ISSN: 3021-7636
International Journal of Science Technology and Health

Research Article
Vol. 2 (1), 2024, page 8-14
https://doi.org/10.63441/ijsth.v2i1.6

Performance Test of Residu Powder Distillation from Fermentation Result Cocoa Fruits (*Theobroma Cacao L.*) as Adsorbent For Metal Ions (Cr^{3+}, Fe^{3+}, Pb^{2+})

Kaharuddin Kaharuddin [1,*], Kurnia Sri Yunita [1], Muh. Edihar [1], Mawaddah Zaqinah Diah[1], Salniati Hade [2], Sapril Kartini [3]

1 Department of Chemistry, Faculty of Science Technology and Health, Institut Sains Teknologi dan Kesehatan (ISTEK) 'Aisyiyah Kendari, Kendari, 93116, Southeast Sulawesi, Indonesia
2 Department of Pharmacy, Akademi Kesehatan Konawe, 93418, Southeast Sulawesi, Indonesia
3 Department of Medical Laboratory Technology, Faculty of Science and Technology, Universitas Mandala Waluya, Kendari, 93231, Southeast Sulawesi, Indonesia

*Correspondence: kaharmr@gmail.com (K.K.)

Received: November 1, 2023	Accepted: January 02, 2023	Published: January 30, 2024

Abstract: Research this which is used as an adsorbent powder obtained through hydrolysis, fermentation and distillation of cacao fruit skin. This study aims to determine the ability of the cacao fruit skin powder to adsorb metal ions chromium (Cr^{3+}), iron (Fe^{3+}) and Lead (Pb^{2+}) with adsorbent mass variation. Adsorption is done on metal chromium (Cr^{3+}), iron (Fe^{3+}) and lead (Pb^{2+}) with three variations of the adsorbent mass of 0.25, 0.50 and 0.75 grams. The results showed that the performance of cacao fruit skin powder the most effective to metal ions lead (Pb^{2+}) with percent adsorption 97.70%, for metal ions iron (Fe^{3+}) with percent adsorption 94.33%, and crom (Cr^{3+}) metal ions with the percent adsorption was 89.71% with adsorbent mass of 0.75 grams.

Keywords: Cacao, adsorbent, metal ions, adsorption

1. Introduction

According to plantation statistics for the Province of Southeast Sulawesi, the cocoa commodity is able to achieve an average production of 119,160 tons per year, with an average rate of increase in production of 6.83% per year. In terms of the area of commodity development, indications were obtained that the development area of the cocoa commodity in Southeast Sulawesi in 2020 had reached 110 770 Ha. The more cocoa production increases, the more the amount of cocoa pod waste produced will also increase. The waste can be utilized to become something that has economic value. Cocoa shell is a lignocellulosic waste containing lignin, cellulose and hemicellulose.

Several studies inform that cocoa pod shell waste can be processed into animal feed, organic fertilizer and alcohol, while the cocoa pulp itself can be used as a metal adsorbent (sorbent). The main current in adsorbent research is the use of agricultural by-products as adsorbents for organic and inorganic compounds. Have also reported several agricultural byproducts that have potential as adsorbents, namely corn cobs, rice grain, soybean grain, cottonseed, straw, bagasse, and peanuts [1,2]. Used cocoa pod skin as an adsorbent for methylene blue dye from textile waste with an adsorption capacity of 1605.99 μg/g adsorbent [3]. Show that modified cellulose in corn cobs was able to adsorb methylene blue from textile waste with an adsorption capacity of 518.07 μg/g adsorbent [4]. The bagasse could adsorb methylene blue dye with an adsorption efficiency of up to 90% [5,6]. Adsorbents that are often used are activated carbon, zeolite and activated sludge [7]. Utilized activated charcoal from cocoa shell (Theobroma cacao L.) as an adsorbent for metal(II) ions [8,9,10]. The results of these studies indicate that agricultural waste containing lignin and cellulose can be further processed as an adsorbent and is expected to increase its added value

The adsorption method is a very efficient method for reducing heavy metal content. Therefore, the by-product (powder) of distillation from fermented cocoa pods can be used to reduce metal content. Adsorbents for waste containing Cr^{3+}, Fe^{3+} and Pb^{2+} metal ions at the same time, can be used in handling laboratory wastewater and waste from the nickel mining industry.

