Study of Pb (II) adsorption by Tannin Based Adsorbent from mangrove bark (Rhizophora mucronata)

Yohanes Sudaryanto, Adriana Anteng Anggorowati, Martinus Edy Sianto
Faculty of Engineering, Widya Mandala Catholic University Surabaya, Surabaya, Indonesia
E-mail: nesto@ukwms.ac.id

Abstract. Mangrove bark (Rhizophora mucronata) is a potential adsorbent for heavy metals adsorption such as lead or Pb (II), because of its tannin content. Prior to be used as adsorbent, the extract of tannin should be polymerized using formaldehyde and produced Tannin Based adsorbent which was not dissolved in water. This research aimed to study the effect of temperature, adsorbent dose and contacting time to% removal of Pb (II). A series of batch adsorption was carried out using 250 mL Pb (II) solution with initial concentration 307.2mg/g. The variation of adsorbent mass was 1-5 gram, the variation of temperature was 30, 40 and 50°C, and the variation of contact time was started at 10 minutes until reached the adsorption equilibrium. The obtained data were also required to determine the adsorption kinetic and adsorption isotherm. The maximum percentage(%) removal was 71.6% which was obtained at temperature 50°C, contact time 70 minutes and TBA dosage 4gram/250 mL solution. Study of adsorption kinetic determines that the pseudo-2 order fitted with this adsorption process. The adsorption coefficient was 0.0099 g/mg.min and the coefficient of determination ($R^2$) was 0.9976. In addition, Langmuir equation described adsorption isotherm better than Freundlich and Temkin equation. The maximum adsorption capacity ($q_e$) was 18.281 mg/g, Langmuir coefficient was 0.0017 L/mg. The research results can be applied to design and to scale-up the process.

1. Introduction
Many industries, such as metal plating, mining, paints and pigments, and battery industries discharge heavy metals such as lead (Pb) [1]. Insufficient treatment process will deliver lead into environment. This action is dangerous for human life, because lead is toxic and accumulates in human body, potential to cause respiratory disorders, neurologic disorders, digestive disorders, cardiovascular disorders, urinary disorders and inflammation [2].

Adsorption is often applied to reduce pollutants in liquid waste, including heavy metals, toxic compounds, dyes and surfactants. The other methods are precipitation, ion exchange and membrane filtration. Compared to the other methods, adsorption is relatively low cost, easy to obtain adsorbent raw material, ease of operation and having relatively high efficiency [3]. In recent years many studies have been carried out on the adsorption of heavy metals and toxic compounds in liquid waste with biosorption technology, which uses adsorbents derived from agricultural waste. Mangrove is a plant that is widely planted along the coast to resist sea water abrasion. As a country that has thousands of islands, Indonesia has a very long beach so that
it is potential as land for mangrove growth. To improve plant growth, rejuvenation is regularly done by cutting some of the stems. Due to containing tannin, mangrove bark obtained from stem can be used as raw material to make adsorbent.

Many researchers have investigated the potential of tannin from agricultural waste to adsorb heavy metals. Kunnambath and Thirumalaisamy (2015) used tannin gels extracted from *Acacia nilotica* to absorb Ni(II) from water [4]. The results showed that the adsorption of Ni(II) followed a pseudo 2nd order equation. Experimental data also confirmed that the Langmuir isotherm adsorption is the most suitable equation with a maximum adsorption capacity = 250 mg/g and KL = 0.037. The application of the Freundlich equation produces KF = 2.511 mg/g and n = 0.434, while the application of the Temkin equation produces KT = 762.3 and BT = 2.814.

