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Regional Case Study

Utilization of Activated Charcoal from Cassava Peel and Straw in Reducing Cadmium Levels in Putri Cempo Landfill Leachate

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Abstract

Contamination of leachate due to excessive rainwater infiltration into landfill sites presents a significant environmental and public health concern. This study aims to address the adverse impacts of cadmium (Cd) pollution in leachate, specifically its risks to human health and the environment. To address this issue, the research investigates the use of natural adsorbents to mitigate agricultural waste. Straw and cassava peel, abundantly available in Indonesia due to the country's substantial rice and cassava production, were selected as potential adsorbents. The findings of this study are important for guiding pollution control measures and evaluating community activities near pollution sources, particularly focusing on Cd pollution originating from Putri Cempo in Jatirejo Village, Mojosongo, Jebres, Surakarta. The research shows that cassava peel waste is highly effective in adsorbing cadmium metal levels in leachate, with a significant total effectiveness (EF%) rating of 0.3144. Additionally, the study identifies the optimal burning temperature for activated charcoal derived from cassava peel as 600°C, resulting in the highest EF% value of 0.515152.

Keywords: Cadmium; charcoal; cassava peel; straw; leachate

1. Introduction

Leachate water is formed when water seeps and extracts dissolved or suspended materials in waste piles that dissolve many compounds (Apriyani & Lesmana, 2019). Leachate water in Final Disposal Sites originates from a series of physical, chemical, and biological changes that decompose easily decomposable solid waste fractions and organisms carried by water and seep through the soil (Youcai, 2018). This results in highly polluted content of dissolved organic matter, inorganic macro components, xenobiotic organic compounds, and heavy metals. The waste type contributing the most to this leachate water decomposition process is organic waste. Organic waste, including leaves, vegetable residues, fruits, and food, constitutes the dominant waste composition in Indonesia, accounting for 57 percent of the total annual waste load. Leachate water pollution originates from excess rainwater entering the waste layer, followed by reactions of organic and inorganic matter with hazardous substances, one of which is Cd (Puspitarini et al., 2023). This type of heavy metal originates from battery rocks, electronic devices, paint pigments, and plastics, which can contaminate and reduce the oxygen supply to nearby surface water bodies. These heavy metals, with their high mass density and high density, are highly toxic to the environment, thus impacting the health of living organisms (Thakare et al., 2021). Several heavy metals entering the human body can disrupt organ function and affect enzyme stability and body metabolism, making them vulnerable to various diseases such as organ damage, nervous system disorders, hormonal disturbances, and serious diseases including cancer and death (Pratiwi, 2020). According to Mitra et al. (2022), most heavy metals cause pollution and become highly toxic when mixed with different environmental elements such as soil, water, and air. The long-term negative impact of this pollution is the disruption of absorption processes by aquatic organisms, affecting the food chain (Wdowczyk & Szymańska-Pulikowska, 2021).

The impact of Cd pollution on the environment requires a series of efforts. The application of natural adsorbents in the form of activated charcoal made from agricultural waste such as straw and cassava peel can separate and absorb pollutants in a specific mixture (Sari and Sari, 2021). The selection of these two materials is based on Indonesia's high production levels of rice and cassava. Rice and cassava are the first and third staple food sources, respectively, with by-products such as straw accounting for 1.5 tons per 1 ton of production (Puspitasari et al., 2022). Meanwhile, cassava peel waste in each annual cassava production is 15% and has yet to be optimally utilized (Utami et al., 2020). Based on research conducted by Sufra et al. (2023), it is stated that activated charcoal sourced from organic waste can function as an adsorbent to absorb heavy metals in liquid waste. This study uses wood bark waste containing lignin and polyphenolic compounds. Research conducted by Nurhidayanti et al. (2022) stated that the use of activated charcoal made from tea dregs can increase the effectiveness of removing heavy metals such as cadmium and arsenic from textile industry waste. Cassava peel waste and straw can be used as natural adsorbents to address heavy metal pollution in a pollutant-containing body. Based on research conducted by Maulinda et al. (2017), cassava peel can be utilized as a natural adsorbent that plays a role in absorbing, attracting, and binding heavy metals in a contaminated body. Cassava peels and straws are rich in cellulose content, which is classified as a natural polymer with the ability to adsorb and retain metal molecules. Research conducted by Utami et al. (2020) found that the use of straw as an adsorbent plays a role in reducing manganese levels in well water at the Krian Health Center, Krian District, Sidoarjo Regency.