2. Materials and Methods

Materials used in this study included blenders, analytical balances, glass tools, reflux equipment, distillation equipment, and Atomic Absorption Spectroscopy (AAS). The materials needed are cocoa pod skin (Theobroma cacao L.) as the main raw material, HCl, NaOH, tape yeast (Saccharomyces sp), standard solutions of Chromium (Cr), Iron (Fe) and Lead (Pb) and Aquades.

This research method consists of 4 stages, namely hydrolysis, drying, distillation and adsorption. 1; The sample to be hydrolyzed is put in a beaker containing water and added HCl, then stirred until homogeneous, then put in a reflux flask, and heated for 1 day at a temperature of ±30 ^{0}C [11], 2; the sample is cooled and a starter is made with 1 gram of yeast mass at a volume of 10% of the volume of the sample to be fermented. The starter was made by taking 70 mL of sample and putting it into a beaker containing tape yeast (Saccharomyces sp) and leaving it in an open space for up to 24 hours. Starter is made to activate the growth of *Saccharomyces sp*, And then, the starter is put into the fermentation container and left for 7 days in a closed condition [12]. 3; sample into the distillation flask that has been assembled and then heated to the alcohol vapor temperature (controlled) and stopped when the temperature passes the alcohol vapor point, then the remaining residue in the flask consisting of air and residue (powder) is cooled. After cooling, filtering is carried out to filter out the water and residue (powder). The powder obtained from the results of filtering with an oven at a temperature of ± 50 ^{0}C will be used as a metal adsorbent [13]. 4; Adsorption was carried out with variations in mass, namely 0.25 grams, 0.5 grams and 0.75 grams (for each type of metal), then put into containers containing 10 ml of Chromium (Cr^{3+}), Iron (Fe^{3+}) metal solution each. and Lead (Pb^{2+}) with a concentration of 20 ppm for each metal that has been prepared and stirred for 30 minutes [14].

3. Results and Discussion

Based on the data in Table 1, the ability of the adsorbent to adsorb Cr^{3+} metal ions in the mass range of the adsorbent tested does not affect the percentage of adsorption. It is presumed that by varying the mass of the adsorbent in the range tested with a metal ion concentration of Cr^{3+} of 20 ppm, the ability of the adsorbent to be maximized. Although the mass of the adsorbent added will not increase the percentage of adsorption of Cr^{3+} metal ions. This is also supported by research conducted by [15] that the addition of adsorbent mass after optimal conditions shows that the adsorption capacity remains constant or tends to decrease. Table 2, the mass variation of the tested adsorbents is optimal and does not affect the percentage of adsorption of Fe^{3+} metal ions. It is presumed that from the addition of 0.25 gram of mass the adsorption conditions have been optimal so that changes in the increase in the mass of the adsorbent do not increase the percentage of adsorption. Table 3, variations in the mass of the adsorbent that were tried at an adsorption time of 30 minutes had no effect on the percentage of adsorption. It is suspected that the mass of the adsorbent is not proportional to the concentration of Pb^{2+} metal ions in the solution. Or in other words, the concentration of Pb^{2+} metal ions in solution is less than the active groups and adsorbent pores to adsorb Pb^{2+} metal ions.

The effect of adsorbent mass on the adsorption capacity of Pb^{2+} metal ions does not appear to be that different. This is probably due to the amount of Pb^{2+} metal ions in solution has been used up and the adsorbent active groups are still present for all variations of the adsorbent masses tested. Thus, even though the mass of the adsorbent is added, it will not affect the percentage of adsorption.

