Adsorbent from coffee grounds to reduce cadmium concentration in leachate water

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Article Info	ABSTRACT			
Article history: Received Feb 1, 2024 Revised May 30, 2024 Accepted Jun 19, 2024 Keywords: Absorbent Cadmium Carbonized-non carbonized Leachate Liquid waste	Wastewater contains a variety of heavy metals, one of which is cadmiu (Cd) which causes adverse effects on both the environment and heal Coffee grounds can be used to reduce Cd in wastewater so this study aims determine the reduction of Cd levels using coffee grounds. The type research used is an experiment to see the decrease in Cd levels usi			
	carbonized and non-carbonized coffee grounds. The samples used were taken from the leachate water source at one of the landfills in Makassar City. Sampling was done using the grab sampling technique. The results showed that the use of uncarbonized and carbonized coffee grounds was effective in reducing Cd levels in Makassar City Tamangapa Landfill leachate water with an average decrease of 0.048 and 0.023 μ g/L. Uncarbonized coffee grounds have a higher ability to reduce Cd in leachate so that it can be used as an alternative in the wastewater treatment process.			
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1. INTRODUCTION

Waste management in Indonesia still uses an open dumping system. This activity causes the soil to be potentially contaminated with leachate, especially if the landfill is in an area with high rainfall and groundwater table. This condition causes environmental pollution by heavy metals due to leachate, which has environmental risks due to its high toxicity and bioaccumulation properties. Cadmium (Cd) is a heavy metal in leachate water. Long-term exposure to Cd in humans can damage bones and kidneys and negatively affect the central nervous system and fertility [1], [2]. Heavy metals, including Cd, lead, copper, and zinc, have been widely dispersed into the environment by anthropogenic activities, such as mining operations, electroplating, industrial activities, and even waste disposal in landfills [3]. Heavy metals are non-biodegradable and easily accumulate in living organisms, resulting in increased concentrations of heavy metals in the environment [4]. Besides some emissions to the atmosphere associated with dust particles, heavy metals largely remain in waters and soils.

Pollutants derived from sewage, industry, mining, and settlements are becoming a problem in the environment, including heavy metal ions such as Cd [5], [6]. These metal ions are toxic and do not easily decompose in the environment. Metal ions can be removed from water using adsorbents such as activated carbon and coffee grounds [7]. Chemical precipitation, membrane filtration, and ion exchange are some of the commonly used techniques for treatment but are expensive [8]. Among other alternative techniques, heavy metal sorption with sorbents is cost-effective and inexpensive [9]. Among the various techniques, removing heavy metals through adsorption on adsorbents is considered the best, as it is a relatively simple

and cost-effective technique. With this technique, the concentration of heavy metals in water can be reduced through adsorption onto the surface of the adsorbent material [10].

Activated carbon to remove heavy metals from water can be obtained from inexpensive and locally available materials with competitive adsorption capacity, such as clay minerals, oyster shells, and certain waste products from industrial facilities. In addition, the use of coffee grounds waste as an adsorbent for heavy metals in contaminated water can be considered [11]. Coffee grounds can be made into activated charcoal as an adsorption or absorbent material through an activation process. Activation is a process used to remove charcoal hydrocarbons, thus increasing carbon's porosity. Charcoal can be activated through chemical and physical activation [12]. The use of activated coal in coffee amps as Cd adsorbent in well water. The results obtained from the quality tests of the activated coal in coffee amps covered fertility (98.5%), water content (7%), ash content (4%), and absorption (687.96 mg/g). There were four groups, namely without treatment 0 gr/l (P0), treatment with 5 gr/l (P1), treatment with 8 gr/l (P2), and 10 g/l (P3), with each group consisting of 6 replications [13], [14].

Coffee is one of the largest agricultural products and is a highly tradable commodity in the international market, resulting in a large amount of coffee waste, especially in the form of coffee waste soil (SCG). SCG is an organic residue in powder form obtained after extracting coffee from coffee beans using hot steam and high pressure. SCG has been used for bio-energy, bioactive compounds, subgrade materials, plastics, and composites [12]. This study examined the effect of using carbonized coffee grounds as an adsorbent for wastewater contaminated with heavy metal Cd. While previous studies investigated the impact of using other coffee-absorbent materials, they did not explicitly discuss the effect of coffee grounds on adsorbing heavy metal Cd in wastewater.