Thus, research related to the use of cassava peel and straw to reduce heavy metal levels still focuses on well water and industrial wastewater, overlooking the threat of leachate water from Final Disposal Sites located in residential areas. Regarding the potential and novelty of utilizing these two materials, by-products can be processed as raw materials for producing activated charcoal, which can be used as a natural adsorbent, especially to reduce heavy metal levels in leachate water at the Putri Cempo Final Disposal Site. This research was conducted to reduce agricultural waste in the form of straw and cassava peel by examining their potential as natural adsorbents and testing their effectiveness in reducing heavy metal content in leachate water at the Putri Cempo Final Disposal Site. The results of this research can be used as a reference and basic material for determining the steps for handling pollution and evaluating activities by the community around the pollution source, which in this case is Cd pollution originating from the Putri Cempo Final Disposal Site located in Kampung Jatirejo RT 03 RW 39, Mojosongo, Jebres, Surakarta.

2. Methods

2.1. Preparation of Tools and Materials

This research employs several tools, including an Atomic Absorption Spectrophotometer (AAS) equipped with a Cd cathode, a furnace, an oven, an analytical balance, measuring flasks, measuring cups, evaporator cups, crucible cups, Erlenmeyer flasks, measuring pipettes, pipette pumps, stirrers, a hot plate, and mortar and pestle. The materials used comprise leachate, straw, cassava peel, 1N hydrochloric acid (HCl), sodium chloride (NaOH), nitric acid (HNO3), deionized water (aqua bidest), filter paper, and aluminum foil. The experimental procedure follows the principles outlined in SNI 06-3730-1995 with several adjustments made to achieve the desired variations in results. Initially, rice straw and cassava peels are washed and dried to reduce their water content. Subsequently, they are chopped into smaller pieces, facilitating drying in an oven and burning in a furnace. Each type of raw material for activated charcoal is dried and burned at different temperatures of 400°C and 600°C.

2.2. Charcoal Activation

Straw charcoal and cassava peel are then activated using a chemical process with a 1N hydrochloric acid (HCl) solution for 24 hours (Verayana et al., 2018). The activated charcoal is subsequently neutralized with a sodium hydroxide (NaOH) solution (Norouzi et al., 2018). The charcoal was dried in an oven for 2 h at 105°C and then ready for use (Hayaati & Ridho, 2020). The activated charcoal is weighed with four mass variations, namely 1, 1.5, 2, and 2.5, at each temperature and charcoal type and is then exposed to leachate samples from the Putri Cempo landfill that have been digested. The digestion process can be done using concentrated oxidizing acids such as $HClO_4$, H_4O_4, H_2O_2, HNO_3, and H_4SO_4 (Armarego, 2022). In this study, digestion is performed using concentrated nitric acid (HNO_3). The purpose of the digestion step is to break down the organic materials within the leachate until the remaining metals are dissolved as ions (Du et al., 2020). Leachate digestion is conducted on a hot plate for 1-3 hours until the solution is reduced, and the yellow vapor dissipates (Erniati et al., 2018). After digestion, 50 mL of the leachate was placed in contact with activated charcoal for 24 h and filtered using a filter paper.

2.3. AAS Testing

Before this stage, it is necessary to prepare standard cadmium solutions with different concentrations. According to Wiyantoko (2020), creating standard solutions involves diluting the cadmium mother solution to create a range of Cd standard solutions. This research employs seven concentration variations, including 0.05, 0.075, 0.1, 0.125, 0.25, and 0.75. The dilution is performed in a 50 ml volumetric flask, which will subsequently be analyzed using AAS. AAS testing is conducted to determine cadmium levels. The testing is performed at a wavelength of 228.8 nm (Nasir, 2020). This test yields absorbance values and Cd levels in samples, which can be used to assess the effectiveness of straw and cassava peel-activated charcoal in reducing cadmium levels in saliva. The relationship between effectiveness and adsorption capacity is directly proportional; the higher the effectiveness value, the more cadmium can be reduced or absorbed into the activated carbon. The data obtained were processed statistically and descriptively and quantitatively analyzed. Data is presented in the form of graphs and tables. The statistical test utilized in this research is a normality test. This test was performed to ascertain the accuracy and normality of the data distribution obtained during the AAS testing (Rahmat et al., 2023).

