Recovery

Effect of $H_3C_6H_5O_7$ Concentration to Pb^{2+} Recovery

Effect of $H_3C_6H_5O_7$ concentration to Pb^{2+} recovery was studied. Pb^{2+} ions that was retained could be recouped by elution using citric acid ($H_3C_6H_5O_7$) at various concentrations. The concentration of citric acid was 0.01, 0.05, and 1 M. The results of the effect of the concentration of citric acid for Pb^{2+} recovery was showed in Figure 4.
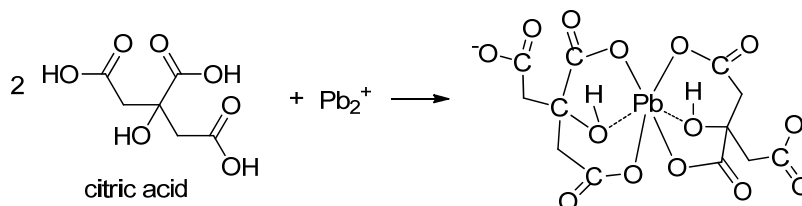

Figure 5. Proposed reaction of complex formation between Pb^{2+} and $H_3C_6H_5O_7$ [9]

The elution of Pb^{2+} was done using citric acid. Citric acid was used to elute Pb^{2+} on SC that unable to be separated using ion exchange mechanism. Citric acid forms a strong complex with metal ions Pb^{2+} to allow recovery over the maximum. Figure 4 showed the recovery of Pb^{2+} increased with increasing of citric acid concentration from 0.01 M to 0.05 M. The highest recovery was achieved at 0.05 M (81.18%). These results indicated citric acid was able to elute the Pb^{2+} which retained on the SC. The citric acid was predicted able to form a stable complex with Pb^{2+} ions (Figure 5) when it forms $C_6H_5O_7^{3-}$ ($Kf = 1.26 \times 10^6$) [10].

Figure 5 showed citric acid used the protonated of carboxylic and hydroxyl group to bind Pb^{2+}. This formed a effective chelate Pb-citric acid. Chelate formation has octahedral geometry with two carboxylic groups from citrate bound to Pb^{2+} ions, while the other carboxylic group was proposed free. This structure revealed that Pb^{2+} was bound by six-oxygen atom donors.

CONCLUSION

Mass composition of SC influences the adsorption of Pb^{2+}. SC 65% has the best adsorption that is 9.326 mg/g. Pb^{2+} ions interact with – OH groups from -Si-OH and -OH groups from chitosan. Pb^{2+} ions undergo electrostatic interaction with -OH groups of the two

compounds. The optimum concentration of Pb^{2+} at SPE was 10 ppm (recovery value 88.25%). The best recovery Pb^{2+} was obtained when using 0.05 M citric acid as an eluent.

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