ADSORPTION OF Pb^{2+} USING HYDROXYAPATITE FROM TUNA BONES

Rizki Amalia Herawati¹, Mahidin² and Muhammad Faisal^{2,3,✉}

¹Balai Riset dan Standarisasi Industri Banda Aceh, Banda Aceh 23232, Indonesia

²Chemical Engineering Department, Faculty of Engineering, Universitas Syiah Kuala Darussalam, Banda Aceh 23111, Indonesia

³Halal Research Center, Universitas Syiah Kuala, Banda Aceh 23111, Indonesia

✉Corresponding Author: mfaisal@unsyiah.ac.id

ABSTRACT

This study aims to evaluate the performance of hydroxyapatite adsorbents from tuna bones to remove lead metal (Pb^{2+}). Hydroxyapatite was prepared through calcination at 700°C for 30 min. Adsorbents were prepared with and without H_3PO_4 activation. The adsorbents' surface structures were analyzed using SEM. Adsorption test was carried out using $\text{Pb}(\text{NO}_3)_2$ solution at 25-150 mg/L concentration, 30-150 min contact time and 100 rpm stirring. The results showed that the best adsorbent characteristics were obtained from the calcined activation and with H_3PO_4 . Contact time and initial concentration affected the adsorption capacity and efficiency. The Pb^{2+} adsorption equilibrium time was obtained at 90 min. with an initial concentration of 125 mg/L. The highest adsorption efficiency of Pb^{2+} was 96.11% with an adsorption capacity of 44.5 mg/g. The adsorption of Pb^{2+} followed the Langmuir isotherm model with the R^2 , Q_m , and K_L values of 0.995, 500 mg/g, and 5.5 L/mg respectively. The adsorption kinetics of the two adsorbates met the second-order pseudo equation with $R^2 = 0.998$. The kinetic parameters of Pb^{2+} adsorption was $K_2 = 0.033 \text{ g.mg}^{-1}.\text{min}^{-1}$ and $Q_e = 50 \text{ mg/g}$. In general, the results indicated that hydroxyapatite from tuna bone waste could be a promising alternative for lead metal adsorption.

Keywords: Tuna Bones, Hydroxyapatite, Adsorption, Lead Metal.

RASĀYAN J. Chem., Vol. 14, No.2, 2021

INTRODUCTION

Pollution from heavy metal liquid waste deteriorates the quality of soil, groundwater, rivers, ponds, lakes, and even oceans. Heavy metal liquid waste comes from various places including domestic use, agriculture, laboratories, and industrial activities, with the later as its biggest contributor. One of the heavy metals in industrial waste that many researchers are concerned about is lead (Pb^{2+}). Industries with Pb^{2+} as their by-product include those manufacturing piping materials, batteries, pigments, ammunition, and additive materials for gasoline.^{1,2} Pb^{2+} is both toxic and difficult to decompose in nature, making it dangerous to the environment and humans as it accumulates in the body.^{3,4} The maximum limit of Pb^{2+} content in drinking water is 0.015 mg/L⁵ and high Pb accumulation in the body causes various health problems including damages to the kidneys, pancreas, brain, and liver.^{6,7}

Heavy metal in liquid waste has to be carefully treated by reducing or removing its hazardous properties.⁸ Methods that have been developed to reduce Pb^{2+} in wastewater include activated carbon adsorption, ion exchange, precipitation, membrane filtration, reverse osmosis, and stabilization.⁹ Adsorption is a technique frequently used to remove Pb^{2+} due to its high effectiveness, low cost, and easy application.¹⁰ Adsorbents used in the adsorption of heavy metal waste include bentonite, biomass cells, activated carbon, clay, zeolite, and rock.¹¹⁻¹⁶ In addition, hydroxyapatite ($\text{Ca}_5(\text{PO}_4)_3\text{COH}$), which is a material containing a hydroxyl group (OH^-), can be used as ion exchange and adsorbent of heavy metal ions.¹⁷⁻²⁰

One material containing hydroxyapatite is fish bones.²¹ The content of inorganic substances in fish bones reaches 60 to 70%, with a tendency in the form of hydroxyapatite and calcium phosphate.²² A study by Zayed et al.²³ on adsorption of Pb^{2+} using hydroxyapatite adsorbent from mullet fish bones activated with acrylic acid found that the maximum adsorption capacity was 855 mg/g at an initial concentration of 300-1000 mg/L and pH 5.

