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Adsorption of Lead (II) From Aqueous Solution by Using Modified and Unmodified Banana Peels

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ABSTRACT

Heavy metals must be avoided from improperly discharged effluent before it pollutes the environment. However, conventional methods have limits, such as low effectiveness and high costs. Agricultural waste can replace conventional methods to remove heavy metals from wastewater. This research aims to utilise modified banana peels (MBP) and unmodified banana peels (UBP) for lead removal from an aqueous solution. The effect of pH and adsorbent dosages on the adsorption behaviour of adsorbents was examined using AAS to find optimal adsorption parameters. The MBP was chemically modified with 0.001 M of sodium hydroxide solution (NaOH) to investigate the improvement in the adsorption capacity compared to UBP. The adsorbent dosage with the maximum adsorption capacity for UBP and MBP is 1.0 g. Regarding the effect of pH, adsorption of the Pb^{2+} ion by UBP and MBP was favoured at pH 6. Based on the adsorption results, MBP is slightly better than UBP in terms of lead removal percentage. The functional groups and thermal studies also showed that both adsorbents are almost similar. The presence of O-H, C=O, C=C, C-H and C-N functional groups on the surfaces of both adsorbents was shown by FTIR analyses. According to the DSC study, the maximum temperatures for UBP and MBP are 170°C and 147°C, respectively.

Keywords: *Adsorption, banana peels, lead removal, adsorbent dosage, pH*

INTRODUCTION

Water contamination is a global issue that threatens the whole ecosystem and affects the lives of millions of people worldwide. Water pollution is one of the leading global risk factors for sickness, disease, and death and causes the ongoing loss of accessible drinking water globally. Research shows that the principal contaminants in water are organic matter, nutrients, pharmaceutical and personal care products, poly-perfluoroalkyl compounds, biocides, heavy metals, dyes, radionuclides, plastics, nanoparticles, and germs [1].

Heavy metal pollution has contaminated around 40% of the world's lakes and rivers [2]. Metals with a heavy atomic weight and density are known as heavy metals [3]. The most toxic heavy metals are mercury, arsenic, lead, and zinc [4]. Heavy metals are frequently present in manufacturing effluent from various industries such as metal plating, refining, smelting, battery manufacturing, petroleum processing, and pesticide manufacturing [5]. Lead is a widespread heavy metal discovered in wastewater, and even at low concentrations of this heavy metal in water, lead ions may threaten human life [6]. If these heavy metals are absorbed and stored in the human body, they may cause serious health problems such as cancer, nervous system damage, organ damage, and even death [3]. Due to the toxicity of heavy metals, it also may affect the environment and aquatic organisms [7]. This is because these pollutants may enhance the fertility of the sediment and water column, resulting in eutrophication, oxygen deficit, growth of algae, and the mortality of aquatic life [8]. Even though heavy metal concentration is minimal, it may build up in a biological system and have long-term consequences called bioaccumulation [9]. Thus, it showed that heavy metals seriously impact the ecosystem and may harm human health.

Many technologies for heavy metal decontamination have been established, including chemical precipitation, chemical coagulation, ion exchange, activated carbon adsorption, and many others [10]. Adsorption has been considered a good process, with significant advantages such as high effectiveness even at low metal concentrations, low expense, no additional nutrient requirements, simple procedure, and no harmful environmental effects [11]. This research focuses on removing lead as a single solute from an aqueous solution utilising agricultural waste. Agricultural waste is an effective, low-cost adsorbent and could replace activated carbon for decontaminating metal-contaminated wastewater [8]. Agricultural waste requires minimal processing and may be found everywhere [3]. The ability of agricultural waste to be easily processed, applied, and recycled without negatively impacting the environment is crucial in industrial applications [10]. It is claimed that recycling agricultural wastes, and by-products for heavy metal treatment can be one of many alternatives to minimise waste in an environment in a responsible manner [11]. These agricultural waste products demonstrate promising removal effectiveness from wastewater for various contaminants, including heavy metals, either in raw material or after specific physical or chemical changes [4].

In recent years, researchers have conducted several experiments to investigate the potential of agricultural waste to eliminate heavy metals such as orange peels, risk husks, sugarcane bagasse,

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peanut shells, and many more [3]. As for this research, banana peel was used as a raw material that acted as an adsorbent to remove heavy metals from wastewater. Banana is the world's second most widely eaten fruit, accounting for 16% of total fruit output [6]. Banana peels include cellulose, hemicellulose, lignin, proteins, polysaccharides, chlorophyll, pectin, and other low molecular weight molecules with functional groups such as hydroxyl, carboxyl, and amine that are important for the adsorption of heavy metals [6, 12]. Banana peels were used as adsorbents due to their vast surface areas, high swelling capacities, and good mechanical strength [5]. They are also easy to use and have a high capacity for adsorbing hazardous pollutants such as lead compared to other agricultural waste. Lastly, banana peels are also readily available and inexpensive. Therefore, the objectives of this research focused on preparing unmodified and modified banana peels for the adsorption of lead from aqueous solution and analysing the effects of pH and adsorbent dosage in percentage removal of lead from aqueous solution by using an Atomic Absorption Spectrophotometer (AAS).