Sengil, et al. (2009) studied the adsorption kinetic and adsorption isotherm of Cu (II) biosorption into valonia tannin, obtaining the adsorption kinetic which following pseudo second order [5]. In addition, the application of the Langmuir adsorption isotherm equation produced the best correlation for the adsorption. The maximum adsorption capacity (Qmax) was 44.24 mg/g, while the Langmuir coefficient was 44.05 L/g. The Freundlich adsorption isotherm equation produces KF = 28.43(mg/g)(mgL)1/n and n = 9.41. In the application of the Temkin equation, the values of KT and or BT are 51.76 and 5.55 L/g, respectively.

Another study is Cr (VI) adsorption using tannin-immobilized activated clay at various temperatures [6]. This study showed that the Freundlich isotherm adsorption produced a higher DETERMINATION coefficient than the Langmuir equation. In the Freundlich equation a value of 1/n obtained = 0.367 to 0.383, while the Freundlich constant value is 2.406 to 3.113 L/g. The application of the Langmuir equation produces a maximum adsorption capacity (Qmax) = 18.34 to 24.09 mg/g, while the Langmuir constant = 0.033 to 0.040 L/mg.

It was examined Co(II) and Pb(II) adsorption using Tannin-Based Adsorbent synthesized from *Rhizopora apiculata* mangrove wood waste [7]. The adsorption kinetics model which was suitable for Co(II) and Pb(II) adsorption is pseudo second order. The application of Langmuir adsorption isotherm for Co(II) and Pb(II) adsorption resulted in better data compatibility than the Freundlich equation. The maximum adsorption capacity of Co(II) is 8.78 mg/g, while the maximum adsorption capacity of Pb(II) is 31.32 mg/g. Langmuir’s constant for Co(II) and Pb(II) adsorption are 0.0498 and 0.1205, respectively.

2. Material and Method

2.1. Material

Mangrove bark *Rhizopora mucronata* used in this study was collected from Ngada District, Flores, East Nusa Tenggara. It was dried, crushed and then extracted by Microwave Extraction Process (MAE) using 80% ethanol at 50°C for 45 minutes. The ratio of mangrove bark mass to solvent volume = 1:10. Then the solvent was evaporated and the tannin gel was dried in oven at 60°C overnight until becoming crude tannin.

Tannin Based Adsorbent was made through the following procedure [4]. Firstly, 5 grams of crude tannin was dissolved into 32 mL 0.125 mol/L Sodium hydroxide (NaOH) and distilled water at 80°C. After obtaining homogenous solution, 5 mL formaldehyde was added and the reaction was kept at the same temperature for 8 hours. The gummy product was dried in oven at 65°C overnight. The dried product was crushed, sieved (70-100 mesh) and washed using distilled water to remove the un-reacted NaOH. Finally, it was dried again at 80°C to produce Tannin Based Adsorbent (TBA).

The chemicals used in this research consisted of commercial grade tannic acid supplied by Sigma Aldrich, ethanol, lead nitrate (Pb(NO₃)₂) and some chemicals supplied by Merck for qualitative and quantitative analysis.
2.2. Characterization
To detect the consisted functional groups, samples of crude tannin, TBA as well as commercial grade tannic acid were analyzed using Fourier Transform Infra Red (FTIR). X-Ray Diffraction (XRD) analysis was also carried out to identify the crystalline structure. In addition, the surface morphology of TBA before and after the adsorption process was analyzed using Scanning Electron Microscopy (SEM).

2.3. Adsorption Experiment
A series of batch adsorption was conducted to investigate the effect of temperature, TBA dosage and contact time to percentage removal. The obtained data were also used to determine the adsorption kinetic and adsorption isotherm.