Hydroxyapatite has also been used to remove cadmium metal with 86.28% efficiency and 44.62 mg/g adsorption capacity obtained at 150 min of contact time and 100 mg/L initial concentration.²⁴ Materials containing hydroxyapatite can remove heavy metals, thus making it a choice in the attempts to overcome the problem of heavy metal pollution.²⁵

This study aims to investigate the use of hydroxyapatite from tuna bone waste as a Pb^{2+} adsorbent. The effect of adsorption time and adsorbate concentration on adsorption efficiency was also examined. Finally, this study evaluates the equilibrium isotherms (Langmuir, Freundlich, and Temkin) and adsorption kinetics of the Pb^{2+} adsorption process using hydroxyapatite adsorbents.

EXPERIMENTAL

Hydroxyapatite was prepared from tuna bones through a calcination process. Tuna bones were washed, boiled (to remove dirt), and dried in an oven at 105°C for one hour. 500 grams of dried tuna bones were then calcined using a furnace (F6000 - Thermolyne) at 700°C for 30 minutes. Hydroxyapatite was then mashed to around 100 mesh. Furthermore, a refinement to make it nano-sized was carried out using a ball mill (pulverisette 6 - Fritsch) for ten hours. Chemical activation was carried out by adding 6M H_3PO_4 into hydroxyapatite with an activator and hydroxyapatite mass ratio of 10:1, heating it at 90°C, adding it with 1M NaOH to pH 10, then leaving it for 24 hours. The activated hydroxyapatite adsorbent was then washed in distilled water to the neutral pH. The adsorbent was then characterized using FTIR (Fourier-transmitting Infrared Spectroscopy) (Prestige 21 - Shimadzu), while morphological analysis was carried out on SEM (Scanning Electron Microscopy). The adsorption process was carried out by contacting 0.1 gram of hydroxyapatite adsorbent with $\text{Pb}(\text{NO}_3)_2$ solution in batches in a glass beaker at $\text{Pb}(\text{NO}_3)_2$ initial concentration of 25, 50, 75, 100, 125 and 150 mg/L, 100 rpm stirring, and contact times of 30, 60, 90, 120 and 150 minutes. The Pb concentration after adsorption was analyzed on an atomic adsorption spectrophotometer (AAS - 6300, Shimadzu).

RESULTS AND DISCUSSION

Morphological Analysis of Hydroxyapatite Adsorbent

The surface shapes of the hydroxyapatite adsorbent prepared from tuna bones through calcination at 700°C, both with and without chemical activation and after being analyzed by SEM, are presented in Fig.-1.

Fig.-1: Morphology of Adsorbent Hydroxyapatite (a) Calcination at 700°C without Chemical Activation, (b) Calcination at 700°C with Chemical Activation.

In Fig.-1(a and b), the hydroxyapatite adsorbent shows empty spaces or pores that will become a transportation pathway for Pb^{2+} adsorption process.^{26,27} In general, the resulting surface morphology of the hydroxyapatite adsorbent was identified to have irregular textures, different structures, fibrous, and porous. This characteristic is consistent with a previous study by Sheha et al.¹⁸ on nano-hydroxyapatite that such a shape enabled hydroxyapatite adsorbents to pull metal ions.

Adsorption Performance Test

Pb^{2+} adsorption efficiency of hydroxyapatite adsorbents

The effect of contact time on the adsorption efficiency of Pb^{2+} at various initial concentrations is presented in Fig.-2. The highest adsorption efficiency was 96%, obtained at 25 mg/L initial concentration, 150 minutes contact time, and with chemical activation (H_3PO_4) added to the adsorbent. Observations

found that the longer the contact time the higher Pb^{2+} metal adsorption would be until it reached equilibrium time. The diminishing removal efficiency was due to the disproportional numbers of ions absorbed to those available in the adsorbate so that the adsorbent surface reached its saturation point and the adsorption efficiency decreased.¹⁸

Fig.-2: The Effect of Contact Time on the Adsorption Efficiency of Pb^{2+}

Different initial Pb^{2+} concentrations affected the adsorption efficiency. As concentration got higher, the adsorption efficiency tended to be static or even decrease. The effect of initial concentration on Pb^{2+} adsorption efficiency at various contact times can be seen in Fig.-2.