2. RESEARCH METHOD

This research uses a true experimental design. This research design is a simple experiment where the research subject is to see the decrease in Cd levels using carbonized and non-carbonized coffee grounds activated charcoal with a Pretest and Posttest design. Leachate water sampling was carried out at the Tamangapa landfill, Makassar City. The sampling location was carried out considering that the location is the main landfill of Makassar City, and there are many settlements close to the location, so there is the potential for groundwater pollution from leachate water. Tamangapa landfill is the main waste disposal site for Makassar city residents, which produces around 4.494.86 m3 of waste/year. The most significant problem arising from the landfill is leachate. Leachate can seep into groundwater and rivers, degrading surface water quality, rivers, and residents' wells. Contamination due to bacteria can cause various diseases. Tamangapa Landfill, located in Tamangapa Village, Manggala District, Makassar City, is the only landfill in the city. Tamangapa landfill services cover all waste in Makassar city. This landfill is very close to residential areas, so residents often complain about the unpleasant odor of the landfill. There are also several activity and residential centers, such as places of worship and schools and offices, about 1 km from the location.

The leachate sampling technique used the grab sample (random sampling technique without special selection), taken directly from the source. Leachate samples were divided into three categories: control samples that were not given interventions in the form of carbonated or non-carbonated coffee grounds, leachate samples given carbonized coffee grounds, and leachate samples given non-carbonized coffee grounds. Each sample was repeated three times. The data that has been processed and presented is then analyzed and interpreted descriptively. In addition, the data were also analyzed statistically using the Crusscall Wallis test using SPSS to determine the comparison of carbonized coffee grounds charcoal and non-carbonized coffee grounds charcoal on the reduction of Cd levels in leachate water. Research Instruments; The preparation phase consists of preparing coal and coffee foil materials until the tools are designed to process coffee coal. Coal and coffee foil production uses ovens to change the coffee foils. The materials used include coffee and aluminum foil. The process of crafting The carbonization process of coffee amps into an adsorbent is carried out by i) drying coffee in the sunlight, ii) then after drying the coffee in an aluminum foil, ii) put into a closed container, iv) then put into the furnace for 2 hours at a temperature of 120 °C to obtain an optimal temperature, and v) after that the coffee amp is ready to be used. For uncarbonized coffee amp be done in a way: i) drying coffee amp under the sun and ii) drying ready coffee amp is used.

3. RESULTS AND DISCUSSION

Figure 1 shows that the initial sample's Cd level was 0.100 μ g/L. In contrast, the Cd level in each control period experienced the largest decrease from the initial sample, namely in the control repeat 2 of 0.002 μ g/L. Repetition was done thrice to ensure the data obtained was valid.

Based on Figure 2, shows that the Cd level in the initial sample was $0.100 \mu g/L$, while the Cd level in each portion of uncarbonized coffee grounds experienced the greatest decrease from the initial sample of uncarbonized coffee grounds, namely in replication 1 of 0.057 $\mu g/L$. Based on Figure 3, shows that the Cd level in the initial sample was $0.100 \mu g/L$, while the Cd level in each carbonized coffee grounds experienced the greatest decrease from the initial sample in carbonized coffee grounds, namely in replication 1 of 0.082 $\mu g/L$. This shows that there is a difference in the decrease in carbonized and non-carbonized coffee grounds.





Cadmium Levels (Uncarbonized Coffee Grounds)



Figure 1. Results of Cd level checks in landfill leachate control in Tamangapa Village, Makassar City 2023





Figure 3. Results of examination of Cd levels in landfill leachate using carbonized coffee grounds Tamangapa Village, Makassar City 2023

Table 1 shows that uncarbonated coffee grounds have a higher ability to remove Cd levels in leachate with the highest presentation in the first replication compared to carbonized coffee grounds. This is due to the higher pH levels in the uncarbonated coffee grounds when compared to the pH in the carbonized coffee grounds. presentation Based on the results of the Kruskal Wallis statistical test, it shows that of all sample testing treatments of Cd levels using carbonized and uncarbonized coffee grounds, the p-value is 0.017>0.05, so it can be concluded that there is no significant difference in the treatment of carbonized and uncarbonated coffee grounds in reducing Cd levels as shown in Table 2.

Table 1.	Reducing	Cd levels	in leachate
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Variable	Treatment	Maximum absorption	Maximum removal	Temp (°C)	Humidity (%)	Optimum pH	
Initial sample	Uncarbonized	0.1	0%	30	62	6	
Replication I		0.082	18%	27	58	6.1	
Replication II		0.08	2%	27	58	6.3	
Replication III		0.069	11%	26	56	6.5	
Initial sample	Carbonized	0.1	0%	30	62	6	
Replication I		0.057	43%	29	60	5.9	
Replication II		0.051	6%	29	59	5.5	
Replication III		0.048	3%	28	59	5.4	

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Table 2. Result of statistic							
Parameter	Treatment	Frequency (n)	Percentage (%)	P-value			
Cadmium	Initial sample	3	100				
	Control	3	100				
	Uncarbonized coffee grounds	3	100	0.017			
	Carbonized coffee grounds	3	100				

From the observation data, it can be seen that the concentration of Cd metal for water samples taken on August 12, 2023, exceeds the quality standard, where Cd metal in the monitoring well (initial sample) reached 0.100 μ g/L. This is because the samples were taken during the dry season, so there was no dilution by rainwater at the sampling location. Apart from that, in the operational stage of the landfill (partially open), the parts that have not been covered with soil will absorb a certain amount of rainwater daily (even though it sometimes still rains during the dry season). This study is in line with research by Kasam *et al.* [14] which states that rainwater entering the landfill area will influence the characteristics of the leachate produced from the landfill. Apart from that, the water detention time in leachate treatment ponds is not optimal because leachate production increases, and the processing ponds do not have sufficient capacity so that leachate quickly overflows from one pond to another.

