Column adsorption of cadmium (II) and lead (II) using rice husks and mango peels

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Abstract

Cadmium (II) and lead (II) are commonly found in industrial wastewaters and have negative effects to the body and the environment with prolonged exposure. Conventional methods to remove these metals are costly and inefficient. An alternative method that is more economical is through adsorption, specifically through the use of fruit and vegetable peels. The adsorption efficiencies of a multi-adsorbent column setup composed of rice husk and mango peels, and single-adsorbent columns individually composed of rice husk and mango peels were determined and compared in the removal of cadmium and lead. The heavy metal solution with an initial concentration of 10 mg/L and 30 mg/L for lead and cadmium, respectively, and a pH of 6.0, was tested on the adsorbent column with a bed height of 15cm and a flow rate of ~10mL/min. It was determined that the combination setup had the lowest adsorption efficiency out of all three setups. This was attributed to a reduction on the masses of the adsorbents to control the bed height variable. The single adsorbent columns achieved a higher adsorption efficiency with rice husk at 94.661% for lead and the mango peel column at 80.860% for cadmium.

Keywords: *bed height, column adsorption, heavy metals, multi-adsorbent setup, agricultural wastes*

Introduction. Heavy metals found in industrial wastewater have been increasing over the years due to industrialization [1]. Among the heavy metals present, cadmium and lead are one of the most common heavy metals in industrial wastewater [2,3]. They are especially prevalent in the Iloilo Batiano River wherein the amount of heavy metals exceeded standard levels [4].

Conventional methods are costly and inefficient in removing heavy metals [5]. Thus, fruit and vegetable peels have been previously studied by researchers as potential adsorbents. Among household wastes, mango peels [2,6] and rice husks [5] are known to be capable adsorbents and are very cheap.

Two common methods in removing heavy metals are the batch and column methods. The column method is preferred since it tests the industrial scale applicability of an adsorbent [7].

Most column biosorption experiments used one type of adsorbent material. However, in some studies like that of Navaratne et al. [8], multiple adsorbents were utilized. Multiple adsorbents whether using the batch [9] or column [8] methods have been observed to increase the adsorption uptake of heavy metals when compared to single adsorbent setups. Although some adsorbents are efficient in removing a single type of heavy metal, industrial wastewater rather contains multi-metal species. Thus, evaluating a multi-adsorbent column setup in a solution containing multiple heavy metals is a more practical simulation to real-world industrial wastewater.

Only a few from previous studies have evaluated the capability of a column setup, composed of two different adsorbents, in adsorbing multiple heavy metals. Thus, the study utilized a multi-adsorbent column setup without well-defined layers. It is hypothesized that the column setup with multiple adsorbents will have a higher adsorption efficiency as compared to single adsorbent columns.

This study aimed to determine the adsorption efficiency of a fixed-bed column composed of rice husks and mango peels combined in equal proportions and compare it to the adsorption efficiency of a fixed-bed column with single adsorbents composed of only rice husks and only mango peels for the removal of cadmium (II) and lead (II) in the same aqueous solution. It specifically aimed to:

(i) determine the influent and effluent concentrations (mg/L) of cadmium (II) and lead (II); and

(ii) calculate and compare the percent adsorption (%) of the fixed-bed column setup composed of rice husks, mango peels, and a combination of both in adsorbing cadmium (II) and lead (II).

Methods. The rice husks and mango peels were washed, oven-dried, crushed, and weighed before

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they were packed inside the column. Three hundred (300) mL of the heavy metal solution containing lead and cadmium was passed through each of the columns with an approximate flow rate of 10 mL/min. A total of three replicates were conducted for each column. The initial and final metal concentrations were analyzed using the Agilent 4200 Microwave Plasma-Atomic Emission Spectrometer (MP-AES) and were used to calculate for the adsorption efficiencies of the different setups. The data obtained were analyzed using One-Way ANOVA with LSD used as a post-hoc test.

Preparation of the adsorbents. One kilogram husks of *Oryza sativa* from Iloilo Central Market was initially washed with tap water and then with distilled water thrice by batches. After washing, the rice husks were oven-dried for eight hours at 70°C to remove any moisture. It was then ground using a blender. Ten kilograms of ripe mangoes, ranging from class four to five on the ripeness chart [15], was obtained from Iloilo Central Market. The mango peels were sliced into small squares and were initially washed with tap water by batch. It was then washed with distilled water thrice and was oven-dried for 72 hours at 70°C [2]. After drying, it was placed inside a plastic container and was crushed manually. Both the adsorbents were sieved to particles larger than 2 mm. After sieving, the adsorbents were stored in separate air-tight containers.