Fig.-3 indicated a tendency that at an initial concentration of 25 mg / L, the efficiency adsorption of Pb^{2+} is higher than at the other initial concentrations. This is because the higher the adsorbate concentration, the more the empty spaces in the adsorbent are filled so that it affects the adsorbate adsorption.²⁶ At 150 minutes contact time, the adsorption efficiency values were 96, 59, 64, 51, 43 and 33% for the initial concentrations of 25 50, 75, 100, 125 and 150 mg/L. Compared to the variable without H_3PO_4 activation, the one with H_3PO_4 activation had higher adsorption effectiveness. That is because the treatment (the addition of chemical activation (H_3PO_4) to the adsorbent) widened the pore surface area so that more Pb^{2+} were adsorbed. The ability of hydroxyapatite to adsorb Pb in this study was higher than that in previous studies using charcoal from the *Cordia Macleodii* tree activated with sodium dodecylbenzenesulfonate.²⁸

Fig.-3: The Effect of Initial Concentration on Pb^{2+} Adsorption Efficiency at Various Contact Times

Pb^{2+} Adsorption Capacity of Hydroxyapatite Adsorbents

The result of the effect of contact time on the adsorption capacity of Pb^{2+} by hydroxyapatite adsorbent can be seen in Fig-4. As seen in Fig-4, as contact time increases, the adsorption capacity increases until it reaches equilibrium time. The highest adsorption capacity of 44.53 mg/g was reached at the 90-minute contact time, with an initial concentration of 125 mg/L and the addition of H_3PO_4 activation into the adsorbent. This value was higher than the adsorption of Pb^{2+} using adsorbent from telescopes nail and

mangrove crab shell powder with a maximum adsorption capacity of about 9.5-9.9 mg/g.²³ In Pb^{2+} adsorption with initial concentrations of 25, 50 and 75 mg/L, the adsorption capacity tended to increase until the 150th minute, but that with initial concentrations of 100, 125 and 150 mg/L, the adsorption capacity after 90 minutes tended to be static, even decreases. That is because as the contact time of adsorption, the adsorbent will experience stagnation and is unable to adsorb more adsorbents.³⁰

Fig-4: The Effect of Contact Time on the Adsorption Capacity of Pb^{2+} by Hydroxyapatite Adsorbent

The observation result in the effect of Pb^{2+} initial concentration on adsorption capacity is presented in Fig-5.

Fig-5: The Effect of Pb^{2+} Initial Concentration on Adsorption Capacity

As shown in Fig.-5, as the initial concentration increases, Pb^{2+} adsorption goes up until it reaches an equilibrium, so that the adsorption capacity becomes static and even tends to decrease. This is because metal ions compete with one another to occupy the adsorbent, and once it is filled, the ions will be released back to the adsorbent surface.

A study by Ain et al.³¹ using hydroxyapatite nanoparticles impregnated magnetic bentonite found the maximum adsorption capacity of 404.56 mg/g, which was higher than that in this study. The different preparation methods made the adsorption capacity in the previous study higher.

Adsorption Isotherm

The calculation of Pb^{2+} adsorption isotherm is an illustration to find out the equilibrium of the adsorption process using hydroxyapatite adsorbent from tuna bones. The evaluation was carried out through the adsorption isotherm tests, namely, Langmuir, Freundlich, and Temkin. The Langmuir isotherm is obtained by plotting the relationship curve between $1/Q_e$ and $1/C_e$ while the Freundlich isotherm by making the relationship curve between $\log Q_e$ and $\log C_e$. Meanwhile, the Temkin isotherm is obtained by plotting a relationship curve between Q_e and $\ln C_e$.

Pb²⁺ Adsorption Isotherm

The results of calculations using the Langmuir, Freundlich, and Temkin isotherm models can be seen in Fig.-6(a-c).

