Adsorption of Pb(II) from aqueous solution by acid-modified water hyacinth cellulose

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Abstract. Water hyacinth has high cellulose content so that its potential to increase the adsorption capacity of heavy metal. Besides has containing cellulose, water hyacinth also contains lignin, which can inhibit the adsorption process. Delignification of water hyacinth was conducted by NaOH so that the cellulose content in water hyacinth increases as the lignin decreases. The research aimed to study the effect of nitric acid-modified on Pb(II) adsorption capacity. The various nitric acid at 0.2, 0.6, and 1 M concentrations. The influence of pH, contact time, and initial metal ion concentration in the adsorption process was studied. The analysis of Pb(II) metal ion contents in a solution used Atomic Absorption Spectrometer (AAS). Results showed that the best of Pb²⁺ adsorption is water hyacinth cellulose adsorbent with nitric acid modification of 1 M (D) was 8.6403 mg/g. The lowest adsorption was observed at 99.8883% for Pb²⁺ ion at pH 4, while the highest adsorption was 99.9477% at pH 7. The optimum contact time for Pb²⁺ adsorption at 100 minutes. The amount of Pb²⁺ ions adsorbed enhancement with an increase in the initial metal ion concentration.

1. Introduction

The contamination of the environment by heavy metal is one of the emerging problems in the world. Accumulation of heavy metals content in the environment was toxic for soil, air, and water, so it could be affected by human health and raised either food contamination [1]. The chemical industry plays an essential role in high environmental pollutants caused by the heavy metal content in waste was toxic and difficult to degrade if discharged into waters without prior treatment [2]. One of the heavy metals caused by contamination in mostly environment water is Pb metal. Lead (Pb) is one of the heavy metal that has a high level of toxicity. The lead (Pb) primary source came from industrial processes such as the battery industry, fuel, casting, purification, and other chemical industry [3].

Therefore, the efforts to decrease heavy metal pollutants were needed, including metal extraction, ion exchange, chemical precipitation, and membrane separation [4]. However, these methods have some drawbacks such as high-cost operation, complicated process, lack of selectivity, imperfect removal of heavy metal, and also producing waste during the process. Another attempt to decrease heavy metal contamination is to use a simple process, low-cost, friendly environment, effective, and high efficiency, such as the adsorption process [5].
Many researchers have developed heavy metal adsorption with natural adsorbent. One of them that can utilize is cellulose. It has functional groups such as hydroxyl and carboxyl groups that hugely affect metal ion bind processes [6]. Water hyacinth (*Eichhornia crassipes*) is aquatic plants consists of lignin, hemicellulose, and cellulose has containing high hydroxyl and carboxyl groups [7]. It could be increased by the modification process or activation to dissolving minerals such as calcium and phosphor, so the efficient and adsorption capacity can be increased [8]. This research aimed to study the effect of nitric acid-modified water hyacinth on Pb$^{2+}$ adsorption capacity in various initial metal ions concentration, pH, and contact time.

2. Materials and methods

The materials used are water hyacinth, collected from Sukosari Village, Malang District, East Java, NaOH, HNO$_3$, Pb(NO$_2$)$_3$, and deionized water.

2.1. Preparation of adsorbent

The adsorbent materials water hyacinth washed by running water and deionized water to remove unwanted particles like dust and mud. The materials dried in sunlight and the oven at 70°C for 24 h. Furthermore, water hyacinth was mashed using grinder and filter using screen until obtained material passes 100 mesh. Water hyacinth was treated with 500 ml of 0.5 N NaOH for one hour while stirring, filtered residue, and washed with aqua dest. Further, mixing the adsorbent and nitric acid at varying concentrations 0.2; 0.6; and 1 M. The adsorbents were dried at 50°C in the oven for 24 h, and then the temperature is raised to 105°C. After acid-modified, the adsorbent rinsed by distilled water. Furthermore, drying the acid-modified adsorbents in the oven at 50°C for 24 h.

2.2. Preparation of aqueous solution

1.6 g of Pb(NO$_2$)$_3$ dissolved with deionized water in a 1000 cm$^3$ volumetric flask. The result concentration was 1000 mg/L to prepare different initial concentrations of Pb$^{2+}$ ion.

2.3. Batch adsorption experiments

2.3.1. Effect of pH. pH variation of adsorption experiments carried out at 4-7, initial pH adjusted using 0.1 M sodium hydroxide (NaOH) or 0.1 M nitric acid (HNO$_3$). 50 ml of Pb$^{2+}$ ions solution of initial concentration (30 mg/L) was added to 0.5 g of adsorbents in 250 ml flat bottom bottle at 40°C temperature, and the mixture was stirred on a shaker at 300 rpm for 1 hr.

