Pineapple Waste as an Adsorbent to Remove Lead from Synthetic Wastewater

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Abstract: This study investigated the potential of pineapple waste and treated pineapple waste as an adsorbent for removal of lead (Pb²⁺) from aqueous solution. The raw materials used are mixed pineapple residues such as stems, leaves and fruit. The treated pineapple waste was prepared using sodium hydroxide (NaOH). Both untreated and treated pineapple wastes are characterized using Fourier Transform Infrared (FT-IR) analysis and serial series of adsorption experiment were performed to evaluate the suitability of product as an adsorbent material. The influence of pH (2, 4, 6), contact time (15, 30, 60, 90 minutes), and the temperature (30, 60, 90°C) on adsorption experiment were also evaluated. Pineapple waste treated with NaOH was found has higher adsorption efficiency for lead ions average at 85.88% than untreated ones by about average at 52.57%. The optimum contact time is at 60 minutes. For pH effect, the biosorption capacity increases sharply from pH 2.0 to pH 4.0 while slightly decreased at pH 6.0 due to the formation of soluble hydroxyl complexes. With increasing the temperature, the Pb²⁺ removal efficiency also increased from 74.31% to 87.28%. The results of this study revealed that pineapple waste is a suitable to remove Pb²⁺ metal ions from aqueous solution and can be applied for wastewater treatment.

Keywords: Adsorption, Bio-adsorbent, Lead, Pineapple waste, Wastewater.

1. Introduction

Water is one of the most valuable resources because water is one of the basic human’s needs besides food, shelter and clothes. Water covers 71% of the Earth’s surface. Most of the living organisms require water to survive longer and to sustain in life rather than food. Nowadays, population growth and urbanization have led to the increasing demand for water consumption and at the same time increasing water pollution level in Malaysia [1]. Consequently, from rapid development has produced large amounts of human wastes, including domestic, industrial and commercial wastes which ends up in the water bodies and in tandem increase the amount of heavy metals in the river.

Heavy metal is a classified chemical element which tremendously dangerous to human and environment since it contains toxicity and give bad effect to human body [2]. One of the major components of heavy metal in wastewater is lead. Lead has the greatest effect on human health. It can cause a rise in blood pressure, brain damage and miscarriage as well as subtle abortion. It also affects brain and nervous system of unborn children when lead enter the fetus through the mother’s placenta [3].

So, due to the growth of these industries, concerns on the lead should not be ignored as the level of lead in the wastewater will potentially increase. Therefore, there are several advanced methods for the treatment of this heavy metals in the wastewaters such as filtration, membrane separation, electrochemical treatment, ion exchange, coagulation, aerobic and anaerobic treatment, advanced oxidation process and adsorption process. Among these methods, adsorption process is widely used to remove heavy metal from wastewater and be considered as a good promising method due to the ability of the adsorbent to bind and sequester the metal ions from wastewater [4]. Further, this process can minimize different type of heavy metals and it is highly efficient process as well as cost effective. For example, activated carbon has been a popular choice as an effective adsorbent for the removal of variety heavy metals from wastewater. However, using the activated carbon as adsorbent for the removal heavy metal will be increasing the cost of operating process because the adsorbent costs are relatively high. Due to this problem, low cost and easily available material need to be develop to be used more economically on large scale.

For that reason, many researchers have focused on alternative low cost adsorbents generated from agricultural wastes. Extensive previous studies have shown that agricultural wastes such as empty fruit bunch, palm shell, corn cob, coconut shell and date palm seed have been found to be suitable precursors owing to their high carbon content and low ash contents [5]. Bhatnagar & Sillanpää, also stated that agricultural wastes material particularly those containing cellulose shows potential sorption capacity for various pollutants [5].
addition, these materials have several advantages such as high sorption capacities, good modifiability and recoverability, insensitivity to toxic substances and simple operation in the treatment processes [6].

