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Joan Jane J. Sanchez
Department of Agricultural and Biosystems Engineering, College of Engineering and Geosciences, Caraga State University

Jonathan M. Yu
Center for Resource Assessment, Analytics and Emerging Technologies (CReATe), Caraga State University

Dale R. Moran

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# Evaluating the Potential of Maize (*Zea Mays*) Cobs for Mercury Removal from Small-Scale Gold Mining Wastewater

Joan Jane J. Sanchez[1], Jonathan M. Yu[2], Dale R. Moran[3]
[1]Department of Agricultural and Biosystems Engineering, College of Engineering and Geosciences, Caraga State University, Butuan City 8600, Philippines
[2]Center for Resource Assessment, Analytics and Emerging Technologies (CReATe), Caraga State University, Ampayon, Butuan City 8600, Philippines
*jjsanchez@carsu.edu.ph

**Abstract:** *Maize (Zea mays) cobs are significant agricultural residues, often disposed of harmfully. Their physical and chemical properties, however, make them suitable for heavy metal adsorption. This study used pyrolyzed maize cobs to remove mercury from wastewater generated by small-scale gold mining (SSGM) at a facility in Andili, Mawab, Davao de Oro. The objective was to evaluate the cobs' efficiency in mercury removal, metal uptake, and compliance with wastewater standards. Batch adsorption experiments utilized 6 g of pyrolyzed maize cob adsorbent per 100 mL of wastewater, with contact times of 2, 4, 6, and 8 hours. The results showed a maximum average adsorption efficiency of 84.38% and a maximum average metal uptake of $3.365x10^{-8}$ mol/g, indicating that maize cobs are effective in adsorbing mercury from SSGM wastewater.*

**Keywords:** Heavy Metals, Mercury, Pyrolyzed Maize Cob, Adsorbent, Batch Adsorption

## 1. INTRODUCTION

A maize cob refers to the central part of the maize ear that remains after the maize kernels have been removed. It is essentially the husk or core of the ear of maize. The maize cob accounts for approximately 75% to 85% of the weight of the entire ear of maize. Maize cobs are typically cylindrical and have a tough outer layer. They comprise a dense matrix of fibers, lignin, and cellulose [1]. The cob serves as a support structure for the maize kernels during the growth and development of the ear. After the maize kernels are harvested for consumption or processing, the maize cobs are often considered agricultural waste. The agricultural sector generates a considerable number of maize cobs, which are inedible remnants of maize production, with a ratio of 18 kg of maize cobs for every 100 kg of maize grain produced [2]. These maize cobs constitute a significant portion of maize residues worldwide annually. The disposal of maize cob remnants has been known to have a negative impact on the environment [3]. Because the disposal of agricultural waste from combustion can negatively impact people and the environment, many researchers focus on exploiting abundant and inexpensive industrial wastes as sustainable materials [4]. It is crucial to emphasize the significance of appropriately disposing of or reutilizing this agricultural waste. Fortunately, the physical and chemical characteristics of maize cobs render them suitable for diverse purposes, including environmentally beneficial applications.

One of the unique environmental remediation applications of maize cob waste is for heavy metal adsorption. Environmental contamination caused by increased industrial activity has become a primary global concern. Heavy metal contamination in the air, soil, and water is among the most common environmental pollutants induced by various industrial processes [5]. It is critical to keep heavy metals out of the natural environment.

Adsorption is a surface process in which a gas or liquid solute adheres to the surface of an adsorbent, forming an adsorbate film. Agricultural wastes, in particular, are an effective material for heavy metal removal. Such biomaterials are low-cost, readily available, produce no sludge, are regenerating, technologically viable, and have engineering applicability [6].

The utilization of maize cob waste and addressing the issue of heavy metals in small-scale gold mining wastewater are both critical areas of research. The study explored the potential of pyrolyzed maize cobs for batch adsorption tests to remove mercury metal from small-scale gold mining wastewater.

### 1.1 Background of the Study

Due to their high propensity to cause environmental issues, the potential applications of maize cobs in several industries have been exhaustively investigated in several research works [3]. In maize, stems, leaves, fastballs, husks, and maize cobs are produced, making up between 47% and 50% of the leftovers. It is also worth noting that, according to the physical and chemical makeup of maize cobs, the raw material is an excellent candidate for removing industrial pollutants as an adsorbent. The microstructure and fiber content of maize cobs contains cellulose, hemicellulose, and lignin, forming porous sponge structures with low density and high bearing capacity.

