Polymerization of the tannin extract from the leave of Acacia mangium and its application as an adsorbent for the removal of lead

M P Laksmi, D A Nurani and D U C Rahayu
Department of Chemistry, Faculty of Mathematics and Natural Sciences (FMIPA), Universitas Indonesia, Kampus UI Depok, Depok 16424, Indonesia

Corresponding author’s e-mail: d.arifa@sci.ui.ac.id

Abstract. Pollution of heavy metal ions in water is a hazardous environmental problem that requires specific methods for handling lead ion contamination. One of these methods involves the use of tannin adsorbent. Tannin adsorbents exhibit renewability, biodegradability, and natural abundance. In this study, the extract from the leaves of Acacia mangium was used as the raw material for the adsorbent. The tannin extract was polymerized by the addition of concentrated H₂SO₄ because the adsorbent was insoluble in water. The resin obtained from the polymerization of the tannin extract (hereafter referred to as PET) was characterized qualitatively by Fourier transform infrared spectroscopy and quantitatively by total organic carbon measurements. To determine its ability as an adsorbent, we estimated the adsorption parameters of PET. The optimum adsorption capacity of PET was 5.261 mg/g at a pH of 7 and a contact time of 120 min.

1. Introduction
Lead metal pollution is one of the prevailing, widespread environmental issues in society, which is extremely deleterious to the environment. Therefore, it is crucial to perform specific methods for handling this pollution. One of the methods involves the use of natural adsorbents such as tannins. Tannin adsorbents exhibit advantages of renewability, biodegradability, and natural abundance [1].

Meanwhile, there has been an increase in the use of natural materials as adsorbents because of economic and environmental reasons. Typically, some natural material–based adsorbents are derived from waste; therefore, in this study, tannins derived from Acacia mangium leaves were investigated.

Nevertheless, the application of a tannin extract from A. mangium leaves as adsorbent for metal ions is disadvantageous because of its facile water solubility; hence, polymerization is initially carried out via crosslinking to enable the A. mangium leaf extract to dissolve easily in an aqueous solution. In this study, preconcentration was carried out using an ion-exchange resin after the polymerization of A. mangium leaf tannin extract for the analysis of the molar Pb²⁺ content.

2. Experimental

2.1. Chemical reagents
A. mangium leaves were obtained from the University of Indonesia, Depok. NaCO₃; 97% H₂SO₄, 37% HCl; Pb(NO₃)₂; and glacial CH₃COOH were purchased from Merck. Technical-grade dichloromethane and chloroform; acetic anhydride; n-hexane; ethyl acetate (EtOAc); NaOH; FeCl₃; Wagner's reagent; K₂Cr₂O₇; Fe(NH₃)₆Cl₃·6H₂O; Aquabidest (from PT Ikapharmindo Putramas); and aquadest were used.

2.2. Synthesis of tannin
First, 1 kg of dried A. mangium leaves was added into a blender and ground to a powder, followed by
maceration with water and NaCO$_3$ for 24 h. Second, the mixture was filtered using a Buchner funnel and freeze dried. The residue was analyzed by TLC using 1:9 n-hexane:EtOAc and 3:7 methanol as the eluents. Subsequently, phytochemical tests were carried out to detect the presence of saponins, tannins, alkaloids, terpenoids, steroids, polyphenols, and flavonoids and were investigated to determine secondary metabolite compounds present in the air fraction [2,3].

2.3. Adsorbent synthesis
The tannin adsorbent was prepared by condensation polymerization. First, tannins were mixed with concentrated HSO$_3$ in a ratio of 1:2, and then the mixture was refluxed for 24 h at 100 °C. After 24 h, the mixture was neutralized using 10 mL of a 2 % NaCO$_3$ solution. The filtrate was washed using Aqua bidestilata pro injection until it became neutral and dried in an oven at 50 °C for 24 h. After drying the precipitate, it was crushed to a homogeneous powder with 300–710 mesh size [4].

2.4. Determination of tannin solubility
The resultant resin obtained from the polymerization of the tannin extract (hereafter referred to as PET) was dissolved in 10 mL of 0.5-M HNO$_3$. The mixture was shaken at 303 K for 24 h using a magnetic stirrer. Next, the mixture was filtered and neutralized using distilled water. The concentration of the total organic carbon (TOC) of the filtrate was measured by the Walkley–Black method.

2.5. Effect of pH
First, 0.2 g of PET at different pH values of 2, 3, 4, 5, 6, 7, and 8 was mixed in a 5-ppm lead solution, followed by stirring the solution using a magnetic stirrer for 1 h. The resulting mixture was filtered, and its absorbance was measured by atomic absorption spectroscopy (AAS) [4].

2.6. Effect of contact time
First, 0.2 g of the PET resin at the optimum pH was added to 5 mL of a 5-ppm lead solution. Second, the mixture was stirred using a magnetic stirrer at different contact times of 30, 60, 90, 120, 180, and 260 min, followed by filtration and AAS absorbance measurements [4].

2.7. Adsorbent capacity determination
First, 0.2 g of the PET resin was added into each of 10-mL lead solutions at concentrations of 1, 3, 5, 10, 50, 100, 200, 500, and 750 ppm at the optimum pH and contact time. After the optimum time was attained, each solution was filtered, and absorbance was measured by AAS [4].