Leads nitrate solution was prepared by dissolving (Pb(NO₃)₂) in deionized water at the concentration needed for the experiment. The initial concentration of Pb(II) was analyzed by Atomic Adsorption Spectrophotometer (AAS). Adsorption was carried out by putting 250 mL (Pb(NO₃)₂) solution in a flask, then 1-5 grams TBA was added. The flask was shaken on a shaking water bath at 30, 40 and 50°C. After certain contact time, the suspension was filtered using No. 42 filter paper, then the Pb(II) in the supernatant was analyzed by AAS. The batch adsorption experiments were done with different time from 10, 20, 30 minutes etc. until reached the equilibrium. Percentage removal of Pb(II) can be calculated by using Eq. 1.

\[ \text{Percentage removal} = \left( \frac{C_0 - C_f}{C_0} \right) \times 100\% \]

and the amount of Pb(II) adsorbed at equilibrium was calculated by using Eq. 2.

\[ q_e = \left( \frac{V(C_0 - C_f)}{W} \right) \]

where,
- \( C_0 \) = the initial concentration of Pb(II) solution, mg/L
- \( C_f \) = the final concentration of Pb(II) solution, mg/L
- \( q_e \) = adsorption capacity, mg/gram
- \( V \) = the volume of solution, L
- \( W \) = the weight of TBA, grams

3. Result and Discussion
3.1. FTIR analysis
Figure 1 shows the spectrum of tannin, commercial grade tannic acid and TBA.

Figure 1 shows the spectrum similarity of crude tannin, commercial grade tannin and TBA analyzed in this research. Hydroxyl groups (-OH) were at around 3400 and 3100 cm⁻¹, (-C-H-) were at around 2900, and (C=O) were at around 1680. Those spectrums were also identical with the spectrum of tannins and tannic acid [8].

3.2. XRD analysis
The XRD analysis was carried out to study the conversion or polymerization from crude tannin to TBA, as shown in Figure 2.

Figure 2 is the result of XRD analysis of crude tannin, with the highest intensity I = 100% at 2θ = 21.69. The peak is not sharp, indicates that crude tannin from mangrove bark is amorphous, mainly because the crude tannin is not homogenous and only consists of 9.23% of pure tannin. After being polymerized to TBA, there are 2 peaks. The first peak is formed with intensity I = 100% at 2θ = 31.53 and the second peak with I = 37.64% at 2θ = 45.28. The two peaks are relatively sharp, indicates that small crystals are formed. In other words, TBA changed into semi crystalline.
3.3. Effect of temperature

The initial concentration of Pb(II) solution analyzed by AAS was 307.2 mg/gram. Effect of temperature, TBA dosage and contact time to % removal is shown in Figure 3.

From Figure 3, it is observed that generally % removal increased in the temperature from 30 to 50°C. It signifies that the adsorption process of Pb(II) onto TBA extracted from mangrove bark requires energy. In other words, the process is endothermic. The energy was required to bond the negative charge of TBA and positive charge of Pb(II). The increasing temperature caused the increasing of activated molecules [6]. Consequently, the frequency of collisions among molecules also increases. In other words, the adsorption of Pb(II) by Tannin Based Adsorbent is chemisorption.

The adsorption of malachite green gave contrast result. Khatti & Singh (2009) studied the effect of temperature on the amount of malachite green adsorbed [9]. The experiments showed that the increasing temperature caused the lowering of amount adsorbed.

3.4. Effect of TBA dose

Prior to convert into Tannin Based Adsorbent, the tannin content of the crude tannin was analyzed by titrimetri method. The result showed that the purity of tannin was only 9.23%. Therefore, in this research the adsorbent mass were slightly high, i.e. 1-5 grams.

Figure 3 also shows that for 250mL Pb(II) solution, % removal increases with the increasing of TBA dose, but 5 grams TBA resulted % removal close to 4 grams. Therefore the use of 4 grams TBA is determined as the best among other TBA mass. The mass of adsorbent used in this study is much higher than some previous research. For 100 mL solution, Only required 20 mg adsorbent derived from tannin extract to adsorb Zn^{2+}, methylene blue and cetyltrimethylammonium bromide (CTAB), but the adsorbents used were commercial grades [8]. The lower mass of adsorbent only required 0.05 grams adsorbent synthesized from natural condensed tannin for lead adsorption, but the purity of the tannin was not reported in this research [10].
3.5. Effect contact time

