Removal of zinc (II) ion from aqueous solution by adsorption onto activated palm midrib bio-sorbent

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Abstract. In this paper, palm midrib that was activated with mixed citric acid and tartaric acid as biosorbent was used to remove Zn (II) ion from aqueous solution. The aim of this research is to activate palm midrib by using a mixed citric acid and tartaric acid and to determine adsorption capacity of activated palm midrib biosorbent on Zn (II) ion uptake from aqueous solution. The effect of several parameters such as contact time, initial Zn (II) ion concentration and activator concentration on the degree of Zn (II) ion removal was examined. Atomic Absorption Spectroscopy method was performed to determine adsorbed amount of Zn (II) ion into activated biosorbent. The result showed that the adsorption process was relatively not so fast and equilibrium was reached after contact time of 120 min. The adsorption capacity of biosorbent reached a maximum when the concentration of mixed citric acid and tartaric acid was 1.6 M. The optimum adsorption capacity was 5.72 mg/g. The result was obtained on initial Zn (II) ion concentration of 80 ppm for 120-min contact time. Langmuir isotherm was found as the best fit for the equilibrium data indicating homogeneous adsorption of metal ions onto the biosorbent surface.

1. Introduction

Recently, the growth of chemical industry moves rapidly so that the disposal of heavy metals into the environment increases accordingly. The heavy metals aqueous wastes have induced many problems for human being and its environment. Electroplating and metal surface treatment processes produce large quantity of wastewater containing heavy metals, which include zinc (II) ion [1].

The presence of zinc (II) ions in aquatic environment, even at low concentrations, is potentially harmful to human health. Zinc may cause some diseases including high blood pressure, infantilism, destruction of red blood cells, impaired wound healing, and kidney damage when it accumulates in the human body [2]. Considering the toxicity and harmful effects of these metals, therefore, before discharging to environment heavy metal has to be treated. There are a lot of treatment processes for heavy metal removal from wastewater such as reverse osmosis, electrocoagulation, ultrafiltration, dialysis/electrodialysis, solvent extraction, precipitation and ion exchange [3,4,5,6].

These separation processes are not entirely economically feasible due to their relatively high costs. Therefore, it is important to study new processes, which are more efficient and economical.

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Adsorption is one of the most widely used methods for the removal of metal ions from contaminated water [7].

Many researchers utilized activated carbons as adsorbent for wastewater treatment industries. Because activated carbon is an expensive adsorbent. Therefore, the searching of cheap adsorbents from agricultural solid waste could be an alternative method [8]. Agriculture, forestry and fisheries have been generating large quantities of various biomass wastes, and some of them contain various natural materials with interesting functional groups, such as carboxyl, hydroxy and so on which are as the active site on the adsorbent.

Palm midrib is one of the valuable biomass wastes but it has been partly utilized as cattle feed while the remaining is mostly wasted into the nature. For application of adsorption process, palm midrib that have variety of pore size inside its particles with a proper activation process, those pores size can be enlarged and adapted to the size of molecules of proper liquid waste of heavy metal so that adsorbate can be adsorbed easily into pore of adsorbent.

So far, some researchers have used other biomaterials to sorb heavy metals including coffee waste, orange peel, banana peel, mangosteen peel, hardwood, corn straw and other adsorbents [9, 10, 11, 12, 13, 14]. The adsorption capacity of biomass-based biosorbent on heavy metals can be enhanced by modifying the physicochemical properties of its surface [15, 16, 17]. The modification has been carried out using various reagents such as some acids such as citric acid, tartaric acid and phosphoric acid can increase the adsorption capacity of heavy metal ions [15, 16, 17, 18, 19, 20, 21]. With this activation, some acid groups can occur and form ester groups [17].

As far as we know, there are no previous studies that deal with the chemical modification of palm midrib by using a mixed citric acid and tartaric acid. Thus, the preparation of biosorbent from this agricultural by-product was here proposed. The purpose of this study is to prepare activated palm midrib biosorbent by using mixed citric acid and tartaric acid as activator, and to investigate the adsorption of zinc (II) ions from aqueous solution toward adsorption capacity. The effect of mixed activator concentration at similar ratio (citric acid and tartaric acid) was studied at neutral pH.