Several studies have been done applying maize cobs to treat various effluents. In a study by Abdelfattah [7], maize cob as an adsorbent exhibited the properties of treating the industrial processing effluent from heavy metal ions like Lead, Zinc, Copper, Iron, Nickel, Chromium ions, and Cyanide. Similarly, studies by Liu et al. [8] and Duan et al. [9] used maize cob as a raw material for removing mercury ions in a simulated solution, demonstrating its viability for heavy metal contaminant adsorption.

Despite the numerous studies on the application of maize cob as an adsorbent for heavy metal removal, there remains a notable gap in its implementation in real-world wastewater, particularly in small-scale gold mining wastewater. This gap presents an opportunity for further research and highlights the relevance of conducting studies to address this issue.

Several artisanal small-scale gold mines have been occasionally seen upstream of Agusan Marsh and Agusan River in the last two decades, adding to the burden of heavy metals, particularly mercury, frequently used in amalgamation, into the river. During the late 1980s in eastern Mindanao, the excessive and inadequately regulated application of mercury (Hg) for gold amalgamation led to multiple cases of poisoning among miners. The initial incident involved 11 individuals getting injured and one fatality [10]. Despite regulations, releasing heavy metal-contaminated water into the natural environment continually impacts the health of organisms in the surrounding area. Harmful industrial contaminants such as heavy metals cause alarming pollution due to their non-destructive nature, health risks, and toxicity to living organisms. Agricultural productivity, as well as food safety and security, rely heavily on soil and water quality. Soil and water are essential environmental variables that can encourage or inhibit species' growth and development in an ecosystem, including humans [11]. It is imperative to ensure the preservation, rehabilitation, and safety of our water bodies because of their significance not only for industrial use, such as irrigation but, most importantly, for human and animal consumption. There is a lack of adequate and affordable treatment methods for small-scale gold mining wastewater. Traditional treatment techniques may be inadequate or economically unfeasible for these operations. Hence, there is a pressing need to explore alternative and sustainable approaches that can be applied, such as the application of maize cobs. By investigating the feasibility and efficiency of maize cob as an adsorbent in small-scale gold mining wastewater treatment, the study can fill the existing gap in knowledge and provide a practical solution for this specific context. The research can yield valuable insights into the performance of the application of maize cob adsorbent. Additionally, it can contribute to developing low-cost, environmentally friendly, and sustainable technologies tailored to the needs of small-scale gold mining communities.

## 2. METHODS AND MATERIALS

This chapter contains the methods used in the study. It also describes the sample, adsorbent material and treatment, apparatus and instruments, and the analysis of the wastewater samples. The general framework of the study is shown in Figure 1.

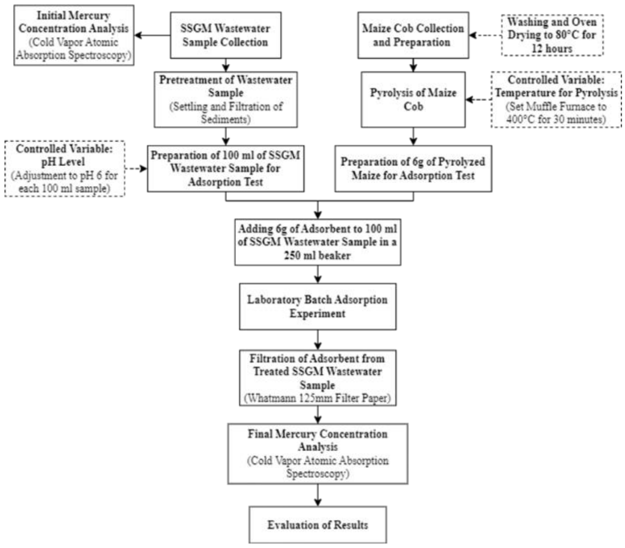


Fig. 1. General Framework of the Study

### 2.1 Collection, Pretreatment, and Preparation of SSGM Wastewater Sample

The sampling pretreatment is integrated into the general framework of the study in Figure 7. This section discusses each step of the sampling and preparation process for SSGM wastewater samples.

### 2.2 SSGM Wastewater Sample Collection

The collection of SSGM wastewater samples described follows the Standard Methods for Examining Water and Wastewater, 23rd edition, which is the advised standard of sampling by Davao Analytical Laboratories Inc. The study utilized grab sampling, which involves collecting a single sample at a specific time from a particular location. In this case, a 2-liter sample of small-scale gold mining wastewater was collected. A 200 mL sampling bottle made of polypropylene was used to gather the effluent from a tailings collection tank at Andili, Mawab, Davao de Oro, Philippines the location is shown in Figure 2. Polypropylene is used in sample containers as it is chemically inert and does not contaminate the sample [12].

