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## Removal of As and Cd Ions from Aqueous Solution Using Biosorption Technique

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**Abstract.** Arsenic (As) and cadmium (Cd) are listed as heavy metals that have contaminated the environment, especially water supplies. Therefore, the goal of this study was to remove heavy metals, particularly As and Cd metal ions, from aqueous solutions by utilizing natural waste adsorbents and at the same time, help in the reduction of waste products. This study was designed to use low-cost and more widely available adsorbents material such as coconut husk and banana peel to remove As and Cd ions in an aqueous solution. The adsorption method was utilized to reduce and remove the As and Cd ions, and their concentrations in an aqueous solution were then determined by Atomic Absorption Spectroscopy (AAS). Various parameters such as types of adsorbents (banana peel and coconut husk), adsorbent dosages (0.1-0.3g), contact time (30-70 minutes), and temperature (25-45°C) were used to carry out the removal process. The FTIR analysis revealed that certain heavy metals were more likely to bind to these adsorbents due to the presence of important functional groups such as hydroxyl (-OH) and carbonyl (C=O). From this study, the optimum removal conditions were 0.1 g dose of adsorbent along with 70 minutes of contact time at a reaction temperature of 25°C. The results revealed that banana peel removed 0.948 mg/L of Cd ions and 0.148 mg/L of As ions from the aqueous solution, suggesting that it was more efficient at removing heavy metals than coconut husk. Meanwhile, Cd ions have a higher affinity (93.9% to 99.9% removal) than As ions (8.3% to 22.2% removal) to adsorb onto the active sites of banana peel and be removed from an aqueous solution. In conclusion, the adsorption technique using natural waste adsorbents can be applied to remove the As and Cd ions from the aqueous solutions. The reduction of these heavy metals' concentration by adsorbents can also help to preserve the quality of water sources under the permissible limit set by WHO.

### 1. Introduction

Most countries throughout the world are currently undergoing significant growth in both urbanisation and industrialisation. These developments have, however, led to a significant increase releasing heavy metals into the environment, particularly water supplies. Due to improper waste management, herbicides, fertilisers, and fast-growing agriculture and metal industries, and heavy metals had been



released into soils, rivers and the environment [1]. Due to the negative impacts of heavy metal to the ecosystem, the contamination of heavy metal is becoming an issue, and creating considerable concern especially to the human health.

Heavy metals are not biodegradable even though they may be found naturally in the Earth's crust. Heavy metals have accumulated in living organisms as a result of uncontrolled and irresponsible human activities like smelting, mining, and industrial operations that causes the alteration of their biochemical balancing and geochemical cycles [2].

Heavy metals can be explained as metalloid elements which have a density of more than 5 g/cm<sup>3</sup> and in comparison to light metal, they have high toxicity [3]. There are variety of heavy metals include chromium (Cr), mercury (Hg), zinc (Zn), thallium (Tl), nickel (Ni), lead (Pb), copper (Cu), As and Cd [4]. There are various factors that might influence how harmful the heavy metals are, including the amount, exposure method, age, gender, heredity, and many more [5].

Due to the harmful effect of heavy metal especially to human health, treatment for heavy metal pollution can be accomplished by utilizing several techniques including membrane filtration, chemical precipitation, adsorption methods, ion exchange, electro-coagulation, electro-flotation, electro-deposition [6]. However, each approach has advantages and disadvantages, and it depends on the nature of each heavy metals used [7].

Among from the other technique, adsorption has been selected as the most effective removal technique for toxic metals from the aqueous solutions. Adsorption is known as an approach of physicochemical treatment that encourages the efficient removal of hazardous metals from the polluted water sources [8]. Its key benefits are selectivity through the use of specialized adsorbents, effectiveness at both high and low pollutant concentrations, the ability to regenerate used adsorbents, and a relatively cheap cost [9].

Various type of adsorbents that we may use in the adsorption process, including activated carbon, nanomaterials, and ion exchange resins, but they are both costly and toxic to the environment [10]. Due to their biocompatibility, biodegradability, distinctive structure, reduced environmental impact and low cost, natural waste adsorbent such as coconut husk and banana peel have recently attracted significant attention as materials used for the treatment of polluted water samples [11,12]. In order to remove Cd and As metal ions from the aqueous solution, natural waste adsorbents of coconut husk and banana peel were used in this study.