EXPERIMENTAL

Chemicals and materials

0.1 M hydrochloric acid solution (HCl), 3.3 M hydrochloric acid solution (HCl), 0.1 M sodium hydroxide solution (NaOH), 0.001 M sodium hydroxide solution (NaOH), lead nitrate salt ($Pb(NO_3)_2$), distilled water, banana peels, gloves, and Whatman No. 1 filter paper.

Sample collection

Banana peel samples were collected from market waste. Distilled water was used to clean and remove contaminants from banana peels before being cut into small pieces in 2 cm using a scalpel blade [13, 14]. Distilled water was used to wash the small pieces of banana peels again and then dried them at room temperature for 24 hours [15].

Preparation of unmodified banana peels (UBP) and modified banana peels (MBP)

Banana peels were dried in the oven for 24 hours at 90°C [8]. After drying, a blender ground the banana peels and sieve to 60 mesh (ASTM) particle size [16, 17]. After that, banana peel powder was dried again for 24 hours at 90°C in the oven [15, 18]. After drying, banana peel powder was divided into two portions. The first portion was labelled as unmodified banana peels (UBP) and distilled water was used to soak UBP for 24 hours [8]. The second portion was soaked into 0.001 M of sodium hydroxide solution, NaOH, for 24 hours and labelled as modified banana peels [16].

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Both UBP and MBP were filtered in the beakers by using filter paper. UBP and MBP were dried in the oven for 24 hours at 90°C [15].

Analysis of UBP and MBP using ATR-FTIR

UBP and MBP were used in the ATR-FTIR analysis. The crystal region has been cleansed, and the background has been collected. A sufficient amount of UBP and MBP were added to the little crystal region to cover it. The pressure arm was placed over the sample. The pressure arm was precisely positioned over the diamond crystal. The sample was then pressed onto the diamond surface by applying force. The spectrum was first evaluated in “Preview Mode" to fine-tune the applied force. The pressure was applied again until the strongest bands with intensities extending beyond 70% were created, from a baseline of 100% to 70% [8]. Once the spectrum was acquired, data was gathered in the usual way. Finally, a solvent, methanol-soaked tissue, was used to clear the crystal region. “Preview Mode” was used to ensure that the crystal area was cleaned before it was utilised again.

Thermal behaviour studies of UBP and MBP using DSC

The DSC analysis was conducted using approximately 15.86 mg of UBP and 16.61 mg of MBP utilising a Perkin Elmer DSC. The samples were scanned in sealed aluminium pans and heated from 220°C using a nitrogen flowing rate of 50 $mLmin^{-1}$ at a heating rate of $10°Cmin^{-1}$ [19].

Preparation of stock solution

Lead nitrate salt ($Pb(NO_3)_2$) was used to prepare the stock solution [20]. 0.1 g of lead nitrate salt ($Pb(NO_3)_2$) was added and dissolved in 100 mL of distilled water in a 100 mL beaker to prepare 1000 mgL^{-1} of lead solution [5, 21]. The solution was transferred into the 1L volumetric flask [5, 21]. The solution was shaken to dissolve, and the distilled water was used to dilute the solution up to the mark [14]. The serial dilution equation, as shown below, was used to prepare the metal of lead ions solution with concentrations of 100 ppm:

$$C_1V_1 = C_2V_2 \qquad (1)$$

where C_1 is the concentration of a stock solution, V_1 is the volume of stock needed to make the expected working solution, C_2 is the concentration of the expected working solution, and V_2 is the volume of the volumetric flask used to prepare the working solution [5].

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Batch adsorption study: Effect of adsorbent dosage in percentage removal of lead

The adsorption efficiency using a different UBP and MBP adsorbent dosage were studied [8, 14]. Different masses of adsorbent powder of UBP and MBP which are 0.2, 0.4, 0.6, 0.8, and 1.0 g, were used for this experiment. 100 mgL^{-1} of lead ion solution was used for this experiment. The required adsorbent doses were added into each 100 mL conical flask containing 100 mL lead solution with a fixed concentration of 100 mgL^{-1}. The temperature was kept constant at 30°C, with the pH at its natural level of 7. Then, each conical flask was placed into the mechanical shaker with an agitation speed of 150 rpm for 1 hour. After that, the solutions were filtered into beakers using a filter funnel and Whatman No. 1 filter paper. The filtrates were analysed by using AAS. The percentage removal efficiency was calculated by using the following equation:

$$\text{Removal Percentage (\%)} = \frac{C_o - C_e}{C_o} \times 100\% \qquad (2)$$

where C_o (mgL^{-1}) and C_e (mgL^{-1}) are the initial and final concentrations of a lead solution, respectively [5].

