



Exploring the Potential of Cacao Pod Husk as an Adsorbent of Simulated Water Pollutants

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DOI : <https://doi.org/10.55248/gengpi.6.0225.0723>

ABSTRACT

This study evaluated the levels of heavy metals, namely cadmium, lead, and mercury, from key aquatic fauna and sediments from seven strategic potentials of the Philippines. The researchers explore the potential of activated carbon using cacao pod husk, using only a single chemical agent to successfully achieve the toxic metal pollution. The results indicate that the 50% KOH concentration yielded the highest mean adsorption efficiency (0.66 ppm), followed by the 70% KOH (0.38) concentration (0.58) concentration, and lastly, the absence of KOH resulted in the lowest average amount of Lead (Pb) and Cadmium (Cd). The computed pvalue (2.920) and coefficient of variation (C.V = 0.53) indicate that there is no statistically significant difference in adsorption efficiency across the different concentrations. These findings highlight how using chemicals to activate the carbon improves its ability to absorb these metals, making it a practical and ecofriendly option for cleaning up polluted water.

Introduction

Water is polluted by the increasing activities including the rising of population and the necessity to provide goods that use water as a vital resource. The contamination of heavy metals is one of the big concerns of humankind, due to consequences of both aquatic ecosystems and human health. Moreover, heavy metals like: cadmium, lead, nickel and others are all around us. Mostly, they are found in lakes, groundwater, rivers, and other water sources by the increased concentration of heavy metal, the water gets more polluted. This water pollution becomes strongly toxic by emerging with different environmental elements such as soil, even in water, air, human and including other living organisms can be exposed to them through food that contains heavy metals.

Heavy metal contamination of the aquatic environment is of worldwide concern, due to the toxicity of metals and their lethal effects on aquatic organisms (Karaouzas, et al., 2021). These metals are discharged from an assortment of sources such as mining, urban sewage, smelters, tanneries, textile industry and chemical industry. Technologies utilized for their expulsion from aquatic bodies incorporate reverse osmosis, ion-exchange, electro dialysis, adsorption, etc. Most of these technologies are quite costly, energy intensive and metal specific. These conventional technologies for the expulsion of the dangerous heavy metals are most certainly not practical and further create colossal amount of harmful chemical sludge (Zehra, et al., 2020). Mining and manufacturing, along with fertilizer and pesticide use, were dominant sources in North America, while four sources (mining and manufacturing, fertilizer and pesticide use, rock weathering, and waste discharge) were responsible for the majority of heavy metal pollution in the river and lake water bodies of South America. Heavy metal concentrations in water, and the number of heavy metals with concentrations above the threshold limits for both WHO and USEPA standards were lower in the developed countries of Europe and North America, and higher in the developing countries of Africa, Asia, and South America (Zhou, et al., 2020).

Diwa, et al (2021) stated that the heavy metal pollution in Manila Bay is attributed to several rivers draining northeast of Manila Bay, particularly the Marilao-Meycauayan-Obando River System (MMORS) which is cited as one of the 30 dirtiest river systems in the world. Laguna de Bay is the largest multipurpose lake in the Philippines. Of the primary uses, fish cultivation and potable water production depend mainly on its water quality. Over the years, this tropical lake has been inundated with pollution from agricultural, industrial and domestic wastewaters. While new contaminants have emerged, traditional contaminants including heavy metals continue to threaten the lake's resources (Sacdal, et al., 2022).

Heavy metals have the ability to accumulate in the human body and disrupt functions of some body organs. These metals can find their way into humans by consumption of metal-contaminated fish (Dacera, et al., 2018). Lake Mainit is one of the largest lakes recognized as one of Key Biodiversity Areas (KBAs) in the Philippines with rich fishery resources. However, the lake is at risk from heavy metal contamination due to inputs of industrial, agricultural effluents and small-scale mining activities. The present work evaluated levels of heavy metals namely cadmium, lead, and mercury from key aquatic fauna and sediments from seven strategic sections of the lake in 2018 (Ebol, et al., 2020).

Adsorbents prepared by introducing active functional groups such as amino, carb.oxyl, ester, and sulfonic acid groups with lignin as raw materials (Zhang, et al., 2023). Biochar is effective for the removal of several toxic metals (As, Cr and Mn) from groundwater and drinking water. Biochar also shows promising performance for the removal of various heavy metals (Cr, Pb, Cu, Cd and Zn) from wastewater (Biswal, et al., 2023). Among various treatment methods, the adsorption process is considered as one of the highly effective treatments of heavy metals and the functionalization of adsorbents can fully enhance the adsorption process. Therefore, four classes of adsorbent sources are highlighted: polymeric, natural mineral, industrial by-product, and carbon nanomaterial adsorbent (Zaimie, et al., 2021). The various studies has its limitations in uses of materials, the porosity and its potential thickness, and many different chemical aspects are used. With these, the researcher to explore the potential of Activated Carbon using Cacao pod Husk, using only single chemical agent to be successfully achieve the toxic metal pollution.

