Indonesian Journal of Chemistry and Environment
Vol. 4, No 2, December 2021, pp. 39 ~ 48
e-ISSN: 2599-3186

Preparation of Magnetite-Tannin Guava Leaves as Pb(II) Adsorbent

Mochamad Hafiz Ghozali Rusmana* and Triastuti Sulistyaningsih
Department of Chemistry, Faculty of Mathematics and Natural Sciences, Universitas Negeri Semarang

Article Info

Article history:

Received: October 15th, 2021
Revised: November 20th, 2021
Accepted: December 16th, 2021

**Corresponding Author:*

Moch. Hafiz Ghozali Rusmana,
Department of Chemistry
Universitas Negeri Semarang

Email: asyifasapni9@gmail.com

ABSTRACT

The increasing use of heavy metals in everyday life causes serious environmental pollution, one of which is the Pb(II) metal ion which is toxic to organisms. This study aimed to modify the tannins extracted from guava leaves with magnetite (Fe_3O_4) by coprecipitation as adsorbent of Pb(II) metal ion. The modified results were characterized using Fourier Transform Infra Red (FTIR), Scanning Electron Microscopy (SEM), Energy Dispersive X-ray (EDX), and X-Ray Diffraction (XRD). Metal ion levels of Pb(II) before and after adsorption were measured by Atomic Absorption Spectroscopy (AAS). The results showed that the tannins increased the magnetite-tannin crystal size from 85.17 to 155.66 nm. Modification of magnetite (Fe_3O_4) in guava leaf tannins is able to provide magnetic properties that facilitate post-adsorption separation. The optimum adsorption conditions were reached at pH 7 for magnetite-tannin and magnetite with optimum contact time. The adsorption of magnetite-tannin and magnetite occurred at 90 and 60 minutes. The maximum adsorption capacity of Pb(II) metal ions by magnetite-tannin is smaller than that of magnetite. Both adsorption processes followed the Langmuir isotherm pattern and Pseudo Order Two (Ho) kinetics.

Keyword: *adsorbent, tannins, magnetite (Fe_3O_4), metal ion Pb(II)*

1. INTRODUCTION

Heavy metal ion waste belongs to toxic waste. Thus, it requires more handling than other wastes such as organic waste. Disposal of heavy metal ion waste in ecosystems can have a negative impact on these ecosystems such as plants and other aquatic ecosystems in the environment (Simamora & Krisna, 2015). One example of heavy metals that pollute the environment is the metal ion Pb(II). Pb(II) metal ion is one of the dangerous heavy metals. The maximum level of Pb(II) metal ions in waters recommended by the Ministry of Health for sanitation purposes is 0.05 ppm (Kemenkes, 2017). The effects of Pb(II) metal ions is quite dangerous for health, these metal ions may cause several organ function disorders if they accumulate in the body in large quantities (Danarto, 2014). Various methods have been used to reduce the levels of heavy metal ions, one of which is the adsorption method. According to Pang et al. (2011), adsorption is one of the most widely used and effective methods for remediation of heavy metal ion pollutants, because the adsorption process offers flexibility in its manufacture and application. According to Syauqiah et al. (2011), adsorption is influenced by several factors including pH, concentration, and contact time. The adsorption method requires a binder specimen as the adsorbent. Tannin compounds found in plants can be applied as bioadsorbents. Tannins are used as adsorbents because of their ability to absorb heavy metals by forming chelates through phenolic hydroxyl groups. The use of tannin as a bioadsorbent of Pb(II) metal ions has been carried out by Kartikaningsih et al. (2011). The findings show that tannins can adsorb Pb(II) metal ions. However, the obstacle faced is the difficulty of separating tannins from the post-adsorption solution.