Effect of contact time to % removal was investigated at 30, 40 and 50°C (Figure 3) and TBA dosage from 1 to 5 grams. It can be seen that % removal increased with increasing of contact time. Initially, the increasing was sharp, but start from 50 minutes the increasing of % removal was small until constant at 70 minutes. Therefore the equilibrium contact time was 70 minutes. The equilibrium contact time depends mainly on the adsorbent and the adsorbate type. The adsorption of Ni(II) ions from water by tannin extract found that at 35 minutes the adsorption reached the equibrium [4], while Ni(II) and Cu(II) removal by modified mangrove barks achieved the equilibrium at 60 minutes [11]. Wen et.al. (2012) carried out Cr(VI) adsorption on tannin-immobilized activated clay, found that at 310, 320 and 310 K the equilibrium contact time was around 100 minutes, while Rajdeo et al. (2016) found that the equilibrium contact time of Cd(II) adsorption by tannin-formaldehyde/acetaldehyde resins derived from Camellis sinensis powder was 120 minutes [6, 12].

Figure 2: XRD Analysis of crude (a) tannin and (b) TBA
Figure 3: Effect of temperature, contact time and adsorbent dose to percentage removal
3.6. Kinetic Study

Adsorption kinetic is the solute removal rate, controlling the residence time of the sorbate in the solute-solution interface. Studies of kinetic can be carried out by using various initial sorbate concentrations, sorbent doses, particle size, agitation speeds and pH values [13].

The kinetic experiment was conducted at 50°C and ratio of TBA dosage 5 grams/50 mL. The values of parameters together with coefficient of determination (R²) for pseudo-1 order and pseudo-2 order are given in Table 1.

Table 1 shows that for pseudo-1 order, the calculated adsorption capacity (qₑ calc.) is closer to the adsorption capacity of the experiment (qₑ exp.) than pseudo-2 order. Contrarily, the coefficient of determination (R²) of pseudo-2 order is slightly higher than pseudo-1 order. Based on R² value, it shows that pseudo-2 order fits better than pseudo-1 order to represent the Pb(II) adsorption by Tannin Based Adsorbent extracted from mangrove bark.

The opposite results when studied the adsorption of Malachite green by rattan sawdust [14]. In this research, the coefficients of determination value of the pseudo-1 order were all higher than those of the pseudo-2 order, and also the calculated adsorption capacity (qₑ calc.) were much more accurate. In contrast, the adsorption of Malachite green by organically modified clay fitted with the pseudo-2 order [15].

3.7. Adsorption Isotherm

The experiment to investigate the adsorption isotherm was carried out at 50°C, TBA dosage 5 gram/50 mL and contact time 70 minutes. The results are given in Table 2.

According to Table 2, Langmuir equation expressed the highest coefficient of determination. Therefore, Langmuir equation described adsorption isotherm better than Freundlich and Temkin equation. It was explained that this equation has 3 assumption, i.e. adsorption is monolayer, all surface site is similar and only can only adsorb one atom, and the independency of each site occupancy [13]. Aside from that, Freundlich equation was also satisfy to represent the adsorption of Pb(II) onto TBA, due to its heterogeneity between 1-10, while Temkin equation was usually applied in gas adsorption.
4. Conclusion

Tannin Based Adsorbent synthesized from mangrove bark (*Rhizopora mucronata*) is potential to adsorb Pb(II). The maximum percentage removal was 71.6% which was obtained at temperature 50°C, contact time 70 minutes and TBA dosage 4gram/250 mL solution. Study of adsorption kinetic determines that the pseudo-2 order fitted with this adsorption process. The adsorption coefficient was 0.0099 g/mg.min and the coefficient of determination ($R^2$) was 0.9976. In addition, Langmuir equation described adsorption isotherm better than Freundlich and Temkin equation. The maximum adsorption capacity ($q_e$) was 18.281 mg/g. Langmuir coefficient was 0.0017 L/mg. The further research is required, especially to study the effect of pH.