The amount of metal ion removed (mgg^{-1}) by the adsorbent representing the adsorption capacity of the adsorbent was calculated by using the following equation:

$$Q_e = \frac{V(C_o - C_e)}{m} \qquad (3)$$

where Q_e (mgg^{-1}) is the amount of lead adsorbed, C_o (mgL^{-1}) and C_e (mgL^{-1}) are the initial and final concentrations of the lead solution, V (L) is the volume of initial lead solution used, and m is the mass of adsorbent used in gram [5, 14].

Batch adsorption study: Effect of pH in percentage removal of lead

The efficiency adsorption by using different pH levels from pH 2, 4, 6, 8, and 10. The lead ion solution with its initial pH of 100 mL at 100 ppm was adjusted to different required pH levels by using 0.1 M sodium hydroxide solution, NaOH and 3.3 M of the hydrochloric acid solution, HCl. Next, the 1.0 g of adsorbent dose UBP and MBP were added into each of the 100 mL conical flasks that contained 100 mL of lead solution. The temperature was kept constant at 30°C. Then, each conical flask was placed into the mechanical shaker with an agitation speed of 150 rpm for 1 hour. After that, the solutions were filtered into beakers using a filter funnel and Whatman No. 1 filter paper. The percentage removal efficiency and the amount of the metal ion removed was calculated using the same formula.

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RESULTS AND DISCUSSION

Adsorption study on the effect of adsorbent dosage by using AAS

The effect of adsorbent dosage on the removal percentage of Pb^{2+} ions by using MBP and UBP is shown in Figure 1. The adsorbent doses vary from 0.2, 0.4, 0.6, 0.8 and 1.0 g. Figure 1 depicts that the removal percentage increases with the amount of adsorbent dosage. However, the removal percentage of Pb^{2+} ions is higher using MBP than UBP of the same mass. This shows the improved ability of MBP to adsorb a higher amount of toxic Pb^{2+} ions per gram of absorbent mass. Modifying banana peels' surface with NaOH improved banana peels' adsorption capacity [15].

The removal percentage of Pb^{2+} ions using MBP increases from 14% with 0.2 g to 59% with 1.0 g. Meanwhile, the removal percentage of Pb^{2+} ions using UBP also increases from 9% with 0.2 g to 56% with 1.0 g. Both graph of UBP and MBP shows a positive trend where the higher the mass of the adsorbent of UBP and MBP, the higher the uptake of the Pb^{2+} ions by the UBP and MBP particles. The adsorbent mass restricts the available number of adsorption sites. The greater the adsorbent mass, the greater the number of adsorption sites. In general, adsorption effectiveness is proportional to the amount of adsorbent used. As the amount of adsorbent increases, so do the accessible binding sites in the adsorbent UBP and MBP for the Pb^{2+} ions to bind [8].

Other studies have shown that smaller particle sizes had a higher metal removal percentage owing to better access to the porous structure and a larger surface area for adsorption [8]. Since the adsorbent used for this experiment is 250 µm in size, the particle size is small, which causes the accessibility of pores and surface area for adsorption to be more significant, that help in higher Pb^{2+} ions removal percentage. Besides, modifying the adsorbent MBP with NaOH seems to improve the Pb^{2+} ions adsorption capacity of the banana peel powder compared to UBP, as the MBP have higher removal percentage compared to UBP.

Therefore, the higher the adsorbent mass of adsorbent dosages, the higher the removal percentage of Pb^{2+} ions due to the higher the number of available active sites for the removal of Pb^{2+} ions and the selected optimum adsorbent dosage for further adsorption study is 1.0 g for both UBP and MBP.