On the other hand, magnetite (Fe_3O_4) is one of the iron oxides that can be used as an adsorbent for heavy metal ions in wastewater. Magnetite has oxygen atoms on its surface that can bind heavy metal ions (Teja & Koh, 2009). Besides being able to bind pollutants in the environment, magnetite has magnetic properties so that it can be attracted by external magnets. However, the weakness of this adsorbent is that it is easily oxidized and agglomerates in aqueous solution systems which can affect its absorption capacity (Maity & Agrawal, 2007). The coating of natural organic matter on the magnetite surface can make magnetite less toxic and more environmentally friendly. The coating can also inhibit autoxidation and agglomeration, which are disadvantages of magnetite adsorbents (Rashid et al., 2017). Therefore, in this study, tannin was prepared from guava leaves and it combined with magnetite. Modification of magnetite with tannins was successfully carried out by Bagtash et al. (2016), the results obtained that tannin compounds coat the surrounding magnetite particles. It is hoped that the incorporation of tannins with magnetite will facilitate the separation of the adsorbent from the post-adsorption solution with the help of an external magnet and prevent the magnetite from agglomerating.

2. RESEARCH METHOD

Samples of 50-gram guava leaf powder were macerated with 400 mL of solvent. The solvent made by mixing the acetone and water with the proportion of (7:3) and the addition of 3 mL of 10 mM ascorbic acid for 3 x 24 hours. The tannin extract was concentrated with a vacuum rotary evaporator and heated with a water bath at a temperature of 40-50 °C until the volume became one third of the initial volume. The concentrated extract was extracted with chloroform (4 x 25 mL) to form 2 layers. The aqueous layer (top) was extracted with ethyl acetate (25 mL). The water layer (at the bottom) is concentrated with a vacuum rotary evaporator. The extract obtained was tested with 1% $FeCl_3$ reagent (Kartikaningsih et al., 2014).

Magnetite-tannin synthesis was initiated by dissolving $FeCl_3{\cdot}6H_2O$ and $FeSO_4{\cdot}7H_2O$ with a mole ratio of 2:3 in 400 mL of demineralized water with 500 rpm stirring at 80°C for 20 minutes. Then the solution was added with 2 M NaOH solution at a temperature of 55ºC so that the pH became 11 (Abdulla et al., 2019). After stirring for 2 minutes, 5 ml of tannin extract was added to the solution and stirred for 30 minutes. After the magnetite-tannin is produced, the magnetite-tannin is separated from the solution by being pulled with a magnet on one side. After the magnetite–tannin was rinsed with distilled water to pH 7 (El-kharrag et al., 2011). The last step is magnetite-tannin drying using an oven at a temperature of 65ºC for 6 hours. Magnetite-tannin and magnetite were characterized using FTIR, SEM, EDX and XRD.

Adsorption was carried out at room temperature with a stirring speed of 250 rpm, adsorbent weight of 0.1 grams, and adsorbate volume of 10 mL. Determination of the optimum pH was carried out by varying the pH of 4, 5, 6, 7 and 8 using a phosphate buffer solution. Determination of the optimum contact time was carried out at the optimal pH with time variations at 5,15,30,60,90,120 and 150 minutes. Determination of the optimal concentration was carried out at pH and optimal contact time with various concentrations of 25, 30, 40, 45, 50, 55 and 60 ppm. The concentration of Pb(II) before and after adsorption was measured using AAS. .

3. RESULTS AND DISCUSSION

Characterization

Magnetite-tannin compounds were successfully synthesized as shown in Figure 1. The solid obtained was black and could be attracted by a magnet, this was due to the dominated black color of the magnetite (Abdulla et al., 2019). Characterization results from the FTIR spectra of guava leaf tannins (Figure 2) obtained a peak at wave number 1612 cm^{-1} indicating a carbonyl group (C=O). C-H bending vibrations appear in the range of 1300-1400 cm^{-1}. The broad band at wavenumber 3400 cm^{-1} was identified as a hydroxyl group (Atacan et al., 2017). The peak at wave number 1000-1210 cm^{-1} is a C–O stretching vibration arising from the pyran ring structure of tannins (Agi et al., 2018). The FTIR spectra of magnetite show that there are peaks at wave numbers 441 and 590 cm^{-1} which show octahedral and Fe-O tetrahedral bonds (Maylani et al., 2016), absorption peaks in the 3448 cm^{-1} region that is the OH stretching vibration (Atacan et al., 2017). In the magnetite-tannin FTIR spectra, an absorption band appears at a wave number of 1072 cm^{-1} which is a CO group (Madubuonu et al., 2020) and a peak at a wave number of 1704 cm^{-1} shows the vibration of the C=O carboxylate functional group which is a typical absorption of tannins (Bagtash et al., 2016). The absorption peak of 1620 cm^{-1} was defined as the stretching vibration of the C=C aromatic group (Poukarim et al., 2020). The absorption peak at 589 cm^{-1} indicates the Fe-O group vibration of magnetite. These results indicate that magnetite-tannin compounds were successfully synthesized.

