Comparison the Adsorption of Pb with Ecofriendly Bio-Adsorbent from Rice Husk Ash and Boiler Fly Ash

Enda Rasilta Tarigan¹, Anna Angela Sitinjak^{1*}, Meriahni Silalahi¹, Switamy Angnitha Purba¹, Yenny Sitanggang, Darry Purba¹

¹Politeknik Teknologi Kimia Industri Medan, Medan, 20228 Indonesia *Corresponding Author: annaangelasitinjak@yahoo.co.id

(Received 10-09-2023; Revised 16-11-2023; Accepted 29-11-2023)

Abstract

The amount of environmental pollution is in line with the increasing of industry. Industry can generate waste in the form of solid, liquid or gas. Utilization of waste as an adsorbent is a solution that can be done in dealing with waste such as metal waste contained in water. Therefore, this research aims to make a bio-adsorbent in the form of silica from rice husk ash and boiler fly ash and know the comparison of the Pb absorbed. The research method used is an experimental method by synthesizing the manufacture of silica. Then testing of Pb based on contact time was 30 minutes, 60 minutes, 90 minutes and 120 minutes. The results showed that the two silica-based bio-adsorbents could adsorb Pb. Bio-adsorbent from rice husk ash absorbed 56.51% of Pb in 30 minutes, 52.93% in 60 minutes, 48.65% in 90 minutes and 43.55% in 120 minutes. The bio-adsorbent from the fly ash boiler absorbed 50.15% of Pb in 30 minutes, 38.48% in 90 minutes and 36.45% in 120 minutes. Bio-adsorbent from rice husk ash absorbs more Pb ions than from boiler fly ash. Because the silica in the rice husk ash forms a collection in the pores, whereas in the fly ash boiler there is silica that is spread out.

Keywords: Bio-adsorbent, Fly ash boiler, Rice husk ash, Waste

1 Introduction

The increased industrial development actually causes high waste or environmental pollution problems [1]. The boiler combustion process from the palm oil processing industry produces various waste products, one of which is fly ash [2-4]. Fly ash is a large amount of solid waste and is simply thrown away or piled up in industrial areas. Likewise with the waste from the rice milling industry, in the form of rice husk ash. Boiler fly ash



and rice husk ash can cause problems for the environment [5], such as by accumulation and when it rains it can be carried into waters so that the water is polluted and the quality of the ecosystem decreases, and disrupts breathing [6,7].

Apart from air and solid waste, environmental pollution also occurs from liquid waste. Water is more often polluted by inorganic components. Initially, liquid waste started from household waste, then developed from industrial activity sources. It is because the industry does not process waste optimally. The content of these metals can be toxic to living things. Because the life cycle of living creatures is very dependent on water, indirectly, living creatures may consume polluted water [8]. The importance of water for the survival of living things is our main task in maintaining water quality.

The utilizing waste into a product is one way to deal with the waste produced, one of which is by turning it into an adsorbent [9]. Adsorbents are solid substances that can absorb certain components in a solution. Adsorbents usually use materials that have pores or at certain locations within the particle. In general, these pores are small so that their surface area becomes larger than the outer surface. Separation occurs due to differences in molecular weight or differences in polarity, which cause some molecules to stick more tightly to the surface than other molecules. In the adsorption process, many factors can influence the rate of the adsorption process and the amount of adsorbate that can be absorbed. The factors that influence the adsorption process [10] are agitation, adsorbent characteristics, adsorbent pore size and contact time. The activating materials used in activating the adsorbent are like NaOH and HCl. Activating ingredients function to degrade or hydrate organic molecules during the process, limiting tar formation and assisting the decomposition of organic compounds during subsequent activation.

Various research has been carried out in dealing with waste. Tandung, Nur and Mardiah [11] researched the effect of boiler ash as an absorption agent and used as an air cathode by analyzing it mathematically (multiple linear regression model). Nurhasni [12] found that the absorption of Cd and Cr metal ions in wastewater can be using rice husks. From the results of previous studies were stated that boiler fly ash and rice husk ash could be modified and useful in absorbing liquid waste.

