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Utilization of Soursop (*Anonna muricata* Linn) Seeds as Heavy Metals Biosorbent.

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ABSTRACT

Biosorption with *Anonna muricata* seeds had been used previously without the isolation of active substance. Soursop seeds dregs that have been macerated with 3 organic solvents can be used as a heavy metal biosorbent. Biosorption process was performed by using the batch method. The metal ions used are Pb (II), Cd (II), Cu (II), and Zn (II). The parameters that will be tested for this biosorption are the variations of pH, time contacts (minutes), stirring speeds (rpm), biomass weights (g), concentration of solutions (mg/L), regeneration of metal ions, and multi-component. Soursop seeds that have been extracted can be used as heavy metals biosorbent. Based on the observations, the biosorption process of Pb, Cd, Cu, and Zn has optimum condition at pH 4, 15 minutes of contact time, 100 rpm of stirring speed, and 0.1 g of biomass weigh. The optimum concentration of Pb and Cd solution was 150 mg/L with 17.065 mg/g and 9.775 m/g absorption capacity. The optimum concentration of Cu and Zn solutions was 100 mg/L with 8.6125 mg/g and 6,185 mg/g absorption capacity.

Keywords: *Anonna muricata* seeds, biosorption, heavy metal,

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INTRODUCTION

Heavy metals are one of the causes of waters pollution. Many sources of heavy metals derived from industrial and non-industrial waste water. Waste water containing heavy metals pollute waters in the city, and can cause a serious problem in some industrialized countries. The release of heavy metals from industry on a large-scale had an adverse impact on the environmental health [1]. Heavy metals that pollute the environment mostly spread through water. Therefore, to control the environmental pollution caused by heavy metals, the limitation of heavy metals content in waste water need to be done. Some chemical processes such as deposition method, ion exchange, and electro-deposition gave unsatisfactory results especially for removing pollutants that have very low concentrations. Absorption process by using carbon has been reported could eliminate or reduce heavy metals from waste water, but the price is relatively expensive and the absorption of heavy metals is less than maximum [2]. Biosorption is an alternative method that absorbs heavy metal ions due to the presence of biological material components that has a large binding capacity [3]. Some of biomaterials and geomaterials that have been used for the absorption of metal ions were perlite [4], moss [5], mangosteen peel [1], soursop seeds [6] and other agricultural waste.

MATERIALS AND METHOD

Treatment of soursop seeds

Anonna muricata seeds were washed with distilled water, and dried at room temperature for 3 days. Dried seeds were peeled to get the seed core. Anonna muricata seeds were pounded to get the powder. Anonna muricata seed powder was extracted by using non-polar, polar and semi-polar (n-hexane, ethyl acetate and methanol) solvents. After extraction process, powder or dregs is used as biosorbent.

Chemical and apparatus

The equipment used in this research are analytical balance, screener, pH meter, shaker, Atomic Absorption Spectrometry, Scanning Electron Microcosope, FTIR and other laboratory glassware. The materials used were in this research are soursop seeds, $Cd(NO_3)_2.4H_2O$, $CuSO_4.5H_2O$, $Pb(NO_3)_2$, $ZnSO_4.7H_2O$, HCl, NaOH, HNO_3, n-hexane, ethyl acetate, methanol, distilled water, phosphate buffer, acetate buffer.

Batch biosorption studies

Absorption process by using batch method was performed to find out the biosorption characteristics of soursop seeds against metal ions. Biosorption process was performed by using the batch method. Adsorption process was carried out at room temperature in a 100 mL Erlenmeyer which contains 0.1 g of adsorbent 180 µm, 25 mL of ion solution 10 mg/L. The pH of solution was adjusted by the addition of HCl and NaOH 1M. The solution was stirred using a shaker at 100 rpm for 1 hour. The solution was filtered with a filter paper to separate the filtrate and residue. The filtrate was filtered and analyzed by SSA for calculating the value of absorption capacity factor.

$$q = \frac{Co - C}{m} \times 0.025$$

RESULT AND DISCUSSION

Effect of pH on Metal Ion uptake

Metal adsorption on the surface of biomass materials has been described in the molecular mechanisms which may include the exchange of cations in the interlayer, and the specific adsorption due to the surface complexation. Hydrogen ions affect metal complexation because it has a great affinity for adsorption. It was well-established that the adsorption of heavy metal ions by biosorbent depends on the pH [7]. The **Fig. 1** shows the adsorption of Cd^{2+}, Pb^{2+}, Cu^{2+}, and Zn^{2+} in pH 4 has the highest adsorption and it increases significantly from pH 3. Ionization constants of various carboxyl groups will be in pH 3-4. In a very acidic pH, ion acts as a positive charged species [8].