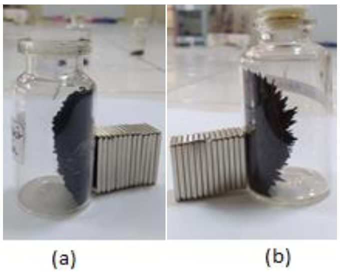

Figure 1. Magnetite-tannin (a), Magnetite (b)

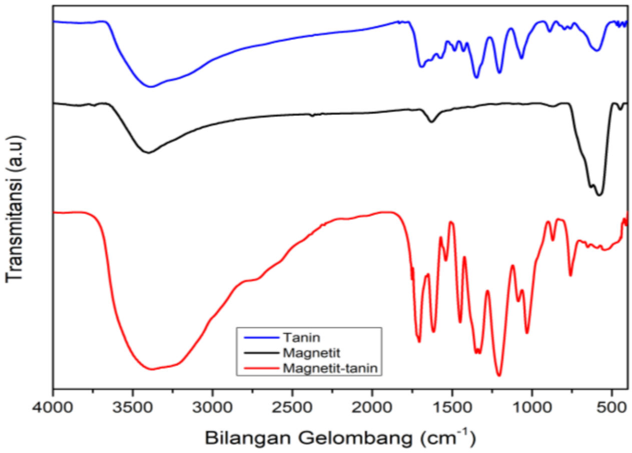

Figure 2. Tannin, Magnetite, and Magnetite-tannin FTIR Spectra

The XRD analysis is shown in Figure 3. Based on JCPDS No.19-629, the phase of the synthesized material is magnetite (Fe_3O_4). The synthesized magnetite diffractogram showed peaks at 2θ: 35.4709°, 43.1181o and 57.1019o. According to Maylani et al. (2016) the peaks of the magnetite diffractogram appear at 2θ: 35.46°, 43.34° and 57.42° so that the diffractogram results show that magnetite compounds have been successfully synthesized. The results of the magnetite-tanin diffractogram appear at peaks of 2θ: 35.8735°, 43.5585° and 57.0731° with a decrease in intensity due to the presence of tannin compounds in magnetite. Based on the calculation of the size of magnetite-tannin and magnetite crystals using the Debye-Scherrer method, the size of magnetite-tannin is 155.66 nm and magnetite is 85.17 nm. The crystal size of magnetite-tannin based on research by Abdulla et al. (2019) has a size of 138.57 nm. Magnetite-tanin crystal size which is larger than magnetite occurs due to the presence of large tannin compounds bound to magnetite compounds. The greater the molar concentration of Fe^{2+} and Fe^{3+} ions, the higher the peak of the magnetite phase formed (Atacan et al., 2017).

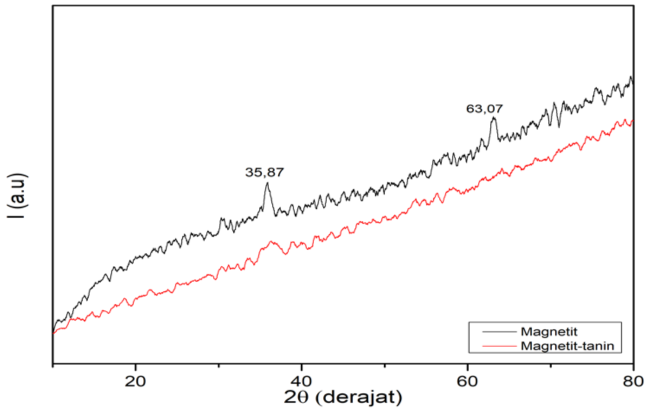

Figure 3. Magnetite and Magnetite-tannin XRD diffractogram

In addition, characterization using EDX (Energy Dispersive X-ray Spectroscopy) obtained the percentage of elements contained in the material (see Table 1). Magnetite-tannin compounds have a higher percentage of carbon content than magnetite however it has fewer Fe atoms than magnetite compounds. The high carbon atom in magnetite-tannins occurs because the organic compounds of tannins have many carbon atoms bonded to magnetite compounds (Bagtash et al., 2016).