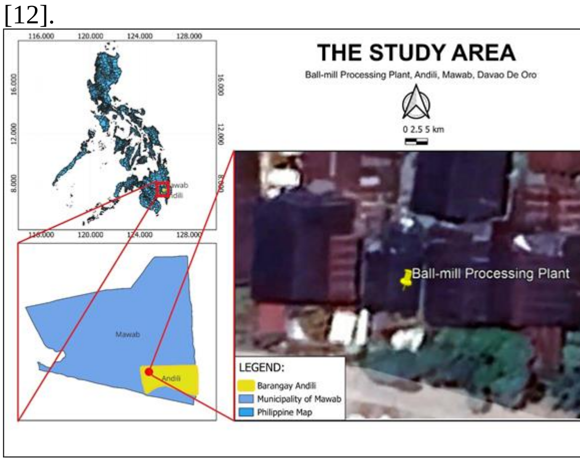


Fig. 2. Study Area: Location of Wastewater Sample Source (Ball-mill Processing Plant, Andili, Mawab, Davao de Oro).

The opened sampling bottle is held on the lower part and submerge to a depth of about 20 cm with the mouth. The collected sample from the 200 mL bottle was poured into a larger polypropylene bottle. In this case, a 7-liter bottle was used due to the unavailability of other sizes. The sample was poured until it reached the 2-liter mark on the larger bottle. This process ensures sufficient sample volume for analysis [12]. From the gathered sample, 300 mL was extracted and sent to Davao Analytical Laboratories Inc for the initial mercury concentration analysis. This portion of the sample underwent Cold Vapor Atomic Absorption Spectroscopy to determine the mercury concentration in the wastewater.

### 2.3 Pretreatment and Preparation of Collected SSGM Wastewater

The process of settling and filtration plays a crucial role in wastewater treatment, as it helps to reduce the presence of sediments and impurities in the collected wastewater.
During the settling process of this study, wastewater is allowed to stand undisturbed for 60 minutes. This period allows the heavier particles and suspended solids in the water to settle down to the bottom of the container, forming a sludge layer [13]. The importance of settling lies in removing settleable solids and sediments from the wastewater. These solids can include organic and inorganic materials such as silt, sand, grit, and other particulate matter. Allowing these particles to settle makes the wastewater more transparent and less turbid, making it easier to treat in subsequent study processes. Filtration is an additional step employed after settling to remove fine suspended solids further. In the study, Whatman 125mm filter paper is used.
The pretreated SSGM wastewater is then prepared for batch adsorption experiments. Studies by Arunkumar [14] and Abdelfattah et al. [7] observed pH 6 as the optimal pH level for the adsorption of heavy metals in maize cob. Hence, in this study, each 100 ml of SSGM wastewater sample used in the batch test is adjusted to a pH of 6.

### 2.4 Collection and Preparation for Pyrolysis of Maize Cob

Figure 3 shows the location where Maize cobs are collected from the maize stockpile at the maize farm located in Sta. Irene, Prosperidad, Agusan del Sur, Philippines. Maize cobs are the outer part of the maize plant that remains after the maize kernels have been removed. The collected maize cob material was rinsed with detergent and distilled water several times. This step is performed to remove any dirt, debris, or impurities that may be present on the surface of the maize cob. After rinsing, the maize cob material is oven-dried at 80°C for 12 hours. The purpose of drying is to evaporate any remaining water on the surface or within the pores of the maize cob [15].

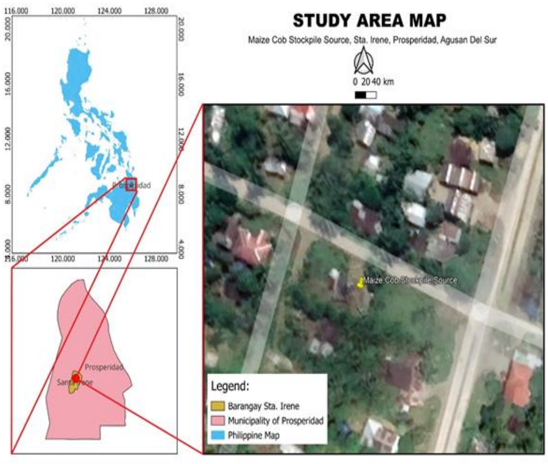


Figure 3. Location of Maize Cob Stockpile Source (Sta. Irene, Prosperidad, Agusan del Sur)

