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Development of Lead Preconcentration on Ion Exchanger Resin With Tannin Extraction From Acacia Mangium Extract (*Acacia mangium* Willd)

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Abstract

The heavy metal ion contained in water tend to be so low that the analysis process requires pre-concentration techniques using ion exchange resins. The use of ion exchange resins in pre-concentration techniques had advantages such as minimizing loss of analyte, using small amount of resins and environmentally friendly. In this study, extracted tannin from Acacia Mangium leaves was used as the raw material for ion-exchange resin production. The polymerization reaction of extracted tannin with the addition of concentrated H_2SO_4 is done so that the resin is not easily soluble in water. The result of polymerization of extracted tannin (PTE) was characterized qualitatively using Fourier Transform Infra-Red (FTIR). To know its ability as ion exchange resin, PTE was examined with retention parameters and analytical validation. The optimum retention parameter was obtained at eluent concentration of HNO_3 2 M in 5 mL. Based on the validation test of the analysis method, the value of repeatability with % RSD is 0.97%, the linearity of R^2 0.9986 in the range of 0.25-100 ppm, the sensitivity of 0.067 ppm, the limit of detection (Limit of Detection/LOD) of 0.019 ppm and the recovery of 102.3% - 110.91%. The result of the sample test shows that the Lead level in Ciliwung River is 105-267 ppb.

Keywords: Lead, Preconcentration, Tanin extract, *Acacia mangium* Willd leaves, Atomic Absorption Spectrophotometer

Introduction

Heavy metal pollution is one of the long-standing and widespread environmental problems in a society that is very harmful to the environment. One of the toxic heavy metals is Lead (Pb^{2+}). Lead is well known to be contained in river water and industrial waste such as color industry, textile and photo industry. The concentrations of metal ions in water tend to have very low levels (trace metals). Therefore, a certain techniques need to be done to determine the content of metal ion with pre-concentration method. Natural adsorbents such as tannins

are renewable, biodegradable and available in large quantities in nature. Some of the natural material-based adsorbents are generally derived from waste, therefore this study used polymer extract tannins (PTE) leaves of Acacia Mangium as ion exchange resins for analysis of Pb^{2+} ion content in small quantities.

Experiment

Sampling

Water samples are taken from the Ciliwung river flows in West Java as many as 3 different points on coordinates are 6.348730,106.865854, -6.348730,106.865854; and -6.347126,106.866546. Each water sample was placed into plastic. The concentrated HNO_3 added to the sample until the pH of the solution was 3. All of the water samples are immediately taken stored in a refrigerator.

Pre-concentrations of Pb^{2+} using ion exchange resins from polymer extracts of Acacia Mangium leaf tannins (PTE)

A total of 0.2 grams of PTE resin was inserted into the column. Then, the PET resin column is set to optimum pH. After the PTE resin is set, standard solution of Pb^{2+} (250 ppb) was flowed through the column. Afterward, each solution of HNO_3 at the concentration 1; 1.5; 2; 2.5 and 3 M are flowed into the same column. The concentration of Pb^{2+} of the filtrate was measured using AAS. After obtaining maximum eluent concentration, the standard Pb^{2+} (250 ppb) was flowed through a column already filled with resin, then the HNO_3 eluent is flowed through the column with the variation of volume are 3; 3.5; 4; 4.5 and 5 mL.

Method validation of analysis

Validity test is conducted include probability, linearity, limit of detection (LOD), sensitivity, sample determination and recovery. Validity test conducted include probability, linearity, limit of detection (LOD), sensitivity, sample determination and recovery.

Result and Discussion

Determination of eluent concentration

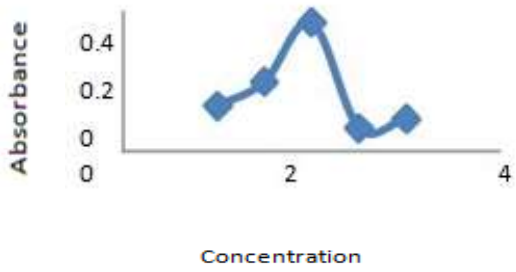

Fig 1. Determination of HNO_3 Concentration

Figure 1 shows that the higher the concentration of the HNO_3 eluent the greater the Pb^{2+} metal can be eluted in the PTE resin. The optimum concentration of eluent to elucidate the Pb^{2+} is 2 M with the difference of absorbance is 0.3636. High concentration of eluent will lead degradation of bond formed on the polymerization resin.