Table 1. EDX Analysis Results

Element Symbol	Element	Element Concentration	
		Magnetite-tannin (%)	Magnetite (%)
Fe	Iron	15,54	27,19
O	Oxygen	52,98	63,74
C	Carbon	28,43	9,07

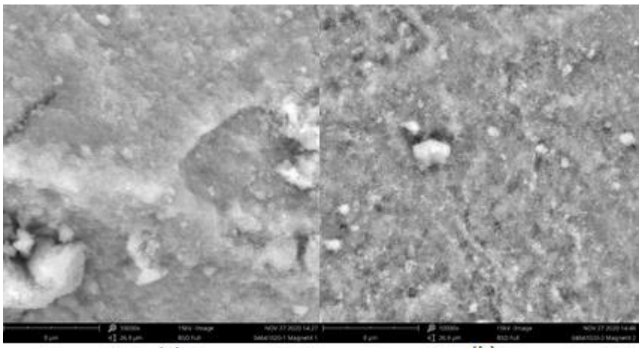

Figure 4. Magnetite (a) and Magnetite-tannin (b) of SEM Analysis

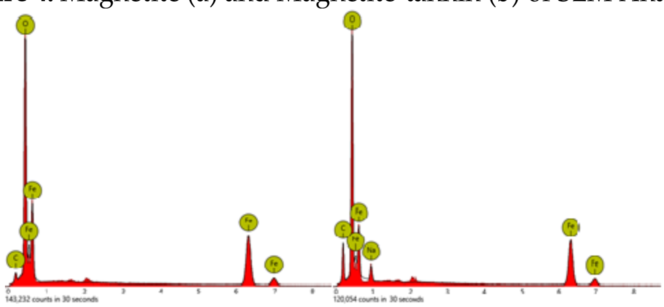

Figure 5. Magnetite (a) and Magnetite-tannin (b) of EDX Analysis

Adsorption Study

The degree of acidity (pH) is an important factor in adsorption. This is because changes in pH can cause the charge of the adsorbent or metal ion species in solution changing. Figure 6 shows that the optimum pH for the adsorption of Pb(II) metal ions by magnetite-tannin and magnetite occurs at pH of 7. At an acidic pH there is competition between metal ions Pb(II) and H^+ ions in getting for the active side on the surface of the adsorbent which is still empty. Therefore, the amount of metal ion Pb(II) which is adsorbed getting less. Along with the increase in pH, the number of Pb(II) metal ions adsorbed will be higher due to the reduced number of H^+ ions in solution. At alkaline pH, the surface of the adsorbent is surrounded by OH^- ions so that the surface is negatively charged due to deprotonation. This results in an attraction between the adsorbent surface and Pb(II) metal ions which is positively charged (Madubuonu et al., 2020). The adsorption of Pb(II) metal ions decreased at pH 8, this was due to the formation of precipitated $Pb(OH)_2$ compounds.

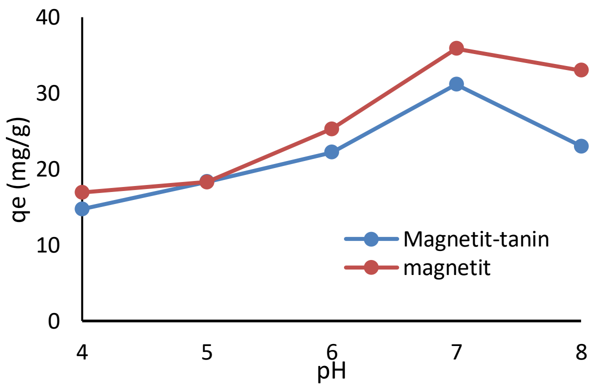

Figure 6. The Effects of pH toward Pb(II) ion metal adsorption power

The adsorption process on magnetite-tannin and magnetite is a physical and chemical adsorption process. In chemical adsorption, the particles adhere to the surface of the adsorbent and form chemical bonds usually in the form of covalent bonds, ionic bonds or both. Adsorption on magnetite-tannin and magnetite is irreversible (Lim et al., 2011). The reaction mechanism of magnetite and magnetite-tannin with the metal ion Pb(II) is presented in Figure 7.