Fig.-6: Model Isotherm (a) Langmuir,(b) Freundlich(c) Temkin

The calculation results show that the correlation factor value (R^2) closest to one (1) in Pb²⁺ adsorption was the Langmuir isotherm model. The R^2 value in the Langmuir isotherm model was the highest compared to that in both Freundlich and Temkin isotherms, that is, 0.995. The Langmuir isotherm was also suitable for Pb²⁺ adsorption using hydroxyapatite-coated³² and palm kernel shells³³ activated carbon. However, this result differs from previous studies using hydroxyapatite-Fe₃O₄-bentonite composite, where the Freundlich isotherm is more suitable in the adsorption of lead metal.²⁵ In the Langmuir isotherm model, the maximum distribution rate in one layer (monolayer) of the adsorbate molecule is on the surface of the adsorbent and there is no adsorbate transmigration in the surface plane.⁹ The assumption used in the Langmuir isotherm model is that adsorption only occurs in one layer so that the interaction between adsorbent and adsorbate is quite weak.²⁵ This shows that one adsorbate molecule can only be adsorbed by one active site on the surface of the adsorbent. Chemical and physical bonds can occur between adsorbent and adsorbate. With strong bonds, the adsorbed molecules will be kept across the surface. The active sites on the adsorbent surface on the Langmuir isotherm are homogeneous, meaning that the adsorbent can only adsorb one Pb²⁺ for each active site and that there is no interaction between Pb²⁺ on the adjacent active sites.⁹ The calculation of the isotherm constants in Pb²⁺ adsorption can be seen in Table-1.

Tabel-1: Isotherm Constants in Pb²⁺ Adsorption

Isotherm Constants		
Langmuir	Freundlich	Temkin
$Q_m \text{ (mg/g)} = 500$	$N \text{ (L/mg)} = 28.571$	$B \text{ (J/mol)} = 3.041$
$K_L \text{ (L/mg)} = 5.5$	$K_F \text{ (mg/g)} = 0.148$	$A_T \text{ (L/g)} = 16548.4$
$R^2 = 0.995$	$R^2 = 0.892$	$R^2 = 0.876$

This study confirms the adsorption study conducted by Utami et al.³⁴, using activated carbon from natural zeolite (by using the hydrothermal method) for Pb^{2+} adsorption. The results of the study followed the Langmuir isotherm where $Q_m = 181.81 \text{ mg/g}$, $K_L = 0.7639 \text{ (L/mg)}$ and $R^2 = 0.995$. The Q_m and K_L values in this study tended to be greater than the study conducted by Pap et al.⁹ This is probably due to the higher calcination temperature in this study (700°C) so that the adsorbent's surface area is wider. The adsorbent pore surface area which tends to be wider allows Q_m (maximum capacity of the monolayer) and K_L (Langmuir isotherm constant) to tend to be greater.²²

Adsorption Kinetics

The mathematical model of adsorption kinetics aims to determine the rate of Pb^{2+} adsorption by hydroxyapatite adsorbents. When the adsorption process takes place, the determination of the adsorption kinetics is described through concentration as a function of time. This research used the approach of first and second-order empirical pseudo models.

Fig.-7: The First (a) and Second-order (b) Kinetic Pseudo Models on Pb^{2+} Adsorption by Hydroxyapatite.

The first and second-order kinetic pseudo models on Pb^{2+} adsorption by hydroxyapatite can be seen in Fig.-7. The experimental Q_e value obtained was 41.30 mg/g . Meanwhile, the Q_e , K , and R^2 values from the calculation results can be seen in Table-2. The pseudo-second-order has a Q_e value closer to the experimental Q_e than the pseudo-first-order does. The pseudo-second-order was more suitable to describe the kinetics of Pb^{2+} adsorption by hydroxyapatite adsorbents. Table-2 presents the values of the kinetic parameters of Pb^{2+} adsorption by hydroxyapatite.

Tabel-2: Kinetic Parameters of Pb^{2+} Adsorption by Hydroxyapatite.

Pseudo First Order			Pseudo Second Order		
$K_1(\text{min}^{-1})$	$Q_e \text{ (mg/g)}$	R^2	$K_2 \text{ (g.mg}^{-1}.\text{min}^{-1})$	$Q_e \text{ (mg/g)}$	R^2
0.021	22.56	0.931	0.033	50	0.998

The results of adsorption kinetics in this study were close to the previous study⁹ using activated carbon from the cherry kernel on Pb^{2+} metal adsorption. The results of that study showed that the Q_e value was almost the same as the value in this study and its kinetics followed the pseudo-second-order. However, the adsorption capacity and adsorption rate of the current study were higher.