2. Experimental procedure and methodology

2.1 Materials and Equipment

Palm midribs, a waste product of palm tree, were used for the removal of Zn (II) ions from aqueous solution. These palm midribs were collected from area of Aceh Besar District, milled, powdered and sieved to get uniform particle size of 40-60 mesh. Some chemicals that used in this research like sodium hydroxide, citric acid 99.9 %, tartaric acid 97.5% and a solution of Zn(NO$_3$)$_2$ were purchased from chemical supplier with brand of Merck and distilled water was collected from our laboratory. Some equipment that used in this research such as hot plate, glasswares, desiccator, digital scale, oven dryer and sieve shaker. The analysis apparatus was Atomic Absorption Spectrometry (AAS) type AA 7000 (Shimadzu) and SEM TM-3000 (Hitachi).

2.2 Research Procedure

Raw material preparation of palm midrib was performed as following: at the beginning, about 10 mm x 10 mm size of raw palm midrib was washed several times with clean water in order to remove impurities on raw materials and after that was dried under sunlight for 1-2 days. Further washing was performed by soaking of dried palm midrib in hot water for 1 hr, then it was dried again under sunlight for a day and finally was dried in oven dryer at 110 °C for 1 hr. A dried palm midrib was then milled and sieved on the particle size of 40-60 mesh. Lastly, powdered palm midrib was dried again at 110 °C for 4 hr and then was stored in a desiccator for further application.

For preliminary activation process, 10 gr of dried palm midrib was mixed with solution of 0.5 M KOH. The mixing was performed at speed of 80 rpm for 30 min at room temperature. After completion of mixing and filtering, palm midrib biosorbent was neutralized several times using a distilled water. Finally a neutral of palm midrib biosorbent was dried at 50 °C for 2 hr. The purpose of
base solution addition is to create some new active sites on the surface of palm midrib so that later would increase adsorption capacity [22].

About 2 gr of neutralized palm midrib was mixed with 200 ml of citric acid and tartaric acid (on the same ratio of 0.4 M) at speed of 80 rpm for 2 hr, then filtered and activated palm midrib biosorbent was then washed with distilled water to remove the activator excess until reached a pH of ± 7, followed by re-drying at 50 °C for 24 hr [16]. The similar procedure was repeated for citric acid/tartaric acid concentrations of 0.8; 1.2, and 1.6 M. For adsorption process, 1 gr of activated palm midrib biosorbent was mixed with 100 ml of 20 ppm of Zn(NO₃)₂ at speed of 80 rpm for different time (0 to 160 min) at room temperature. After the adsorption process was completed, the filtered solution was analyzed by using AAS. The above treatment was repeated for initial concentrations of Zn (II) ion of 40, 60, and 80 ppm (15, 44, 54 and 73 ppm of AAS actual results).

3. Results and Discussion

3.1 Effect of Contact Time Toward Adsorption Capacity

Based on the literature study it is known that the longer of contact time between biosorbent and adsorbate then the concentration of metal ion that adsorbed will increase until the equilibrium occurs where the largest adsorption capacity occurs at the beginning of the adsorption process. So in order to know the effect of the contacting time on the adsorption capacity of Zn (II) ion by the activated biosorbent, the preliminary experiment has been carried out at different contact time until 160 min. The effect of contact time on the adsorption capacity of Zn (II) ion can be seen in Figure 1.

![Figure 1](image)

**Figure 1.** The relationship between contact time (min) and the adsorption capacity (mg/g) at initial concentration of 20 ppm Zn (II) ion after biosorbent activation by using citric acid and tartaric acid concentration of 0.4 M.