Statement of the Problem

This research aimed to investigate the potential of cacao husk as an adsorbent for reducing water pollutants such as Lead and Cadmium that are mostly in processed water. Specifically, this research aimed to answer the following questions:

1. What is the number of adsorption efficiency of Cacao husk activated carbon when treating water with cadmium in terms of concentration level;
 - 1.1 No KOH
 - 1.2 50%; and
 - 1.3 70%
2. What is the number of adsorption efficiency of Cacao husk activated carbon when treating water with lead in terms of concentration level;
 - 2.1 No KOH
 - 2.2 50%; and
 - 2.3 70%
3. Is there a significant difference in the adsorption efficiency of each concentrations of cacao husk activated carbon in treating water with cadmium and lead?

Research Hypothesis

This study was tested at 0.05 level of significance.

H₀: There is no significant difference in the amount of cadmium and lead adsorbed when treated with cacao husk activated carbon across different concentrations.

Literature Review

This section contains the literature and empirical studies relevant to the study. These are selected for their relevance and significance to the topic under investigation the following topics: Cacao pod husk waste, Heavy metal problem and effectiveness of Cacao pod husk as heavy metal adsorbent.

Cacao pod husk problem

The Philippines is one of the countries in Asia seen to have a competitive advantage for cacao production due to its strategic location, good climatic condition, and favorable soil. However, despite its competitive advantage, cacao production in the country is still unable to meet the current requirements of the growing cacao-based industry due to several problems affecting the industry, and thus resort to importing cacao beans from other producing countries (Philippines

Statistics Authority., 2024). Andres and Tuates Jr. (2020) stated that the cacao (*Theobroma cacao*) pod is generally composed of husk and mucilaginous pulp surrounding the bean. About 90% of the pod is discarded as waste and remains underexploited. The pod husks are traditionally disposed to rot in the farms resulting in a waste management problem, especially because the demand for chocolate increases. The cacao (*Theobroma cacao* L.) pod is generally composed of husk and mucilaginous pulp surrounding the bean. About 90% of the pod is discarded as waste and remains underexploited. The pod husks are traditionally disposed to rot in the farms resulting in a waste management problem, especially because the demand for chocolate increases. An economical and environmentfriendly way to deal with this is to extract pectin from the pod husks (Tuates Jr, et al., 2020).

Effectiveness of cacao husk to use as activated carbon

Cacao husk (CH) have several significant advantages compared to similar adsorbents, such as activated carbon, zeolites, and sawdust. One of the main advantages of cacao husk is their abundant availability and low cost. In comparison, activated carbon still requires special raw materials and a complex activation process. Zeolites have a microporous structure that is good for adsorption, but often requires more complicated synthesis (Saleem, et al., 2019). Sawdust has a lower adsorption capacity than modified cacao husk and often requires additional treatment to increase its efficiency. Another

advantage of cacao husk is their ability to be activated and modified easily, such as through thermal treatment and the addition of polymer synthesis (da Silva, et al., 2019). The removal efficiency of the cacao pod husk as an adsorbent for toxic metals was above 90%. Hence, cacao pod husk biochar is a very good precursor for the development of adsorbents from the aqueous phase (Abbey, et al., 2023).

Heavy metal problem

Heavy metals are highly toxic elements which are persistent in the natural environment, resulting in magnification throughout the food chain, adversely affecting both human and environmental health (Wang, et al., 2022). The scarcity of clean water resources leads to many scientific and technological advancements in wastewater treatment processes. The recalcitrance of heavy metals in wastewater has been proven to be a challenging concern. Therefore, there is a need for more water treatment technologies to completely remove heavy metals down to a non-hazardous level (Saleh, et al., 2022). Anthropogenic activities are identified as the main source of the increasing amounts of heavy metals found in aquatic environments. Some of the health hazards derived from repeated exposure to traces of heavy metals, including lead, cadmium, mercury, and arsenic, are outlined (Zamora-Ledezma, et al., 2021).