2.3.2. Effect of initial metal ions concentration. 50 ml of Pb$^{2+}$ ions solution of different initial concentrations (10, 30, 50, 70, and 90 mg/L) was added to 0.5 g of adsorbents in 250 ml flat bottom bottle at 40°C temperature, and the mixture was stirred on a shaker at 300 rpm for 1 hr.

2.3.3. Effect of contact time. 0.5 g of adsorbents and 50 ml of Pb$^{2+}$ ions solution of initial concentration (30 mg/L) was mixed in 250 ml flat bottom bottle at 40° C temperature, and the mixture was stirred on a shaker at 300 rpm with a contact times (20, 40, 60, 80, 100 and 120) minutes.

2.3.4. Calculation of metal uptake. The Pb$^{2+}$ adsorption was calculated by:

$$q_e = \frac{(C_o - C_e)}{m} \times V \quad (1)$$

where $q_e$ is Pb$^{2+}$ adsorption capacity in mg/g, $W$ is the amount of the adsorbent in gram, $V$ in liters is the volume of the Pb$^{2+}$ ion solution in liters, $C_o$ and $C_e$ are initial and final Pb$^{2+}$ ions concentrations in mg/L, respectively. The removal efficiency of the Pb$^{2+}$ ions was also determined using:

$$R.E\% = \frac{(C_o - C_e)}{C_o} \times 100 \quad (2)$$

Where R. E % is the percentage of Pb$^{2+}$ ions removed.
3. Result and discussion

3.1. Effect of pH

The degree of acidity (pH) is an essential factor influencing the adsorption process. Adsorption of Pb\(^{2+}\) ions as a function of pH carried out to understand the adsorption mechanism \([9,10]\) and the results shown in Figure 1.

Based on Figures 1a and 1b, the water hyacinth (WH) adsorbent shows that the best adsorption capacity has achieved at pH 4 of 2.9883 mg/g with 99.611% removal. After pH four, the adsorption capacity was decreased, from 2.98 mg/g to 2.9669 mg/g. In water hyacinth modified with 0.2 M, 0.6 M, and 1 M nitric acid (HNO\(_3\)), the adsorption capacity has increased, namely from 2.9899 to 2.9955 mg/g (WHM 0.2M), 2.9850 to 2.9971 mg/g (WHM 0.6M), and 2.9967 to 2.9984 mg/g (WHM 1M). It shows that the adsorption capacity of Pb\(^{2+}\) metal increased as pH increases. At low pH, the Pb\(^{2+}\) adsorption capacity intensively decreased due to the active site of high H\(^+\) ion and the competition raised between H\(^+\) ion and Pb\(^{2+}\) ion. Besides that, the adsorbent surface has surrounded by hydroxonium ions (H\(_3\)O\(^+\)) was prevented metal ions from binding to the adsorbent \([12]\).

The enhancement of pH causes the electrostatic repulsion to decrease due to the high OH\(^-\) ions in the solution and the negatively charged adsorbent functional groups. Therefore the competition between the positive charge of proton ions and Pb\(^{2+}\) metal ions at the adsorbent adsorption site decreased so that more Pb\(^{2+}\) ions were adsorbed \([13]\). However, the adsorption capacity of (WH) and (WHM 0.2M) adsorbent slightly decreased at pH 4 and 7. According to Bashyal et al. \([11]\), it was due to a reaction between Pb\(^{2+}\) and OH\(^-\) formed precipitates of Pb(OH)\(_2\) and blocking the adsorption process.

3.2. Effect of Contact Time

One of the influences of adsorption is time, and to reach equilibrium by contacting the adsorbent and the sample solution at a specific time. Therefore it is essential to evaluate the effect of contact time on the adsorption capacity of Pb\(^{2+}\). The optimum contact time for Pb\(^{2+}\) metal adsorption is to obtain the best adsorption capacity \([14]\). Determination of the effect contact time on Pb (II) adsorption shows in Figure 2.
Figure 2a and 2b water hyacinth adsorbent (WH) showed that the adsorption capacity increased from 20 minutes of 2.74 mg/g with efficiency adsorption 91.3317%, up to 60 minutes 2.7807 mg/g and 92.6897% (optimum contact time). At 80 minutes, the adsorption capacity decreased by 2.779 mg/g, with % removal 92.6323%, up to 120 minutes 2.7676 mg/g, with % removal 92.2527%. In determining the optimum contact time, it is necessary to know that the longer the adsorption time, the electrostatic stability effect will be disturbed. The adsorption capacity after 60 minutes of contact time tends to be constant or decrease. At 60 minutes, the adsorption capacity increased because still many available active sites of adsorbents, so the ions were adsorbed faster and higher. Meanwhile, after reaching the maximum time, the adsorption capacity decreased because the active site of water hyacinth adsorbent (WH) covered or blocked up by lignin, so the absorbent's ability active sites in the binding process of Pb$^{2+}$ ions start to slow down and inhibited [8,10]. The water hyacinth adsorbent modified with nitric acid 0.2 M, 0.6 M, and 1 M (Figure 2a and 2b) have increased its adsorption capacity from 20 minutes of 2.8478 mg/g with 94.9257% removal (WHM 0.2M), 2.8668 mg/g with 95.5607% removal (WHM 0.6M) and 2.8768 mg/g with 95.8940% removal (WHM 1M) up to 100 minutes of 2.8884 mg/g with adsorption efficiency 96.2783% (WHM 0.2M), 2.8988 mg/g with 96.6253% removal (WHM 0.6M) and 2.9207 mg/g with 97.3580% removal (WHM 1M). The enhancement of adsorption capacity at the initial period (20 - 100 minutes) because of an increase in nitric acid (HNO$_3$) treatment causes more available active sites of the adsorbent surface, and the –OH hydroxyl group was increased. Moreover, the Pb$^{2+}$ ion can rapidly be adsorbed and higher [6].