Table 1. Percent adsorption of Cr^{3+} metal ions

Adsorbent Mass (grams)	Contact Time (Minute)	C_0 metal ion (ppm)	C_e metal ion (ppm)	adsorbed (%)
		Cr^{3+}	Cr^{3+}	Cr^{3+}
0.25	30	20	2.3279	88.36
0.50	30	20	2.2131	88.93
0.75	30	20	2.0574	89.71

Table 2. Percent adsorption of Fe^{3+} metal ions

Adsorbent Mass (grams)	Contact Time (Minute)	C_0 metal ion (ppm)	C_e metal ion (ppm)	adsorbed (%)
		Fe^{3+}	Fe^{3+}	Fe^{3+}
0.25	30	20	1.1756	94.12
0.50	30	20	1.1463	94.27
0.75	30	20	1.1341	94.33

Table 3. Percent adsorption of Pb^{2+} metal ions

Adsorbent Mass (grams)	Contact Time (Minute)	C_0 metal ion (ppm) Pb^{2+}	C_e metal ion (ppm) Pb^{2+}	adsorbed (%) Pb^{2+}
0.25	30	20	0.4719	97.64
0.50	30	20	0.4649	97.68
0.75	30	20	0.4605	97.70

Table 4. Classification of acids and bases based on the HSAB concept

Hard Acid	Soft Acid
H^+, Li^+, Na^+, Be^{2+}, Mg^{2+}, Ca^{2+}, Sr^{2+}, BF^{3+}, $B(OH)_3$, AlH_3, $AlCl_3$, $AlMe_3$, CO_2, RCO^+, NC^+, Si^{4+}, CH_3Sn^{3+}, N^{3+}, Cl^{3+}, I^{5+}, I^{7+}, Al^{3+}, Sc^{3+}, Ga^{3+}, In^{3+}, La^{3+}, Cr^{3+}, Fe^{3+}, Co^{3+}, Ti^{4+}, Zr^{4+}, HF^{4+}	Cu^+, Ag^+, Au^+, Hg^+, CH_3Hg^+, Ti^+, Pd^{2+}, Pt^{2+}, Cd^{2+}, Hg^{2+}, BH_3, $GaMe_3$, $GaCl_3$, GaI_3, $InCl_3$, CH_3, Carbena, Br_2, I_2, Br^+, I^+, atom-atom logam
Medium Acid	
Fe^{2+}, Ru^{2+}, Os^{2+}, Co^{2+}, Rh^{3+}, Ir^{3+}, Ni^{2+}, Cu^{2+}, BMe_3, GaH_3, R_3C, $C_6H_5^+$, Sn^{2+}, Pb^{2+}, NO^+, Sb^{3+}, Bi^{3+}, SO_2	
Hard Base	**Soft Base**
CO_3^{2-}, $CH_2CO_2^-$, NH_3, RNH_2, N_2H_4, H_20, OH^-, ROH, RO^-, R_2O, F^-, Cl^-, NO_3^-, PO_4^{3-}, SO_4^{2-}, ClO_4^-	CO, CN^-, RNC, C_2H_4, C_6H_6, R_3P, $(RO)_3P$, R_3AS, $R_{2A}S$, RSH, H^-, R^-, I^-, SCN^-, S_2O_3
Medium Base	
N_2, N_3, NO_2^-, C_2H_5N, $C_6H_5NH_2$, Br^-	

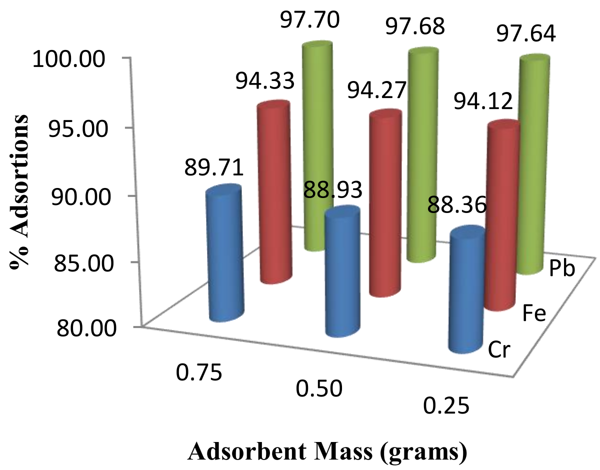

Figure 1. Comparison of the percentage of metal ion adsorption Cr^{3+}, Fe^{3+} and Pb^{2+}