(Hegazi, 2013) did the research on the utilization possibilities of less expensive adsorbents for the elimination of heavy metal from wastewater [7]. Agricultural and industrial waste by-product such as rice husk and fly ash have been used for the elimination of heavy metals from wastewater for the treatment of the EL-AHLIA Company wastewater for electroplating industries. He has found that low cost adsorbents can be fruitfully used for the removal of heavy metals with a concentration range 20-60 mg/L. He also found that using real wastewater showed that rice husk was effective in the simultaneous removal of Fe, Pb and Ni, while fly ash was effective in the removal of Cd and Cu where the percentage of the removal of heavy metals was dependent on the dose of low cost adsorbent and adsorbent concentration. The contact time necessary for maximum adsorption was found to be 2 hours while the optimum pH range for the heavy metals adsorption was 6.0-7.0. Meanwhile, Mopoung & Kengkhkit, 2016 used pineapple wastes to remove methylene blue from aqueous solutions. According to their findings, it was found that dried pineapple leaves are also used for Cr (VI) adsorption and decolourization of Basic Green 4 from synthetic wastewater.

In this study, pineapple waste is choosing as an adsorbent since it is abundantly available in Malaysia especially in Johor. Johor is the largest pineapple (Ananas Comusus) producer in Malaysia which is producing 168,830 metric tons of pineapple in 2010. According to Malaysia Pineapple Industry Board, 40% represents the pineapple fruit from the overall pineapple tree and 60% w/w is pineapple farm waste (Portal Rasmie Lembaga Perindustrian Nanas Malaysia, n.d.). This farm waste is often useless and will be discarded or will be sent to the landfill for disposal. As a result, this waste breaks down and produces methane gas that cause greenhouse effect and is harmful to human and the environment. Indeed, the utilization of pineapple waste as an adsorbent to remove heavy metal from wastewater can greatly reduce the amount of waste produced and would directly solve part of the environmental problem. Hence, the objective of this research is to study the potential of using pineapple waste as a low cost bio-adsorbent for the adsorption of lead in synthetic wastewater. In order to accomplish the goal, the effects of operating parameters such as pH, contact time and temperature on lead adsorption are also studied.

2. Methodology

2.1 Preparation of Raw Materials and Synthetic Wastewater

2.1.1 Preparation of raw materials

Pineapple wastes (crown, leaf and peel) were obtained from Pontian, Johor. The collected wastes were cleaned with distilled water several times to remove dust and impurities. The pineapple wastes sample were later dried in oven at 100 °C for 24 hours to remove any surface moisture. Then the samples were then ground and screened by 125 microns (125 µm) sieveer and then stored in plastic container for further use.

2.1.2 Preparation of synthetic wastewater

The 30 mg/L lead solution was prepared by diluting 1000 mg/L stock solutions of lead solution (Merck) with distilled water. The pH of the dilute solution was adjusted to 6.0 using 0.1 M NaOH (Merck). The final solution was poured into conical flask.

2.2 Adsorbent preparation

2.2.1 Preparation of untreated pineapple waste

The collected wastes were washed with distilled water several times to remove dirt particles. The washed wastes were then oven dried by using oven at 100 °C for 24 hours. The dried wastes were ground to a desired size (125 µm) and then stored in plastic container for further use. The characterization of untreated pineapple waste was performed by using Fourier-transform infrared spectroscopy (FTIR), Bruker.

2.2.2 Preparation of treated pineapple waste

The dried wastes were treated with 1 M NaOH using a 1:10 ratio of weight/volume. The slurry mixtures were boiled for 2 hours with stirring at 300 rpm in incubator shaker. After that, boiled slurry mixtures were washed for several times with distilled water until pH 7. The washed slurry mixtures were oven dried at 100 °C for 24 h. The dried wastes were ground and screened and then stored in plastic container for further use. The characterization of treated pineapple waste was performed by using Fourier-transform infrared spectroscopy (FTIR), Bruker.
2.3 Batch Adsorption Study

Batch adsorption studies were carried out using 250 ml conical flasks containing 100 mL of a 30 mg/L solution of lead with 1 g of dry NaOH treated adsorbents. The slurry mixtures were agitated at 200 rpm in rotary shaker at room temperature for 1 hour. The supernatants were separated by filtration with filter paper. The heavy metals in the supernatant were measured using an inductive coupled plasma (ICP) (Perkin Elmer, Optima 8000). All experiments were carried out in triplicate. The NaOH untreated adsorbents were also studied in a same manner as NaOH treated adsorbents. The metal adsorption efficiencies were calculated for comparison of NaOH treated adsorbents and the untreated ones.