With heavy metals in lakes, rivers, groundwater, and various water sources, water gets polluted by the increased concentration of heavy metals and metalloids through release from the suddenly mine tailings, disposal of high metal wastes, growing industrial areas, leaded gasoline and paints, usage of fertilizers inland, animal manures, E-waste, sewage sludge, pesticides, wastewater irrigation, coal, etc. Exposure to heavy metals has been linked to chronic and acute toxicity, which develops retardation; neurotoxicity can damage the kidneys, lead to the development of different cancers, damage the liver and lungs; bones can become fragile; and there are even chances of death in case of huge amount of exposure (Singh, et al., 2022).

Effectiveness of Activated Carbon using Cacao as Heavy metal adsorbent Activated carbon refers to a wide range of carbonized materials of high degree of porosity and high surface area. Activated carbon has many applications in the environment and industry for the removal, retrieval, separation and modification of various compounds in liquid and gas phases (Heidarinejad, et al., 2020). Activated carbon (AC) is an important material in various fields owing to its low cost, well-developed porosity, and favorable chemical stability. Key factors for the optimal synthesis of AC are the carbon precursors, activation pathways, activating agents, and design of the procedure parameters (Gago, 2020). Additionally, activated carbon has recently attracted the attention of wastewater treatment industries because of its significantly high adsorption capacity against heavy metals. The large surface area, suitable surface functional groups, and appropriate pore diameter make activated carbon a potential adsorbent (Mariana, et al., 2021).

The mechanism of adsorption of the evaluated metals onto cocoa pod husk was attributed to cationic exchange and microprecipitation due to the presence of Ca, K, and Si in the structure of the bio-adsorbent (Tejada-Tovar, et al., 2022). Traditional removal methods of these heavy metals, like chemical precipitation, oxidation/reduction, filtration, ion exchange, membrane separation, and adsorption, are costly, inefficient, and have drawbacks. As an efficient and low-cost adsorbent, biochar has the potential for heavy metal remediation from water. Biochar is a versatile carbonaceous material produced through pyrolysis of organic wastes, emerged as a powerful adsorbent for heavy metal removal from contaminated water. The unique property of biochar makes it an effective medium immobilizing and capturing of heavy metals like Pb, Cd, As and Hg (Bajar, et al., 2024).

METHODS

This chapter represents the research methodology of the study, including the research design, preparing of material, carbonization and activation process, testing adsorption, waste disposal, and data analysis.

Research design

The study utilized an experimental quantitative research method, also a true experimental design. Bell, S. (2009) stated that a true experimental design relies on testing the relationships between and among variables; generally speaking, one variable, the independent variable, is controlled in order to measure its effect on other, dependent, variable. Moreover, a statistical technique in experimental design procedures enables the researcher to better comprehend and assess the variables that affect a certain system. These methods combined theoretical understanding of experimental designs with practical experience in dealing with the specific issues under study. Initial experimental planning was crucial, even though the decision of an experimental design ultimately depended on the experiment's goals and the number of components being examined.

Preparation of Materials

The primary materials used, cacao pod husk (*Theobroma cacao*), was sourced from the local community in the Panacan and Calinan District Davao City, due to its complimentary nature. The collected cacao husk samples were sent to

Community Environment and Natural Resources Office (CENRO) for verification. The researcher will follow the washing process, the cacao husk was washed thoroughly to remove dirt particles such as tannins, resins, reducing sugars, and coloring agents (Tejada-Tovar, et al., 2020), wherein the cacao husk contained impurities due to its usually disposing anywhere. Therefore, the next method that applied is sun-drying. The cacao pod husks were initially washed with tap water to remove dirt particles and mulicage. Then, the husk were chopped into small pieces. Afterwards, the cacao dried in an oven at 150, 200, 250C for 1.5, 2.0, 2.5h to remove moisture. The cacao pod husks, dried and finely ground using mortar and pestle, and blender to make it fine. They were carefully sifted to ensure uniform particle sizes between 1 and 1.7 milimeter. The carefully measured particles have been placed in the ziplock plastic bag to be weighed and brought to the PJAC for activated laboratory. On the other hand, another primary material, the Potassium hydroxide (KOH) was acquired from Philippine-Japan Activated Carbon Corporation (PJAC). The other essential material that are necessary

in the experiment processes such as: tap water, ziplock plastic bags, knife, and mortar and pestle, were procured from the researchers individual establishment. The magnetic stirrer with heater used for activating the carbon were acquired by the Philippine Japan Active Carbon Corp.