## **2. Methodology**

This study was focused at the efficacy of the adsorption method for removing the Cd and As metal ions in aqueous solutions utilising natural waste as adsorbents. To study the effectiveness of these adsorbents as removal agents, several natural waste adsorbents, including banana peels and coconut husk, were utilised with various doses, temperatures and contact times.

### *2.1. Preparation of Aqueous Solutions*

For each element, 1000 mg/L stock solutions were obtained from MERCK KgaA, Germany, and used to prepare the 1.0 mg/L aqueous solutions of As and Cd . To prepare 1.0 mg/L of As and Cd solution, 50  $\mu$ L of As and Cd solution was pipetted from a 1000 mg/L As and Cd stock solution and diluted into a volumetric flask (50 mL).

### *2.2. Preparation of Natural Waste Adsorbents*

Coconut husk and banana peel were utilized as two different natural waste adsorbents in this study. The banana was purchased at the Econsave and consumed first while the peel were used in the treatment process. The coconut husk was obtained from a household in Kampung Paloh Palekbang, Tumpat, Kelantan. Coconut husk and banana peel were washed with tap water and rinsed with deionized water to get rid of any impurities or dirt on their surfaces. The adsorbents were then placed in hot air oven overnight at 70°C until a consistent weight was attained. After the adsorbents fully dried, they were sieved, ground using a grinder/blender to a powder of about 120 mesh, and placed in the air tight container [13].

### 2.3. Batch Adsorption Experiments

Banana peel and coconut husk were used as two different adsorbents in the treatment of the samples. A fixed dosage of each adsorbent (0.1 g) was combined with 50 mL of known metal solutions (1.0 mg/L) in a 100 mL beaker. At a temperature of 25°C, the mixture was stirred for 30 minutes. After the treatment, the sample was filtered and transferred into a falcon tube where it was examined using an atomic absorption spectrometer to determine the concentration of metal ions which had been removed. The variables was altered throughout a range of values to analyze the influence of additional factors such adsorbent dose (0.1 to 0.3g), contact time (30 to 70 minutes), and temperature (25 to 45°C). The removal efficiency were calculated by using the formula below:

$$\%R = \frac{C_0 - C_e}{C_0} \times 100 \quad (1)$$

where,

%R = percentage removal of Cd and As ions

$C_0$  = initial concentration of Cd and As in the solution before adsorption process

$C_e$  = concentration of Cd and As in the solution after adsorption

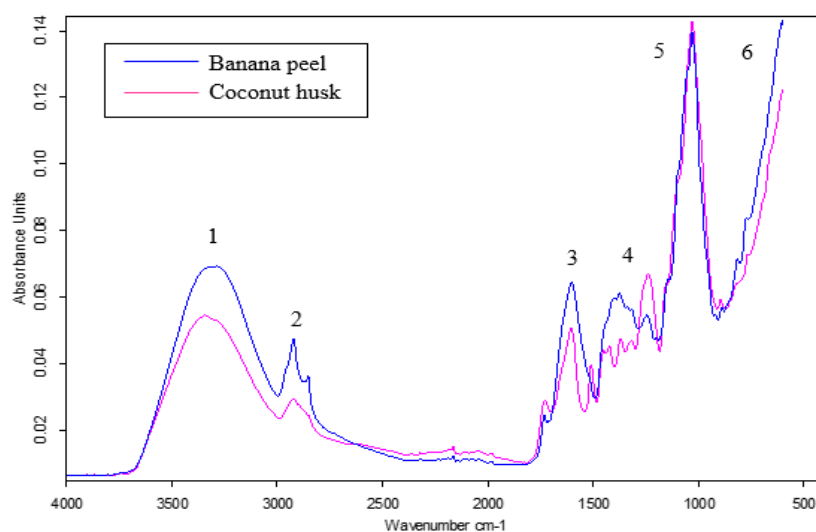
### 2.4. FTIR Analysis of Adsorbents

The composition of functional group in banana peel and coconut husk adsorbents was determined by using attenuated total reflectance-Fourier transform infrared spectroscopy (ATR-FTIR) (Bruker Corporation, Billerica, MA) at Kampus Kesihatan, Universiti Sains Malaysia. In order to determine the absorbance in the mid-infrared spectrum, the absorbance was measured in a wavenumber range between 4000  $\text{cm}^{-1}$  and 600  $\text{cm}^{-1}$ .