Figure 1 shows that Pb^{2+} metal was adsorbed the most (97.70%), followed by Fe^{3+} metal (94.33%) and Cr^{3+} metal adsorbed the least (89.71%), with the same adsorbent mass of 0.75 gram. This shows that Pb^{2+} is more easily adsorbed than Fe^{3+} and Cr^{3+}. This difference is probably due to the match in the pore size of lignin as a polymer with the radius of the Pb^{2+} metal ion which is also larger when compared to the Fe^{3+} and Cr^{3+} ions. The suitability of the lignin pore size with the radius size of the Pb^{2+} metal ion causes metal ions that have been trapped into the pores to be trapped into the polymer. On the other hand, Fe^{3+} and Cr^{3+} ions which have smaller ionic radii than Pb^{2+} metal ions may be due to a mismatch between the ionic radii and the lignin pore size, so that the trapped Fe^{3+} and Cr^{3+} metal ions can come out again from the pore [16]. The interaction model of metal ions with active groups trapped in the polymer.

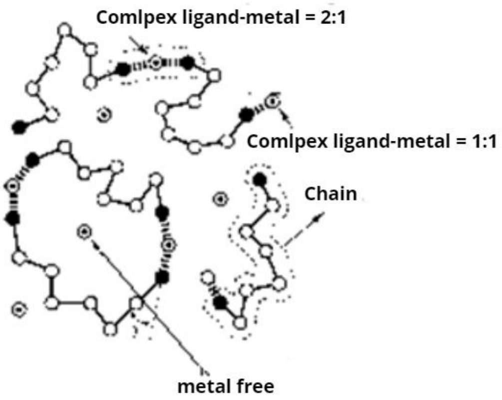

Figure 2. Complex formation at varying constants

Another parameter that determines the percentage of adsorption is the strength of the chemical interaction between metal ions and active groups in lignin. Based on the active groups present in the lignin structure, the active groups that play a role in bond formation are CH_3-O-, OH, and C-O-. In the formation of complex bonds or coordination bonds between metal ions and active groups on lignin molecules as ligands or adsorbents based on the hard acid-soft base concept (Table 4), the Pb^{2+} metal ion belongs to the intermediate acid group and the C-O ether active group includes soft bases and the presence of OH groups in lignin which being a strong base will reduce the softness of the C-O ether group so that its nature will tend to be medium. The large size of the metal ion as well as the size of the ligand or adsorbent (lignin) makes it difficult for them to be polarized or their polarizability becomes lower [17].