In general, the method used in this study is almost similar to previous studies. The difference lies in the selection of the dose of activated charcoal and the standard series of Cd. The dose of activated charcoal from cassava peel used in previous studies was activated charcoal with a mass variation of 0.5; 0.25 and 0.125 grams (Maria et al, 2021). Meanwhile, the standard series that has been used in the analysis of heavy metal Cd in previous studies consists of 5 concentration variations consisting of 0.1 ppm; 0.2 ppm; 0.3 ppm; 0.5 ppm; and 1 ppm of 10 ppm cadmium mother solution (Andriani et al, 2022). In addition, differences in methods also exist in the selection of raw materials for making activated charcoal and active ingredients used as charcoal activators. Raw materials that are widely used in the manufacture of natural adsorbents by previous studies are rice husks (Halim et al, 2021; Sasmita et al, 2021; Siswandi et al, 2022; Yati & Dewi, 2022), corn cobs, coconut shells, and wood powder (Hatina & Winoto, 2020; Kusumo et al, 2022; Moelyaningrum & Ellyke, 2022). The active ingredient used as a charcoal activator in this study is hydrochloric acid (HCl) solution, while in other studies using other activators such as Potassium Hydroxide (KOH), Phosphoric Acid (H_3PO_4), Zinc Chloride ($ZnCl_2$), Sulfuric Acid (H_2So_4) (Aji et al, 2022; Dewi et al, 2021; Wijaya et al, 2022; Yunus et al, 2021).

3. Result and Discussion

3.1. Result

Based on the research results, it was found that activated charcoal made from cassava peels has higher effectiveness compared to activated charcoal made from straw. The ratio of cadmium reduction in leachate water is presented in Table 1. Based on the table, it can be seen that the contact of leachate water with activated charcoal yields effective output in six samples and highly effective results in seven samples, with the highest cadmium reduction value in samples contact with activated charcoal made from burnt cassava peelings at 600 °C with a dosage of 2 g.

Table 1. Ratio of cadmium levels (mg/L)

Charcoal Type	Temperature	CA Quantity (gr)	Final Concentration of CD (mg/L)	Initial Cd Level (mg/L)	Ratio of Cd Levels (mg/L)	Effectiveness Level
Straw	400	1	0.005	0.0066	0.0016	Effective
		1.5	0.0102		-0.0036	Ineffective
		2	0.0054		0.0012	Effective
		2.5	0.0049		0.0017	Effective
	600	1	0.0122		-0.0056	Ineffective
		1.5	0.0052		0.0014	Effective
		2	0.006		0.0006	Effective
		2.5	0.0036		0.003	Very Effective
Cassava peel	400	1	0.0055		0.0011	Effective
		1.5	0.0043		0.0023	Very Effective
		2	0.0062		0.0004	Effective
		2.5	0.0042		0.0024	Very Effective
	600	1	0.0045		0.0021	Very Effective
		1.5	0.0045		0.0021	Very Effective
		2	0.0032		0.0034	Very Effective
		2.5	0.0038		0.0028	Very Effective

Source: Research (2023)

After calculating the effectiveness of activated charcoal for cadmium reduction in leachate water, it was found that the average effectiveness of activated charcoal made from cassava peel and rice straw had a large difference (Table 2). The average effectiveness of rice straw activated charcoal produced from the 400°C heating process was 0.00341% and from 600°C heating was -0.0227%. The average effectiveness of cassava peel activated charcoal produced from the 400°C heating process amounted to 0.2348% and from 600°C heating amounted to 0.3939%. This means that in general, the average effectiveness of cadmium reduction on activated charcoal of rice straw heated for 18 hours is very small, namely 0.0057%. While the effectiveness of cadmium reduction on cassava peel activated charcoal heated for 18 hours is quite good, namely 0.3144%.