Determination of resin volume

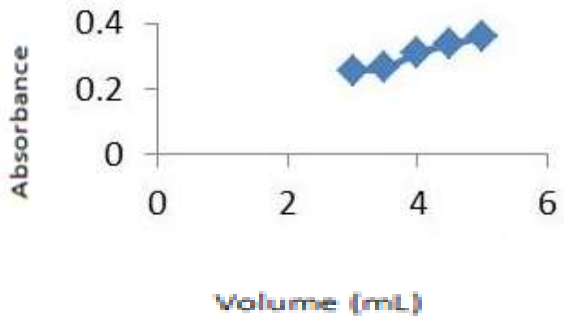

Fig.2 Determination of HNO_3 Eluent Volume

Figure 2 shows the greater the volume of the HNO_3 eluent, the greater the Pb^{2+} metal eluting in the tannin resin. The optimum volume of HNO_3 2 M to elucidate Pb^{2+} is at the absorbance difference of 0.3572.

Characterization using FTIR

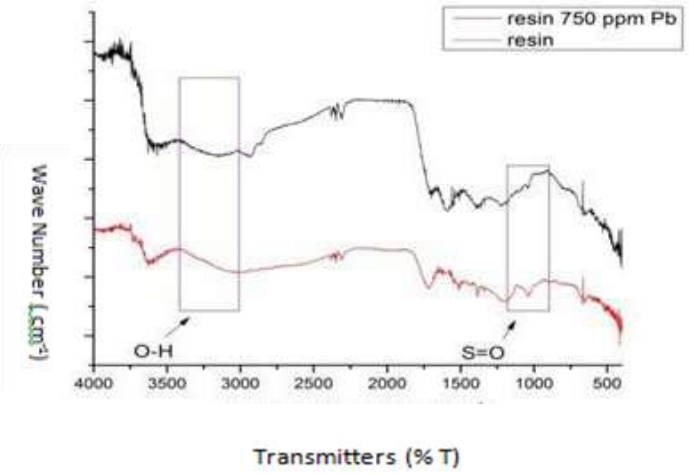

Fig 3. FTIR spectrum for pure tannin resin (red) and tannin resin bonded Pb^{2+} (blue)

Fig 3 shows that at 3240 cm^{-1} there was a decrease of intensity –OH spectra due to the bonding of Pb^{2+} and at 1160 cm^{-1} there was decrease of S=O spectra due to bonding of Pb^{2+} on sulphonate groups as replacing H atoms. The suggested structure of tannin polymer of Acacia Mangium leaves can be seen at Fig 4.

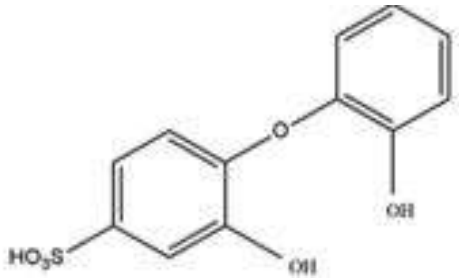

Fig 4. Suggested structure of extracted tannin polymer from Tanin Acacia Mangium Leaves

Based on FTIR spectrums, the possible of mechanism of tannin structure has shown by Fig 5.