### 2.5 Pyrolysis and Preparation of Adsorbent for Batch Adsorption Test

The dried maize cob sample is subjected to pyrolysis. Pyrolysis is when organic material is heated without oxygen to decompose and transform into various byproducts [16]. In this study, pyrolysis is carried out in a muffle furnace. The temperature for pyrolysis of maize cob in the experiment is based on a study by Opia [15], where a high adsorption rate of heavy metal is observed after pyrolyzing the maize cob. The maize cob sample is subjected to a pyrolysis temperature of 400°C for 30 minutes. This specific temperature and duration transform the maize cob into the desired adsorbent material**.**
After the pyrolysis process, the pyrolyzed maize cob sample is left inside the muffle furnace to cool down to room temperature. Cooling is necessary to ensure safe handling of the sample and prevent any potential hazards associated with high temperatures. Once the pyrolyzed maize cob sample has cooled to room temperature, it is weighed according to the required adsorbent dosages needed for the study. For each trial, 6 grams of pyrolyzed maize cob is prepared and mixed with the 100 ml SSGM wastewater. The adsorbent dosage with respect to the chosen volume of wastewater sample is based on a study by Abdelfattah and Sayed [7] using maize cobs as adsorbent to remove heavy metals by batch adsorption experiment. Arunkumar [14] also observed that beyond 6 grams further increase in the dosage does not cause any change due to the availability of more binding sites on the surface of the adsorbent.

### 2.6 Batch Adsorption Experiment

The batch adsorption experiment was started by preparing a known amount of pyrolyzed maize cob adsorbent. The exact amounts of the adsorbent were 6 grams per batch. A 100 mL volume of wastewater with a pH of 6 was taken in a 250 mL beaker. The prepared adsorbent was then added to the beaker containing the wastewater. The system was stirred adequately using a magnetic stirrer at a speed of 260 rpm. Stirring helps achieve better contact between the adsorbent and the wastewater, facilitating adsorption [14]. The parameter of interest for the adsorption process was the contact time, which refers to the duration for which the adsorbent and the wastewater were allowed to interact. In this study, the contact time was varied between 2, 4, 6, and 8 hours. The treatments and the general batch adsorption experiment framework are shown in Figure 9. The range of contact times was based on the study of Abdelfattah and Sayed [7], where desirable adsorption efficiencies by maize cob are observed. After the desired contact time was achieved, a Whatman 125 mm filter paper was used to separate the two phases, i.e., the adsorbent and the treated wastewater. Filtration helps in removing the solid adsorbent particles from the liquid phase. The treated wastewater, after filtration, was carefully stored in specimen bottles. Storing the treated wastewater is to preserve it for transport to Davao Analytical Laboratories, Inc. for final mercury metal analysis**.**

## 3. RESULTS AND DISCUSSION

### 3.1 Concentration of Mercury Metal on Untreated and Treated SSGM Wastewater Samples

The study aimed to treat SSGM wastewater samples using pyrolyzed maize cobs. The untreated and treated samples were then sent to Davao Analytical Laboratories, Inc. for analysis. The laboratory utilized Cold Vapor Atomic Absorption Spectroscopy (CVAAS) to determine the initial mercury concentration in a 100 mL sample of untreated SSGM wastewater.

CVAAS is considered the most favorable instrument for mercury analysis due to its high sensitivity, selectivity, and accuracy. It is designed to determine mercury and offers several advantages over other techniques. CVAAS can detect and quantify mercury at deficient levels, even to parts per billion (ppb) or parts per trillion (ppt). This level of sensitivity is crucial when analyzing samples containing trace amounts of mercury, such as wastewater from gold mining operations. The detection limit of the CVAAS instrument in the study is 0.02 parts per billion.

### 3.2 Initial Concentration of Mercury Metal on Untreated SSGM Wastewater

The results of the mercury analysis of the untreated SSGM wastewater samples are shown in Table 1. The mercury concentration values are expressed in milligrams per liter (mg/L) as stated from the original results given by the laboratory.

Table 1. Mercury Concentration of Small-scale Gold Mining Wastewater Samples.

| Description | Mercury Concentration Ci (mg/L) |
|---|---|
| **Untreated SSGM Wastewater Sample** | **0.0160** |

The initial mercury concentration in the untreated small-scale gold mining wastewater, which amounts to 0.0160 mg/L, exceeds the set limit of the water quality standards for wastewater established by the Philippines. This indicates that the level of mercury in the wastewater is higher than what is considered safe for discharge into the environment.