The metal removal efficiency was calculated as:

\[
\text{Metal ions removal efficiency (\%)} = \left(\frac{C_i - C_f}{C_i}\right) \times 100
\]

where \(C_i\) and \(C_f\) are the initial and final \(\text{Pb}^{2+}\) concentrations.

2.4 The effect of contact time, pH, and temperature

The dilute 30 mg/L solution of lead (100 mL) was added to a series of 200 mL volumetric flasks containing adsorbents 1 g. The pH values of the solutions were adjusted to 2, 4, or 6 using 0.1 M HNO\(_3\) or 0.1 M NaOH to get the optimum pH value. Meanwhile, for the effect of contact time, the slurry mixtures were shaken at 200 rpm for 15, 30, 60, or 90 minutes. 30°C and 60°C were selected as effect of temperature for lead adsorption study. Then, the supernatants were separated by filtration with filter paper. The heavy metals in the supernatant were measured using an inductive coupled plasma (ICP) (Perkin Elmer, Optima 8000).

3. Results and discussion

3.1. Characterization

The FTIR analysis was performed to determine the different types of functional groups and bonds present on the surface of pineapple waste. Every chemical bond oscillates with a specific frequency that corresponds to a certain amount of energy. The frequency of oscillation of any chemical bond is related to a quantity known as the wavenumber. The greater the frequency of oscillation of the chemical bond, the greater the wavenumber is. The dips on the figure above, corresponds to a chemical bond that absorb the energy. The higher the transmittance, the less energy is absorbed by the chemical bond and the more is transmitted and as the wavenumber increases, the frequency increases and the energy of that oscillating chemical bond increase. So, the bonds that located to the left are the stronger bonds while the bonds that located to the right are the weaker bond. According to Ahmad, Mohd-Setapar & Rafatullah, 2016, the broad band that appeared around 3,200–3,600 cm was mainly ascribed to the free or hydrogen bond O–H and/or NH (amino) symmetrical stretching variations. Based on the FTIR, the peak that appeared at 2,918 cm was assigned to the aliphatic C–H groups. However, after the pineapple was treated with NaOH new sharp band at 2,852 cm appears due to the C–H stretching. The strong peak at 1,593 cm was mainly due to the C–O bond of the carboxylic group, and after the pineapple waste is treated with NaOH, a new sharp peak appeared at 1,732 cm which was also due to the carbonyl group of ester, C=O. The peak at 1,417 cm corresponds to the C–H bending vibration. The peaks in the region from 1,369 to 1,245 cm may be attributed to the O–H bending and O–H-stretching or C–H bending vibrations (Yue Qi, 2013). The absorption band at 1,161 cm corresponds to C–O antisymmetric bridge stretching of cellulose moiety of pineapple waste (Xiaolin Yu & Shengrui Tong, 2013). The strong band at 1,103 cm is due to C–O of –OCH group which belongs to lignin structure in pineapple fruit peel. Thus, the appearance of a new peak and shift in the absorption band of FTIR spectrum demonstrated that pineapple waste was successfully treated with NaOH.
3.2 The effects of untreated and NaOH treated adsorbents

Based on Table 1, the Pb\(^{2+}\) adsorption on NaOH treated pineapple waste was significantly higher than adsorption on untreated ones. This is because the treatment with NaOH removed surface impurities present on the adsorbents and exposed the active sites for metal adsorption (Rerngnaporn Mopoung & Nanthaya Kengkhetki, 2016). Furthermore, a deprotonation of the waste materials should have taken place and the Na cation from NaOH which is more electropositive than Pb\(^{2+}\) allows the displacement between Na and Pb cations from the synthetic wastewater (Rerngnaporn Mopoung & Nanthaya Kengkhetki, 2016). Those Na ions were eventually exchanged with Pb\(^{2+}\) from the synthetic wastewater during the sorption process. In addition, the result might also be allocated to the ion exchange that is associated with carboxylate and hydroxylate anions as acidic groups (Yang, X., & Cui, X., 2013). The \(-\text{OH}\) group from NaOH, which is the functional group, was responsible for metal ion adsorption (Weng, Sharma & Tripathi, K., 2014). Hence, the metal binding capability was greatly improved, causing to a higher metal ions adsorption on NaOH treated wastes compared to the untreated ones. For untreated wastes, the low metal ions adsorption levels suggest that adsorption occurs mainly on unsaturated alkenes (CH\(_2\)–) of untreated wastes, which react weakly with metals ions (Ponou, J. & Fujita, T., 2011).