## 3. Results and Discussion

### 3.1. Characterization of Adsorbents

In order to identify the presence of significant functional groups, such as carbonyl and hydroxyl, on the surface of the adsorbents, the characterisation of coconut husk and banana peel was carried out using FTIR. These functional groups are crucial in the adsorption of heavy metals because they bind trace metal ions strongly and speed up the removal process [14]. Figure 3.1 displays the spectrum obtained from a combination of a banana peel and a coconut husk.

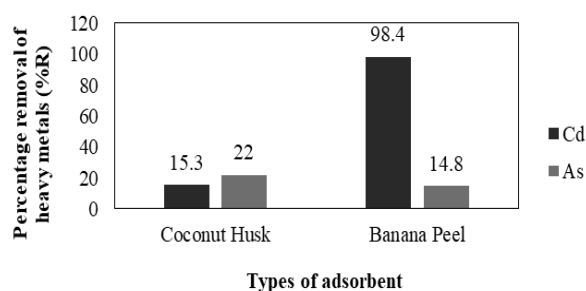


**Figure 3.1:** The FTIR spectrum for the banana peel (blue) and coconut husk (pink) which show several peaks; 1- (O-H) groups, 2- (C-H) groups, 3- (C=O) groups, 4,5,6- fingerprint region.

Banana peel and coconut husk surfaces were found to have a variety of functional groups, including hydroxyl (O-H), carbonyl (C=O), and (C-H) groups, according to the results of FTIR analysis. The functional groups present in both adsorbents were most likely similar, although their intensity varied. The (O-H) groups from the polyphenols that were initially present in both adsorbents are responsible for the peak at a range of 3500–3000  $\text{cm}^{-1}$  [13]. Additionally, the stretching vibration of (C-H) groups was attributed to the adsorption band at about 2900  $\text{cm}^{-1}$  and (C=O) stretching vibrations are seen at their peak between 1630–1800  $\text{cm}^{-1}$ . These functional groups have shown that heavy metals are more likely to attach to the surface of adsorbents, notably (O-H) and (C=O). The coconut husk and banana peel adsorbents have sufficient (C=O) and (O-H) functional groups, which anticipated that they would be successful in removing the heavy metals from the aqueous solution.

### 3.2. The Effects of Different Types of Adsorbents

Figure 3.2 compares the performance of several adsorbents, including banana peel and coconut husk, in removing the metal ions As and Cd from aqueous solutions. Other factors were kept constant, including the dose of 0.1 g, the reaction time of 30 minutes at 25°C. As a consequence of the removal procedure using coconut husk, the concentration of the Cd and As ions were 0.153 mg/L and 0.22 mg/L while the percentage removal were of 15.3% and 22.0%, respectively. However, when Cd and As ions were removed using banana peels, the final concentration were 0.984 mg/L and 0.148 mg/L while removal percentage was 98.4% and 14.8%.

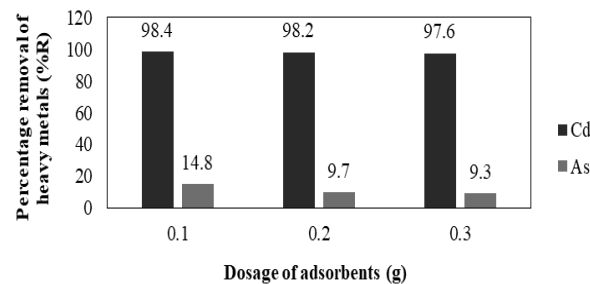


**Figure 3.2:** The percentages removal of Cd and As ions after treatment with 0.1 g of banana peel and coconut husk for 30 minutes at 25°C.

As shown in Figure 3.2, coconut husk was less effective at removing Cd and As ions as higher concentrations of both metal ions could be found and low removal efficiency were found following the removal procedure. However, due to the observation of extremely low amounts of Cd ions after removal, banana peel demonstrated greater efficacy in removing Cd and As ions. The banana peel was considered to have much more functional groups for metal ion coordination because the peaks corresponding to the hydroxyl and carboxyl groups are well resolved in the FT-IR spectrum (Figure 3.1), which contrasts it with the coconut husk [15]. Additionally, the structure of banana peels is very porous, which plays a significant role in the adsorption process. These pores have a high surface energy, which attracts and stores ions [16]. As a result, it was determined that banana peel is more effective than coconut husk in removing Cd and As ions, and it has been chosen as the next parameter.