### 3.3 Final Concentration of Mercury Metal of the Treated SSGM Wastewater

Table 2 below shows the average mercury concentrations in the SSGM wastewater sample after the batch adsorption test. The test involved using pyrolyzed maize cob as an adsorbent material and varying the contact times between the adsorbent and the wastewater sample. The concentrations of mercury were analyzed using Cold Vapor Atomic Absorption Spectroscopy. The contact times for the adsorption test were 2, 4, 6, and 8 hours.

Table 2. Average Mercury Concentration of SSGM Wastewater After Adsorption Treatment

| Contact Time | Treatment | Mean Hg Concentration Cf (mg/L) |
|---|---|---|
| 2 | T1 | 0.0041 |
| 4 | T2 | 0.0032 |
| 6 | T3 | 0.0025 |
| 8 | T4 | 0.0030 |

Based on the results, it is evident that the adsorbent (pyrolyzed maize cob) has effectively removed a substantial amount of mercury from the SSGM wastewater sample. The average mercury concentrations significantly decreased in the treated samples compared to the untreated wastewater.

The untreated wastewater sample had a mercury concentration of 0.0160 mg/L. After 2 hours of contact time, the treated sample, A, showed reduced mercury concentration at an average of 0.0041 mg/L. As the contact time increased to 4 hours, the treated sample, B, exhibited a much lower mercury concentration of 0.0032 mg/L, meaning that mercury ions were substantially removed through a longer elapsed contact time with the adsorbent. The lowest mercury concentration, which passed the DENR guidelines, was observed during the 6-hour mark, C, where 0.0025 mg/L of mercury metal concentration was measured. However, at 8 hours, a slight spike to a higher concentration than the 6-hour mark was exhibited. The slight increase of mercury concentration during this longer contact time can be explained by the surface adsorption capacity of the adsorbent has saturated and has reached an equilibrium between the concentration of mercury in the adsorbent and its environment so that absorption of the pyrolyzed maize cob at the contact time above 6 hours have slightly lowered or reached constant adsorption [17].

### 3.4 Adsorption Efficiency of the Pyrolyzed Maize Cob Adsorbent

Adsorption efficiency measurements allow us to assess how successfully the adsorbent material removes the target contaminant from wastewater. By monitoring the efficiency at different contact times, we can determine the optimal duration for adsorption and understand how the performance of the adsorbent evolves [18].

Actual SSGM wastewater at a pH of 6 was stirred with 6 g of maize cob adsorbent at 260 rpm for 2 hours, 4 hours, 6 hours, and 8 hours. The mean adsorption efficiencies for three replicates for each contact time are shown in Table 3 below.

Table 3. Adsorption Efficiencies for each Adsorption Experiment

| Contact Time | Treatment | Average Adsorption Efficiency (%) |
|---|---|---|
| 2 | T1 | 74.17% |
| 4 | T2 | 80.21% |
| 6 | T3 | 84.38% |
| 8 | T4 | 81.46% |

As shown in Table 3, the adsorption efficiencies were measured for all the batch adsorption experiments done at various treatments T1, T2, T3, T4, with respect to contact times. The measurements appear to be relatively consistent for each group. These data show a relationship between each contact time with adsorbents and average adsorption efficiencies for each treatment.

Within the first 2 hours of contact time, the maize cob adsorbent removed significant contaminants from the wastewater at an average of 74.17% efficiency. The adsorption efficiency slightly increased at 4 hours of contact time compared to the 2-hour mark, with a value of 80.21%. The adsorption efficiency in this study was observed at its maximum at 6 hours, at 84.38%. However, at 8 hours of contact time, the adsorption efficiency value slightly decreased compared to the 6-hour mark, at 81.46%.

Results suggest that the adsorption process becomes more effective as the contact time increases. This indicates that a longer contact time allows for more effective removal of contaminants by the adsorbent [19]. The increased efficiency suggests that the adsorption process is reaching equilibrium, where the adsorbent has a higher chance of capturing additional contaminants.
However, at 8 hours of contact time, the adsorption efficiency values slightly decreased compared to the 6-hour mark, suggesting a saturation point beyond which extending the contact time does not substantially improve pollutant removal [20]. The observed slight decrease in metal ion adsorption occurs due to the hydrolysis of the adsorbent, which disrupts the bonds between the metal ions and the surface functional groups of the adsorbent. This phenomenon is particularly relevant when the adsorbent material is exposed longer to the wastewater [21, 22].