![Figure 1: Transmittance (%) of NaOH treated and untreated pineapple waste on FTIR](image)

Figure 1: Transmittance (%) of NaOH treated and untreated pineapple waste on FTIR

For untreated wastes, the low metal ions adsorption levels suggest that adsorption occurs mainly on unsaturated alkenes (CH\(_2\)–) of untreated wastes, which react weakly with metals ions (Ponou, J. & Fujita, T., 2011). Figure 2 shows the effect of temperature on the Pb\(^{2+}\) removal efficiency of untreated and NaOH treated pineapple wastes. As the temperature is increased from \(30^\circ\text{C}\), and \(60^\circ\text{C}\), Pb\(^{2+}\) adsorption efficiency is increased from 50.57%, and 55.96% (untreated pineapple waste) and for NaOH treated pineapple waste, increased from 86.3% and 87.26%, respectively. It was suggested that the adsorption process for Pb\(^{2+}\) is naturally endothermic (Nasuha, N., & Hameed, B. H., 2011). The result makes it clear that pineapple waste that is treated with NaOH works better to adsorb lead on wastewater compared to original pineapple waste because of the higher efficiency of adsorption.

<p>| Table 1: Comparison between the removal efficiency of NaOH treated and untreated pineapple waste at temperature 60°C and pH 4 |</p>
<table>
<thead>
<tr>
<th>Sample</th>
<th>NaOH treated adsorbent</th>
<th>Untreated adsorbent</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>84.90</td>
<td>52.10</td>
</tr>
<tr>
<td>2</td>
<td>84.73</td>
<td>52.52</td>
</tr>
<tr>
<td>3</td>
<td>88.01</td>
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<td>Average</td>
<td>85.88</td>
<td>52.27</td>
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</table>
3.3 The effects of contact time and pH on NaOH treated pineapple waste

The effect of contact time on adsorption of Pb\textsuperscript{2+} using NaOH treated pineapple waste at 30°C and 60°C is shown in Table 2 and Figure 3. Adsorption efficiency over 80% is observed and the result could be considered as a relatively fast adsorption process. From the experiment, it is found that the adsorption efficiency of Pb\textsuperscript{2+} cation was higher at 60°C than at 30°C when using NaOH treated pineapple waste. It can be seen from the graph that the adsorption rate at 60°C only required about 30 minutes to reach efficiency equilibrium compared to absorption rate at 30°C that needed about 60 minutes to reach equilibrium. This could be because of the structure of the wastes that were quite spongy at high temperature (Abdullah, A. Z., Salamatinia, B., & Kamaruddin, A. H., 2009). As a result, it made it easier for the diffusion of metal ions from solution onto the surface of the adsorbent (Abdullah, A. Z., Salamatinia, B., & Kamaruddin, A. H., 2009). At lower pH, H\textsubscript{3}O\textsuperscript{+} ions compete with the metal ions for the exchange sites in the adsorbents. While at higher pH, more metal ions were presented compared to the number of H\textsubscript{3}O\textsuperscript{+} ions, causing a less competition between the ions and resulting in more exchange sites available for metal ions (Zheng, L., Zhu, C., Dang, Z., Zhang, H., Yi, X., & Liu, C., 2012). Also from Table 2, it is shown that the adsorption efficiency of Pb\textsuperscript{2+} using NaOH treated pineapple waste is more rapid at pH 4 than at pH 2. At lower pH values, the H\textsubscript{3}O\textsuperscript{+} ions occupy the sites and cover the surface of waste based adsorbents (Rafatullah, 2009). As a result, competition between H\textsubscript{3}O\textsuperscript{+} ions and metal ions happened for the exchange sites in the adsorbents. On the other hand, the number of H\textsubscript{3}O\textsuperscript{+} ions is lesser than the number of metal ions at higher pH that leads to a higher and better efficiency of heavy metal adsorption (Ponou, J., Dodhiba, G., & Fujita, T., 2011). At pH 4, the treated adsorbent became deprotonated and negatively charged due to the adsorption of OH\textsuperscript{-} ions and the electrostatic attractive force between treated adsorbents and metal ions. However, at a higher pH which is higher than pH 6, a slight decrease in Pb\textsuperscript{2+} adsorption happens due to the formation of soluble hydroxyl complexes. This finding is similar to (Rafatullah, 2009), where increasing pH above pH 6 will cause to decreasing of removal efficiency.

