Adsorption of Heavy Metals on Banana Peel Bioadsorbent

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Abstract. Heavy metals have become a serious pollutant in water as a result of its non-biodegradable and toxicity properties. In this research, banana peel was synthesized as bioadsorbent to remove heavy metals from contaminated water. The major problem associated with banana peel bioadsorbent is that the activated carbon produces from biomass materials possess insignificant adsorption capability compared to its commercial counterpart. Besides that, large quantity of banana peel wastes contributes to its significant disposal problem. Thus, the present work is expected to solve the problems of banana peel disposal by converting it into bioadsorbent. The objectives of this research are to synthesize banana peel bioadsorbent and to evaluate heavy metals adsorption performance of the banana peel bioadsorbent. The bioadsorbent were treated using KOH in its preparation. The materials then undergo characterization using FTIR and AAS. The carboxylic and hydroxyl functional groups were confirmed by FTIR. The maximum removal efficiency for Pb and Fe ions were 100% and 64% respectively. The comprehensive utilization of low-cost raw material as bioadsorbent in wastewater activities are highly suggested due to its facile processing, abundantly available and environmental friendly.

1. Introduction
Water is the resource for nutriment of all the species in the earth. The increased demand of potable water is parallel with the rapid population and industrial growth since the last few decades. Water pollution is a global crisis and capable to affect human health and it is increasingly harming the earth with uncontrollable anthropogenic activities. The burgeoning industrialization plays a key role to the extreme release of heavy metals into the water ways In recent days, besides other pollutants, heavy metals concentrations in wastewater have reached an excessive level of toxicity for aquatic life. Heavy metals can gradually accumulate in human tissues and are non-biodegradable; thus the effective removal of heavy metals from the wastewater is vital before they enter the environment [1].

At present, there are various methods being used to effectively eliminate the heavy metals from waters, including chemical precipitation, ion exchange, ultrafiltration, adsorption, reverse osmosis, coagulation, flocculation and membrane filtration process [2]. Among them, adsorption assures several attractive features for example high efficiency, effective in removing variety of heavy metals, cost effective and simple process and application. Nevertheless, the broad application of adsorbent has been impede by the high production cost of commercial adsorbent such as silica, alumina and activated carbon, hence resulting to the need of alternative and inexpensive adsorbents [3]. The pursuit of economical and easily available adsorbent has directed to the utilization of biomass.

Bioadsorbent, adsorbent material obtained from biomass, has gain remarkable attention owing to its high surface area, plentiful resources, various surface groups, economical process and environmentally safe [4]. Thus, bioadsorbent is believed to be a capable material for elimination of heavy metals [5].
The main factor that contributes to the adsorption property of bioadsorbents is its surface functional groups, where the presence of oxygen, carbon and mineral fractions led to the chemical adsorption reaction.

As one of the most utilized fruits in the world, banana peel is the banana fruit main residue, at 30-40% of the fruit weight [6]. Banana peel (BP henceforth) is an ordinary waste that contains high cellulose and minerals. Huge quantity of BP leads to major disposal problems as well as massive waste of resources. A range of functional groups present on the BP surfaces such as carboxyl, hydroxyl and amide groups have been proven as the crucial feature in the biosorption processes. It also contains carbon at 41.37% [7]. An attractive approach to resolve the disposal of BP is by reclaims it as sorbent. Due to its porous structure with various surface groups, pure and treated BP had been used as sorbent to remove dissolved heavy metals in wastewater [8]. Nonetheless, chemical treatment with alkaline and acid of the pure BP is still required because of its low adsorption capacity.

Several research groups have used raw and chemically treated BP and banana stalks for the removal of toxic heavy metal ions from aqueous solutions and industrial wastewater [9]. In the present work, fresh BPs were used as raw materials, and then treated with KOH at different concentration to produce effective bioadsorbent. As a result, BP bioadsorbent with oxygen containing surface functional groups was obtained. The characteristics of the as-prepared bioadsorbents from BP had been investigated using FTIR and the adsorption performance of Pb$^{2+}$ and Fe$^{2+}$ ions were investigated.

2. Methodology

Bananas were bought from a local market. Collections of BPs were done followed by washing process with distilled water for several times to remove impurities. The clean BPs were chopped into small pieces (0.5-1.0 cm), and then were used as feedstock. Potassium Hydroxide (KOH) was supplied from Permula Sdn. Bhd. Working solutions of Pb$^{2+}$ and Fe$^{2+}$ ions were prepared and after that diluted to few concentrations. All chemicals used in the experiment were as received at analytical purity. Distilled water was used in the preparation of all solutions.

For bioadsorbent obtained from fresh BP, the peels were consumed as the basic material. The BPs were modified in KOH, where 40 g of BPs were added into 50ml of solution (gradient concentration 0, 30 wt%, 50 wt%) and soaked for 2 hours. After soaking, the sample was filtered and transferred into a furnace, heated at 230°C for 2 hours. Next, the sample was cooled to room temperature and washed with distilled water until neutral. Then the sample was dried for overnight at 80 °C in an oven. Finally, the sample was crushed into powder and ready for the characterization step.

Fourier Transform Infrared (FTIR) (Perkin Elmer) was being used to characterize the surface groups of the samples. Atomic Absorption Spectrophotometer (AAS) was carried out to verify the ions concentrations to determine the adsorption performance. Samples were prepared in triplicate and tested to obtain average results together with blank solution as control. The adsorption tests were performed with two heavy metals, Pb$^{2+}$ and Fe$^{2+}$ ions. The experiments were carried out in Erlenmeyer flasks containing 50ml of aqueous solution of M (II) ions (M= Pb and Fe) and 0.1 g BP bioadsorbent. The mixture was shaken at room temperature for 3 h. The concentrations of heavy metals before and after the adsorption were analysed by AAS.