### 3.3. Effects of different dosages of banana peel

The significant effects of dose variations on the elimination of Cd and As metal ions from aqueous solutions were examined using the banana peel. Figure 3.3 illustrates how the various banana peel dosages which were 0.1 g, 0.2 g, and 0.3 g affected the amounts of Cd and As ions removed, whereas the temperature and contact time were held constant at 25°C and 30 minutes. Following the treatment procedure, the concentrations of Cd ions removed were 0.984 mg/L, 0.982 mg/L, and 0.976 mg/L, respectively, with removal percentages of 98.4%, 98.2%, and 97.6% using adsorbent dosages of 0.1 g, 0.2 g, and 0.3 g. After being treated with 0.1 g, 0.2 g, and 0.3 g of banana peels, the percentages of As ions removed from the aqueous solution were 14.8%, 9.7%, and 9.3%, respectively. As ions were recovered at concentrations of 0.148 mg/L, 0.097 mg/L, and 0.093 mg/L, respectively.

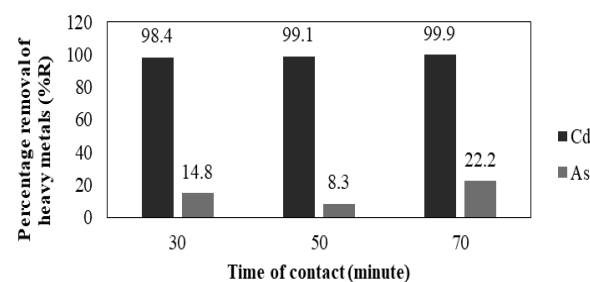


**Figure 3.3:** The percentages removal of Cd and As ions after treatment with 0.1 g, 0.2 g, and 0.3 g of banana peel for 30 minutes at 25°C.

From Figure 3.3, the highest percentage removal of As and Cd ions by banana peel can be seen at 0.1 g of dosages. A prior study by [17] found that as adsorbent weight increases, so does the percentage of metal ions removed. The increased adsorbent dosage in the solution may actually provide more metal ion exchangeable sites and a larger surface area. After the adsorption procedure utilising banana peel, the findings showed a patchy pattern in the percentage removal of Cd and As ions. At doses as low as 0.1 g, both of them have the maximum adsorption rates, and as dosages rise, the clearance percentages decrease (concentrations rise). This could be because when the adsorbent dosage was raised, the adsorption capacity decreased [18].

#### 3.4. Effects of different contact time of banana peel

For the aim of eliminating heavy metals from aqueous solutions, the efficacy of banana peel as an adsorbent was examined at three different contact times. Figure 3.4 illustrates how the removal of As and Cd ions from banana peels changed with varied contact times, which were 30, 50 and 70 minutes while other variables were kept constant. Following the application of the banana peel, the percentages of Cd ions removed from the aqueous solution at 30, 50, and 70 minutes were 98.4%, 99.1%, and 99.9%, respectively. The amounts of Cd ions removed were 0.984 mg/L, 0.991 mg/L, and 0.999 mg/L, respectively. While the percentage removal of As ions in the aqueous solution were 14.8%, 8.3%, and 22.2%, respectively. As ions were recovered at concentrations of 0.148 mg/L, 0.083 mg/L, and 0.222 mg/L, respectively. At 70 minutes of contact time, banana peel removal of Cd and As ions reaches its highest percentage.



**Figure 3.4:** The percentages removal of Cd and As ions after treatment with 0.1 g of banana peel for 30 minutes, 50 minutes, and 70 minutes at 25°C.

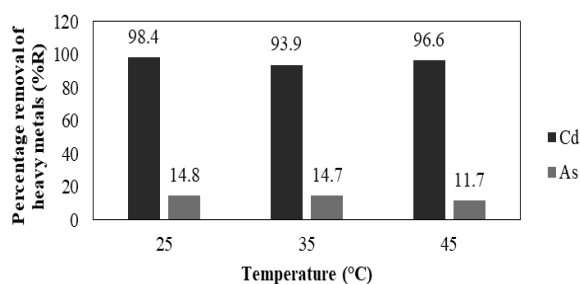
As the contact time increased, there was an increasing trend in the removal of Cd ions. The amount of unbound metal ions in the aqueous solution will decrease and finally reach saturation while there are still enough of binding sites available [19]. According to a previous study by [20], the biosorption process gradually increases with increasing adsorbent concentration and time of contact, but it almost remains constant when these values are reached.