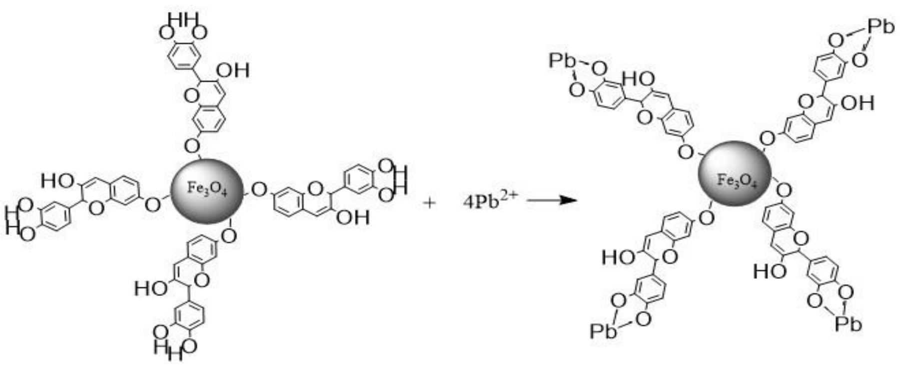

Figure 7. Illustration of Magnetite-tannin reaction with metal ion Pb(II) (Bagtash et al., 2015)

On the other hand, Figure 8 shows that the optimal contact time of metal ion Pb(II) adsorption by magnetite-tannin and magnetite are occurred at contact time of 90 and 60 minutes, respectively, with adsorption magnitudes of 14.415 and 19.855 mg/g. At the beginning of adsorption, the longer the contact time of the adsorbent with the adsorbate, the higher the amount of adsorbate that interacts with the active site of the adsorbent until it reaches a state of equilibrium. The adsorption rate is determined by the interaction between the adsorbent and the adsorbate at a certain time until it reaches an equilibrium state, namely the stability of the adsorption ability with increasing time. The faster the equilibrium time, the faster the adsorption rate. The adsorption rate was determined by adsorption kinetics model. This research uses adsorption kinetics model to determine the rate constant of the adsorption reaction. The kinetic model used is the first order pseudo kinetics of Lagergren and the pseudo second order Ho. Lagergren's pseudo-first order kinetics is determined by constructing a curve of *ln (qe-qt) vs. t,* while pseudo-second-order kinetics of Ho is determined by constructing a curve among *t/qt vs t*. The results of the calculation of the adsorption kinetics are presented in Table 2.

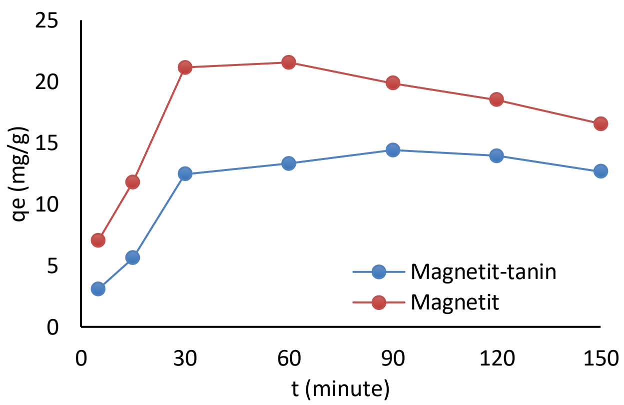

Figure 8. The optimal contact time of metal ion Pb(II) adsorption by magnetite-tannin and magnetite

Table 2. The results of the calculation of the adsorption kinetics of Pb(II) metal ions on magnetite-tannin and magnetite

Adsorbent	Pseudo Orde Satu Lagergren			Pseudo Orde Dua Ho		
	K_1 (minute^{-1})	Qe (mg/g)	R^2	K_2 (g/mg.minute)	h (mg.g^{-1}.minute^{-1})	R^2
Magnetite-tannin	0,0125	0,4025	0,311	0,5618	1,4734	0,9722
Magnetite	0,0062	0,5655	0,1205	3,4662	1,7937	0,9736

Table 2 shows that the value of the correlation coefficient (R^2) of adsorption metal ion Pb(II) with magnetite-tannin and magnetite is 0.9722 and 0.9736, respectively, so that the adsorption kinetics of both are in accordance with the pseudo second-order kinetics model. Ho which is indicated by the value of R^2 closest to 1. The graphs of adsorption kinetics in this study are presented in Figures 9 and 10.