Another factor is the lack of optimal leachate processing at the Tamangapa spill, which relies solely on aerobic and anaerobic processes and short retention times due to the discharges that come during the high rainy season. The composition of leachate is influenced by several factors, such as the type of waste stored, the amount of rainfall in the landfill area, and the specific conditions of the landfills. In addition, the age of the capture site also affects the quality of the mud produced, where the longer the storage site's age, the lower the level of organic pollutants produced compared to the new site. This research is in line with El-Salam and Abu-Zuid's research that heavy metal content in leachate water is influenced by many factors such as rainfall, total dissolved solids (TDS), and total suspended solids (TSS) [15].

The pH effect on Cd adsorption is determined by adjusting the pH of the initial solution. The pH of a solution affects the rate of metal adsorption because it strongly affects metal species and their precipitation, according to research by Li *et al.* [16] and Babu *et al.* [17], which stated that the effect of pH on the Cd absorption was determined through adjustment of the pH. This pattern of change in the level of elimination of Cd corresponds to the solution's end point of pH after the balance between SCG and Cd in the solution, which suggests that the pH regulates the speed of Cd elimination. The zero charge point of SCG was determined experimentally to pH 5.5, using additional methods of solid. Another possibility may be due to the possibility of reduced bonding as the metal bonding ligands in the SCG are destroyed under strong acidic conditions.

Further increases in the transfer rate of Cd were observed with an increase in the pH above 8, where the endpoint pH also increased but never reached 100% due to chemical leakage under experimental conditions [18]. This is associated with increased density of negative surface load on the SCG through deprotonation produced by an increased concentration of OH. The pH-dependent removal of Cd that was inconsistent in previous studies was suspected to be due to a lack of pre-treatment SCG and different properties of the SCG used in this study. Despite the inconsistent rate of elimination of Cd at high pH, an increasing trend with an increase in the pH of the solution from pH 2 to pH 7 has been frequently observed in most previous studies [19].

Coffee grounds waste contains carbon atoms processed into active carbon, used as an absorbent or adsorbent. Activated carbon is a porous solid produced from carbon-containing materials activated by heating at high temperatures. Increasing the surface area of activated carbon will further increase its adsorption power. Utilizing coffee grounds processed into active carbon as a biosorbent can help clean contaminated wastewater and reduce coffee grounds waste in the environment [3]. An activation process must be carried out to increase capacity and efficiency in the adsorption process of adsorbents. Activation can be done by chemical treatment, such as reacting with acids and bases. Fdez-Sanromán *et al.* [20] conducted research, namely making activated carbon from tea dregs using NaOH as an activator with variations in carbonization temperature and concentration of NaOH as an activator. The research results show that the initial sample's Cd level was 0.100 μ g/L. In contrast, the Cd level in each uncarbonized coffee ground decreased most from the initial sample in carbonized coffee grounds, replication 1 of 0.082. μ g/L. Further examination showed that the initial sample's Cd level was 0.100 μ g/L. In contrast, the Cd level in each carbonized coffee ground had the largest decrease from the initial sample in carbonized coffee grounds, replication 1 of 0.082. μ g/L.

Based on the results of the Cruskal Wallis statistical test, it shows that from all treatments examining samples for Cd levels using carbonized and uncarbonized coffee grounds, the p-value was 0.017>0.05, so it can be concluded that there is no significant difference in the treatment of carbonized and uncarbonized coffee grounds in reducing Cd levels. In leachate. Different removal efficiencies in the media

used (carbonized and uncarbonized coffee grounds) in liquid waste processing will affect the saturation of the media used. Saturation indicates the volume of water that passes (through) the media before the maximum concentration of the effluent is reached, indicating that the media used must be regenerated. Another factor that can influence adsorption is the adsorbent concentration. Adsorbent concentration is an important parameter because it determines the optimum adsorbent capacity in adsorbate adsorption. This study's optimum concentration for adsorbing Cd metal was 0.100 μ g/L. This is because as the adsorbent dose increases, the surface area for adsorption also increases. So carbonized coffee grounds more easily bind Cd metal ions in leachate. It can be concluded that as the concentration increases, the interaction between the adsorbent and the adsorbate becomes greater so that adsorption tends to increase [3], [10], [17].

