Synthesis Pb(II)-ion imprinted polymer using tannins from mango leaves (*Mangifera indica L.*)

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**Abstract.** This work reports the synthesis of Pb(II)-Ion Imprinted Polymer (Pb-IIP) using tannin extract from Mango leaf (*Mangifera Indica L.*) as functional ligand (chelating agent and monomer). Pb-ion found to form a stable compound at 1:1 complex with tannin in aqueous solution. The resulting complex of Pb- and tannin extract was polymerized using phenol-formaldehyde as cross-linker in acidic medium. The structure and properties of Pb-IIP were compared to Pb-IIP gallic acid and Non Imprinted Polymer (NIP) that were synthesized with similar conditions. These polymers were characterized by Fourier Transform Infrared (FTIR) and Scanning Electron Microscopy-Energy Dispersive X-Ray (SEM-EDX). The template of Pb(II) ion was completely removed from the polymeric matrix using 1 mol/L HNO₃. The optimum pH of maximum sorption was 5 on IIP-tannin and IIP-gallic acid at 120 mins contact time. Maximum capacity of tannin Pb-IIP, gallic acid Pb-IIP, and NIP were 153.159 mg/g, 147.959 mg/g, and 138.218 mg/g, respectively. It was found that the tannin Pb-IIP sorbent is more selective than gallic acid Pb-IIP and NIP.

**Keywords:** ion imprinted polymer, lead, tannin, *Mangifera Indica L.*

1. **Introduction**

   Recently, industrial activity is growing rapidly to fulfill the people’s needs. But, as we know, the impact of industrial wastes contributes to the environmental pollution. One of the wastes that give major effect to human body is Pb [1]. Low level of lead in blood can cause lifelong health effects. Therefore, the removal of Pb(II) in the wastewater is very important [2].

   There are so many metal separation methods that had been developed; however, these conventional technologies show lots of disadvantages, such as secondary pollution [3,4]. Ion imprinted polymer (IIPs) known as selective adsorption that widely used for metal separation [1,5,6]. The important things in IIP synthesis are the template ions, ligand, cross-linking agent, and solvents [7].

   Mango (*Mangifera indica L.*) is rich in phenolic compounds [8]. Tannins due to high content of phenolic compounds are inexpensive and can be easily isolated from plants. With phenolic compounds, tannins can have the ability to chelating the metallic compound [8,9].

   In this study, a new ion imprinted polymer, adsorption and desorption behavior of Pb-IIP tannin have been compared to Pb-IIP gallic acid as tannin monomers and non-imprinted polymer (NIP). The aim of this research is to prepare a solid-phase adsorbent which has a high capacity and selectivity to Pb(II) ions.

2. **Experimental**

2.1. **Chemicals**

   NaCO₃ (Merck); dichloromethane; H₂SO₄, 97 % (Merck); acetic acid anhydride; chloroform; n-hexane;
2.2. Apparatus
Freeze dryer (Buchner), magnetic stirrer with hot plate, Scanning Electron Microscopy-Energy Dispersive X-Ray (SEM-EDX), UV-vis Spectrophotometer (Shimadzu 2450), Fourier Transform Infrared Infrared (FTIR) Spectrophotometer (Shimadzu Prestige 21) and Atomic Absorption Spectrophotometer (AAS) (Shimadzu AA 6800).

2.3. Preparation of Pb-IIP
Preparation of Pb-IIP comprises two steps. First, 1 mmol Pb(NO$_3$)$_2$ was dissolved in 100 mL of double distilled water. The functional ligand (tannins isolated from mango leaves) was added dropwise to achieve mole ratio of metals/ligand 1:1. The complex solution was stirred for 3 h. 100 mmol phenol, 50 mmol formaldehyde and 50 mL 0.4 M H$_2$SO$_4$ were added to the complex solution, respectively. The mixture was stirred until homogeneous and the nitrogen gas was removed from the solution by purging for 10 minutes. The polymerization was carried out in a reflux system with a temperature of 65 °C–70 °C for 12 h. The resulting polymer particles were filtered and washed with double distilled water to remove unreacted materials. In the second step, the imprint metal ions Pb(II) were leached from polymer matrix by 1M HNO$_3$ and washed by double distilled water until neutral pH. The polymer was dried overnight. The Non Imprinted Polymer (NIP) was prepared by the same manner in the absence of Pb$^{2+}$ template ions. Characterization of IIP and NIP were performed using FTIR and SEM-EDX.