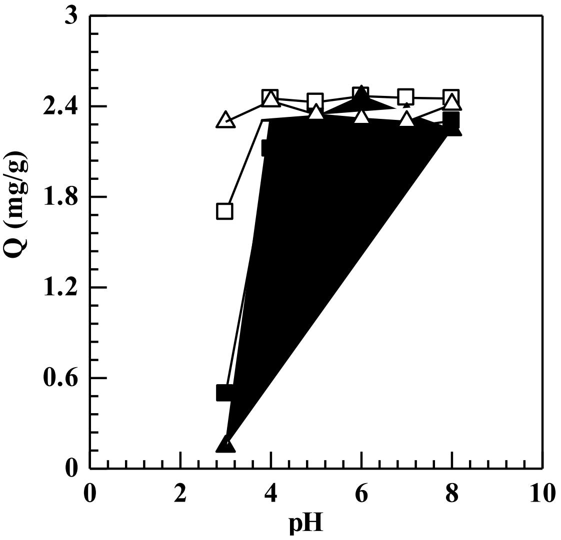

Figure 1: Effect of pH on the absorption of Pb (II), Cu (II), Cd (II), and Zn (II); metal ions solution = 25 mL; concentration of solution = 10 mg/L; biomass weight = 0.1 g; contact time = 60 min; stirring speed = 100 rpm. of Pb (-■-), Cd (-□-), Cu (-Δ-), and Zn (-▲-)

The maximum absorption capacity of Cd^{2+} was 2.34 mg/g and Zn^{2+} was 2.1773 mg/g at pH 4. There is a very significant increase of maximum absorption capacity from pH 3 to pH 4. Ions in pH 5-8 have a linear increased capacity. The maximum absorption capacity of Pb^{2+} was 2.495 mg/g at pH 4. It decreases at pH 5. The maximum absorption capacity of Cu^{2+} was 2.475 mg/g at pH 4. It has a linear decreased capacity in pH 5-8.

Effect of Contact Time

Ion adsorption was performed based on the effect of contact time against an initial concentration (10 mg/L) and an optimum pH of each metal (pH 4). The assay was carried out by various contact time 15-90 minutes with a 15 minute interval. Adsorption by using Electric Arc Furnace Slag shows the maximum value after 300 minutes [9], Adsorption by using Xanthium Pensylvanicum shows the maximum value after 90 minutes [10].

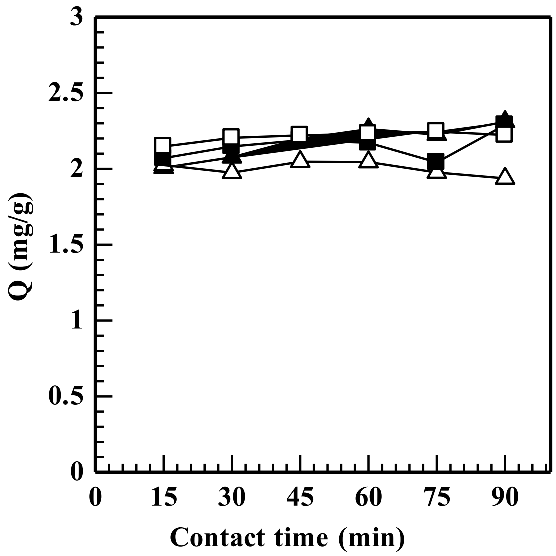

Figure 2: Effect of time contacts on the absorption of Pb (-■-), Cd (-□-), Cu (-Δ-), and Zn (-▲-); pH = 4; metal ions solution = 25 mL; concentration of solution = 10 mg/L; biomass weight = 0.1 g; stirring speed = 100 rpm.