Based on Figure 1 we can see that at the beginning of the adsorption process, the adsorption rate increases rapidly until 30 min and later the increasing of adsorption tends to stabilize from the 120 min until reaching equilibrium at the 160 min. The condition of this research was performed by using biosorbent that was activated by citric acid and tartaric acid concentration of 0.4 M while for adsorbate concentration was at initial concentration of 20 ppm Zn (II) ion. The initial rapid uptake of metal ions may be ascribed to the presence of large number of vacant sites available for metal ions, and afterwards the remaining free metal ions are difficult to be occupied, because of repulsive forces between the free and adsorbed metal ions.
The adsorption capacity reached 1.38; 1.48; 1.48; 1.50; 1.49; 1.50 mg/g at different contact time of 0, 30, 60, 90, 120, 140 and 160 min, respectively. Equilibrium time occurred after contact time of 120 min, where the adsorption capacity of Zn (II) ion reached 1.5 mg/g on the initial adsorbate concentration of 20 ppm. With increasing of contact time, the capacity of biosorbent to bind to surface of biosorbent will be higher that is enabling more and more bonds to be formed between surface of biosorbent particles and heavy metal ions in solution of adsorbate.

Citric acid and tartaric acid that used as activator during activation process plays an important role on modification of biosorbent surface. The presence of citric acid and tartaric acid during the activation process resulted in degradation of materials on the surface of biosorbsents that will form the more pore on particles that later can be also seen on SEM graph in Figure 4. By increasing the concentration of citric acid and tartaric acid, it might be proportional to the increase the pore distribution and surface area of the biosorbent causing a number of binding metal ions of zinc increases and as well as adsorption ability also increases during adsorption process.

Other researcher [23] found that the adsorbed amount of Zn (II) ion on the first 40 min of adsorption process increased significantly and after contact time of 60 min it still remains increasing but reached equilibrium after contact time of 120 min as our finding. The quite fast adsorption of metal ions in the early minutes of adsorption process may be due to at the beginning of the adsorption process many sites and pore of biosorbent is still empty so that the tendency of the metal ion solution to be adsorbed into the biosorbent is much higher with increasing contact time and slow the rate of adsorption began to decline until they reach equilibrium time. Similar to biosorbent that activated by activator of citric acid and tartaric acid in this study, [24] suggested that some natural biosorbent contains cellulose and lignin which is a material with huge potential to be used as biosorbent.

3.2 Effect of Initial Zn (II) Ion Concentration on Adsorption Capacity

To study the effect of initial concentration of Zn (II) ion on the adsorption capacity, the research was done by varying the Zn (II) concentration of 20, 40, 60 and 80 ppm and the adsorption process was done at contact time of 120 min. The effect of the initial concentration of adsorbate on adsorption capacity is shown in Figure 2.

![Figure 2. Effect of initial concentration of adsorbate (ppm) and activator concentration (M) on adsorption capacity (mg/g) at the contact time of 120 min (CA = Citric Acid).](image)
Figure 2 showed that the adsorption capacity increases with increase of initial adsorbate concentration. The highest adsorption capacity was 5.72 mg/g that obtained after adsorption process was performed at initial adsorbate concentration of 80 ppm. On the other hand, the adsorption capacity on others initial adsorbate concentration of 20, 40, 60 and 80 ppm using biosorbent that activated by mixed citric acid and tartaric acid of 1.6 M were 1.56; 3.99; 4.69; 5.72 mg/g, respectively. The utilization of mixed citric acid and tartaric acid as chemical activator to activate the palm midrib biosorbent has improved the adsorption capacity of zinc (II) ion. As comparison, from Figure 2 it can be seen that the adsorption capacity of zinc (II) ion on activated palm midrib by using mixed citric acid and tartaric acid was higher than that of by using only citric acid. Based on the previous study [25, 26, 27], the presence of hydroxyl groups in the biosorbent caused the metal ion interact easily with the hydroxyl group (O-H) from both acids and improving adsorption capacity. The adsorption capacity on the biosorbent increases linearly with increasing adsorbate concentration. This is because when the initial concentration of the solution was increased, the mass transfer driving force became larger, resulting greater adsorption capacity. It can be clarified also that the more concentration, the more adsorbate molecules and adsorbents interact in the adsorption process. This causes adsorption tends to increase its capacity.