Apart from that, the length of contact time can affect adsorption; the longer the adsorption time, the greater the collision frequency between the adsorbent and the adsorbate particles. The research results showed that the carbonized coffee grounds group had the highest percentage reduction in Cd levels. The maximum adsorption capacity of the adsorbent occurs at the equilibrium time, so the contact time must be determined to obtain the maximum adsorption capacity. The equilibrium time is influenced by several factors, including the adsorbent type, the adsorbent's size and physiology, the ions involved in the adsorption system, and the metal ion concentration [21], [22].

One material with a great opportunity as a source of porous active carbon is Robusta coffee bean dregs because, so far, research on the use of Robusta coffee bean dregs as a supercapacitor electrode has not been optimal. Besides being natural and non-toxic, coffee bean dregs are also one of the most common wastes in everyday life [23]. Examined activated carbon from tea dregs as an adsorbent in the adsorption process of β - carotene contained in crude palm oil. This research will study the carbonization process of tea dregs at various temperatures and activation with various concentrations of sulfuric acid (H2SO4) and its methyl blue absorption capacity.

The adsorption process at longer contact times will indicate that heavy metals must diffuse slowly into the pores of the coffee grounds due to the deficit in the available binding network. Moreover, heavy metals will have difficulty sticking to some of the tissues available for adsorption due to the repulsive force exerted between heavy metal ions in large quantities, solutions, and contaminants adsorbed on solid adsorbents. Adsorbent absorption is influenced by the volume used and the specific surface area. There are adsorbent characteristics needed for a good adsorption process, including the larger the surface area, the smaller the adsorption capacity area because the adsorption process occurs on the surface of the adsorbent; there is no significant volume change during the adsorption and desorption processes; adsorbent that has a high level of purity has better adsorption capacity; and the properties of the atoms on the surface are related to the molecular interactions between the adsorbate and the adsorbent which is greater in certain adsorbate [24].

In principle, the carbonization process eliminates the hydrogen and oxygen elements bound in the raw material so that only carbon remains, which is the dominant element. The carbonization process will produce three main components: carbon or charcoal, tar, and gas. At the carbonization stage, carbon will be produced with a weak pore structure because the crystal structure is irregular, so cavities are still filled with the elements that make up the raw material. These elements can cover pores so that their adsorption capacity is low. Therefore, charcoal still needs to improve its pore structure through activation [25].

Leachate seeping into residents' wells can decrease the quality of well and river water. If the well water is used for daily needs such as cooking, washing, and bathing, it will be dangerous for human health. Not only that, if well water containing heavy metals is used for agricultural purposes, it will pollute the soil and can accumulate in plants. If humans consume the plant, the concentration of the heavy metal Cd in the human body will increase due to the bioaccumulation process [26].

Cd is often used as a main or additional material in the industry, including in the electroplating industry, nickel-Cd batteries, coating materials, stabilizers in the plastics industry, and other synthetic goods. Cd harms health through the food chain. Animals easily absorb Cd from food, accumulating in tissues such as the kidneys, liver, and reproductive organs. Cd is bioaccumulative, biomagnifying, toxic, and carcinogenic, so heavy metals in the environment can accumulate in the body tissues of living creatures in that environment so that if they reach toxic concentrations, they can poison all biotic components (animals, plants, and humans. Cd toxicity can damage the physiological system, respiratory system, blood circulation system, and heart, damage the reproductive system and nervous system, and can even cause bone fragility kidney damage, and reduce pulmonary function in the body [27]-[31].

Our research suggests that the ingredients of natural materials are primarily organic wastes such as coffee amps capable of reducing heavy metals in wastewater using carbonization methods, this discovery is tougher than the use of chemicals as absorbents so that future research can look at organic garbage such as coffee amps and other organic materials that have absorbent properties able to reduce Cd heavy metal, the discovery provides a practical method for producing large-scale coffee maps for absorbing heavy metal on wastewater.

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4. CONCLUSION

The level of Cd in Tamangapa waste, Makassar City, is 0.100 μ g/L. The use of non-carbonized coffee soil is effective in reducing the level of Cd in Tarangapa Landfill, Makasar City with an average decrease of 0.048 μ g / L. Carbonizing coffee soils are effective in decreasing the levels of Cd in the Tamangaka Landfill waste, Macassar City with the average decreases of 0.023 μ g/L. Our findings offer definitive evidence that this phenomenon is linked to the ability of coffee to absorb as a heavy metal absorbent Cd not only due to increased concentration but also to other factors such as temperature and pH. However, to deepen the absorption capacity of coffee, further research is needed such as increased absorbence concentration and the addition of absorbents from other organic materials.

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