Preparation of metal solution. Solutions with a concentration of 10 mg/L and 30 mg/L for lead and cadmium respectively were prepared from the following salts: $3CdSO_4 \cdot 8H_2O$ (cadmium sulfate octahydrate, Scharlau) and $Pb(NO_3)_2$ (lead nitrate, Farco) [3]. Using an analytical balance, 60.44 mg of $3CdSO_4 \cdot 8H_2O$ and 47.95 mg of $Pb(NO_3)_2$ were weighed. The salts were then poured into three one-liter volumetric flasks. Deionized water was poured to mark into each of the volumetric flasks. The flasks were agitated until there were no visible solid salt particles in the solution. A pH of 6.0 was obtained using 0.1 M of hydrochloric acid. A strip of pH paper with an accuracy of 1 pH was used to determine the pH of the solution prior to adsorption. The three liter heavy metal solution was transferred and stored in a four-liter HDPE bottle.

Column Design. Before the columns were packed, they were washed with distilled water thrice and were left to air-dry. Using a wooden rod, glass wool was packed inside the column up to a height of 2 cm. After making sure that that layer was flat, the adsorbent layer (rice husks for setup A; mango peels for setup B; a 50:50 bed height combination of rice husk and mango peels for setup C) was then poured inside the column until a 15 cm layer was formed. The sides of the column were tapped for even distribution of the adsorbents. A final layer of glass wool with a height of 1cm was placed on top of the setup. As a primer, 100 mL of deionized water was passed through the column.

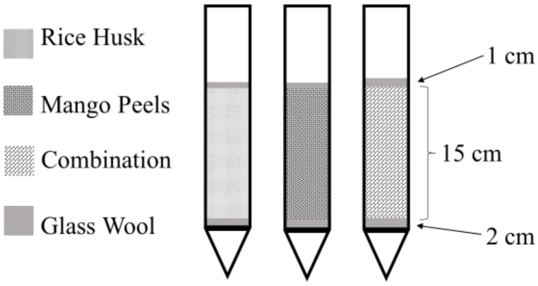

Figure 1. The schematic diagram of the column setups composed of A) rice husks only, B) mango peels only, and C) combination of rice husks and mango peels.

Column Adsorption Experiment. Three hundred mL of the heavy metal solution containing cadmium (II) and lead (II) was passed through the setup. Using a burette as an alternative to a peristaltic pump, the first batch of 50 mL of the 300 mL stock solution was poured into the burette using a funnel. After some of the 50 mL of the solution has finished passing through, the next 50 mL was added into the burette. The procedure was repeated six times. The effluent solution was collected in a 500 mL beaker. The procedure went on until the influent had been fully poured. The effluent solution was transferred from the beaker to an HDPE container for analysis. Concentrated nitric acid was added dropwise to the solution. The column adsorption experiments were done for all setups with each setup having three replicates.

Data Analysis. The heavy metal concentrations were analyzed using the Agilent 4200 MP-AES with a maximum sensitivity of 1 mg/L, and the minimum concentration it can detect is 0.001 mg/L and 0.003 mg/L for lead and cadmium, respectively at the Department of Science and Technology - Region VI. The standard method used was the direct aspiration and digestion of the samples that was done prior to analysis. The total percent adsorption was determined using the initial and final concentrations in mg/L of cadmium (II) and lead (II) ions present in the solution. The percent adsorption was calculated using the formula [8]:

$$Percentage\ Removal\ = \frac{Ci - `Cf}{Ci} \times 100$$

Where C_i is the initial concentration and C_f is the concentration of the metal ion present in the effluents collected from columns.

Statistical Analysis. A test for homogeneity was conducted for the adsorption capacities for the replicates of each setup. One-way ANOVA for the three means using the R Programming Language version 3.5.3 (March 2019) was used to analyze the adsorption efficiencies. A significance level of 0.05 was used. When a significant difference was observed, the Least Significant Difference (LSD) was used as a post-hoc test.

Safety Procedure. The leftover influents, effluents, and greywater collected from the washing were stored separately in properly-labeled air-tight polyethylene (PET) bottles and were handed over to the PSHS-WVC Science Research Assistant for proper storage and disposal. While the used adsorbents were tightly wrapped with paper and were stored inside properly-labeled air-tight plastic bags. The liquid and solid wastes were stored separately. Both waste disposal methods were in accordance with the protocol of the Department of Science and Technology Region VI.