Table 2. Total Effectiveness (EF%)

Charcoal Type	Temperature	CA Quantity (gr)	EF%	Average EF%	Total EF%
Straw	400	1	0.2424	0.0341	**0.0057**
		1.5	-0.5455		

Charcoal Type	Temperature	CA Quantity (gr)	EF%	Average EF%	Total EF%
		2	0.1818		
		2.5	0.2576		
	600	1	-0.8485	-0.0227	
		1.5	0.2121		
		2	0.0909		
		2.5	0.4545		
Cassava Skin	400	1	0.1667	0.2348	**0.3144**
		1.5	0.3485		
		2	0.0606		
		2.5	0.3636		
	600	1	0.3182	0.3939	
		1.5	0.3182		
		2	0.5152		
		2.5	0.4242		

Source: Research (2023)

The cadmium calibration curve in this study has an R^2 value of 0.998. This can also be observed in the calibration result points where all the data lie close to the normal line and form an almost straight line. The R^2 value close to 1 indicates that the AAS test data distribution is normal and accurate. The results obtained in this study were compared with those of previous studies that used the same method and object of research (Cd content in leachate). The difference between this research and that research (Lestari, 2023) lies in the time variable and the type of charcoal. As seen from Table 3, Lestari (2023) who used apu wood as the basic ingredient of activated charcoal and with a much longer treatment time, namely 10 days, got maximum results.

Table 3. Comparison of treatment durations

Bioremediation Media	Average Treatment Duration	Average Effectiveness
Straw	18 hours	0.0057 %
Cassava peel	18 hours	0.3144 %
Apu wood	24 hours × 10 days	31.58 %

Source: Research (2023) & Lestari (2023)

4. Discussion

Based on the research conducted, it is known that the provision of activated charcoal is considered effective in reducing the cadmium levels in leachate water. The output produced based on the contact of leachate water with activated charcoal can result in ineffective, effective, and highly effective outcomes. The negativity of the ratio value is caused by several factors influencing the effectiveness of activated charcoal in absorbing cadmium metal in leachate water. These factors can include the charcoal dosage, burning temperature, and type of activated charcoal used. The provision of activated charcoal has been proven effective in reducing heavy metal levels in various studies. The research by Syauqiah et al. (2021) shows that activated charcoal from rice husks can reduce Cd metal values in *Sasirangan* liquid waste (Syauqiyah et al., 2021). The study by Rahman et al. (2020) also found that the lower the volatile substance content of activated charcoal, the better its absorption capacity for heavy metals (Rahman et al., 2020). Another study conducted by Baryatik et al. (2019) also confirmed that activated charcoal made from coffee grounds effectively reduces cadmium levels in water (Baryatik et al., 2019).

4.1. Calibration Curve

The Cd calibration curve results from processing the absorbance values in each standard solution. The curve depicted above follows a linear equation in the form of $y = mx + c$. In this equation, the coefficient 'y' represents the absorption value in each standard solution, the variable 'X' represents the heavy metal's cadmium (mg/L) content, and the constant 'c' is a laboratory-derived value, specifically -0.0042. The 'R^2' value on the curve indicates linearity. A value closer to 1 signifies greater significance (Manikasari & Mahayani, 2018).

4.2. Effect of Dose Variables

The SSA test results showed that the cadmium content in the pure diluted leachate was 0.0066 g/L. This value was used as a reference for assessing the effectiveness of each variable used in this study. The mass variable of activated charcoal is considered to have no significant impact on reducing cadmium content in leachate water. This can be seen in Table 2. The changes in values that occur tend to go up and down irregularly, meaning that other factors are not included in the current research variables. However, the effectiveness value of 1 gram of activated charcoal is always smaller than the effectiveness value of 2.5 grams of activated charcoal. Both in the categories of straw and cassava skin, temperatures of 400°C and 600°C. The hypothesis regarding the mass of activated charcoal is usually directly proportional to the adsorption capacity of activated charcoal, in line with studies conducted by Nurafriyanti et al. (2017) and El-Bery et al. (2022). They stated that the adsorption capacity of activated charcoal increases with the amount of adsorbent used, so the adsorption surface area is directly proportional to the mass of the adsorbent. However, there are exceptions if excessive adsorbent mass is used, which can cause a decrease in adsorption capacity due to the formation of lumps, thereby reducing the overall surface area (Pandia and Warman, 2016 & Waseem et al., 2012). Our experimental results showed that the level of adsorption capacity did not change significantly between doses of 1 gram to 2.5 grams of activated charcoal powder. This shows that activated charcoal from straw and cassava peel has a fairly large adsorption capacity for the heavy metal Cd. This adsorption ability can also be influenced by the saturation point. According to Mauriza et al. (2020), if it has not yet reached the saturation point, the adsorption capacity value is still likely to increase. In this case, the volume of leachate does not have a significant effect because the volume of solution used is the same in each sample, which is 50 ml.