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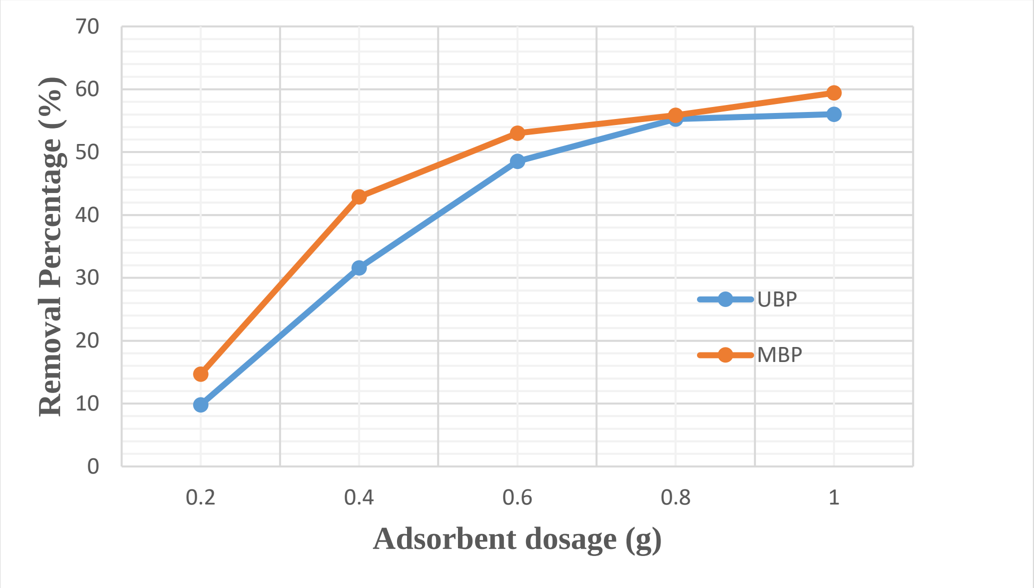

Figure 1: Effect of adsorbent dosage on the percentage of Pb^{2+} ions removal using MBP and UBP

Adsorption study on the effect of pH by using AAS

The effect of pH on the removal percentage of Pb^{2+} ions by using MBP and UBP is shown in Figure 2. The pH varies from pH 2, 4, 6, 8, and 10. Figure 2 shows that the removal percentage of Pb^{2+} ions by using both MBP and UBP is increasing to pH 6. However, the removal percentage of Pb^{2+} ions using MBP and UBP steadily decreases as the pH increases to pH 10.

The removal percentage of Pb^{2+} ions by using MBP increases from 18.72% at pH 2 to 38.94% at pH 6 and slowly decreases to pH 10 with a 23.88% of removal percentage. Meanwhile, the removal percentage of Pb^{2+} ions using UBP also increases from 10.00% at pH 2 to 31.81% at pH 6 and gradually decreases to 3.77% at pH 10. A similar study was conducted on adsorption using banana peels to remove Pb and Cu from an aqueous solution [8].

The minimum adsorption at low pH 2 may be due to the high mobility and high concentration of H^+ [21]. H^+ ions compete with metal cations which are Pb^{2+} ions, to bind at available adsorption sites [8]. The removal percentage of Pb^{2+} ions is low because H^+ metal ions are adsorbed more than Pb^{2+} ions on the binding sites of UBP and MBP. However, at a very high pH value (basic conditions) which is at pH 8 to 10, metal cations of Pb^{2+} ions react with hydroxide ions, OH^- which precipitated as lead hydroxide, $Pb(OH)_2$ [8]. As a result, the optimum pH of UBP and MBP for removing Pb^{2+} ions from an aqueous solution is pH 6.

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Figure 2 also depicts that overall, MBP has the highest removal percentage of Pb^{2+} ions compared to UBP. This is due to the MBP is modified with NaOH. The modification chemically alters the structure, hence increasing the adsorption capacity of the Pb^{2+} ions. Besides, a metal solution's pH influences the adsorption of Pb^{2+} ions because it changes the surface characteristics of adsorbents, the ionic state of functional groups, and metal species. This is because when the pH increases, the carboxylic groups deprotonate and become negatively charged, increasing the number of available binding sites for positively charged metal ions which is Pb^{2+} [8]. Hence, sodium hydroxide, and NaOH solution modified and improved the adsorption capability of the MBP effectively compared to UBP and the optimum pH 6 for both MBP and UBP.