Boiler fly ash and rice husk ash have similarities in terms of the main compounds in the cell walls, namely polysaccharides (coarse fibre or cellulose, lignin and hemicellulose) which have hydroxyl groups that can play a role in the adsorption process, so in this study used oil palm boiler fly ash and rice husk ash as an active metal bioadsorbent in liquid waste as an effort to tackle wastewater pollution and in which the differences between the two will be seen in terms of their ability to absorb Pb based on contact time.

2 Material and Methods

Materials

The materials used in this research are NaOH NaOH for analysis Merck, HCl 37 % Merck, DI water, double distilled water, Pb(NO₃) for analysis Merck, boiler fly ash, rice husk ash.

Instrumentation

Rice husk ash and boiler fly ash were characterized by SEM-EDX JEOL JSM-6510LA, FTIR Perkin-Elmer UATR Spectrum Two, AAS.

Methods

Synthesis SiO₂ from Palm Oil Boiler Fly Ash.

Fly ash from palm oil mill waste is calcined at a temperature of 500 °C for 5 hours, Fly Ash is mixed with 5M HCl with a ratio of 1:4, stirred and heated at a temperature of 70 °C for 4 hours using a magnetic stirrer with a rotation speed of 300 rpm, then the solution was filtered to obtain the precipitate. The fly ash precipitate formed was added with NaOH in a ratio of 1:4 for 4 hours at a temperature of 70 °C and stirred with a magnetic stirrer at a rotation speed of 300 rpm for 8 hours and silica powder was formed. Next, washed with distilled water until the pH was neutral and dried in an oven at 105 for 2 hours. Hydrothermal for 8 hours at 180°C. Furthermore, silica powder was interacted with Pb ions with a mass of 1 gram of silica powder and varied the contact time of the adsorbent with Pb and tested with AAS.

Synthesis SiO₂ from Rice Husk Ash

Rice husk ash from palm oil mill waste is calcined at a temperature of 500 °C for 5 hours, rice husk ash is mixed with 5M HCl at a ratio of 1:4, stirred and heated at a

temperature of 70 °C for 4 hours using a magnetic stirrer with a rotation speed of 300 rpm , then the solution was filtered to obtain a precipitate. The rice husk ash precipitate that was formed was added with NaOH at a ratio of 1:4 for 4 hours at a temperature of 70°C and stirred with a magnetic stirrer at a rotation speed of 300 rpm for 8 hours and silica powder was formed. Furthermore, it was washed with distilled water until the pH was neutral and dried in an oven at 105 for 2 hours. Hydrothermal for 8 hours at 180 °C. Furthermore, silica powder was interacted by SEM/EDX to determine surface morphology. Next, the silica powder was interacted with Pb ions with a mass of 1 gram of silica powder and varied the contact time of the adsorbent with Pb and tested with AAS.

Testing of Bio-Adsorbent on Pb Metal

A concentration of 1000ppm of Pb metal was prepared by dissolving 1.56gr of PbNO₃ in 1000mL of DI water. Rice husk bio-adsorbent was weighed as much as 1 gr and put into 100 mL of PbNO₃ solution and stirred at 300rpm with variations in contact time of 10 minutes, 20 minutes, 30 minutes, 60 minutes and 120 minutes. Doing the same thing to the bio-adsorbent made from fly ash boiler.

3 Results and Discussions

The initial concentration of Pb metal was 1000 mg/L. Table 1 below shows the concentration of Pb metal left in the solution after contact with samples of rice husk ash and fly ash with a sample mass of 1 gram.