4.3. Effect of Temperature Variables

In this research, burning was carried out at a temperature of 600°C with two different materials, namely straw and cassava skin. Cassava peel charcoal burned at 600°C has a higher absorption capacity than straw charcoal burned at the same temperature. Generally, charcoal produced at higher temperatures has a larger specific surface area compared to charcoal produced at lower temperatures (Ahmad et al., 2012; Rodriguez et al., 2020). For example, the surface area of charcoal produced from wheat straw that is well carbonized at temperatures between 500 and 700 °C is reported to be 300 m2 g-1, whereas the surface area of charcoal produced at temperatures between 300 and 400 °C is reported to be due to poor carbonization. sufficient is 200 m2 g-1 (Erdem, 2021). However, temperatures that are too high can damage the pores of activated charcoal, thereby reducing its ability to bind metal ions (Imelda et al., 2019). This difference in results is also caused by differences in the characteristics of each material used in activated charcoal production, as supported by research by Astuti et al. (2021). Straw is more fragile than cassava skin (Sumarmo et al., 2021 & Kosim et al., 2022). If both are heated at a high temperature for the same duration, the resulting activated charcoal structure will differ. In addition, the absorption capacity of metal ions in activated charcoal is influenced by the ash content. High ash content is caused by burning at too high a temperature (Sartova et al., 2019). The brittle nature of straw makes it more flammable and accelerates the formation of ash compared to cassava peel. High ash content clogs the pores of the charcoal, thereby reducing its surface area (Wahyuni, 2019). As a result, the ability to bind or adsorb metal ions becomes reduced (Moelyaningrum & Ellyke, 2022).

4.4. Effect of Variable Types of Activated Carbon

The two previous variables, namely temperature and mass, show that activated charcoal made from cassava peel tends to have better effectiveness than straw-activated charcoal. This could happen due to other variables that were not tested in this study, namely the size of the activated charcoal particles and the stirring speed (Siskayanti et al, 2020). Another variable that can be taken into consideration is the ingredients of the activated charcoal itself, namely straw and cassava skin. The cadmium content in the straw may cause an increase in cadmium levels in samples treated with straw-activated charcoal. Straw is a by-product of rice which is the staple food in Indonesia. To meet high productivity demands, farmers often use fertilizers, including inorganic fertilizers containing phosphate, which can cause an increase in cadmium levels in the soil. Research conducted by Mutiara et al. (2023) confirmed that phosphate fertilizer can contain Cd in the range of 0.1-170 ppm. Continuous and prolonged use of these fertilizers can result in the accumulation of cadmium in the soil, which ultimately moves to rice plants. The accumulation process involves the absorption and transport of cadmium mixed with nutrients from fertilizer through the plant's roots and into its tissues. These metals will later accumulate in plant body parts such as stems, leaves, and fruit (Suryandani et al, 2021). These metals accumulate in various parts of plants, including stems, leaves, and fruit, a process called bioaccumulation (Susilowati, 2019). The cadmium content accumulated in the straw remains during conversion to activated charcoal, contributing to the relatively high cadmium content in samples treated with activated charcoal from rice straw at combustion temperatures of 400°C and 600°C, resulting in negative effectiveness compared with activated charcoal. made from cassava skin. As shown in Table 2, cassava peel showed higher effectiveness than straw-activated charcoal. This is proven by calculating the average and total effectiveness of samples treated with both types of charcoal, as detailed in the table above.