CONCLUSION

The maximum Pb^{2+} adsorption efficiency of 96.11% and its adsorption capacity of 44.53 mg/g was achieved through the adsorbate's 125 mg/L initial concentration, 90 minutes contact time, 700°C adsorbent calcination and H_3PO_4 activation. Three isotherm equilibrium models (Langmuir, Freundlich, and Temkin) have been evaluated, showing that the Langmuir model was more suitable for lead metal adsorption using hydroxyapatite from tuna bones. The results of Pb^{2+} adsorption isotherm followed the Langmuir isotherm model, with $R^2 = 0.995$, $Q_m = 500 \text{ mg/g}$, and $K_L = 5.5 \text{ L/mg}$. The calculation results of Pb^{2+} adsorption kinetics followed the second-order pseudo equation, with the R^2 , K_2 , and Q_e values of 0.998, $0.033 \text{ g.mg}^{-1} \text{ min}^{-1}$, and 50 mg/g respectively.

ACKNOWLEDGEMENT

The authors acknowledge Universitas Syiah Kuala and the Ministry of Research and Technology for funding and provided research facilities.

REFERENCES

1. R.Verma and P. Dwivedi, *Recent Research in Science and Technology*, **5(5)**, 98(2013)
2. A. T. Paulino, M. R.Guilherme, A. V.Reis,E. B.Tambourgi, J. Nozaki, E. C. Muniz, *Journal of Hazardous Materials*,**147(1-2)**, 139(2007), [DOI:10.1016/j.jhazmat.2006.12.059](#)
3. J. K.Bediako, W. Wei, Y. S. Yun, *Journal of Industrial and Engineering Chemistry*, **43**, 61(2016), [DOI:10.1016/j.jiec.2016.07.048](#)
4. O. K. Ince, M. Ince, V. Yonten, A. Goksu, *Food Chemistry*, **214**, 637(2017), [DOI:10.1016/j.foodchem.2016.07.117](#)
5. Guidelines for Drinking Water, US Environmental Protection Agency (US EPA), 2001.
6. Y.Zhou, L. Zhang, , Z. Cheng, *Journal of Molecular Liquids*, **212**,739(2015), [DOI:10.1016/j.molliq.2015.10.023](#)
7. M. K.Sahu, S. Mandal, S. S. Dash, P. Badhai, R.K. Patel, *Journal of Environmental Chemical Engineering*, **1(4)**, 1315(2013), [DOI:10.1016/j.jece.2013.09.027](#)
8. P.Lu, Q. Feng, Q. Meng, T.Yuan,*Separation and Purification Technology*, **98**, 216(2012), [DOI:10.1016/j.seppur.2012.07.010](#)
9. S. Pap, J. Radonić, S. Trifunović, D. Adamović, I. Mihajlović, M. V. Miloradov, M. T. Sekulić, *Journal of Environmental Management*, **184(2)**, 297(2016), [DOI:10.1016/j.jenvman.2016.09.089](#)
10. M.Baláž, Z. Bujňáková, P. Baláž, A. Zorkovská, Z. Ková, J. Briančin, *Journal of Colloid and Interface Science*, **454**, 121(2015), [DOI:10.1016/j.jcis.2015.03.046](#)
11. M. Faisal, Jurnal Teknik Kimia USU, **4(1)**, 20 (2015), [DOI:10.32734/jtk.v4i1.1455](#)
12. R. Raihan, A. Setiawan, L.Hakim, Muhammad, M. Arif, H. Hosseiniamoli, *Jurnal Rekayasa Kimia dan Lingkungan*, **15(2)**,104 (2020), [DOI:10.23955/rkl.v15i2.17618](#)
13. M. Faisal, Abubakar, S.P. Kelana, D.E. Nanda, H. Daimon, *International Journal on Advanced Science, Engineering and Information Technology*, **10(6)**, 2560(2020), [DOI:10.18517/ijaseit.10.6.8037](#)
14. A. Gani, M. Faisal, *Rasayan Journal of Chemistry*, **13 (3)** 1451(2020), [DOI:10.31788/RJC.2020.1335872](#)
15. M.Faisal, A.Gani, A. Muslim, *International Journal of GEOMATE*, **17 (64)**, 252(2019), [DOI:10.21660/2019.64.93855](#)
16. M. Faisal, A. Gani, Abubakar, *International Journal of GEOMATE*, **15(48)**, 143(2018), [DOI:10.21660/2018.48.28153](#)
17. N. A.Medellin-Castillo, R. Leyva-Ramos, E. Padilla-Ortega, R. O. Perez, J. V. Flores-Cano, M. S. Berber-Mendoza, *Journal of industrial and Engineering Chemistry*, **20(6)**, 4014(2014), [DOI:10.1016/j.jiec.2013.12.105](#)
18. R. R. Sheha, S. I., Moussa, M. A, Attia, S. A. Sadeek, H. H.Someda, *Journal of Environmental Chemical Engineering*, **4(4)**, 4808(2016),[DOI:10.1016/j.jece.2016.11.005](#)
19. K.Lin, J. Pan, Y. Chen, R. Cheng, X. Xu, *Journal of Hazardous Materials*, **161(1)**, 231(2009), [DOI:10.1016/j.jhazmat.2008.03.076](#)
20. Y.Feng, J. L. Gong, G. M. Zeng, Q. Y. Niu, H. Y.Zhang,C. G.Niu, M.Yan, *Chemical Engineering Journal*, **162(2)**, 487(2010), [DOI:10.1016/j.cej.2010.05.049](#)
21. S.Santhosh andB. S.Prabu, *Materials Letters*, **97**, 121(2013),[DOI:10.1016/j.matlet.2013.01.081](#)
22. N. H. Herpandi, A.Rosma, N. W. A. Wan, *Comprehensive Reviews in Food Science and Food Safety*, **10(4)**, 195(2011),[DOI:10.1111/j.1541-4337.2011.00155.x](#)
23. E. M. Zayed, H. H. Sokker, H. M. Albishri, A. M. Farag, *Ecological Engineering*, **61**, 390(2013), [DOI:10.1016/j.ecoleng.2013.09.010](#)
24. R. A. Herawati, M. Faisal, Mahidin, In IOP Conference Series: Materials Science and Engineering,**845(1)** p. 012025. IOP Publishing, (2020) [DOI:10.1088/1757-899X/845/1/012025](#)
25. A.Kamari,N. Yusof, F. C.Isbak, E.Philip, G.Yuliani, (2014), In Proceeding of International