However, Figures 2a and 2b showed that at 120 minutes, the capacity and efficiency adsorption of adsorbent WHM 0.2M decreased. It was possible because of the high concentration of Pb$^{2+}$ ions so that the desorption process occurs or the adsorbate release during the agitate process. Desorption occurs due to the adsorbent surface's active site was saturated and causing the adsorption rate to decrease [15]. Meanwhile, the adsorption capacity and efficiency adsorption of adsorbent WHM 0.6M and WHM 1M tend to be constant after 100 minutes because of the active site of the adsorbent begin to decrease so that the ability to bind ions is slower and indicates an equilibrium in the uptake of Pb$^{2+}$ ions [13,16].

3.3. Effect of Initial Concentrations of Pb$^{2+}$ Aqueous Solution
The Pb$^{2+}$ ion solution's initial concentration is also an essential factor affecting the adsorption process, which acts as the driving force to overcome the resistance to mass transfer between aqueous solutions and adsorbents [14]. The effect of initial metal ion solution concentration on adsorption capacity of Pb (II) metal by adsorbent water hyacinth and nitric acid-modified water hyacinth (HNO$_3$) 0.2; 0.6; and 1 M shown in Figure 3.
In the adsorbent WH, WHM 0.2M, WHM 0.6M, and WHM 1M, there is an increase in the adsorption capacity (Figure 3a), and the efficiency adsorption decreased (Figure 3b) along with the increase in the initial concentration (Co) of Pb²⁺ ion. At the initial concentration of ion (Co) 10 mg/L, there was an adsorption capacity of 0.952 mg/g with efficiency removal of 95.2% (WH), 0.9878 mg/g with 98.78% removal (WHM 0.2M), 0.9891 mg/g with 98.909% removal percent (WHM 0.6M) and 0.9987 mg/g with 99.873% removal (WHM 1M). Co 30 mg/L of 2.7807 mg/g with removal 92.6897% for adsorbent (WH), 2.8799 mg/g with 95.9953% removal for adsorbent (WHM 0.2M), Co 30 mg/L of 2.8968 mg/g with 96.5607% removal (WHM 0.6M) and 2.9181 mg/g with 97.2697% removal (WHM 1M), Co 50 mg/L of 4.6299 mg/g with 92.5976% removal (WH), 4.7046 mg/g with 94.0918% (WHM 0.2M), 4.8021 mg/g with 96.0416% (WHM 0.6M) and 4.8607 mg/g with 97.213% removal (WHM 1M), Co 70 mg/L of 6.4940 mg/g with 92.7713% removal (WH), 6.5918 mg/g with 94.1691% (WHM 0.2M), 6.7033 mg/g with 95.7617% (WHM 0.6M) and 6.8020 mg/g with 97.1716% removal (WHM 1M), and Co 90 mg/L 8.3790 mg/g with 93.0999% removal (WH), 8.4860 mg/g with efficiency removal 94.2888% (WHM 0.2M), 8.5918 mg/g with 95.4646% (WHM 0.6M) and 8.6403 mg/g with 96.0038% removal (WHM 1M). Based on the result, high adsorption capacity produces by adsorbent WHM 1M. It proves that the higher of nitric acid (HNO₃) concentration in the adsorbent modification will increase the negative group of hydroxyl –OH in cellulose, so the adsorbent's ability to bind Pb²⁺ ions greater. Therefore, the positive charge of metal ions can better interact with the active site adsorbent [6,8]. Meanwhile, the increase of adsorption capacity and the decrease of efficiency because of the higher ionic solution concentration causes the availability of the adsorbent surface's active sites to decline and saturate due to more ion molecules interacting with the adsorbent [19,20]. The value of adsorption capacity and adsorption efficiency (%) of the WH adsorbent is small because of still has lignin contained, so it can be a supporting factor the adsorption process to slow and was inhibited [8].