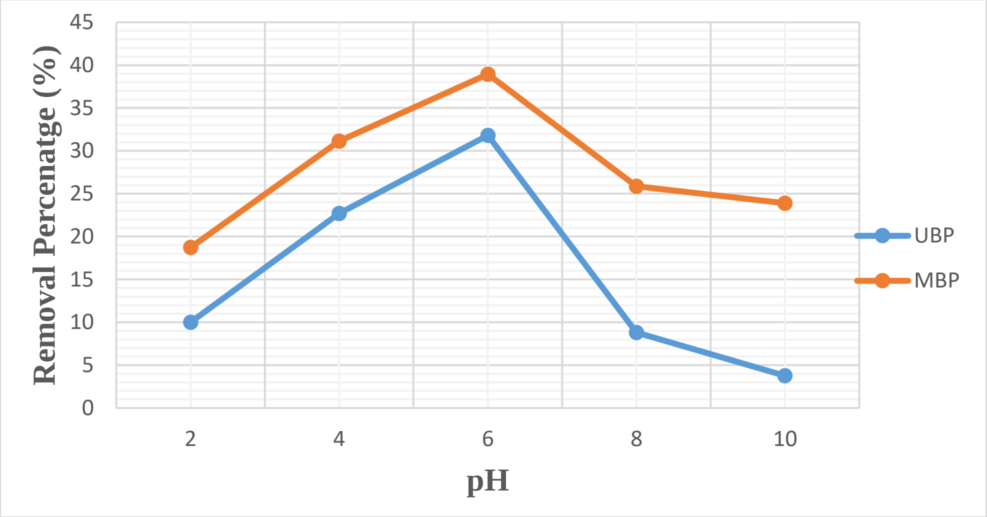

Figure 2: Effect of pH on the percentage of Pb^{2+} ions removal using MBP and UBP

FTIR spectrum of UBP and MBP

The FTIR spectrum of UBP is demonstrated in Figure 3. It is shown that there is a strong and broad peak at 3344 cm^{-1} of UBP signifies the O-H group found in banana peels. The peaks observed at 2918 cm^{-1} and 2850 cm^{-1} are attributed to the C-H stretching of alkane. The peak at 1733 cm^{-1} was observed and indicated to the C=O stretching band of aldehyde. The peak at 1620 cm^{-1} represents the C=C stretching of alkene. The peak at 1449 cm^{-1} shows the presence of the C-H bending of alkane. Lastly, C-N is stretching at peaks 1244 cm^{-1} and 1029 cm^{-1}.

The FTIR spectrum of MBP is demonstrated in Figure 4. It is shown that there is a strong and broad peak at 3346 cm^{-1} of MBP signifies the O-H group found in banana peels. The peaks observed at 2918 cm^{-1} and 2849 cm^{-1} are attributed to the C-H stretching of alkane. The peak at 1734 cm^{-1} was observed and indicated to the C=O stretching band of aldehyde. The peak at 1620

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cm^{-1} represents the C=C stretching of alkene. The peak at 1453 cm^{-1} shows the presence of the C-H bending of alkane. Lastly, C-N is stretching at peaks 1245 cm^{-1} and 1030 cm^{-1}. The results of the FTIR spectrum for both UBP and MBP are summarised in Table 1.

Table 1: FTIR peaks of UBP and MBP

Wavenumber (cm^{-1})		Functional group	Compound class
UP	**MBP**		
3344	3346	O-H stretching	Alcohol
2918 & 2850	2918 & 2849	C-H stretching	Alkane
1733	1734	C=O stretching	Aldehyde
1620	1620	C=C stretching	Alkene
1449	1453	C-H bending	Alkane
1244 & 1029	1245 & 1030	C-N stretching	Amine