Results and Discussion. Presented in Table 1 are the mean ± standard deviation of the influent and effluent concentrations. The mean initial concentration of cadmium was 29.630 mg/L with a standard deviation of 0.668. The mean initial concentration of lead was 9.370 mg/L with a standard deviation of 0.014. Among the three setups, setup B achieved the lowest final concentration at 5.672±2.028 mg/L for cadmium adsorption. It was followed by setup A at 7.498±1.871 mg/L of cadmium and then, setup C at 10.242±0.956 mg/L of cadmium. Among the three setups, setup A achieved the lowest final concentration for lead at 0.050±0.387 mg/L. It was followed by setup B at 1.509±0.329 mg/L of lead and then, setup C at 1.975±0.324 mg/L of lead.

Table 1. Mean ± standard deviation of the concentrations (mg/L) of the influents and effluents for cadmium and lead.

Adsorbent	Cadmium (mg/L)	Lead (mg/L)
Initial	29.630 ± 0.668	9.370 ± 0.014
Rice Husk *(setup A)*	7.498 ± 1.871	0.050 ± 0.387
Mango Peel *(setup B)*	5.672 ± 2.028	1.509 ± 0.329
Combination *(setup C)*	10.242 ± 0.956	1.974 ± 0.324

The comparison between the adsorption efficiency for each setup is shown in Figure. 2. Among the three setups, setup A achieved the highest percent adsorption in removing lead at 94.66%. On the other hand, setup B achieved the highest percent adsorption for cadmium at 80.86%. For both heavy metals, setup C achieved the lower percentages adsorption.

As denoted by an asterisk (*) in Figure 2, it was determined that setup A has a significantly higher percent adsorption for lead compared to both setup B (0.012 ≤ 0.05) and setup C (0.002 ≤ 0.05). For cadmium adsorption, setup B was found to have a significantly higher percent adsorption compared to setup A and setup C. Additionally, there was a significant difference observed in the percent adsorption for the other two setups. Generally, the adsorption efficiencies of the single-adsorbent column setups were much higher than the combination setup.

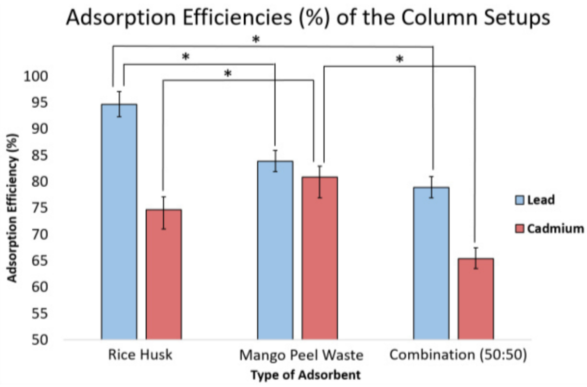

Figure 2. The percent adsorption (%) and standard deviations of each setup for cadmium and lead (* denotes that the p ≤ 0.05, thus there is a significant difference between the means of the setup).

The results of the study suggest that both rice husks and mango peels vary in the efficiency of removal of a specific heavy metal in a multi-metal solution. It was also determined that the combination of these two adsorbents in the combination column setup reduced the adsorption efficiency.

The three columns were able to achieve adsorption efficiencies ranging from 65.438% to 94.661%. However, it was observed that setup C composed of both adsorbents having a 50:50 bed height ratio had a lower adsorption efficiency for both metals. The lower adsorption efficiency of a combination column setup can be attributed to the reduction of their adsorbent mass that specializes in the adsorption of a specific heavy metal [5]. Having a much lower adsorbent mass would result in less binding sites for the metal ions; thus, the total adsorption efficiency would also decrease. In conjunction with the study by Navaratne et al. [8], the multi-adsorbent setup did not have the highest efficiency. Instead, the single adsorbent column composed of brick clay had the highest adsorption efficiency for both cadmium and lead. Similarly, in this study, both the single adsorbent setups, the rice husk and mango peel columns, had the highest adsorption efficiencies compared to the combination setup in removing lead and cadmium, respectively. However, the results of this study are in contrast to the findings of Binabaj et al. [9] which determined that the multi-adsorbent batch setup had the highest adsorption efficiency compared to single adsorbent setups due to the diversity of the functional groups existing on the surfaces. A 50:50 adsorbent ratio was not guaranteed to produce the highest adsorption efficiency as observed in the study of Binabaj et al. [9] which conducted the batch method rather than the column. Their multi-adsorbent setup, composed of coal and zeolite, had the highest adsorption efficiency at a coal to zeolite ratio of 75:25.