The adsorption capacity Q (mg/g) of Pb$^{2+}$ and Fe$^{2+}$ ions on BP bioadsorbents were determined by using equation (1) below:

\[
Q = \frac{(C_e - C_0) \times V}{m}
\]

where $C_e$ and $C_0$ are the equilibrium and the initial ions concentrations (mg/L), respectively. m is the weight of the BP bioadsorbent in gram while V is the solution volume in mL. The removal efficiency of ions, adsorption %, is determined from equation (2):

\[
\text{Adsorption \%} = \left(1 - \frac{C_e}{C_0}\right) \times 100\%
\]
3. Results and Discussion

3.1. Characterization of Biochars

Fresh banana peels were treated with KOH after simple wash and cut, followed by heating in the furnace. After the heating process, powders in dark brown in colour were achieved, which meant for carbonized product.

![Figure 1: FTIR spectra of BP bioadsorbent](image)

To classify the surface groups on BP bioadsorbent, FTIR examination was done as depicted in Figure 1. It was found that the similar IR band showed that all samples had resemblance chemical nature with sample at 50 wt% showed stronger and broader peaks. In all of the samples signal around 3374 cm\(^{-1}\) was detected, which match up to the hydroxyl groups. The bands at 1645 cm\(^{-1}\) and 1085 cm\(^{-1}\) correspond to C=O (C-O) carboxyl groups, verifying the oxygen group that is essential for metal adsorption. Band assigned to O=C=O also detected at 2349 cm\(^{-1}\).

It is recognized that surface area and porous structure influenced the heavy metals physical adsorption on bioadsorbent, with high surface energy and holes for attraction and storing of ions. The nature of BP is highly porous in structure play a major role in the adsorption process. But this factor alone is not enough where chemical reaction is also needed to increase the adsorption capacity through stronger bindings such as electrostatic attraction, ion-exchange and surface complexation [10].

The potassium hydroxide added in the pretreatment of BP bioadsorbent help to hydrolyse and decompose the BP bioadsorbent, encourage the formation of the surface functional groups such as hydroxyl and carboxyl groups. From all of the samples, increasing in KOH concentration showed broader and stronger peaks, appointed to hydroxyl and carboxylic groups. This suggests that the pretreatment could boost the formation of oxygen containing groups. Two main mechanisms of heavy metals adsorption are ion exchange and surface complexation, with carboxyl and hydroxyl groups play the important role. The high amount of these oxygen containing functional groups on the bioadsorbent leads to the improvement of metal adsorption.

3.2. Adsorption Studies

The effects of BP bioadsorbent on the removal for heavy metal ions were investigated and the results are shown in Figure 2 and 3. Gradient amounts of KOH concentrations were used as the pretreatment of the BP bioadsorbent. The bioadsorbent were added into the ions solution and shaken at room temperature for 3 hrs.
As depicted in Figure 2, the adsorption capacities of both Pb$^{2+}$ and Fe$^{2+}$ samples increased steadily with the increase of KOH concentrations. The adsorption of both ions displayed excellent adsorption performance even without any treatment of KOH (0 wt%). For Pb$^{2+}$, as the KOH concentration increased, a higher adsorption capacity of 0.9595 mg/g was showed by BP bioadsorbent treated at 30 wt%, and the same value showed with 50 wt% KOH treated BP. For Fe$^{2+}$ adsorption, adsorption capacity of 0.7735 mg/g (KOH at 30 wt%) is shown and an even higher value of 1.0505 mg/g was achieved at 50 wt% KOH. The removal efficiency for both ions is shown in Figure 3. The maximum removal efficiency for Pb$^{2+}$ and Fe$^{2+}$ were 100% and 64% respectively at KOH concentration of 50 wt%.

The porous BP precursor through KOH pretreatment was found to be an effective bioadsorbent for removal of and Pb$^{2+}$ and Fe$^{2+}$ ions from aqueous solution. Banana peels biomass containing a variety of chemical groups such as carboxylic acid and hydroxyl groups which act as active centers for the adsorption of metal ions from aqueous media and industrial wastewater. The presences of these functional groups were shown in the FTIR spectra. Increment in KOH concentration encourage more formation of active functional groups and thus improve the removal of Pb$^{2+}$ and Fe$^{2+}$ ions as the concentration increase. The adsorption properties of BP bioadsorbent on both ions exhibit excellent removal at 50 wt % KOH. It is suggested that KOH could promote more formation of the oxygen-contained functional group and contribute to the adsorption of heavy metals, besides the nature of porous structure of the BP itself.
4. Conclusions
The porous BP bioadsorbent fabricated from banana peel precursor through KOH pretreatment was found to be an effective adsorbent for removal of Fe$^{2+}$ and Pb$^{2+}$ ions from aqueous solution. The obtained results proved a great potential to apply the low-cost banana peel-derived bioadsorbent with the well-defined adsorption characteristics for environmental treatment. Inexpensive, locally available and effective banana peels could be used in place of commercial activated carbon for the elimination of metal ions from industrial effluents. Undoubtedly banana peels bioadsorbent offer a lot of promising advantages for commercial purposes in the future.

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