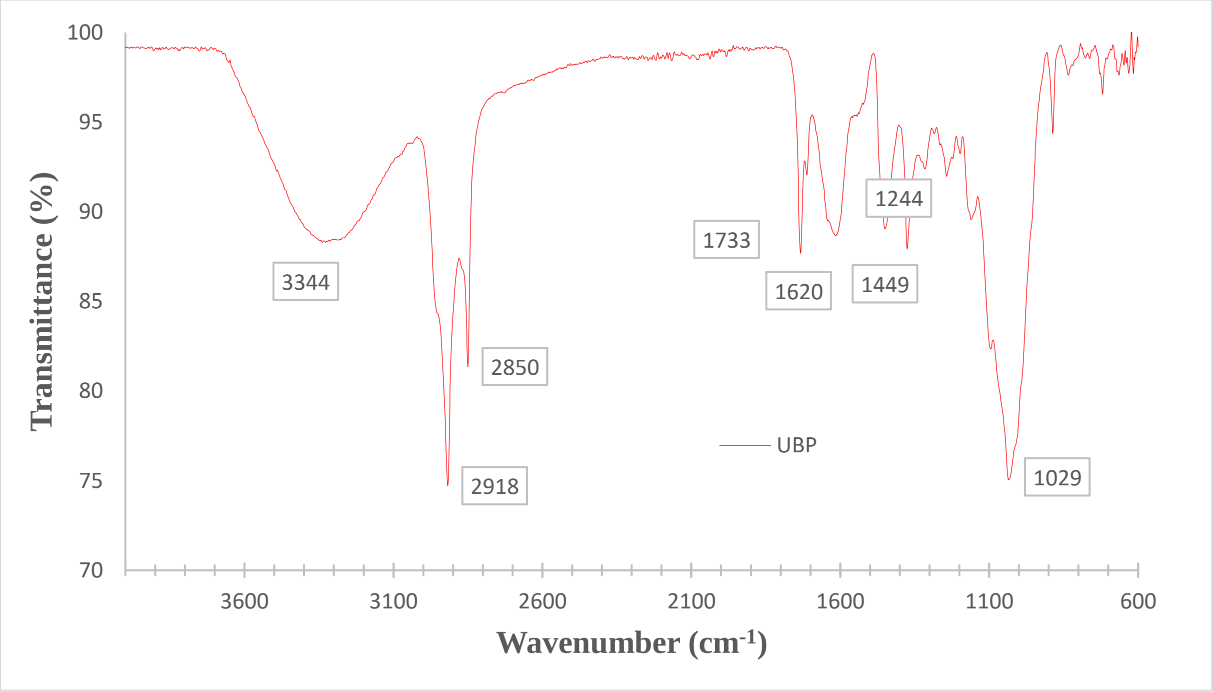

Figure 3: FTIR spectrum of UBP

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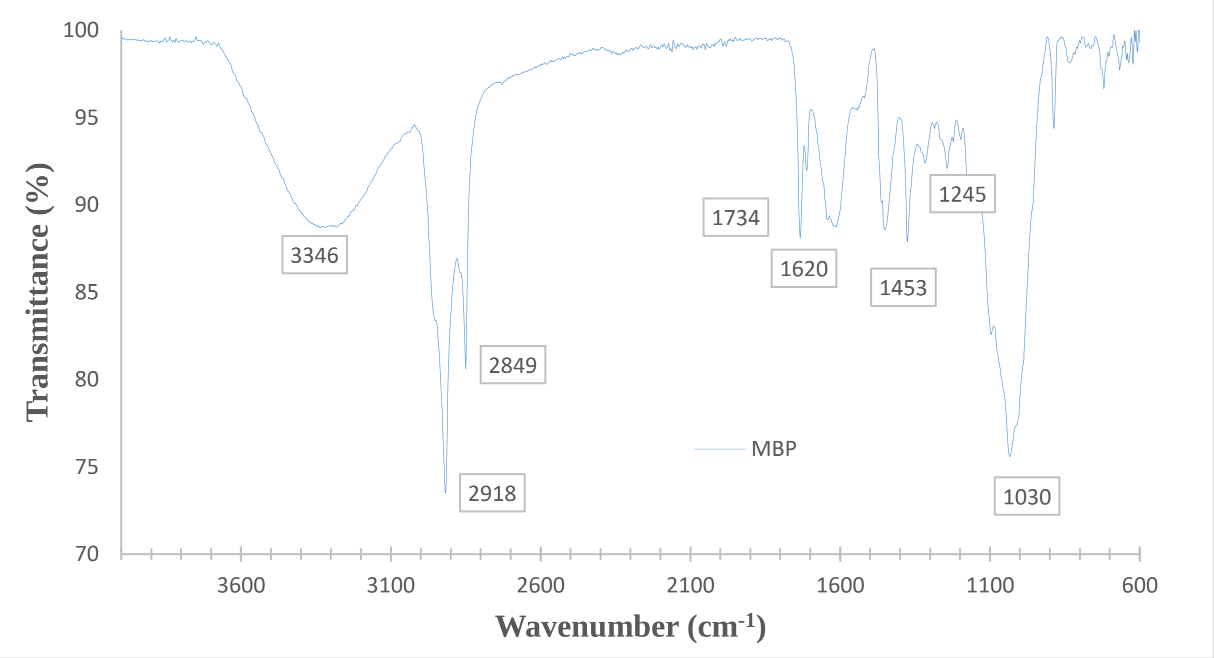

Figure 4: FTIR spectrum of MBP

Comparison of FTIR spectrum between UBP and MBP

According to Figure 5, the FTIR spectrums of UBP and MBP illustrate slightly different values but are within a similar range. However, it is observed that MBP has a higher peak intensity (per unit volume) than UBP, implying an increased amount of functional groups associated with the molecular bond. MBP peaks are sharper than UBP peaks, indicating that MBP is purer. This is because the UBP may retain more moisture than the MBP, causing the water to inhibit the UBP's IR adsorption [8]. Besides, MBP that was modified with sodium hydroxide, NaOH promotes the production of surface functional groups such as hydroxyl and carboxyl groups [22]. As oxygen-containing functional groups increase, metal adsorption will be improved. Next, MBP is modified with NaOH, resulting in a higher pH of MBP (basic condition) with pH 6. When the pH of the solution is increased, the carboxylic groups deprotonate and become negatively charged [8].