3. Results and discussion
3.1. Phytochemical test
The fraction from the water extract of A. mangium leaves only contained a tannin compound (figure 1), while freeze-drying did not alter the tannin compound in the water fraction of the
Table 1. Phytochemical test results obtained from the water and freeze-dried fractions of *Acacia mangium*.

| Test    | Water Fraction |
|---------|----------------|
| Flavonoid | +              |
| Terpenoid | −              |
| Steroid  | −              |
| Alkaloid | −              |
| Tannin   | +              |
| Saponin  | −              |

Figure 3. Mechanism of tannin complex formation.

Figure 4. TLC results using various eluents: (a) *n*-hexane:EtOAc = 1:9 (b), *n*-hexane:EtOAc = 3:7 and (c) methanol.

A. mangium leaf extract (figure 2). The Phytochemical test results are shown in table 1. The detection of black color resulting from complex formation with FeCl3 and HCl revealed positive results for the phytochemical tests of tannins. The formation mechanism of tannin complexes is shown in figure 3.

3.2. Thin layer chromatography (TLC) test.

The A. mangium extract results revealed no shifts with the use of various eluents, indicative of the presence of only tannin compounds (figure 4).

3.3. FTIR characterization.

The FTIR spectrum of the A. mangium leaf extract is shown in figure 5. The A. mangium leaf extract exhibited peaks at 3414 cm\(^{-1}\) (–OH); 1639 cm\(^{-1}\) (C=O); 1310 cm\(^{-1}\) (C–O); and 2830 cm\(^{-1}\) (C–H sp). The presence of –OH and C=O revealed that the A. mangium leaf extract contains active components of tannin compounds, which is also verified by the results obtained from phytochemical tests and TLC.
Figure 5. FTIR spectrum of the *Acacia mangium* leaf extract.

Figure 6. FTIR spectra of the polymer resin at various contact times.

3.4. Polymerization of the tannin extract (PET).
Tannin is a water-soluble polar compound that needs to be modified for the purpose of decreasing the water solubility of tannins by polymerization using the crosslinking method [5]. Polymerization was carried out by the addition of concentrated sulfuric acid under heating, affording a crosslinked between the active group of tannin compounds and sulfuric acid (72.93%). The content of lead from a water sample was analyzed using PET.

Polymerization was carried out using the tannins from the *A. mangium* leaf extract, followed by the addition of concentrated H$_2$SO$_4$ in 6, 12, 18, and 24 h at 90°C–100°C. FTIR spectra of the polymer resin at various contact times are shown in figure 6.

On the basis of the FTIR spectra, the resin comprised –OH, C–H, C–O, and S=O functional groups. With the variation of the contact time, the vibrational intensities of –OH and –CH decreased, indicating that crosslinking occurs by the condensation of phenolic hydroxyl and the formation of S=O. The lower the intensity of –OH, the lower the water solubility. The higher the intensity of S=O, greater the formation of a crosslinking network between PET and H$_2$SO$_4$. With different times, the vibration intensity of –OH decreased, and the desired S=O was formed at 24 h. The proposed reaction for the crosslinking network formation between PET and H$_2$SO$_4$ is shown in figure 7.
3.5. Determination of tannin solubility.
The higher the HNO₃ concentration, the lower the amount of carbon produced because solubility can increase in the presence of acid (figure 8). The TOC of PET (blue) was greater than that of the tannin extract (ET, red) because of the formation of crosslinking network between PET with H₂SO₄.

3.6. pH optimization.
Optimum conditions were observed at pH 7 with the absorbance of 0.0767 (figure 9). At low pH, the absorbance considerably changed, indicating that PET cannot be used at low pH because of the competition with protons and the possible damage to the tannin resin because of extremely low pH. On the other hand, if the [H⁺] concentration is extremely high, a majority of PET is protonated [6]. At high pH, the amount of Pb⁺ adsorbed on the resin decreased because of the formation of Pb(OH)₂. The Pb(OH)₂ solution easily settled at extremely high pH because the Pb(OH)₂ solution exhibited a Kₘₐₜ of 2.8 × 10⁻¹⁶; hence, the adsorption of lead metal ions on the resin decreases.

3.7. Contact time optimization.
With increasing contact time, the adsorption of Pb⁺ on the resin increased (figure 10). The optimum adsorption capacity of Pb⁺ by the resin was observed at a contact time of 120 min with the difference of absorbance of the standard solution being 0.0759. An extremely rapid contact time corresponded to low absorbance, probably because of incomplete bond formation between lead metal and the active group of the adsorbent [6]. The increased contact time possibly increased the probability of interactions between Pb⁺ and the active resin; hence, considerable amount metal ions are adsorbed. On the other hand, at a long contact time, the bond between Pb⁺ and the resin was thought to break.
3.8. Adsorption capacity.

The higher the metal ion concentration, the higher the adsorption capacity of PET (figure 11). The adsorption capacity increased because at high concentrations, the number of metal ions in the solution increased; hence, the metal ions interacting with the active sites of the adsorbent increase, while at an extremely high concentration, the adsorbent possibly becomes saturated because of the complete binding of the active sites of the adsorbent by lead. The highest resin adsorption capacity in a 500-ppm solution was 5.261 mg/g.

4. Conclusions

In this study, the tannin extract from *Acacia mangium* leaves was investigated as an adsorbent, which was prepared by condensation polymerization via crosslinking (72.93%) under optimum conditions at 90 °C–100 °C for 24 h. The optimum conditions for the adsorption of Pb⁺ on the tannin resin was at a pH of 7, contact time of 120 min., and resin adsorption capacity of 5.261 mg/g. Thus, on the basis of the test parameters, the polymer obtained from the tannin extract from *A. mangium* leaves can be used as an adsorbent for lead.

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