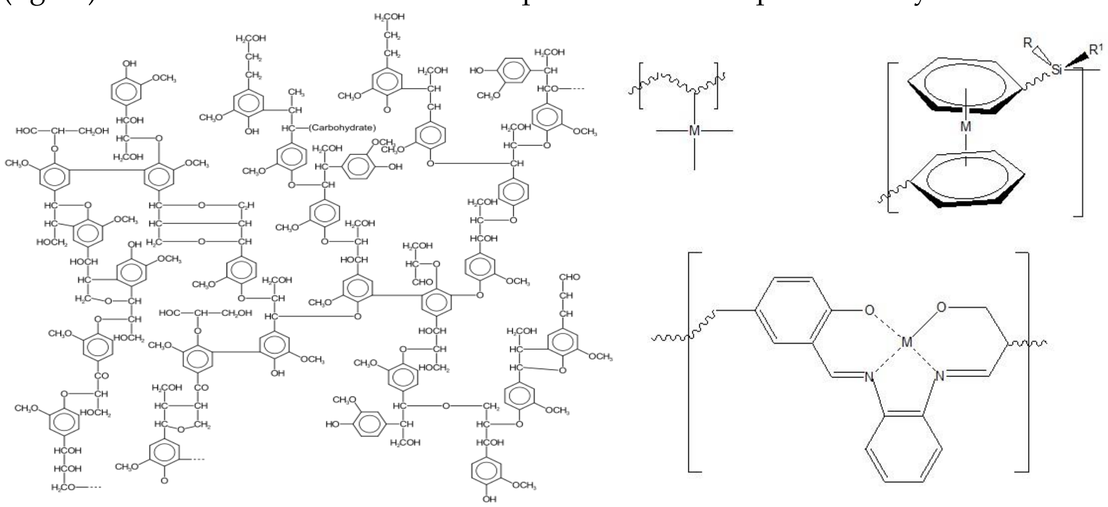

Figure 3. (a) Lignin polymer structure; (b) polymeric structures bond metal ions

As a result, chemical compatibility to form bonds between Pb^{2+} metal ions and active groups on lignin will have a greater probability when compared to Fe^{3+} and Cr^{3+} metal ions. This will cause the Pb^{2+} metal ion to have a greater adsorption percentage when compared to the Fe^{3+} and Cr^{3+} metal ions.

Conclusions

Based on the research results, it can be concluded that the ability of fermented cocoa pod (*Theobroma cacao L.*) powder to act as an adsorbent to adsorb metal ions Pb^{2+}, Fe^{3+} and Cr^{3+} has an adsorption capacity of 97.33%, 94.33% and 89,71%, respectively with a mass of 0.75 gram adsorbent.

Acknowledgments

We acknowledge the financial support from the Institut Sains Teknologi dan Kesehatan 'Aisyiyah Kendari under the Beginner Lecturer Research (PDP) award grant no. 09/K.PI/LPPM/ISTEK-AK/II/2023.

Conflicts of Interest

The authors declare no conflict of interest.

References

[1] Rojo-Poveda, O., Barbosa-Pereira, L., Zeppa, G., & Stévigny, C. Cocoa Bean Shell—A By-Product with Nutritional Properties and Biofunctional Potential. *Nutrients*, **2020**, *12*(4), 1123. https://doi.org/10.3390/nu12041123

[2] Gardner R. Nutritional Outlook. Cacao Pulp: It's Not Just a Waste Product of Cocoa Anymore [(accessed on 20 January 2020)]; Available online: https://www.nutritionaloutlook.com/herbs-botanicals/cacao-pulp-its-not-just-waste-product-cocoa-anymore

[3] Ferkous, H., Rouibah, K., Hammoudi, N.-E.-H., Alam, M., Djilani, C., Delimi, A., Laraba, O., Yadav, K. K., Ahn, H.-J., Jeon, B.-H., & Benguerba, Y. The Removal of a Textile Dye from an Aqueous Solution Using a Biocomposite Adsorbent. *Polymers*, **2022**, *14*(12), 2396. https://doi.org/10.3390/polym14122396

[4] Rakesh M, T.V. Mallesh. Adsorption of Dyes from Textile Effluent Using Low Cost Adsorbents-A Comprehensive Review. *The Journal Of Industrial Technology*, **2020**, 17(03),16-27. https://www.thaiscience.info/view_content.asp?id=10995637

[5] Andrade Siqueira, T. C., Zanette da Silva, I., Rubio, A. J., Bergamasco, R., Gasparotto, F., Aparecida de Souza Paccola, E., & Ueda Yamaguchi, N. 2020. Sugarcane Bagasse as an Efficient Biosorbent for Methylene Blue Removal: Kinetics, Isotherms and Thermodynamics. *International Journal of Environmental Research and Public Health*, **2020**, *17*(2), 526. https://doi.org/10.3390/ijerph17020526

[6] Al-Mokhalelati, K., Al-Bakri, I., & al Shibeh Al Wattar, N. 2021. Adsorption of methylene blue onto sugarcane bagasse-based adsorbent materials. *Journal of Physical Organic Chemistry*, **2021**, *34*(7). https://doi.org/10.1002/poc.4193