Thus, the availability of binding sites for positively charged metal ions, such as Pb^{2+}, is increased [8]. There is a slight difference between peaks of UBP and MBP because the concentration of NaOH solution for the modification of MBP is low, with 0.001 M of NaOH solution. This is because a higher concentration of NaOH solution can alter the structure of banana peels, which also can cause the banana peels to become a paste texture, as this will cause difficulty

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in the filtration and adsorption process. Thus, the sodium hydroxide, and NaOH solution effectively modified and improved the MBP's adsorption characteristic.

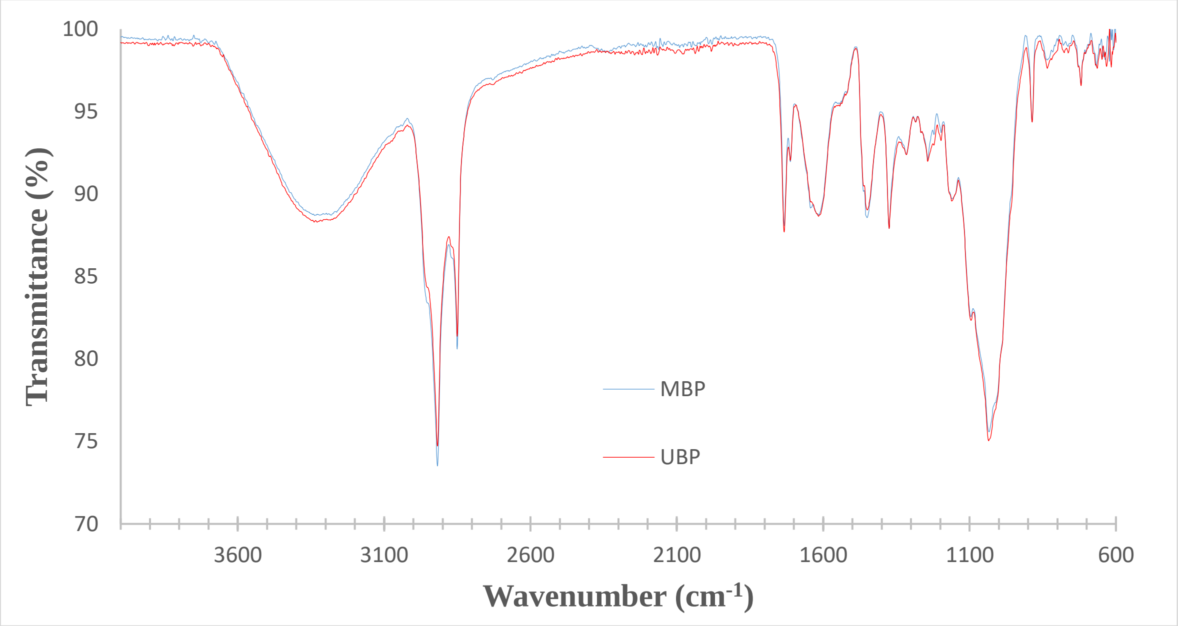

Figure 5: FTIR spectrum of UBP and MBP

Thermal behaviour studies of UBP and MBP

The thermal properties of UBP and MBP were investigated using DSC, as shown in Figure 6. The mass used for MBP and UBP are 16.61 mg and 15.86 mg. The mass must be greater than 15 mg to allow the instrument to pass through the aluminium pans and reach the samples. The exothermic reaction is depicted in Figure 6. According to Figure 6, temperatures below 100°C corresponding to mass loss in the UBP and MBP could be attributed to water loss due to moisture in the UBP and MBP. Although the UBP and MBP were dried before analysis, complete water removal was difficult due to the banana peels' hydrophilic nature, which persists even as structurally bound water molecules [19].

Next, the UBP and MBP demonstrate thermal stability between 100°C and 200°C. The maximum temperature that can be used is 170°C for MBP and 147°C for UBP, as mass loss is high above these temperatures. Moreover, the high difference in the adsorption study is attributable to the thermal stability of UBP and MBP as measured by DSC. Because UBP's hemicellulose structure degrades at a lower temperature than MBP's, it has a lower efficiency. Perhaps the structure of UBP was destroyed during the drying process, and no modifications were made to

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UBP in comparison to MBP, which had modifications that increased the structural banana peels, such as functional groups. The experiment is carried out at a temperature of 220°C because the maximum temperature of the majority of peels is between 100°C and 200°C [19, 23].