The rice husk setup achieved the highest adsorption efficiency for lead at 94.661% with a standard deviation of 4.192%. The efficiency of rice husks in removing lead ions from water is mainly attributed to the presence of functional groups such as carboxyl, silanol, and hydroxyl wherein the different electronegativity charges enable the metal ion to attach itself unto the functional groups [5]. The initial concentration of 10mg/L also has an effect on removal efficiency because having a lower concentration results in lesser saturation onto the available adsorption sites [5]. Similar to the results of this study, both Prabha and Udayashankara [5] and Sadon et al. [10] have identified rice husks as an efficient adsorbent in the removal of lead without being subjected to any form of chemical modification. Furthermore, it is worth noting that Sadon et al. [10] found multi-layered fixed-bed column setups to be more favorable in the adsorption of a multi-metal solution as compared to a single-layered setup which was what was utilized in this study.

The mango peel adsorbents achieved the highest adsorption efficiency for cadmium at 80.860% with a standard deviation of 6.845%. Mango peel adsorbents have high adsorption efficiencies due to the presence of hydroxyl and carboxyl functional groups which have different electronegativity charges [6,11]. The results of this study go in accordance with the result of the study of Iqbal et al. [2] which determined a high adsorption efficiency of mango peels for cadmium at 68.92 mg/g as well as for lead at 99.05 mg/g. Similar to the case of rice husk adsorbents, the removal efficiency of mango peel adsorbents can be affected by the initial concentration of the solution. At low metal concentrations, adsorption sites take up the available heavy metal more quickly due to the fewer metal ions competing for adsorption sites [11]. In this study, the adsorbent's uptake for lead is greater than cadmium since the initial concentration of the former is greater than the latter.

As observed in previous column studies, the adsorbent mass and column bed height could have also affected the individual efficiencies of each column. The adsorbent mass inside the column is proportional to the bed height. A taller bed height corresponds to a higher adsorbent mass and an increased surface area, hence, it results in a higher adsorption efficiency [5,11,12,13]. Thus, when the bed height is increased, there are more binding sites for the adsorbents which allows for an increased adsorption of heavy metal ions. Since the bed height was controlled, the combination column had lesser adsorbent masses to maintain a 15-cm bed height. At the same time, it is worth noting that increasing adsorbent mass does not always result in a higher adsorption efficiency. In a column setup with a higher bed height, all of the adsorbents may not be fully utilized [12,13]. This indicates that the adsorbent mass is in excess. Essentially, the amount of metal ions on the adsorbents and the amount of free ions remains constant even with the increase of the adsorbent mass. Determining the least possible amount of adsorbent to achieve maximum adsorption efficiency is significant in terms of economic viability [14]. Moreover, even though bed height is an important factor in column studies, adsorbent mass should also be looked into when implementing a multi-adsorbent column because the number of binding sites are also dependent on the adsorbent masses. It is important to consider that adsorbent masses for a certain bed height are different for each adsorbent due to the differences in their bulk density.

Lastly, it has been noted that when implementing a column setup, factors such as adsorbent mass, bed height, initial metal concentration, particle size, contact time, and pH level must be tested at different values in order to determine at which parameter values can the optimum adsorption efficiency be achieved.

Limitations. The study determined the potential use of multi-adsorbents in a column setup in removing multiple heavy metals. Primarily, it was focused on the comparison of the adsorption efficiencies of the (a) rice husk column, (b) mango peel column, (c) and the combination column composed of rice husk and mango peels. A burette was used instead of a peristaltic pump in controlling the influent flow rate due to material unavailability. pH paper was used to measure the pH because of the unavailability of a pH meter. Due to lack of resources, the study did not subject the column setups to positive and negative controls as well as different initial concentrations, adsorbent mass ratio, pH levels, flow rate/contact time, particle sizes, and there was no use of mathematical models and breakthrough curves.

Conclusion. It was determined that the single adsorbent column achieved the higher adsorption efficiency with rice husk at 94.661% for lead and the mango peel column at 80.860% for cadmium while the combination setup had the lowest adsorption efficiency which can be attributed to a reduction on the masses of the adsorbents to control the bed height variable. Since a reduction of adsorbent mass can affect the adsorption capability, the adsorption efficiency for the combination column was the lowest. Even though the combination column had a much lower efficiency, the use of multiple adsorbents in a column is a better design because it was considered to be capable of addressing multiple heavy metals; however, some design factors still need to be explored.

Recommendations. It is recommended to manipulate the ratio of the adsorbent mass in the combination column and test the column at different metal concentrations and pH levels to optimize operating parameters. Moreover, implementing a combination column with three or more adsorbents at different ratios in adsorbing multiple heavy metals may further expand the column design and including mathematical models and breakthrough curves can better explain the adsorption process.

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