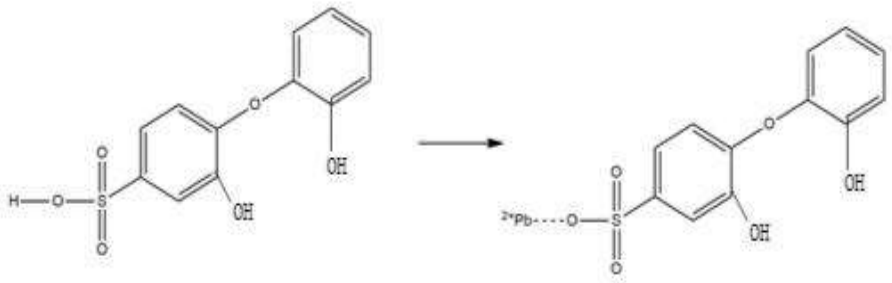

Fig 5. Suggested mechanism of ion exchange of Pb^{2+} with resin PTE

Validation Method

Precision

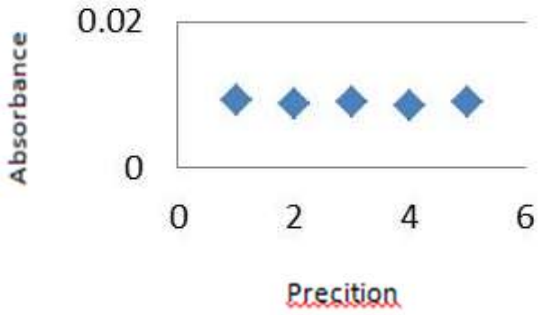

Fig 5. Precision

From the calculation, it was obtained that % RSD and CV Hotwizt were 0.97% and 1.282% respectively. A precision was considered good value when it have % RSD lower than CV Hortwozt so in this study, the pre-concentration method was concluded as had a good precision due to have a constant value for 5 repetitions.

Linearity

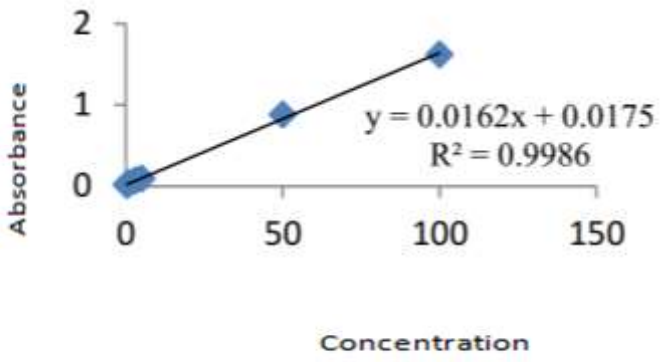

Fig 6. Linearity

The calculation result obtained was y = 0.0162x - 0.0175 and sensitivity of R^2 was 0.9986. Therefore, it can be concluded that preconcentration method using resin PTE result a good linearity due to have a low error rate and can approve the linear relationship between analytes concentration and response of detectors with a value close to 1.

Limit of detection (LOD)

The limit of detection (LOD) was the smallest number of analyte as a detectable sample which still gives a significant response compared to the blank. The result of LOD in this study showed that the limit value of tannin resin detection obtained was 0.019 ppm.

Sensitivity

The sensitivity test was performed to see the ratio between the measurement tool response (AAS) to the sample concentration measured. The sensitivity value obtained in this study was 0.067 ppm.

Accuracy

Accuracy test can be conducted by approaching recovery. The method was considered its validitation when the recovery ranges were 80-110 %.

Table 1. Result of recovery test

Point	% recovery
6.348730,106.865854	102,3
6.349318,106.865570	110,91
6.347126,106.866546	109,09

From the calculation of sample 1, 2 and 3, the % recovery obtained were 109.36 %, 110.9%, and 109.09%. So it can be concluded that analysis using resin PTE preconcentration method had a good accuracy due to have a suitability between actual concentration and measured concentration obtained using preconcentration.

Application of Analysis Method

Table 2. Concentration of Pb^{2+} in the sample

Point	Concentration (ppb)
-6.348730,106.865854	105
-6.349318,106.865570	267
-6.347126,106.866546	143

Based on the government regulation number 82 of 2001 for the permissible limit for Pb^{2+} in the waters was 30 ppb. Based on the analysis result of water sampled from Ciliwung river, it was known that the concentration of Pb^{2+} were 105 ppb, 267 ppb and 143 ppb. Sampling was conducted on the coordinate points were 6.349318,106.865570; - 6.348730,106.865854; - 6.347126,106.866546. The result showed that Pb^{2+} in the Ciliwung's water was in high concentration. Thus it needs to periodic monitoring and further waste treatment.

Conclusion

Optimum condition characterization of eluent retention of HNO_3 at concentration 2 M and volume of eluent HNO_3 5 mL.. The result of validation method obtained were the value of probability % RSD of 0,97%, linearity of R^2 0,9986, sensitivity of 0,067 ppm, limit of detection (Limit of Detection / LOD) of 0,019 ppm and recovery of 102,3%, 110 , 91%, and 109.09%.

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