Table 2: Pb\textsuperscript{2+} removal efficiency of NaOH treated pineapple waste with various temperatures 30°C & 60°C, and pH 2, pH 4 & pH 6.

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>Time (min)</th>
<th>pH</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>2</td>
</tr>
<tr>
<td>30</td>
<td>15</td>
<td>74.39</td>
</tr>
<tr>
<td>30</td>
<td>30</td>
<td>80.70</td>
</tr>
<tr>
<td>60</td>
<td>60</td>
<td>83.73</td>
</tr>
<tr>
<td></td>
<td>90</td>
<td>84.30</td>
</tr>
<tr>
<td>60</td>
<td>15</td>
<td>74.71</td>
</tr>
</tbody>
</table>
3.4 The effects of temperature on NaOH treated pineapple waste

According to Table 2, it shows the effect of temperature on Pb\textsuperscript{2+} adsorption efficiency by using NaOH treated pineapple waste. It is shown that as the temperature increases from 30\(^\circ\)C to 60\(^\circ\)C, the percentage of adsorption efficiency increases too. It was suggested that the adsorption process for Pb\textsuperscript{2+} is naturally endothermic (Nasuha, N., & Hameed, B. H., 2011). Higher temperature is required to be used to prepare the adsorbent. This is because it improves the trend by either increasing the number of available active sites or decreasing the thickness of the boundary layer surrounding the adsorbent (Nguyen, T. A.H., 2013). As shown in the Table 2, when temperature increases, the removal efficiencies of Pb\textsuperscript{2+} also increases. From the result, it can be conclude that adsorption ability of the pineapple waste improves at higher temperature.

4. Conclusion

The result of this research shows that pineapple wastes that are treated with sodium hydroxide, NaOH, have higher adsorption efficiency of Pb\textsuperscript{2+} ions rather than untreated pineapple wastes. This explains that NaOH is a good reagent for the conversion of pineapple waste to have a higher Pb\textsuperscript{2+} ions adsorption efficiency. The increase of adsorption efficiency that can be observed upon the three times treatment on average is 85.88%. Based on the experiment made, it is found that the Pb\textsuperscript{2+} ions adsorption on NaOH treated pineapple waste reaches efficiency equilibrium as early as at 30 minutes. In addition, the adsorption efficiency increases respectively from the 30 minutes to the 90 minutes. Other than that, different temperatures also affect the adsorption efficiency. The adsorption rate of Pb\textsuperscript{2+} at 60\(^\circ\)C is higher than at 30\(^\circ\)C. When included the effect of pH, times needed to reach equilibrium for Pb\textsuperscript{2+} adsorption on NaOH treated pineapple with pH 2 waste are 30 minutes, 60 minutes, and 90 minutes, respectively. The adsorption efficiency increases when NaOH treated pineapple waste with pH 4 is used to adsorb Pb\textsuperscript{2+} ions from the synthetic wastewater. However, the adsorption efficiency of adsorbent with pH 6 decreases slightly, which shows that adsorbent with pH 2 and pH 4 is higher than pH 6 that is not be quite effective to adsorb heavy metals from wastewater. Finally, overall of this experiment, it can be concluded that pineapple waste is suitable to be a widely used adsorbent in our country because it has structural formula that has been one of the main reasons to a high heavy metals adsorbent efficiency. Other than that, pineapple waste can be found easily from all around our country because of its abundant numbers in Malaysia. Moreover, the price of pineapple waste that is cheap and affordable gives an extra reason to the uses of pineapple waste as heavy metals adsorbent from wastewater on a large scale. The most important part is pineapple waste have high potential for conversion to Pb\textsuperscript{2+} ion adsorbents by treatment with NaOH.
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