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References

[1] Ergun, M.E., Dursun, S., Ozdemir, C., & Karatas, M. (2007). Heavy metal adsorption by modified oak sawdust: Thermodynamics and kinetics. Journal of Hazardous Materials, 141: 77-85.

[2] Boskabady, M., Marefat, N., Farkhondeh, T., Shakeri, F., Farshbaf, A., & Boskabady, M.H.(2018).The effect of environmental lead exposure on human health and the contribution of inflammatory mechanisms, a review. Environment International, 120, 404-420

[3] Demirbas, A. 2008. Heavy metal adsorption onto agro-based waste materials: A review. Journal of Hazardous Materials, 157: 220-229

[4] Kunnambath P.M. & Thirumalaisamy, S., 2015. Characterization and utilization of tannin extract for the selective adsorption of Ni (II) Ions from water. Journal of Chemistry, 2015: 1-9.

[5] Sengil, L.A., Ozacar, M. & Turkmenler, H., 2009. Kinetic and isotherm studies of Cu(II) biosorption onto valonia tannin resin. Journal of Hazardous Materials, 162: 1046-1052.

[6] Wen Li, Yankui Tang, Yutao Zeng, Zhangfa Tong, Dawen Liang, Weiwei Cui, 2012. Adsorption behaviour of Cr(VI) ions on tannin-immobilized activated clay. Chemical Engineering Journal, 193-194: 88-95.

[7] Oo, C.W., Kassim, M.J. and Pizzi, A., 2009. Kinetic and isotherm studies of Cu(II) biosorption onto Rhizophora apiculata mangrove polyflavonoid tannins in the adsorption of copper (II) and lead (II). Industrial Crops and Products, 30: 152-161.

[8] Martin, J.S., Beltrand-Herrera, J. & Gibello-Perez, P.(2011). Adsorbent biopolimers from tannin extracts for water treatment. Chemical Engineering Journal, 168: 1241-1247.

[9] Khati, S.D. & Shing, M.K.(2009). Removal of malachite green from dye wastewater using neem sawdust by adsorption. Journal of Hazardous Materials, 167: 1089-1094.

[10] Xin-Min, Z. & Xuan Zhao (2003). Mechanism of lead adsorption from aqueous solutions using an adsorbent synthesized from natural condensed tannin. Water Research, 37: 3906-3912.

[11] Rozaini, C.A., Jain, K., Oo, C.W., Tan, K.W., Tan, L.S., Azraa, S. & Tong, K.S. Optimization of nickel and copper ions removal by modified mangrove bark. International Journal of Engineering and Application, 1(1):84-89.

[12] Rajdeo, K.S., Ponrathnam, S., Tambe, S.S.& Chavan, N.N.(2016). Adsorption studies of Cd(II) with tannin-formaldehyde/acetaldehyde resins derived from Camellia sinensis powder. International Journal of Researches in Biosciences, Agriculture and Technology, 4(1): 57-61.

[13] Febrianto, J., Kosasih, A.N., Sunarso, J., Yi-Hsu, J. Indraswati, N. & Ismadji,S. (2009). Equilibrium and kinetic studies in adsorption of heavy metals using adsorbent: A summary of recent studies. Journal of Hazardous Materials, 162: 616-645.

[14] Hammed, B.H. & El-Khairy, M.I. (2008). Malachite green adsorption by rattan sawdust: Isotherm, kinetic and mechanism modelling. Journal of Hazardous Materials, 159: 574-579.

[15] Arellano-Cardenas, S., Lopez-Cortez, S. & Cornejo-Mazon, M. (2013). Study of malachite green adsorption by organically modified clay using a batch method. Applied Surface Science, 74-78. doi: https://doi.org/10.1016/j.apsusc.2013.04.097.