Fig. 2 indicated that the increasing of absorption capacity is not significant in each of metals. The maximum absorption capacity for each of metals are 2.00725 mg/L of Pb, 2.0705 mg/L of Cd, 2.0245 mg/L of Cu, and 2.14745 mg/L of Zn.

Effect of Stirring Speed

Effect of stirring speed shows the value of the biosorption capacity. The assay was carried out by various stirring speed at 50-200 rpm in **Fig. 3**. Cu and Zn have maximum values at 100 rpm. Cd has an increasing value but it was not significant. Pb has a linear value. Cd and Pb have optimum values at 100 rpm. The rate of adsorption is controlled by a thin layer or pore diffusion, depending on the amount of agitation [11]. The increasing of stirring speed did not show an increase in biosorption efficiency whereas at low speeds the solution was suspended and it will take more time to reach the equilibrium condition.

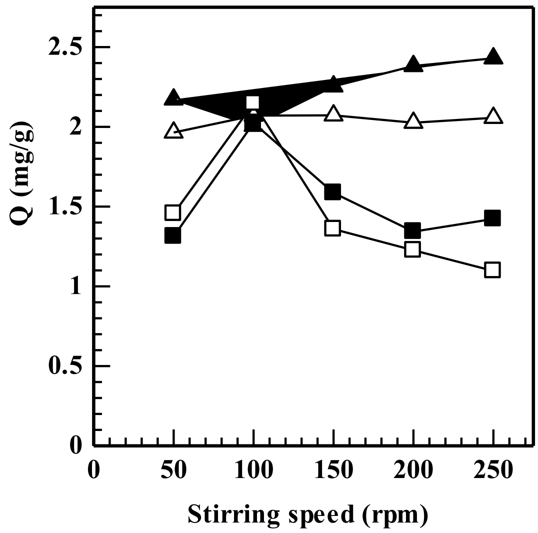

Figure 3: Effect of stirring speeds on the absorption of Pb (-■-), Cd (-□-), Cu (-Δ-), and Zn (-▲-); pH = 4; metal ions solution = 25 mL; concentration of solution = 10 mg/L; biomass weight = 0.1 g; contact time = 15 min.

Effect of Biomass Weight

The absorption capacity of metal ions per unit mass will decrease if the weight of adsorbents tended to increase. Maximum absorption capacity of Cu on Ocimum bacillium showed at 1.5 g of adsorbent with a decreased weight of adsorbent [12]. The absorption capacities of Pb and Zn on Phanerochaete chrysosporium decrease if the weight of adsorbents tended to increase [13]. The **Fig. 4** shows the absorption capacity decreased with the increasing of the biomass weight.

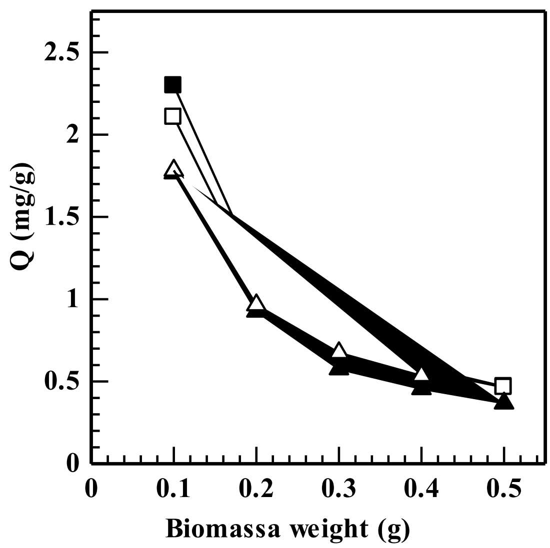

Figure 4: Effect of biomass weight on the absorption of Pb (-■-), Cd (-□-), Cu (-Δ-), and Zn (-▲-) pH = 4; metal ions solution = 25 mL; concentration of solution = 10 mg/L; stirring speed = 100 rpm; contact time = 15 min

Effect of Solution Concentration

The amount of metal ions per biomass increased with the increasing of the solution concentration. The possibility of interaction between the metal ions and biomass at low concentrations is less than at high concentrations. It can be seen in the **Fig. 5**. The maximum absorption capacity of Pb and Cd showed at 150 ppm whereas Cu and Zn showed at 100 ppm. Significant valsue of adsorbed ions at initial concentration can be related to two main factors, the ability of collision between the metal ions and the metal surface and the ability to diffuse into biosorbent surface [14], a high concentration of metals on species will increase the metal strength and reduce the transfer mass barriers [15].