Furthermore, at a concentration of 10 mg/L (Figure 3a and 3b) were a small adsorption capacity with a high % removal because the number of active sites available is more than the ion concentration in the solution so that the adsorption efficiency is high and adsorption capacity small [17,18]. However, at the concentrations of 70 mg/L and 90 mg/L, the efficiency adsorption for adsorbent WH and WHM 0.2M (Figure 3b) were increased. According to Adelaja et al. [3], it due to the enhancement of the number of molecules adsorbed at the adsorbent binding site, besides the adsorbent resistance of WH in adsorption Pb²⁺ ions start to weaken so that the percent removal increases at high Pb ion concentrations [14].

Figure 3. Effect of Initial Concentrations of Pb(II) in Adsorption Process: (a) Adsorption capacity (mg/g) and (b) Efficiency Adsorption (%)
4. Conclusion
The Pb$^{2+}$ adsorption of an aqueous solution using water hyacinth cellulose was influenced by pH, contact time, and metal ion concentration was studied. The following conclusions from this study, the best of Pb$^{2+}$ adsorption is using water hyacinth cellulose adsorbent with a modification of 1 M nitric acid (WHM 1M). The highest maximum adsorption capacity obtained 8.6403 mg/g. The lowest adsorption efficiency at pH 4 99.8883%, and the highest adsorption at pH 7 was 99.9477%. The optimum contact time obtained at 100 minutes and the enhancement of Pb$^{2+}$ ions adsorbed with the initial metal ion concentration increase was observed.

Based on the adsorption parameters, water hyacinth cellulose adsorbent with acid-modified proved to increase adsorption capacity and efficiency due to the hydroxyl group in cellulose increased by nitric acid-modified (HNO$_3$) and to be a very effective adsorbent for bind or removal Pb$^{2+}$ metal ion from water.

References
[1] Arunakumara K, Walpola B C and Yoon M H 2013 Korean J. Environ. Agric 32 2 108–16
[2] Cerino-Córdova F J, Díaz-Flores P E, Garcia-Reyes R B, Soto-Regalado E, Gómez-González R, Garza-González M T and Bustamante-Alcántara E 2013 Int. J. Environ. Sci. Technol 10 3 611–22
[3] Adelaja O a, Amoo I a and Aderibigbe a D 2011 Arch. Appl. Sci. Res 3 6 50–60
[4] Sadeek S A, Negm N A, Hefni H H H and Abdel Wahab M M 2015 Int. J. Biol. Macromol 81 2015 400–09
[5] Sarkar M, Rahman A K M L and Bhoumik N C 2017 Water Resour. Ind 17 1–6
[6] Saxena A, Bhardwaj M, Allen T, Kumar S and Sahney R 2017 Water Sci 31 2 189–97
[7] Kumar P and Chauhan M S 2019 J. Environ. Chem. Eng 7 4 103218
[8] Pinem D A, Mimpin G and Ginting A 2018 Int. J. Sci Technol. Eng 4 9 23–8
[9] Abdel-Rahman L H, Abu-Dief A M, Abd-El Sayed M A and Zikry M M 2016 Chem. Mater. Res 8 4 23-8
[10] Chakravarty P, Sen Sarma N and Sarma H P 2010 Desalination 256 2010 16–21
[11] Bashyal D, Homagai P L and Ghimire K N 2010 J. Nepal Chem. Soc 26 53–60
[12] Egila J N, Dauda B E N and Jimoh T 2010 African J. Biotechnol 9 48 8192–8
[13] Wang G, Zhang S, Yao P, Chen Y, Xu X, Li T and Gong G 2018 Arab. J. Chem 11 1 99–110
[14] Liu W, Liu Y, Tao Y, Yu Y, Jiang H and Lian H 2014 Environ. Sci. Pollut. Res 21 3 2054–63
[15] Huang Y, Li S, Chen J, Zhang X and Chen Y 2014 Appl. Surf. Sci 293 2014 160–8
[16] Zou C, Jiang W, Liang J, Sun X and Guan Y 2019 Environ. Sci. Pollut. Res 26 2 1315–22
[17] Shakeri A, Hazeri N, Valizadeh J, Hashemi E and Motavalizadeh Kakhkhy, A R 2012 Iran. J. Chem. Chem. Eng 31 3 45–50
[18] Mousavi H Z and Seyedi S R 2010 J. Chil. Chem. Soc 55 3 307–11
[19] Cheng Y, Yang C, He H, Zeng G, Zhao K and Yan Z 2016 J. Environ. Eng. (United States) 142 9 1–7
[20] Haloi N, Sarma H P and Chakravarty P 2013 Appl. Water Sci 3 3 559–65