3.3 Effect of Activator Concentration on Adsorption Capacity
The addition of different concentration citric acid and tartaric acid during activation process would affect the adsorption capacity of the adsorbate solution on palm midrib biosorbent. This effect was illustrated in Figure 3.

![Figure 3](image3.png)

Figure 3. Addition effect of citric and tartaric acid concentration (M) and the initial concentration of adsorbate (ppm) on adsorption capacity (mg/g) at the contact time of 120 min.

The increase of citric and tartaric acid concentration that used to activate biosorbent affected adsorption capacity on each samples with different uptake capacity of Zn (II) ion. The highest adsorption capacity of 5.72 mg/g was obtained when we used biosorbent that activated by using citric acid and tartaric acid concentration of 1.6 M at initial concentration of 80 ppm Zn (II) ion. While the lowest adsorption capacity was obtained at citric acid and tartaric acid concentration of 0.4 M with the uptake capacity of 1.52 mg/g.
The higher concentration of the activator would be the higher the adsorption capacity value of the Zn (II) ion. The increase of citric acid and tartaric acid concentration increases proportionally pore numbers and surface area of the biosorbent, causing the number of Zn ion-binding sites to increase and their adsorption capacity increased as well. Therefore as observed in SEM images analysis, the presence of citric acid and tartaric acid during activation results in the cleaning of impurities materials on the surface of biosorbent to form more pores and active sites.

3.4 Morphological Analysis on Biosorbent Surfaces
To know the morphology on the surface of the biosorbent, SEM analysis of biosorbent has been done and the results can be seen in Figure 4 below.

![Figure 4. SEM photographs of (a) palm midrib biosorbent before activation (b) palm midrib biosorbent after activation with citric acid and tartaric acid of 1.6 M.](image)

Figure 4 (a) showed clearly that the pores and cavities present in the unactivated biosorbent are still covered by many impurities and the pores and cavities are not clearly visible on the surface of the biosorbent. However, after activation by citric acid and tartaric acid as seen in Figure 4 (b), the surface of the biosorbent has been cleaned and broaden and we can see clearly there are many pores and cavities appeared that are some parts look quite regular.

3.5 Adsorption Isotherm
Determination of Langmuir adsorption isotherms was obtained by creating a relationship curve between the equilibrium Zn (II) ion concentration in aqueous solution (Ce) with Ce/qe (qe, represents the equilibrium adsorption capacity). In Figure 5 it can be seen that the correlation value of $R^2$ obtained is 0.998.
The determination of Freundlich adsorption isotherms was obtained by creating a relationship curve between the log $C_e$ and the log $q_e$. Freundlich adsorption isotherm graphs can be seen in Figure 6 where the correlation value obtained is 0.9934.

The determination of Langmuir or Freundlich adsorption isotherms is known from the value of $R^2$ obtained. The adsorption isotherms of zinc (II) ions using palm midrib biosorbent followed the equation having $R^2$ value close to 1. Based on Figure 5 and Figure 6 it can be seen that Langmuir's isotherm equation has $R^2$ value close to 1 that is 0.9989, so it can be concluded that adsorption of zinc (II) ions on activated palm midrib follows Langmuir's isotherm equation. The adsorption isotherms show that the initial Zn (II) ion concentration increase is followed by the increase in the amount of adsorbed so as to achieve a balanced state.

The Langmuir equation is used to obtain the maximum adsorption capacity value ($q_m$) and the Langmuir adsorption constant ($k_L$) where by obtaining this value, we can know the amount of adsorbate adsorbed on 1 gr of biosorbent. For this biosorbent the $q_m$ value obtained is 4.23 mg/g and the value of $k_L$ is 0.62.
4. Conclusions

The adsorption capacity of Zn (II) ion on activated palm midrib reached the equilibrium time at 120 min. The highest adsorption capacity of 5.72 mg/g by using palm midrib that was activated using mixed citric and tartaric acid concentration of 1.6 M was obtained at adsorption condition of initial concentration of 80 ppm zinc (II) ion.