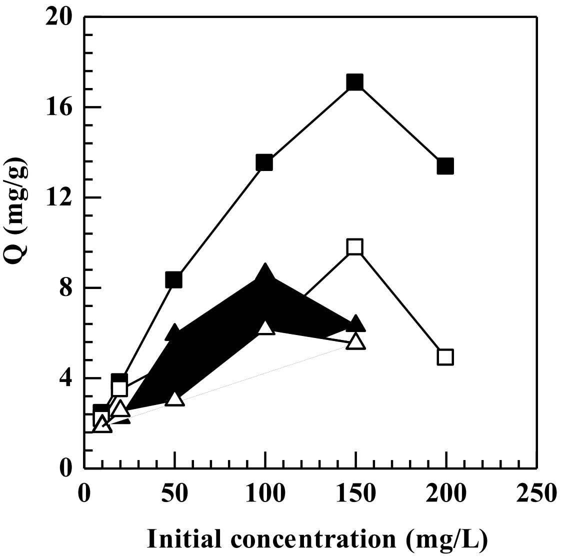

Figure 5: Effect of ion concentrations on the absorption of Pb (-■-), Cd (-□-), Cu (-Δ-), and Zn (-▲-), and Zn (II); pH = 4; metal ions solution = 25 mL; biomass weight = 0.1 g; stirring speed = 100 rpm; contact time = 15 min;

Regeneration of Metal Ions

Cadmium metals in various concentrations were transferred to the regeneration medium. Concentrations of cadmium that were more than 100 M inhibit the callus induction and plant regeneration of *Eleusine coracana* [16]. The regeneration of the metal ions on soursop seeds (*Anonna muricata* Linn) was carried out by using HNO_3 with variations of pH 1-4. The highest regeneration percentage of Pb showed at pH 1, whereas the highest regeneration percentage of Cd, Cu and Zn showed at pH 2. The results can be seen in the **Fig. 6**.

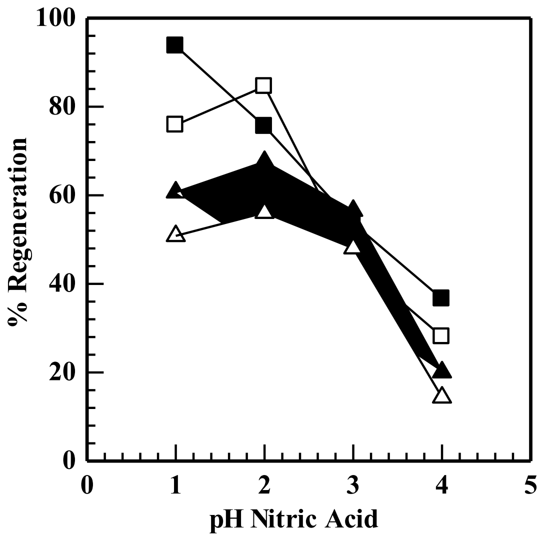

Figure 6: Regenerations of Pb (-■-), Cd (-□-), Cu (-Δ-), and Zn (-▲-); HNO_3 solution = 25 mL; biomass weight = 0.1 g; stirring speed = 100 rpm; contact time = 15 min.

Multi-components of Metal Ions

Metal ions will compete with other metals. In the **Fig. 7** shows that Pb was able to survive, but other metals such as Cd, Cu, and Zn had a decreased concentration. Because the metal ions Pb has a greater electronegativity than other metals