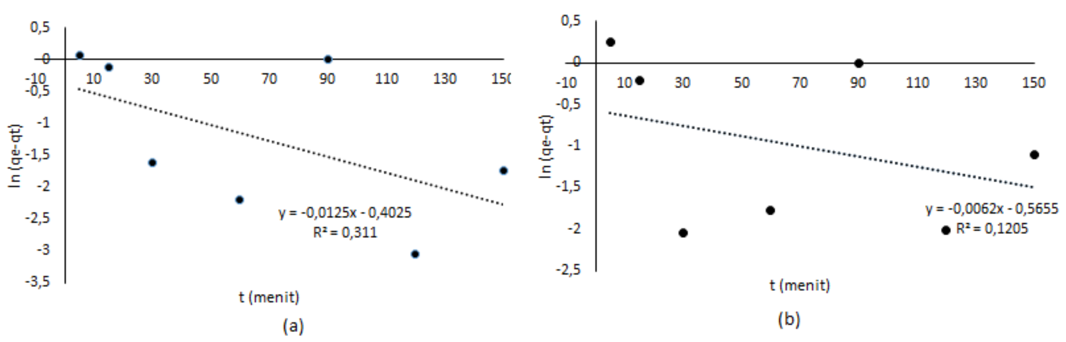

Figure 9. Linear plot of pseudo first-order kinetic equations, for the adsorption of Pb(II) metal ions against (a) magnetite-tannin and (b) magnetite

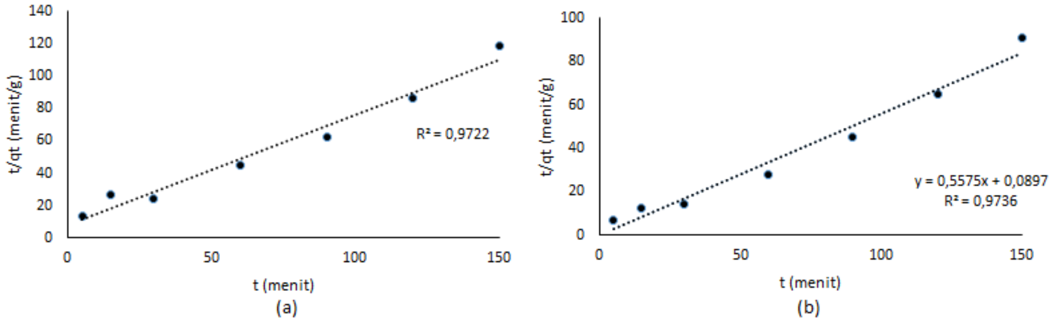

Figure 10. Linear plot of pseudo second-order kinetic equations, for the adsorption of Pb(II) metal ions on (a) magnetite-tannin and (b) magnetite

In addition, optimum adsorption of metal ion Pb(II) in magnetite-tanin occurs at an equilibrium concentration of 52.4 ppm with a total adsorbed of 13.3883 mg/g, while in magnetite it occurs at an equilibrium concentration of 52 ppm of 15.3689 mg/g. (Figure 11). At low concentrations, the active site of the adsorbent is only slightly filled with Pb(II) metal ions. Furthermore, the adsorption process increased until it reached the optimum concentration. The optimum condition was obtained at the concentration with the highest amount of Pb(II) metal ion adsorbed. After reaching the optimum concentration, the adsorption of Pb(II) metal ions will decrease. This is because the pores and surface of the adsorbent have been filled with Pb(II) metal ions or have been saturated. In addition, the release of Pb(II) metal ions on the adsorbent causes the adsorption power to decrease (Luo et al., 2017).