However, the pattern that appeared from in As elimination following the adsorption procedure using banana peel was uneven. The percentage removal for each dosage was quite low, despite the fact that

this adsorbent was able to reduce the concentration of As ions in the solution. The trend was irregular, as seen by the sudden increase in the proportion of As ions removed as well as the decrease in the removal rate. In order to increase the adsorption of heavy metals, [21] found that a highly specific surface area can create more active sites on the adsorbent's surface. The difference in removal efficiency was affected by the metal's adsorption affinity and the metal ions' ability to remove themselves from the aqueous solution [22].

### 3.5. Effects of different temperatures of banana peel

Other than that, the removal of Cd and As metal ions from aqueous solution was observed using a banana peel to evaluate the significant effects of temperature variations. The absorption of As ions using banana peel was observed by the three different temperatures, 25°C, 35°C, and 45°C, as shown in Figure 3.5. The removal percentages of Cd ions in the aqueous solutions following the treatment with banana peels at 25°C, 35°C, and 45°C were 98.4%, 93.9%, and 96.6%, respectively. There were 0.984 mg/L, 0.939 mg/L, and 0.966 mg/L of Cd ions removed, respectively. After being treated to banana peels at 25°C, 35°C, and 45°C, the percentages of As ions removed from the aqueous solution were 14.8%, 14.7%, and 11.7%, respectively. There were 0.148 mg/L, 0.147 mg/L, and 0.117 mg/L of As ions eliminated, respectively. At a temperature of 25°C, banana peels remove the highest percentage of Cd and As ions.



**Figure 3.5:** The percentages removal of Cd and As ions after treatment with 0.1 g of banana peel for 30 minutes at 25°C, 35°C, and 45°C.

Following the adsorption procedure utilizing banana peels, the removal of Cd and As ions showed an uneven pattern. When the reaction temperature is just 25°C, both of them have the maximum adsorption rates, and as the temperature increases, their removal percentages decrease. The endothermic adsorption process may be seen in the early stages of temperature as enhanced heavy metal adsorption capability and absorption [23]. This phenomenon could be driven on by rapid ion exchange and a change of pore size of the adsorbent. The proportion of adsorption decreases as temperature increases, which may be caused by the lowering of equilibrium constant at higher temperatures, in line with Le Chatelier's principle [24]. Therefore, as the temperature increased, the equilibrium of adsorption in a particular system decreased.

The removal efficiency of Cd was higher than As ions, as shown in Figures 3.3 to 3.5. The variance in percentage removal may be caused by the different affinity of binding between metal ions and active sites of banana peel [22]. Ionic radius was one of the elements that impacted the affinity of metal ions. Compared to As ions, the Cd ions have a higher ionic radius, which facilitates the rapid saturation of adsorption sites and increases adsorption capacity [25]. From this, it has a stronger affinity for adsorbents and may be removed out of aqueous solutions more easily.

## 4. Conclusion

By employing two distinct types of natural waste adsorbents which were banana peel and coconut husk, the biosorption method efficiently removed Cd and As metal ions from the aqueous solution. After observation in the effects of several adsorbents on four different parameters, banana peel was selected as the next parameter. The removal efficiency of As and Cd ions by banana peel were 14.8% and 98.4%, respectively, showing that it was more effective than coconut husk. With regard to other factors, the range of heavy metal removal in the aqueous solution for Cd ions employing banana peel as the

adsorbent was 93.9 to 99.9%. While the percentage removal of As ions in aqueous solutions using banana peel ranged from 8.3% to 22.2%.

From this study, the optimal conditions for employing this procedure to the both metal ions were 0.1 g of adsorbents for 70 minutes of 25°C. The banana peel was observed as an excellent adsorbent to remove Cd ions based on the results of this study since a high percentage removal was achieved. Additionally, both adsorbents have undergone FTIR analysis. The investigation showed that the presence of certain groups, such as the (C=O) and (O-H) groups, increased likelihood that these heavy metals would bind to these adsorbents.

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