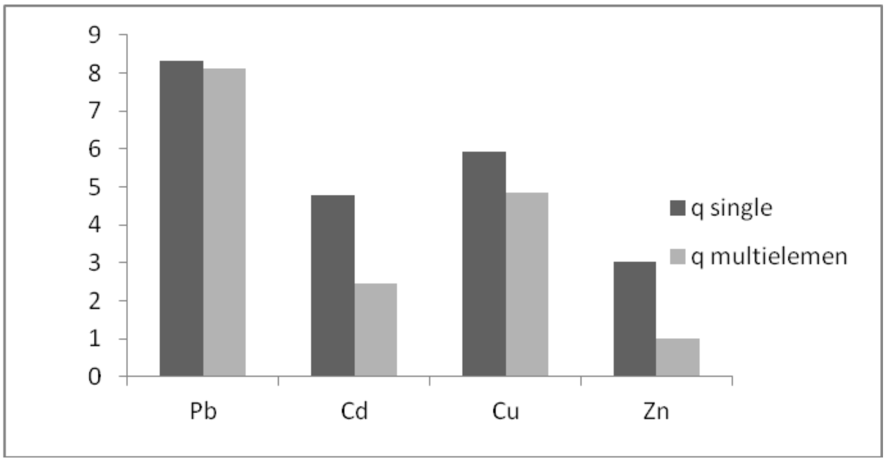

Figure 7: Multi-components of Pb (II), Cu (II), Cd (II), and Zn (II); HNO_3 solution = 25 mL; biomass weight = 0.1 g; stirring speed = 100 rpm; contact time = 15 min; solution concentration = 50 ppm.

SEM Analysis

The surface morphology of soursop seed (Anonna muricata) before and after the metals absorption can be observed by using SEM analysis **Fig. 8**. Before the absorption of metal ions, the sample surface had many pores like shards. After the absorption of metal ions Pb, the sample surface looks rough and fused.

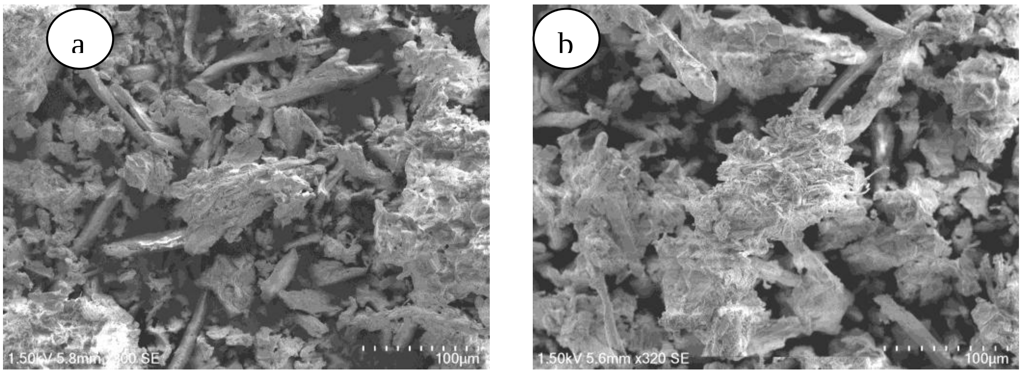

Figure 8: SEM Results (a) before thebiosorption (b) after the biosorption

FTIR Analysis

Fig. 9 is a characterization of FT-IR analysis of the major functional groups menyerapap metal ions Pb (II). At 3421.48 visible wave numbers indicate the width of the hydroxyl group (OH), after the OH absorption peak shifted to 3429.80. C–H bonds at wave numbers 2952.43 slight shift occurred after the uptake of metal ions into 2886.90. In the wave number 1734.97 C=O groups are, after absorption of a change in the rate of absorption. At wave numbers 1654.43 no C=C group, which also experienced a shift to smaller wave numbers after the absorption process. In the absorption spectrum before C-O group are the wave numbers 1058.11 unchanged after absorption into 1111.97. A shift to a smaller number of all functional groups after the absorption process. Where this is due to the interaction of these groups with metal ions absorbed. The interaction with the metal ions resulted in a change in the bond energy of all the functional groups to the lower energy so that all the functional groups shifted to lower wave numbers.