Contact No Time (Minute)		Concentration of Pb metal remaining after contact with the rice husk ash sample which was activated physically and chemically (mg/L)	Concentration of Pb metal remaining after contact using fly ash which is activated physically and chemically (mg/L)	
1	30	434,9190	498,4790	
2	60	470,7070	557,1720	
3	90	513,4530	615,1210	
4	120	564,4800	635,5050	

Table 1. The Remaining Pb Metal Concentration in Solution

From the research results it was found that after being contacted for 30 minutes, 60 minutes, 90 minutes and 120 minutes, absorption of Pb metal occurred in both bioadsorbents. This means that rice husk ash silica and boiler fly ash can absorb Pb metal in water and can be used as an adsorbent that is environmentally friendly because it does not dissolve easily in water [13-15].

FTIR characterization in this study was only carried out on rice husk ash which had absorbed Pb, to determine the main functional groups. The FTIR results of rice husk ash silica are shown in the Fig. 1.

The results of the Fourier Transform Infra-Red (FTIR) Spectrum show that the O-H (Stretching) functional group has an absorption band of around 3325.04 [16] and O-H sending around 1637.64 [17]. In the figure above, the silica functional group is no longer visible. In the adsorption of Pb, ion exchange occurs where silica containing silanol (Si-OH) and Siloxane (Si-O-Si) functional groups are bonded with certain metal ions, in this case Pb ions [18]), so that level of Pb in water decrease.

The comparison of absorption results between bio-adsorbent from rice husk ash and boiler fly ash, it can be seen that the optimum contact time for the absorption of Pb is around 30 minutes, after which there is a decrease in the absorption of both bio-adsorbents. Because the longer the two bio-adsorbents are in contact with Pb, the bonding between the H^+ ions in the solution and the hydroxyl groups in cellulose to form OH_2^+

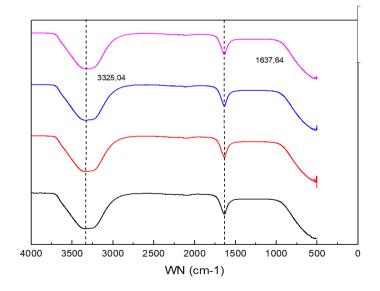


Figure 1. Test Result of FTIR

17

increases, resulting in rejection of the metal ions so that the pores of the bio-adsorbent become saturated and absorption decreases. This is in line with the research of Mujiyanti, Nurmasari and Nurhikmah [19] which states that the optimum time of absorption for Pb is about 30 minutes. From the graph it is also found that the highest absorption of Pb is bio-adsorbent from rice husk ash at 43% to 57%, while in boiler fly ash it is between 36% to 50%.

ZAF Method Standardless Quantitative Analysis(Oxide) Fitting Coefficient : 0.0382 Total Oxide : 24.0									
Element K	(keV)	Mass ⁸	Sigma	Mol%	Compound	Mass%	Cation		
к СК 2.9069	0.277	11.04	0.33	39.02	С	11.04	0.00		
0		45.24							
Mg K 0.7126	1.253	0.44	0.05	0.78	MgO	0.74	0.16		
Si K 84.5326	1.739	37.68	0.46	56.94	SiO2	80.62	11.39		
P K 1.1617	2.013	0.76	0.10	0.52	P205	1.74	0.21		
к к 9.5541	3.312	4.31	0.10	2.34	K20	5.20	0.94		
Mn K	5.894	0.51	0.07	0.40	MnO	0.66	0.08		
1.1320 Total		100.00		100.00		100.00	12.77		

Table 2. Physically activated rice husk composition (Test results with EDX)

Table 3. Physicall	y activated Fly ash	a composition (Test re	esults with EDX)
--------------------	---------------------	------------------------	------------------