Calculations based on samples treated with cassava peel-activated charcoal produced an average total effectiveness of 0.3144. The high effectiveness of cassava peel-activated charcoal is due to the significant carbon content in the white layer of cassava peel. This is supported by research conducted by Pratiwi et al. (2021) which shows that the white layer of cassava skin contains 59.31% carbon. The carbon compounds in cassava skin can be lignin and cellulose which function as raw materials for making natural adsorbents (Sari & Sari, 2021). Cassava peel cellulose consists of around 43.63%, lignocellulose 10.38%, hemicellulose 1.76%, and other components (Artiyani & Soedjono, 2019). Cellulose in cassava peel contains hydroxyl groups (-OH) so it is suitable for use as an absorbent material (Varghese et al., 2019). Utilizing cellulose-containing raw materials to produce activated charcoal improves its structural regularity. In addition, the presence of cellulose increases the macropore size on the surface area of activated charcoal and increases its crystallinity. Thus, activated charcoal made from cellulose has a higher quality than activated charcoal produced without cellulose (Li et al., 2020). Although straw also contains cellulose and lignin, cassava skin has a higher cellulose content. This was confirmed by Laya et al. (2022), who revealed that straw contains 37.71% cellulose, 21.99% hemicellulose, and 16.62% lignin.

The efficacy of utilizing activated charcoal is also contingent upon the attributes of leachate water. The characteristics of the viscous liquid utilized in this study include its dark brown color, distinctive odor, and presence of suspended solids, commonly referred to as TSS, which represents the residue of total solids retained by a filter with a maximum particle size of 2 micrometers. Various constituents typically found in leachate include metal oxides, sulfides, mud, clay, algae, bacteria, and fungi (Apriyani and Lesmana, 2019). Pagiling et al. (2017) indicated that parameters such as DO, COD, BOD, and Cd remained within acceptable quality standards, whereas NO2 levels fell short of the standards at the Santiago Tahuna. Astuti (2006) conducted a leachate analysis and noted elevated levels of parameters such as BOD, COD, Cd, nitrates, nitrites, as well as oils and fats at the Putri Cempo Mojosongo Surakarta Final Waste Disposal Site. Essentially, the characteristics of leachate vary based on the waste composition and processes occurring within the waste pile.

4.5. Effect of Treatment Duration Variable

The duration or length of treatment in a study is an important variable to consider. In this study, the average duration of contact treatment between leachate water and activated charcoal is 18 hours. This 18-hour period yields an average effectiveness of 0.0057% and 0.3144% (Table 3). Meanwhile, in a phytoremediation study of leachate water using cadmium for 10 days conducted by Lestari (2023), the average effectiveness was 31.58% (Table 3). This indicates that the time variable significantly influences the results of leachate water bioremediation. The difference in average bioremediation effectiveness between 10 days of treatment using *apu* wood plants and 18 hours of treatment using straw contact reaches 5540 times.

Meanwhile, the difference in average bioremediation effectiveness between 10 days of treatment using *apu* wood plants and 18 hours of treatment using cassava peel contact reaches 100 times. From these calculations, bioremediation using activated charcoal made from cassava peelings potentially has the same high effectiveness as bioremediation using *apu* wood plants. Provided that the activated charcoal is in contact with leachate water for 24 hours × 10, as noted.

5. Conclusions

This study demonstrates that cassava peel waste is the most effective material for absorbing cadmium levels in every 50 mL of leachate water. This is indicated by a high total effectiveness (EF%) value of 0.3144. Meanwhile, the optimal combustion temperature of cassava peel waste-based activated charcoal is 600 °C. Combustion at this temperature produces the highest EF% value, which is 0.515152. It is recommended to conduct further research focusing on doubling the volume of leachate water with the mass of activated charcoal contacted. This research can provide a deeper understanding of the effectiveness of using activated charcoal, particularly derived from cassava peel waste, in reducing heavy metal levels in leachate water. Additionally, further research can explore the influence of other variables, such as contact time and pH, on the adsorption process of heavy metals by activated charcoal. Thus, a more comprehensive understanding of the potential use of activated charcoal as a natural adsorbent in addressing leachate water pollution at final disposal sites can be achieved.

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