Conference On Research, Implementation and Education Of Mathematics And Sciences, Yogyakarta State University, **C(1)**,1-8.

26. S. B.Chen, Y. B.Ma, L.Chen, K.Xian, *Geochemical Journal*, **44(3)**, 233(2010), DOI:10.2343/geochemj.1.0065
27. S., Hokkanen, A. Bhatnagar, E.Repo,S. Lou, M.Sillanpää, *Chemical Engineering Journal*, **283**, 445(2016), DOI:10.1016/j.cej.2015.07.035
28. A. K.Wanjari andU. E. Chaudhari, *Rasayan Journal of Chemistry*, **10(1)**,82(2017), DOI:10.7324/RJC.2017.1011556
29. H.Darmokoesoemo, P. T. Magdhalena, H. S. Kusuma, *Rasayan Journal of Chemistry*, **9(4)**, 680(2016)
30. M.Iqbal, N.Iqbal, I. A. Bhatti, N.Ahmad, M. Zahid, *Ecological Engineering*, **88**, 265(2016),DOI:10.1016/j.ecoleng.2015.12.041
31. Q. U.Ain, H.Zhang, M. Yaseen, U.Rasheed, K. Liu, S. Subhan, Z. Tong, *Journal of Cleaner Production*, **247**, 119088(2020), DOI:10.1016/j.jclepro.2019.119088
32. Y.Long, J.Jiang, J.Hu, X.Hu, Q.Yang, S. Zhou, *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, **577**, 471(2019),DOI:10.1016/j.colsurfa.2019.06.011
33. M. Faisal, A.Gani, Z.Fuadi, *International Journal of GEOMATE*, **20 (78)**, 81(2021), DOI:10.21660/2021.78.6135
34. A.R.Utami, S.Sugiarti, P.Sugita, *Rasayan Journal of Chemistry*, **12(2)**, 650(2019), DOI:10.31788/RJC.2019.1222056

[RJC-6141/2020]