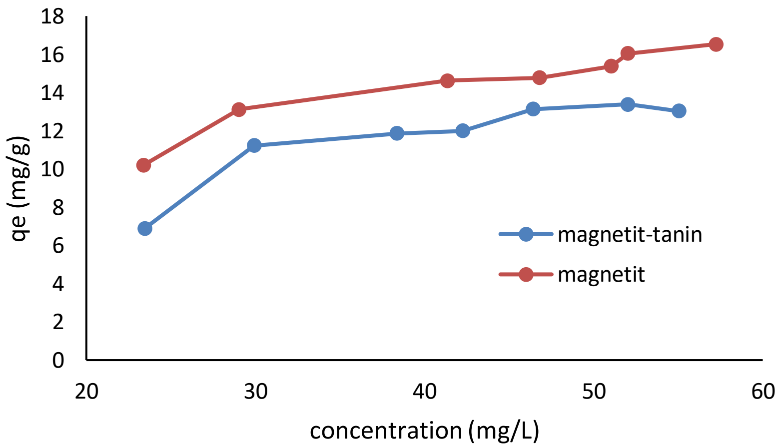

Figure 11. The curve of the effect of concentration on the adsorption power of Pb(II) metal ions.

The adsorption capacity of the Pb(II) metal ions was determined using an adsorption isotherm. The adsorption isotherm model used is the Langmuir and Freundlich isotherm model. The Langmuir isotherm model is assumed to cover monolayer adsorbents on a homogeneous surface, while the Freundlich isotherm model is based on multilayer adsorption on a heterogeneous adsorbent surface (Maylani et al., 2016). The calculation results of the adsorption Pb(II) metal ions adsorption isotherm are presented in Table 3.

Based on the calculation results in Table 3, it shows that the adsorption of Pb(II) metal ions with magnetite-tannin and magnetite both follows the Langmuir isotherm pattern. This is because the Langmuir isotherm has a correlation factor (R^2) greater than the correlation factor (R^2) of the Freundlich isotherm. The suitability of the Langmuir isotherm model for this research shows that the adsorption process occurs on the surface of the adsorbent which is homogeneous. The adsorption ability of magnetite after modification with tannins is decreased.

Table 3. The results of the calculation of the adsorption isotherm of Pb(II) metal ions by magnetite-tannin and magnetite.

Adsorbent	Isoterm Freunlich			Isoterm Langmuir		
	k_f (mol/g)	n	R^2	q_{max} (mg/g)	k_L (L/mol)	R^2
Magnetite-tannin	1,8522	1,8274	0,681	25,1256	0,0305	0,9678
Magnetite	4,3161	2,7746	0,8032	31,1526	0,0499	0,9376

4. CONCLUSION

Optimal conditions for adsorption of Pb(II) ions using magnetite-tannin and magnetite occurred at pH of 7 with optimum contact times of 90 and 60 minutes, with maximum adsorption capacities of 25.1256 and 31.1526 mg/g, respectively. The adsorption isotherms of Pb(II) ions by magnetite-tannin and magnetite both followed the Langmuir isotherm pattern, while the adsorption kinetics of both followed the pseudo-second order (Ho) kinetics pattern.

REFERENCES

Abdulla, N. K. Siddiqui, S. Tara, N. Adil, A. & Chaudhry, S. A. (2019). Psidium guajava leave-based magnetic nanocomposite γ-Fe2O3@GL: A green technology for methylene blue removal from water, *Journal of Environmental Chemical Engineering*, 7(6).

Agi, S., Zamanian, A., & Sohrabijam, Z. (2015). Characterization and synthesis of magnetite nanoparticles by innovative sonochemical method. *Procedia Materials Science*, 11, 265–269.

Atacan, K., Çakıroğlu, B. & Özacar, M. (2017). Efficient protein digestion using immobilized trypsin onto tannin modified Fe_3O_4 magnetic nanoparticles. *Colloids and Surfaces B: Biointerfaces*, 156, 9–18.

Bagtash, M. Yamini, Y. Tahmasebi, E. Javad, Z. & Dalirnasab, Z. (2016). Magnetite nanoparticles coated with tannic acid as a viable sorbent for solid-phase extraction of Cd(II), Co(II) and Cr(III). *Microchimica Acta*, 183(1), 449–456.

Chen, F., Liu, R., Xiao, S., & C Zhang. (2015). solvothermal synthesis in ethylene glycol and adsorption property of magnetic Fe_3O_4 microspheres. *Materials Letters*, *55(14)*, 38–42.