2.4. Extraction procedure
Adsorption test was performed using batch method. 50 mg dried polymer was added to the 10 mL aqueous solution consists of various concentrations of Pb(II) and stirred to reach an optimum contact time with a magnetic stirrer. pH was adjusted to pH 2–12 to obtain optimum condition. The reusability of polymer was tested by desorption step. Elution Pb(II) ions from IIP was performed in 1M HNO$_3$. The concentration of Pb(II) in the solution was confirmed by FAAS.

3. Results and discussion

3.1. Characterization
IIP was synthesized by polymerization of Pb--tannin complex as a template and phenol-formaldehyde as cross-linker monomer using thermal method. The absorbance of ligand (tannin) solution was regarded as a function of metal ion/ligand mole fraction in order to obtain stoichiometry and stability of complex. The mole fraction plot revealed a sharp inflection point at mole fraction 0.5, indicating the formation of 1:1 ligand to metal complex in aqueous solution.

FTIR spectroscopy was used to study the chemical structure of the synthesized polymer (figure 1).
The typical and intense tannin backbone could be observed in all FTIR spectra, O-H stretching vibration at 3414 cm$^{-1}$, C=O and C-O ester stretching band at 1639 cm$^{-1}$ and 1310 cm$^{-1}$ appeared respectively. The sulphonic acid adsorption S=O at 1096 cm$^{-1}$ was observed in the imprinted polymers. The presence of Pb$^{2+}$ ions in Pb-IIP polymer leads in decreasing adsorption intensity and shifts the adsorption to lower wave numbers.

The morphology of Pb--tannin was assessed by SEM, and the resulting SEM pattern is shown in figure 2. In figure 2a, the polymerization resulted in irregular shape and surface particle with the size about (300–400) μm. The morphology of the particle depends on type of solvent, metal salt, cross-linker, ligand, polymerization temperature, time and stirring speed on polymerization process [10]. Moreover, the surface morphologies of polymer after leaching process were rougher than that of the unleached Pb-IIP. As shown in figure 2b the circular mold was formed in leached Pb-IIP, indicating Pb$^{2+}$ removal from polymer matrix.

The EDX analysis was used to determine the composition of polymerized particle before and after leaching process. It can be seen in figure 3 that unleached Pb-IIP contains C, O, and Pb whereas in Pb-IIP after leaching, there are C and O. This result confirms that Pb$^{2+}$ ions were completely leached from matrix of polymer using 1 M HNO$_3$.

3.2. Effect of pH and adsorption time

pH is an important parameter for adsorption of metals in aqueous solution. Batch experiments were carried out to study the effect of pH on adsorption performance. As shown in figure 4, the absorbance of Pb$^{+}$ increases slowly as the pH increases. In lower pH, the amount of H$^+$ formed increased, so H$^+$ competed with Pb(II) to be bonded with cavities in polymer matrix. At the higher pH shows the decrease of Pb$^{2+}$ absorbance. It is because OH$^-$ was formed, had interaction with Pb(II) and precipitated at pH> 8. Based on the result, pH 5 was selected as the optimal pH value for adsorption study in this work.
Figure 4. Effect of pH in adsorption performance, 10 mL 5 ppm Pb(NO₃)₂, 50 mg IIP

Figure 5. Effect of absorption time, 10 mL 5 ppm Pb(NO₃)₂, 50 mg IIP

Figure 6. Adsorption capacity of Pb-IIP tannin (red triangle, dotted line) Pb-IIP gallic acid (asterisk, dashed line) and NIP (filled circle, solid line) 10 mL Pb²⁺ 20-1000 mg/L, 50 mg adsorbent

Adsorption rate is an important factor that should be determined in the application. Variation of adsorption time as the function of absorbance was investigated and the result is shown in figure 5. The absorbance slightly increases at the beginning and sharply increases at 60–120 min. The optimum contact time was found at 120 min with the highest adsorption of Pb²⁺ ions. At longer contact time, the adsorption of Pb²⁺ was decreased due to the weak bonding between polymer matrix and Pb(II). From figure 5 and figure 6, it is obtained that NIP, Pb-IIP tannin, and Pb-IIP gallic acid have optimum adsorption at the same pH and contact time.
Table 1. Selectivity coefficient of Pb-IIP tannin, Pb-IIP gallic acid and NIP

| Metals | Pb-IIP Tannin | Pb-IIP Gallic Acid | NIP |
|--------|---------------|--------------------|-----|
| Fe     | 8.767         | 3.661              | 0.072|
| Ni     | 44.102        | 8.034              | 0.161|
| Cu     | 57.475        | 14.550             | 0.242|
| Pb     | -             | -                  | -   |