ZAF Method Standardless Quantitative Analysis(Oxide) Fitting Coefficient : 0.0326								
Total Öxide : 24.0								
Element K	(keV)	Mass ⁸	Sigma	Mol%	Compound	Mass%	Cation	
C K	0.277	14.41	0.34	45.73	C	14.41	0.00	
4.0288	0.277	14.41	0.54	43.75	C	14.41	0.00	
4.0200 O		39.63						
Na K	1.041	7.72	0.16	6 40	Na2O	10.41	3.25	
14.6926	1.011	1.12	0.10	0.10	Mazo	10.11	5.25	
Mq K	1.253	0.37	0.05	0.59	MqO	0.62	0.15	
0.5482					5-			
Al K	1.486	1.19	0.08	0.84	A1203	2.25	0.43	
2.1237								
Si K	1.739	29.86	0.40	40.53	SiO2	63.88	10.30	
62.8020								
Cl K	2.621	1.89	0.05	2.04	Cl	1.89	0.00	
4.3513								
K K	3.312	1.75	0.06	0.85	К2О	2.11	0.43	
3.9540								
Ca K	3.690	3.17	0.10	3.02	CaO	4.44	0.77	
7.4994								
Total		100	.00	100	0.00	100	0.00 15.33	

From Table 2 and 3 regarding to the EDX test results, it is found that the SiO_2 content in rice husk ash is 80.62% and in boiler fly ash is 63.88%. From the table it also appears that the presence of carbon is 11.04% in rice husk ash and 14.41% in boiler fly ash. Then chemical treatment was added and the EDX results were obtained as listed in Tables 4 and 5.

From Table 4 and 5, it was found that silica in rice husk ash after physical and chemical activation was 79.53% and carbon 17.94%. Silica in the fly ash boiler after physical and chemical activation was 80.35% and carbon 17.02%. From result experimental, only given physical treatment (before chemical treatment) silica in rice husk ash was higher than boiler fly ash but carbon in rice husk ash was lower than boiler

ZAF Method Standardless Quantitative Analysis(Oxide) Fitting Coefficient : 0.0371									
Total Óxide : 24.0									
Element	(keV)	Mass ⁸	Sigma	Mol%	Compound	Mass ^{&}	Cation		
K			_		_				
СК	0.277	17.94	0.39	52.36	С	17.94	0.00		
5.2345									
0		42.93							
Mg K	1.253	0.30	0.04	0.44	MgO	0.50	0.11		
0.5259									
Si K	1.739	37.18	0.43	46.39	SiO2	79.53	11.84		
90.3234									
ΚK	3.312	0.89	0.05	0.40	К2О	1.07	0.20		
2.1286									
Cu K	8.040	0.76	0.10	0.42	CuO	0.95	0.11		
1.7876		100 00		100 00		100 00	10.00		
Total		100.00		100.00		100.00	12.26		

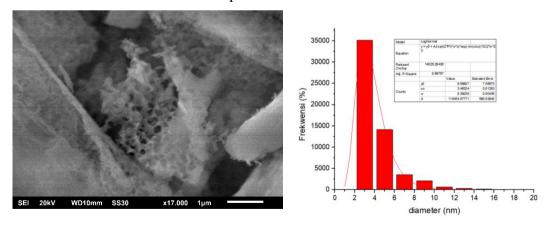
Table 4. Physically and chemically activated rice husk composition

Table 5. Summary of Physically and chemically activated rice husk composition

No	Sample	Parameter	Unit	Value of Analysis Result	Test Method
	SP 23-	С		17.02	
	1088-06- 01-1 (Ash Akt)	Na ₂ O		0.67	SEM/Jeol
1		SiO_2	%	80.35	Jsm 6510
1		K ₂ O		0.59	
		CaO		0.45	La
		CuO		0.91	

fly ash. After physical and chemical treatment, there was a decrease in silica in rice husk ash but the carbon content increased and was the highest compared to carbon fly ash, although there was an increase in silica and carbon content. The bio-adsorbent that is connected with Pb metal in water is a bio-adsorbent that has received physical and chemical treatment. This means that through the addition of chemical activation, it causes an increase in the carbon content, in which carbon helps or facilitates silica in the uptake of Pb metal. This is because physical and chemical activation forms pores so that they can effectively absorb various kinds of heavy metals. From this research, knowledge was obtained that if the adsorbent contains silica and carbon, the metal absorption can be higher. This is in line with previous research [20] that silica-activated carbon composites can be formed and have a greater adsorption capacity for heavy metals compared to silica and activated carbon itself.