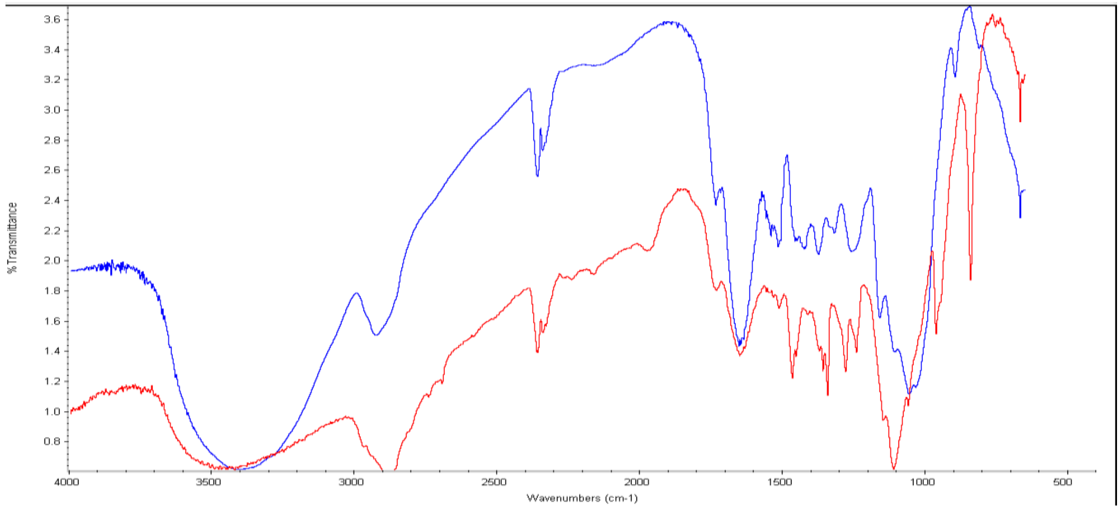

Figure 9: FTIR Analysis

CONCLUSION

Anonna muricata seed dregs that has been extracted can be used as a heavy metals biosorbent. The maximum absorption capacity of heavy metals is 17.065 mg /g of Pb, 9.775 mg/g of Cd, 8.6125 mg/g of Cu, and 6,185 mg/g of Zn. The maximum absorption efficiency of heavy metals is 90.93% of Pb, 90.72 % of Cd, 75.41% of Cu, and 86.82% of Zn. Biosorbent that has absorbed metal ions can be regenerated by $HN0_3$. The regeneration percentage of each metal is 93.73% of Pb, 84.58% of Cd, 67.56% of Cu, and 56.06% of Zn. The competition between the metal ions caused a decreased absorption capacity of Cd, Cu, and Zn whereas Pb was stable at 8.11 mg/g.

REFERENCES

[1] R Zein, R Suhaili, F Earnestly, Indrawaty and E Munaf. Hazardous materials2010;181:52-56.
[2] M Ghasemi and M Rahimnejad. Biokemistri 2008;20(2):41 – 46.
[3] N Ahalya, TV Ramachandra, RD Kanamadi. Res J Chem Environ 2003;7:4.
[4] E Munaf, R Suhaili, Y Anwar, Indrawat and R Zein. Asian J Chem 2009;21(3):2059-2066.
[5] Refilda, E Munaf, R Zein, Deswati and E Kayora. J Andalas Chem 2000; 6:49-53.
[6] Meilia Innes Kurniawan, Zulfi Abdullah, Ayu Rahmadani, Rahmiana Zein and Edison Munaf. Asian J Chem 2014;26(12):3588-3594.
[7] Olu-owolab BI, Oputu and OU Adebowale. Sci Res Essays 2012;7(15):1614-1629.
[8] Umar Farooq, Janusz A. Kozinski, Misbahul Ain Khan and Makshoof Athar. Biores Technol 2010;101:5043–5053.
[9] X Chen, WH Hou, GL Song, and QH Wang. Chem Biochem Eng 2011;25(1):105–114.
[10] Jaber Salehzadeh. Leonardo Journal of Sciences 2013;97-104.
[11] Ekmekyapar, F, Aslan, A, Bayhan, Y. K, and Cakici, A. Int J Environ Res 2012; 6(2):417-424.
[12] Hafiz Muhammad Adeel, Bushra Parveen. Int J Chem Biochem Sci 2013;4:38-45.
[13] R Marandi, F Doulati Ardejani, H Amir Afshar. Int J Min Environ 2010; 1(1).
[14] Wang L, Chen Z, Yang J and Ma F. Desalin Water Treat 2013; 1-9.
[15] Wiwid Pranata Putra, Azlan Kamari, Siti Najiah Mohd Yusoff. J Encapsul Adsorp Sci 2014; 4:25-35.
[16] Krishania Suman and Agarwal Kalpana. Res J Recent Sci 2013;2:24-28.