Carbonization and Activation of Cacao pod husk

In this section, the KOH can be attributed in leading to the formation of carbon pores. The activation process was conducted in Philippine Japan Activated Carbon Corporation (PJAC), by preparing two with KOH solutions: (250 g) of KOH for 50% concentration, (350 g) of KOH for a 70% concentration, both dissolved in 500 ml of distilled water. The KOH was mixed thoroughly in the distilled water until fully dissolved. Once dissolved, cacao husk carbon was gradually added to the solution while stirring continuously to ensure that the carbon did not settle and remained suspended in the liquid. After all the carbon was added, the mixture was placed on a magnetic stirrer and heated. The solution was brought to a boil for 3 hours, with stirring every 30 minutes to prevent the cacao husk carbon from settling at the bottom while boiling. Once the boiling process was complete, the mixture was stirred again before transferring it to a tray for oven drying. The mixture was dried in an oven at 100°C for 28 hours, with stirring every 20 minutes to prevent burning at the bottom. After the successful drying, the mixture formed into a fine powder.

Testing adsorption

The Atomic Absorption Spectrophotometry (AAS), is a analytical technique that involves the measurement of the absorption of electromagnetic radiation by atoms in the gas phase. This involves the determination of the concentrate of elements present in a liquid sample by measuring the amount of energy absorbed from specific wavelengths of light, typically ranging from 190 to 900 nm (Sharma, 2023).

This testing were conducted in Davao Analytical Laboratories,

Inc. (Dalinc), which they used to define the concentration of heavy metals were identified in the surface area and pore volume of every grain of activated carbons. This showed that the analysis of the laboratory result in the activated carbon is more efficiently.

Waste Disposal

Disposing of the excess cacao with the fungi and seeds was done by sealing the materials in biodegradable bags. The researchers used boiling water to sterilize the waste, maintaining a temperature of 100 °C for 20 minutes to ensure the elimination of microorganisms. Additionally, leftover waste from the experiment was safely discarded into a compost pit designed for organic decomposition. Nonbiodegradable waste, such as used gloves and other materials, was segregated and disposed of according to local environmental regulations. This process was carried out at the STEM laboratory in Carlos P. Garcia Senior High School.

Data Analysis

To analyze the data collected, the researchers used the following statistical tools.

Mean. This used to measure the adsorption of each concentrations of cacao husk activated carbon. Then proceed with the chemical process in treating water with cadmium and lead using Atomic Adsorption Spectrophotometry (AAS).

In terms of different concentration levels; No KOH concentration; 50% KOH concentration; and 70% KOH concentration.

Kruskal Wallis. This was used to determine the significant difference in the cadmium and lead adsorbed when treated with cacao husk activated carbon across different concentrations.

RESULTS

The presentation is organized into three(3) sections; first, the lead (pb) when treated by Activated carbon with 70% KOH concentration, 50% KOH concentration and with No KOH; second, the cadmium (cd) when treated by

Activated carbon with 70% KOH concentration, 50% KOH concentration and with No KOH, and third, significant difference in the adsorption efficiency when analyzed according to the different concentrations.

Lead (Pb) when treated by Activated carbon prepared using 70% KOH concentration, 50% KOH concentration and without KOH treatment.

Presented in Table 1 is the lead (Pb) when treated by Activated carbon, according to the 3 different concentration levels: 70%, 50% and No KOH. As observed, this laboratory experiment was conducted in three trials. Wherein, it shows that the 50% KOH, obtained the highest value of the adsorption efficiency among the two concentration levels (0.89ppm), followed by the 70% KOH, that has a minimal differences to the highest value of adsorption efficiency (0.893ppm) and No KOH that has the lowest value of adsorption efficiency (0.08ppm).

Table 1.

Lead (pb) when treated with activated carbon prepared using 70% KOH concentration, 50% KOH concentration, and without KOH treatment.

| Concentrations | Parameter |
|--------------------|-------------|
| 70% KOH | 0.83 |
| 50% KOH | 0.89 |
| Without KOH | 0.08 |
| Total Mean | 0.6 |

The results indicate that the overall mean adsorption efficiency of Cacao Husk Activated Carbon for Lead (Pb) is 0.6. This suggests that activated carbon treated with higher KOH concentrations (70% and 50%) exhibits comparable efficiency in adsorbing Lead (Pb), while untreated carbon shows a slightly lower performance. Additionally, the data highlights that the variation in adsorption efficiency across these treatments is minimal, demonstrating the potential of Cacao Husk Activated Carbon as a sustainable material for Lead (Pb) removal.

Cadmium (Cd) when treated by Activated carbon prepared using 70% KOH concentration, 50% KOH concentration and without KOH treatment.