Citric acid and tartaric acid that used as activator during activation process plays an important role on modification of biosorbent surface. The presence of citric acid and tartaric during the activation process resulted in degradation of materials on the surface of materials. The adsorption capacity of biosorbent was influenced significantly by addition of citric and tartaric acid as mixed activator during activation process. The cleanliness and opening of pore and cavities would also increase the adsorption capacity significantly. Adsorption of zinc (II) ion on activated palm midrib follows Langmuir's isotherm equation.

References

[1] Malamis S and Katsou E 2013 J. of Hazardous Materials 252 428-461
[2] Anastopoulous I, Bhattacharya A, Bikiaris D N and Kyzas G Z 2017 Int. J. Mol. Sci. 18 114
[3] Kurniawan T A, Chan G Y, Lo W H and Babel S 2006 Chem. Eng. J. 118 (1) 83–98
[4] Ali I, Khan T A and Asim M 2012 Environ. Sci. Poll. Res. 19(5) 1668–76
[5] Ghosh G and Bhattacharya P K 2006 Chem. Eng. J. 119(1) 45–53
[6] Khattab I A, Shafeei M F, Hussein H S and El-Rehim S A 2013 Egypt J. Petrol. 22(1) 205–10
[7] Sharma P, Kaur H, Sharma M and Sahore V 2011 Environ. Monit. Assess. 183 151–195
[8] Grassi M, Kaykioglu G, Belgioirno V and Lofrano G 2012 Emerging Compounds Removal from Wastewater G. Lofrano (ed.) Springer Science
[9] Rossner A, Snyder S A and Knappe D R U Water Res. 43 3787–3796
[10] Lafi R, Rezma S and Hafiane A 2014 Desalin. Water Treat. 1 12
[11] Ponou J, Wang L P, Matuo S and Fujita T 2014 Environ. Eng. Manage. J. 2 1070–1081
[12] Huang K, Xi Y and Zhu H 2013 Environ. Sci. Pollut. Res. 20 5930–5938
[13] Chen X, Chen G, Chen L, Chen Y, Lehmann J, McBride M B and Hay AG 2011 Bioresour Technol 102 8877–84
[14] Gisi S D, Lofrano G, Grassi M and Notarnicola M 2016 Sustainable Mater. Tech. 9 10-40
[15] Marshall W E, Wartelle H, Johns M and Toles C A 1999 Bioresource Technol. 69 263–268
[16] Marshall W E, Wartelle L H, Boler D E and Toles C A 2000 Environ. Technol. 21 601–607
[17] Marshall W E, Chatters A Z, Wartelle L H and McAloon A 2001 Ind. Crop. Prod. 14 191–199
[18] Wong K K, Lee C K, Low K S and Haron M J 2003 Chemosphere 50 23–28
[19] Wafwoyo W, Seo C W and Marshall W E 1999 J. Chem. Technol. Biotechnol. 74 1117–1121
[20] McSweeney J D, Rowell R M and Min S H 2006 Journal of Natural Fiber 3 43-58
[21] Yang J S, Park Y T, Baek K and Choi J 2010 Sep. Sci. Technol. 45 1963-1974
[22] Mulana F, Muslim A, Alam P N and Mariana 2015 Adsorption of Pb (II) Heavy Metals from Wastewater Using Modified Rice Husk as Adsorbent Proc. of The 5th AIC Unsyiah In conjunction with The 8th ICChESA 9-11 September, 2015, Banda Aceh, Indonesia
[23] Pratama Y Triandri R and Darjito 2015 Kimia Student Journal 1 741 – 747
[24] Okafor C P 2012 Inter. J. Electrochemical Science 7 12354 – 12369
[25] Mulana F, Mariana, Alam P N and Muslim A 2016 Activation of Palm Midrib by Using Mixed Citric Acid and Tartaric Acid and its Application for Adsorption of Zn (II) Heavy Metals from Wastewater Proc. of the 6th AIC Unsyiah in conjunction with The 12th ICMSA 4-6 October 2016, Banda Aceh, Indonesia
[26] Muslim A 2017 J. Eng. Sci. Technol. 12(2) 1823–4690.
[27] Muslim A, Aprilia S, Suha T A and Fitri Z. 2017 J. Korean Chem. Soc. 61(3), 89–96.