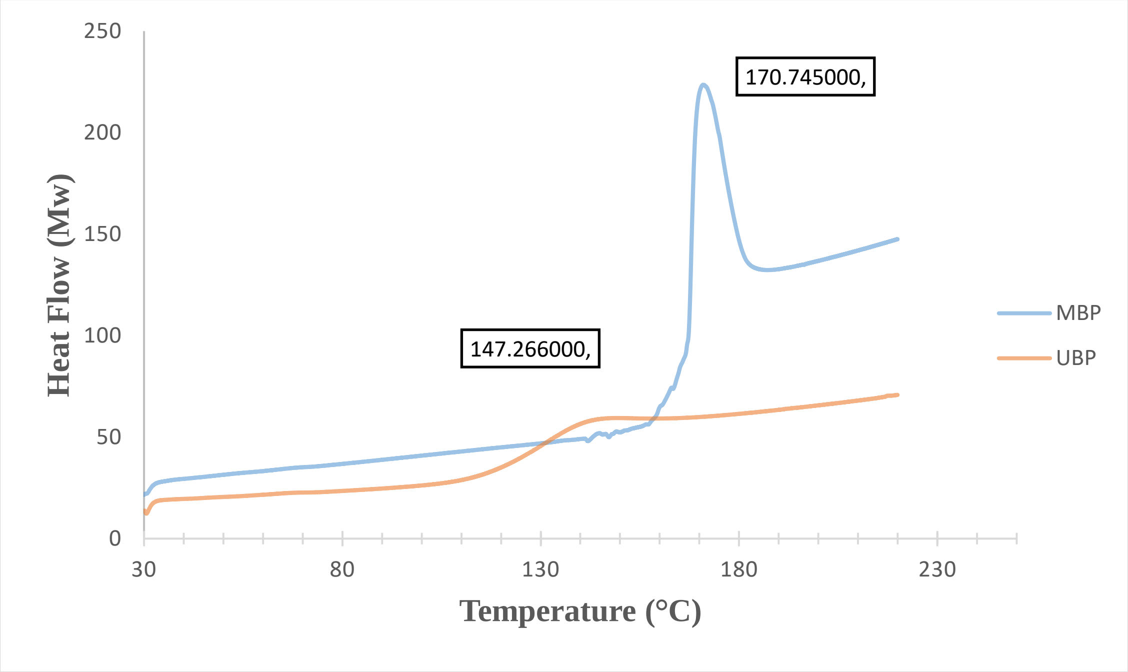

Figure 6: Thermal behaviours studies of UBP and MBP using DSC

CONCLUSION

According to the results of this study, UBP and MBP can be utilised for lead adsorption from an aqueous solution. The amount of Pb^{2+} ions adsorbed by UBP and MBP was observed to increase as the adsorbent mass increased. This is attributed to an increase in the binding sites of UBP and MBP for Pb^{2+} ion adsorption. The optimal adsorbent dose for UBP and MBP is 1.0 g. The amount of Pb^{2+} ions adsorbed by UBP and MBP increased with pH at pH 6 and gradually decreased until pH 10. This is because, at lower pH, the concentration of H+ ions is greater and competes with Pb^{2+} ions for binding to UBP and MBP, but at higher pH, the concentration of OH^- ions is higher, causing Pb^{2+} ions to bind with OH^- to produce $Pb(OH)_2$. As a result, pH 6 is the optimal pH for the adsorption of Pb^{2+} ions from an aqueous solution. FTIR analysis of UBP and MBP reveals the existence of functional groups suggesting the characteristics of banana peels. The presence of O-H, C=O, C=C, C-H, and C-N functional groups on the surfaces of adsorbents before and after modification was shown by FTIR analyses, whereas DSC analysis reveals that the maximum

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temperatures for UBP and MBP are 170°C and 147°C, respectively. That above 200°C, the UBP and MBP cannot be utilised due to hemicellulose and lignin degradation. The results of this investigation demonstrate that MBP modified with NaOH has a slightly better ability to remove Pb^{2+} ions from an aqueous solution than UBP. Thus, rather than being disposed of as garbage, banana peels will help society. This will not only protect the environment, but it can also be a low-cost natural adsorbent.

For recommendation, non-hazardous agricultural waste materials such as banana peel are excellent substitutes for non-economic adsorbents such as activated carbon and silica to remove heavy metals. Therefore, more studies and research should be done to enhance the adsorption capacity using these adsorbents. The effect of temperature, pH, adsorbent size, and contact time should be studied as they can alter the adsorption rate and mechanisms. Lastly, the effectiveness of these adsorbents on the removal of other types of heavy metals, such as iron or zinc, should be explored.

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AUTHOR’S CONTRIBUTION

All the authors have contributed to the study design, analysis and writing of the manuscript.

CONFLICT OF INTEREST STATEMENT

The authors hereby declare that there are no conflicts of interest whatsoever.

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