[7] Maulina, S., Kamny, E. R., & Amalia, R. Comparison of activated zeolite and activated carbon as adsorbent on liquid smoke purification. *IOP Conference Series: Materials Science and Engineering*, **2021**, *1122*(1), 012102. https://doi.org/10.1088/1757-899X/1122/1/012102

[8] Pabbenteng, Samawi, F. W., & Maming. The utility of cocoa pods husk M45 (Theobroma cocoa) as adsorbent of heavy metals, iron (Fe) and copper in the laboratory wastewater. *IOP Conference Series: Earth and Environmental Science*, **2020**, *473*(1), 012042. https://doi.org/10.1088/1755-1315/473/1/012042

[9] Eletta, O. A. A., Adeniyi, A. G., Ighalo, J. O., Onifade, D. V., & Ayandele, F. O. Valorisation of Cocoa (*Theobroma cacao*) pod husk as precursors for the production of adsorbents for water treatment. *Environmental Technology Reviews*, **2020**, *9*(1), 20–36. https://doi.org/10.1080/21622515.2020.1730983

[10] Tejada-Tovar, C. N., Villabona-Ortíz, A., Colpas-Castillo, F., Sanmartín-Álvarez, Z., & Landázury-Galé, D. Cocoa husk-derived Biochars synthesized at low temperature impregnated with zinc chloride for removal of ibuprofen in different solutions. *Ingeniería Y Competitividad*, **2021**, *24*(1). https://doi.org/10.25100/iyc.v24i1.10941

[11] Rahmiati, Zubair, S., Rahmah, B. Y. A., Mustikasari, I., Afgoni, A., & Gunawan, E. R. Formulation and antibacterial test traveling paper soap made from virgin coconut oil and durian seeds. *Jurnal Pijar Mipa*, **2022**, *17*(4), 549–553 https://doi.org/10.29303/jpm.v17i4.2914

[12] Micelyn Amelia Ngamput, H., & Herrani, R. The Effect of Differentiation of Hydrolysis Time towards Ethanol Levels Produced Through Ulva Lactuca Fermentation. *Journal of Physics: Conference Series*, **2019**, *1241*(1), 012010. https://doi.org/10.1088/1742-6596/1241/1/012010

[13] Korzenszky, P., Barátossy, G., Székely, L., & Géczi, G. A case study comparing distillation technologies for plum palinka production. *Potravinarstvo Slovak Journal of Food Sciences*, **2020**, *14*, 1191–1199. https://doi.org/10.5219/1472

[14] Putra, A. H., Jannah, M., Hidayah, E. N., and Cahyonugroho, O. H. Adsorption Capacity of Activated Carbon of Peanut Shells on Fe Removal. (2020). *Nusantara Science and Technology Proceedings*, **2019**, 350–357. https://doi.org/10.11594/nstp.2019.0450

[15] Tejada-Tovar, C., Villabona-Ortíz, A., & González-Delgado, Á. Adsorption Study of Continuous Heavy Metal Ions (Pb^{2+}, Cd^{2+}, Ni^{2+}) Removal Using Cocoa (Theobroma cacao L.) Pod Husks. *Materials*, **2022**, *15*(19), 6937. https://doi.org/10.3390/ma15196937

[16] Liu, X., Lu, J., Fang, X., Zhou, J., & Chen, Q. Complexation modelling and oxidation mechanism of organic pollutants in cotton pulp black liquor during iron salt precipitation and electrochemical treatment. *Chemosphere*, **2022**, *308*, 136374. https://doi.org/10.1016/j.chemosphere.2022.136374

[17] Ge, Y., & Li, Z. (2018). Application of Lignin and Its Derivatives in Adsorption of Heavy Metal Ions in Water: A Review. *ACS Sustainable Chemistry & Engineering*, **2018**, *6*(5), 7181–7192. https://doi.org/10.1021/acssuschemeng.8b01345