Presented in Table 2 is the Cadmium (Cd) when treated by Activated carbon, according to the 3 different concentration levels: 70%, 50% and No KOH. As observed, this laboratory experiment was conducted in three trials. Wherein, it shows that the 50% KOH, obtained the highest value of the adsorption efficiency among the two concentration levels (0.44ppm), followed by the 70% KOH, that has a minimal differences to the highest value of adsorption efficiency (0.34ppm) and No KOH that has the lowest value of adsorption efficiency 0.04ppm).

Table 2.

Cadmium (Cd) when treated with Activated Carbon prepared using 70% KOH concentration, 50% concentration, and without KOH treatment.

| Concentrations | Parameter |
|--------------------|-------------|
| 70% KOH | 0.34 |
| 50% KOH | 0.44 |
| Without KOH | 0.04 |
| Total Mean | 0.27 |

The results show that the adsorption efficiency of Cacao Husk Activated Carbon varies across the treatments, with 70% KOH achieving an efficiency of 0.34, 50% KOH achieving 0.44, and untreated activated carbon showing a significantly lower efficiency of 0.04. The overall mean adsorption efficiency for Cadmium (Cd) is 0.27, equating to 27%. This indicates that activated carbon treated with higher KOH concentrations significantly enhances Cadmium (Cd) adsorption, underline the importance of chemical activation for improved performance in heavy metal removal.

Difference in the adsorption efficiency when analyzed according to the different concentrations.

Presented in Table 3 is the difference in the adsorption efficiency in Lead and Cadmium when analyzed according to the following concentrations : 70% KOH concentration, 50% KOH concentration and without KOH.

Table 3.

Difference in the adsorption efficiency when analyzed according to the different concentrations.

| Concentrations (ppm) on Ho | Mean | df | C.V | p-value | Decision |
|-------------------------------|------|----|------|---------|----------|
| 70% KOH | 0.58 | 2 | 0.53 | 2.920 | Ho is |
| 50% KOH | 0.66 | | | | |
| No KOH | 0.06 | | | | |

accepted.

The data presented in Table 3 shows the difference in the adsorption efficiency of Lead and Cadmium when analyzed under three different concentrations: 70% KOH, 50% KOH, and without KOH.

The results indicate that the 50% KOH concentration yielded the highest mean adsorption efficiency (0.66 ppm), followed by the 70% KOH concentration (0.58 ppm), and lastly, the absence of KOH resulted in the lowest mean adsorption efficiency (0.06 ppm). The computed p-value (2.920) and coefficient of variation

(C.V = 0.53) indicate that there is no statistically significant difference in adsorption efficiency across the different concentrations. As such, the null hypothesis (H_0) is accepted. This suggests that while the concentration of KOH has an observable impact on adsorption efficiency, it is not statistically significant in this study.

DISCUSSION

The researchers evaluated the adsorption efficiency of Lead (Pb) and Cadmium (Cd) using activated carbon treated with 70% KOH, 50% KOH, and no KOH. Results showed that 50% KOH consistently achieved the highest efficiency for both metals, with Lead showing higher adsorption values than Cadmium.

The total mean adsorption efficiency for Lead was 0.6 ppm and 0.27 ppm for Cadmium. Although 50% KOH-treated carbon performed slightly better, the Kruskal-Wallis test (p-value = 2.920) indicated no statistically significant difference across treatments. These findings suggest that KOH-activated carbon, particularly at 50%, is effective and sustainable for heavy metal removal, though further optimization is needed for improved performance.

CONCLUSIONS

1. This indicates that the overall mean adsorption efficiency of Cacao Husk Activated Carbon suggests that activated carbon treated with higher KOH concentrations (70% and 50%) exhibits comparable efficiency in adsorbing

Lead (Pb), while untreated carbon shows a slightly lower performance. Additionally, the data highlights that the variation in adsorption efficiency across these treatments is minimal, demonstrating the potential of Cacao Husk Activated Carbon as a sustainable material for Lead (Pb) removal.

2. This shows that the adsorption efficiency of Cacao Husk Activated Carbon varies across the treatments, with 70% KOH achieving an efficiency of 0.34, 50% KOH achieving 0.44, and untreated activated carbon showing a

significantly lower efficiency of 0.04. This indicates that activated carbon treated

with higher KOH concentrations significantly enhances Cadmium (Cd) adsorption, underline the importance of chemical activation for improved performance in heavy metal removal.

Recommendations

Based on the conclusions, the following recommendations are offered:

1. Avoid excessive addition of KOH to the carbon to prevent a potential decrease in its adsorption efficiency.
2. Further explore other potential applications of cacao husk as an activated carbon aside from water applications.
3. If the future researchers plan to use it for water treatment, alternative methods should be explored to remove the black color of the activated carbon. So that the water can be reusable again after undergoing activated carbon treatment.

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