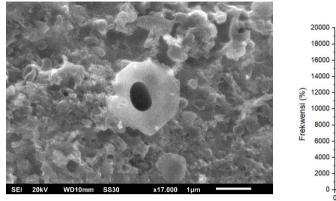
From the SEM test above to see the morphology or topography of the AKF ash samples from the Fig. 2(a) and 3(a). Fly Ash it shows that the morphology of the two samples is not homogeneous or has an uneven size distribution and algomerization is formed. By using the image J and Origin applications, pore diameters were obtained in both samples, namely around 3.43 nm (Fig. 2(b) for fly ash and 3.58 nm for rice husk Fig.3(b). The particle size of the active ash sample is larger than rice husk, indicating that the absorption capacity of rice husk is higher in adsorbing the active metal Pb which has an atomic radius of around 30 -300 pm.



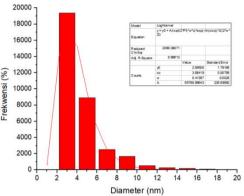
(a) Morphology of rice husk samples

(b) Particle size distribution of rice husk samples

Figure 2. Characterization results of rice husk samples that were physically and chemically activated using SEM



(a). Morphology of the physically and chemically activated boiler fly ash sample



b). Particle size distribution of fly ash

Figure 3. Characterization results of fly ash sample that were physically and chemically activated using SEM

The particle size distribution of the sample can be seen in the Fig. 2(a) rice husk and Fig. 3(b) is the fly ash. This particle size distribution can also show the absorption capacity of the active ash and active husk samples against the contact time, where as the contact time increases the adsorption of the metal Pb decreased, this was because the diameter of the sample particles, both active ash and active husk, was greater than the atomic radius of Pb.

4 Conclusions

Waste can be processed into products that can overcome the waste problem. Utilizing rice husk ash and boiler fly ash waste into bio-adsorbent in the form of silica can be done, especially since the price of these two bio-adsorbents is relatively cheap and does not dissolve easily in water. From the research it was found that both bio-adsorbents from rice husk ash and boiler fly ash can absorb Pb. Then, after physical and chemical activation, porous silica is formed and there is an increase in carbon. The silica in rice husk ash forms clusters that are visible from the morphology so that it binds Pb ions more strongly, whereas in boiler fly ash the silica is dispersed, plus the carbon content in rice husk ash is higher than boiler fly ash. For this reason, the ability to absorb Pb by bioadsorbents from rice husk ash is higher than boiler fly ash.

Acknowledgements

The researcher would like to thank PTKI Medan through the UPPM unit for the financial assistance provided so that this research could be carried out well.

References

- [1] A. F. Dashti, M. O. Fatehah, M. A. Zahed, "Waste management of the palm oil industry: present status and future perspective," *Journal of Enviironmental Engineering and Science*, vol. 17, no. 2, pp. 75-88, 2022.
- [2] J. J. P. Telaumbanau, "Using Fly Ash and Bottom Ash Boiler of Palm Oil Factories as Adsorbents for Adsorption of Color in Artificial Liquid Waste," *Jurnal Mekintek*, vol. 11, no. 2, pp. 59-67, 2020.
- [3] R.Y. Farandia, M. Olivia, L. Darmayanti, "Kinerja Beton High Volume POFA," *Jurnal Online Mahasiswa (JOM) Bidang Teknik dan Sains*, vol. 1, no. 1, 2015.
- [4] M. Liu, C. P. Chua, U. J. Alengaram, and M. Z. Jumaat, "Utilization of Palm Oil Fluel Ash as Binder in Lightweight Oil Palm Shell Geopolymer Concrete, "*Hindawi Publishing Corporation Advances Amterial Science and Engineering*, vol. 12, 2014.
- [5] S.K.S. Hossain, L.Mathur & P.K. Roy, "Rice Husk ash as an alternative source of silica in ceramics: a review," *Journal of Assian Ceramic Societies*, vol. 6, no. 4, pp. 299-313, 2018.
- [6] PTPN., Material Balance Pengolahan Kelapa Sawit. Pekanbaru, 2011.
- [7] M. Riyadi, "Pemanfaatn Abu Sekam Padi sebagai Substitusi Sebagian Semen pada Mortar Semen Pasir," *Politeknologi*, vol. 12, no. 5, pp. 39-46, 2013.
- [8] R. Pratiwi, D.P.S. Prinajati, "Adsorption for lead removal by chitosan from shrimp shells,"*Indonesian Journal of Urban and Environmental Technology*, vol. 2, no. 1, pp. 35-46, 2018.