### 3.5 Effect of Contact Time of Pyrolyzed Maize Cob on the Batch Adsorption Treatment

The effect of contact time on the adsorption efficiency and metal uptake of pyrolyzed maize cob as an adsorbent can provide valuable insights into the optimal operating conditions for this material. The adsorption efficiency and metal uptake of pyrolyzed maize cob increase with increasing contact time up to a certain point, after which they tend to level off or even decrease.
The trend observed in this study can be explained by the adsorption process involving the diffusion of metal ions from the solution to the surface of the adsorbent. At the beginning of the process, the surface of the adsorbent is relatively clean and available for metal ion adsorption. Higher mercury metal concentration was due to the availability of more binding sites at the initial stage of the adsorbent. As the contact time increases, more metal ions diffuse to the surface of the adsorbent, increasing adsorption efficiency and metal uptake [23].
However, after a certain point, the surface of the adsorbent either becomes saturated with metal ions or the adsorption rate slows down. This means that there are lesser active sites to accommodate mercury metal ions [20]. The hydrolysis of the adsorbent, which breaks apart the connections between the metal ions and the surface functional groups of the adsorbent, causes the modest drop in metal ion adsorption that has been reported. This phenomenon is critical when the adsorbent material is exposed to wastewater for longer. Some of the metal ions initially adsorbed onto the surface may be displaced by the hydroxyl groups or other hydrolysis products. This displacement weakens the bonding between the metal ions and the adsorbent, leading to a slight decrease in adsorption efficiency and metal uptake in the study [21, 22].

## 4. CONCLUSIONS AND RECOMMENDATIONS

### 4.1 Conclusion

The study investigated the wastewater collected from the SSGM ball mill facility and discovered that it contained a significantly high amount of mercury, with a concentration of 0.0160 mg/L. Batch adsorption experiments were carried out using actual wastewater samples, with an adsorbent dose of 6g per 100 mL of wastewater at various contact times 2, 4, 6, and 8 hours. The overall performance of pyrolyzed maize cob as an adsorbent was excellent, with maximum average adsorption efficiency of 84.38% and maximum average metal uptake of 3.365x10-8 mol/g reached at 6 hours contact time. The experiment showed that the adsorption efficiency and metal uptake of pyrolyzed maize cob increased with increasing contact time up to a certain point. Since, at an extended contact time of 8 hours, there was a slight decrease in adsorption efficiency and metal uptake due to the saturation of the adsorbent surface and hydrolysis exhibited by the solution.
The study also found that the treated wastewater met the government regulatory limit as stated in DENR Administrative Order 2016-08 for Class C waters, which specifies a maximum allowable mercury concentration of 0.002 mg/L. The treated wastewater achieved an average mercury concentration of 0.0025 mg/L after 6 hours of contact time. The statistical treatment using paired t-tests in the study further supported the effectiveness of using pyrolyzed maize cob as an adsorbent. The calculated t-value was considerably large, indicating a substantial difference between the initial and final mercury concentrations. The p-value obtained was smaller than the significance level (0.05), providing strong evidence against the null hypothesis. These results support the alternative hypothesis and suggest that using pyrolyzed maize cob as an adsorbent can reduce mercury contamination in small-scale gold mining wastewater.
The study results indicated good adsorption efficiency and metal uptake, which shows the potential of pyrolyzed maize cob as an adsorbent for SSGM wastewater. The findings can be utilized to optimize the treatment process and achieve the desired mercury concentration within the regulatory limits.

### 4.2 Recommendations

Following the conclusion and the limitations of the study conducted, the following are the recommendations of the researchers for future works and improvements on the research about the application of maize cobs as an adsorbent for wastewater:

- Future pilot-scale studies would be necessary to determine the practicality and efficiency of using maize cob beyond laboratory-scale scenarios.
- Future studies should incorporate samples from multiple sites to account for variations in mining practices and wastewater characteristics to comprehensively understand the potential of maize cobs.
- Investigations should explore the influence of other parameters, such as adsorbent dosages, temperature, and other contaminants, on the adsorption efficiency of maize cob.
- Factors such as the cost of acquiring the adsorbent, its preparation, and the disposal or desorption of spent adsorbents should be considered to evaluate the viability of using maize cob in practical applications.

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