Danarto, Y. C. (2014). Pengambilan tanin dari kulit kayu bakau dan pemanfaatannya sebagai adsorben logam berat Cuprum (Cu) dan Timbal (Pb), *Ekuilibium*, 23–27.

El-kharrag, R., A. Amin, & Y.E. Greish. (2011). Low temperature synthesis of monolithic mesoporous magnetite nanoparticles. *Ceramics International, 38*(1), 627-534/

Fan, R. Min, H. Hong, X. Yi, Q. Liu, W. Zhang, Q. & Luo, Z. (2018). Plant tannin immobilized $Fe_3O_4@SiO_2$ microspheres: A novel and green magnetic bio-sorbent with superior adsorption capacities for gold and palladium. *Journal of Hazardous Materials*, 364, 780–790.

Kartikaningsih, D., A.B., M. A., & Danarto, Y. (2014). Pengambilan tanin dari kulit kayu bakau dan pemanfaatannya sebagai adsorben logam berat Cuprum (Cu) dan Timbal (Pb). *Ekuilibium*. 37–41.

Kemenkes, RI. (2017), *Buletin Kesehatan Lingkungan.* Jakarta: Kementrian Kesehatan RI.

Luo, H. Zhang, S. Li, X. Liu, X. Xu, Q. Liu, J., & Wang, Z. (2017). Tannic acid modified Fe_3O_4 core–shell nanoparticles for adsorption of Pb(II) and Hg(II). *Journal of the Taiwan Institute of Chemical Engineers, 72*, 163–170.

Lim, K. D. (2011). Structural characterization of mesoporous magnetite nanoparticles synthesized using the leaf extract of calliandra haematocephala and their photocatalytic degradation of malachite green dye. *Applied Nanoscience*, *8*(4), 675–683. http://dx.doi.org/10.1007/s13204-018-0698-8.

Madubuonu, N. Samson O. Aisidia, M. Ahmad, I. Botha, S. Zhao, T. Maaza, & M. Ezema, I. (2020). Bio-inspired Iron Oxide nanoparticles using psidium guajava aqueous extract for antibacterial activity. *Applied Physics A: Materials Science and Processing*, *126*(1).

Maylani, A., Sulistyaningsih, T., & Kusumastuti, E. (2016). Preparasi nanopartikel magnetit dan aplikasinya sebagai adsorben ion logam kadmium. *Indonesian Journal of Chemical Sciences*, *5*(2), 1–6.

Maity, D., & Agrawal, D. C. (2007). Synthesis of iron oxide nanoparticles under oxidizing environment and their stabilization in aqueous and non-aqueous media. *Journal of Magnetism and Magnetic Materials*, *308*, 46–55.

Morel, M., Martínez, F., & Mosquera, E. (2013). Synthesis and characterization of magnetite nanoparticles from mineral magnetite. *Journal of Magnetism and Magnetic Materials*, *343*, 76–81.

Pang, Z., & Nikpassand, M. (2020). Synthesis, characterization and application of Fe_3O_4@SiO_2@Tannic acid nanoparticles: A novel and magnetically recyclable catalyst for one-pot synthesis of novel 5-pyrazolin-1,2,4-triazolidine-3-ones (thiones). *Journal of Molecular Structure*, *542*, 21–30.

Rashid, M., Price, N. T., Pinilla, M. A., & O'Shea, K. E. (2017). Effective removal of phosphate from aqueous solution using humic acid coated magnetite nanoparticles. *Water Research*, *123*, 353-360

Simamora, P., & Krisna. (2015). Sintesis dan karakterisasi sifat magnetik nanokomposit Fe_3O_4-montmorilonit berdasarkan variasi suhu. *Prosiding Seminar Nasional Fisika (E-Journal) SNF 2015* (hal. 75-80).

Syauqiah, I., Amalia, M., & Kartini, H. A. (2011). Analisis variasi waktu dan kecepatan pengadukan pada proses adsorpsi limbah logam berat dengan arang aktif . *Info teknik, 12*(1), 11-20.

Teja, A. S. & Koh, P. (2009). Synthesis, properties , and application of magnetic iron oxide nanoparticles. *Progress in crystal growth and characterization of materials*, *55*, 22.