- [9] S. Arita, D. Kristianti, L. N. Komariah, "Effectiveness of Biomass-Based Fly Ash in Pulp and Paper Liquid Waste Treatment," *South African Journal of Chemical Engineering*, vol. 41, pp. 79-84, 2022.
- [10] I. Syauqiah, M. Amalia, H. A. Kartini, "Analisis Variasi Wkatu dan Kecepatan Pengaduk pada Proses Adsorpsi Limbah Logam berat dengan Arang Aktif," *Info Teknik*, vol. 12, no. 1, pp. 11-20, 2011.
- [11] M.R. Tandung, S. Nur, Mardiah, "Utilization of Palm Boiler Ash as Air Catode Material in Air Aluminium Battery," *Jurnal Chemurgy*, vol. 4, no. 2, pp. 38-44, 2020.
- [12] Nurhasni, Penyerapan Ion Logam Cd dan Cr dalam Air Limbah Mneggunakan Sekam Padi, Tesis Universitas UIN Syarif Hidyatullah: Jakarta, 2014.
- [13] H. K., Okoro, S. M. Alao, S. Pandey, S. Jimoh, K. A. Basheeru, Z.Caliphs, J.C. Ngila, "Recent Potential Application of Rice Husk as an Eco-friendly adsorbent for removal of heavy metals," *Springer Applied Water Science*, vol. 12, no. 259, 2022.
- [14] P.S. Utama, R.Yamsaengsung, C. Sangwichien, "Silica Gel Derived from Palm Oil Fly Ash," *Songklanakarin J.Sci. Technol.*, vol. 40, no. 1, pp. 121-126, 2018.
- [15] Y. Poo-arporn, et al., "The Investigation of SiO₂ structure obtained from the combustion of rice husk", *International Conference on Engineering and Industrial Technology-IOP Publishing*, 2020,
- [16] N. P. S. N. Utari, I W. Sudiarta, dan P. Suarya, "Sintesis Dan Karakterisasi Silika Gel Dari Abu Vulkanik Gunung Agung Melalui Teknik Sol-Gel," *Jurnal Kimia* (*Journal of Chemistry*), vol. 14, no. 1, pp. 30-36, 2020.
- [17] F. Huang, H. Hao, W. Sheng, X. Lang, "Dye-TiO₂/SiO₂ assembly photocatalysis for blue light-initiated selective aerobic oxidation of organic sulphides," *Chemical Engineering Journal*, vol. 423, 2021.
- [18] I. S. Hardyanti, et al., "Pemanfaatan Silika (SiO₂) dan Bentonit sebagai Adsorben Logam Berat Fe pada Limbah Batik," *Jurnal Sains Terapan*, vol. 3, no. 2, pp. 37-41, 2017.
- [19] D. R. Mujiyanti, R. Nurmasari, Nurhikmah, "Adsorption Pb(II) on Silica Gel from Rice Husk Ash," *Sains dan Terapan Kimia*, vol. 10, no. 1, 33-38, 2016.

[20] M. H. Givianrad, M. Rabani, M. Saber-Tehrani, P. Aberoomand-Azar, M. Hosseini Sabzevari, "Preparation and characterization of nanocomposite, silica aerogel, activated carbon and its adsorption properties for Cd (II) ions from aqueous solution," *Journal of Saudi Chemical Society*, vol. 17, pp. 329-335, 2013.