3.3. Adsorption capacity
The adsorption capacity is defined as the amount of adsorbate in mg, units which can be absorbed in 1 gr of adsorbent. Figure 6 shows that the adsorbent being saturated at different concentrations. In order to reach the saturation point, the Pb(II) concentration was increased until the adsorption capacity values were obtained. The adsorption capacity was calculated using following equation:

$$Qe = \frac{(Co - Ce) V}{W}$$

where Co is the initial concentration of Pb(II), Ce is the concentration of Pb(II) that did not adsorb by the adsorbent, V is the volume of Pb(II) and W is the mass of adsorbent. From figure 6, It can be observed that the adsorption capacity of Pb-IIP tannin, Pb-IIP gallic acid, and NIP were 52.87 mg/g, 50.75 mg/g, and 48.50 mg/g, respectively. Pb-IIP tannin has a higher adsorption capacity than Pb-IIP and NIP. The uniform and accessible imprinted binding sites could enhance the adsorption performance of Pb- by imprinted polymer [11]. Furthermore, the high molecular weight of tannin might affect the amount of binding sites cavities in the polymer matrix.

3.4. Selectivity
This test aims to compare the adsorption performance between lead-ion imprinted polymer (Pb-IIP) and non-imprinted polymer (NIP) in samples containing various types of metal ions i.e. Cu^{2+}, Ni^{2+}, Fe^{2+}. In figure 7 it can be seen that Pb-IIP tannin has a higher adsorption capacity to Pb metal ions than other polymers. Since Pb-IIP absorbs the metal not only on the basis of affinity but also on the shape and size of the metal ions. This is due to the cavity of recognition site possessed by Pb-IIP, whereas the NIP absorbs the metal only based on the affinity of the metal ion.

The selectivity coefficient represents the degree of Pb-IIP and NIP selectivity towards other metal ions. From table 1 it can be seen that Pb-IIP tannin has the highest selectivity coefficient compared to Pb-IIP gallic acid and NIP. High selectivity coefficient value indicates that the metal ions Pb (II) can still be detected even though there are other metal ions, so that the presence of other metal ions against Pb metal ions as an interfering metal is not very significant. Ion imprinted polymer possess an even allocation and cavities which related to the imprint ion size and coordination geometries [7]. The chelating ligand also affects the selective affinities for the imprint ion.
3.5. Reusability

Reusability is one of the important performances of IIP due to its application. In this research five times repetition of adsorption-desorption test were performed using the same Pb-IIP tannin. Figure 8 shows that adsorbent could be repeatedly used without significant loss of binding cavities. It was also found that %RSD of five replicates were 0.304 % and CV Hortwitz 1.314 %. Pb-IIP tannin has good performance and it has a lower %RSD value than CV Hortwitz.

4. Conclusions

A novel Pb-IIP using tannins as functional ligand from mango (*Mangifera indica* L.) leaves with phenol-formaldehyde crosslinker in acidic medium has been successfully synthesized. Pb-IIP tannin was more selective than Pb-IIP gallic acid and NIP because of its recognition sites and it is also effective as chelating agent in synthesis of IIP due to high selective coefficient value. Pb-IIP tannin has higher adsorption capacity than the others due to the large amount of active group.

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References

[1] Liu H, Kong D, Sun W, Li Q, Zhou Z and Ren Z 2016 *Chem. Eng. J.* 303 348–58
[2] Shukla V, Shukla P and Tiwari A 2018 *Indian J. Med. Spec.* 93 146–9
[3] Juang R S and Shiau R C 2000 *J. Membrane Sci.* 165 159–67
[4] Qin J J, Wai M N, Oo M H and Wong F S 2002 *J. Membrane Sci.* 208 213–21
[5] Behbahani M, Bagheri M, Taghizadeh M, Salarian M, O Sadeghi, Adlnasab L and Jalali K 2013 *Food Chem.* 138 2050–56
[6] Hu S, Xiong X, Huang S and Lai X 2016 *Anal. Sci.* 32 975–80
[7] Shamsipur M, Besharati-Seidani A, Fasihi J and Sharghi H 2010 *Talanta* 83 674–81
[8] Luo F, Fu Y, Xiang Y, Yan S, Hu G, Huang X, Guodi H, Sun C, Li X and Chen K 2014 *J. Funct. Foods* 8 282–91
[9] Fan R, Xie F, Guan X, Zhang Q and Luo Z 2014 *Bioresour. Technol.* 63 167–71
[10] Shamsipur M and Besharati-Seidani A 2011 *React. Funct. Polym.* 71 131–9
[11] Zhou Z, Kong D, Zhu H, Wang N, Wang Z, Wang Q, Liu W, Li Q, Zhang W and Ren Z 2018 *J. Hazard. Mater.* 341 355–64

Figure 8. Repetition test of Pb-IIP tannin, 10 mL 5.0 mg/L Pb(II), eluent 0.5 M HNO₃.