Jurnal Presipitasi
Media Komunikasi dan Pengembangan Teknik Lingkungan
e-ISSN : 2550-0023

Vol 19, No 1, 2022, 11-23
Article available at [homepage presipitasi]

Case Study

Effectiveness of Lead and Cadmium Reduction with Adsorption Method using a Combination of Chitosan and Coffee Grounds (Case Study of Industrial Wastewater PT.X Indonesia)

Nisa Nurhidayanti[1,2*], Nur Ilman Ilyas[2], Dhonny Suwazan[2], Sandy Fajar Nugraha[2], Supriyanto[2]

[1]Doctoral Study Program in Environmental Engineering, Faculty of Civil and Environmental Engineering, Bandung Institute of Technology, Jl. Ganesha No.10, Lb. Siliwangi, Coblong District, Bandung City, West Java 40132, Indonesian
[2]Environmental Engineering Program, Faculty of Engineering, Universitas Pelita Bangsa, Jalan lnspeksi KaIimaIang TegaI Danas Arah DeIta Mas, Kecamatan Cikarang Pusat, Kabupaten Bekasi, Jawa Barat lndonesia 17530
*Corresponding author, e-mail: nisa.kimia@pelitabangsa.ac.id

Abstract
PT. X Indonesia (PXI) is a company engaged in laboratory services in Bekasi Regency. Based on a preliminary study, the concentration of cadmium and lead in wastewater shows that it exceeds the quality standard of PerMenLHK No. P12 of 2020. The presence of cadmium and lead in PXI's wastewater must be resolved immediately to avoid dangerous human activities and polluting the environment. The research was initiated by taking wastewater samples and synthesizing the adsorbent from the combination of chitosan and activated carbon from coffee grounds. The method used in this study is an experimental approach with quantitative descriptive methods based on laboratory data using FT-IR, SEM EDX and AAS instruments. The results showed that chitosan biosorbent and 1.4-gram coffee grounds activated carbon resulted in the highest cadmium metal reduction efficiency of 94.35% and led to a metal reduction efficiency of 90.86%. The results concluded that the adsorbent of chitosan-activated carbon coffee grounds is very effective in reducing cadmium and lead metals in the wastewater of PXI. This research needs to follow up by increasing the mass of activated carbon of coffee grounds to meet quality standards.

Keywords: Adsorption; coffee grounds; cadmium; activated carbon; chitosan; lead

1. Introduction

Heavy metal pollution in water as a result of human activities or industrial activities in the form of heavy metal cations such as Zn2+, Pb2+, Cd2+, Ni2+ and As3+. Ketika logam berat seperti arsen, kadmium, kobalt, tembaga, timbal, nikel atau seng terkandung dalam limbah cair dan masuk ke lingkungan tanpa pengolahan maka akan menghasilkan dampak negatif bagi lingkungan dan makhluk hidup (Panighari & Santhoskumar, 2020). When heavy metals such as arsenic, cadmium, cobalt, copper, lead, nickel or zinc are contained in wastewater and enter the environment without treatment, it will harm the environment and living things (Velusamy et al., 2021). Therefore, removing heavy metal contaminants in drinking and industrial water is an urgent and essential task. Wastewater treatment is a significant problem many countries face (Mosivand et al., 2019).

Removing heavy metals in wastewater has been conducted using several methods, including electrochemistry, chemical oxidation, chemical stabilization, coagulation, precipitation, adsorption, ion exchange, membrane filtration, phytoremediation, etc. These methods have their respective advantages and disadvantages. Adsorption is a physical and chemical process in which the liquid pollutant molecules touch and stick to the surface of the solid/adsorbent (Pratiwi & Prinajati, 2018). Adsorption is an appropriate technique for removing heavy metals in low concentrations from wastewater. The adsorption efficiency depends on the type of adsorbent and the deposition method (Obaid et al., 2018; Prathna et al., 2018). In general, adsorption is proven efficient, cost-effective, and easy to do. The abundance of natural adsorbents in nature is quite a lot. Efficiency and selectivity are high and do not pollute the environment (Naushad et al., 2017; Botahala, 2019).

Coffee is consumed by many populations worldwide and is considered one of the most popular drinks after tea in the world (Ahsan et al., 2021). In Indonesia, coffee is one of the plantation commodity products with high economic potential. It has an essential role as a source of foreign exchange for the country. In addition, coffee is also a source of income for 1.5 million coffee farmers in Indonesia (Rahardjo, 2012). In 2007, coffee production in Indonesia experienced a relatively rapid increase in production, reaching 676.5 thousand tons/year and increased production in 2013 as much as 691.16 thousand tons/year (Badan Pusat Statistik, 2015). Public interest in coffee consumption is high in Indonesia, resulting in extensive waste of coffee grounds. Coffee grounds that are disposed of directly into the environment can be toxic because of the presence of tannin, caffeine and polyphenol compounds (Iqbal et al., 2018).

Coffee grounds waste contains carbon atoms to be processed into activated carbon used as an absorbent or adsorbent (Irmanto, 2009). Activated carbon is a porous solid produced from carbon-containing materials activated by heating at high temperatures. The increased surface area of activated carbon will further expand its adsorption power (Sembiring dan Sinaga, 2003; Rengganis et al., 2017). Utilization of coffee residue/dregs that is processed into activated carbon as a biosorbent can help clean contaminated wastewater and reduce coffee grounds waste in the environment (Ahsan et al., 2021).

In recent years, chitosan has been widely used as a metal adsorbent. Chitosan can be used as a coagulant to reduce the colour content of sasirangan wastewater at a dose of 600 mg/L with an efficiency of 50.5% (Arifin et al., 2017). Chitosan can adsorb chromium (III) metal as much as 138 mg/g at pH 3.5 and a temperature of 20 ^oC (Pietrelli et al., 2020), nickel (II) metal as much as 49.9 mg/g at a temperature of 60 ^oC (Liao et al., 2016), zinc metal (II) 196.1 mg/g at pH 5 and 25 ^oC (Seyedmohammadi et al., 2016), lead (II) 843.9 mg/g at pH 4 and 25 ^oC (Rodrigues et al., 2019). Chitosan can bind lead metal ions 5-6 times greater than chitin (Supriyantini, 2018). The use of chitosan and activated carbon from coffee grounds as adsorbents can reduce metal levels of cadmium by 74.54% and nickel by 73.43% (Sari, 2019) and can minimise micropollutant compounds in pharmaceutical wastewater such as acetaminophen, metamizole, acetylsalicylic acid and caffeine (Lessa et al., 2018).

PT. X Indonesia (PXI) is one of the companies in Bekasi Regency engaged in laboratory services ranging from inspection, testing, certification and training for loCal and multi-national companies/industries in Indonesia. PXI operates ISO 17025 accredited state-of-the-art laboratories for food, pharmaceutical, cosmetic and textile testing. PXI generates hazardous and toxic waste, handed over to third parties. Based on the test results of wastewater samples from PXI, the metal concentration of cadmium (Cd) was 1.15 mg/L, and lead (Pb) was 1.02 mg/L. Based on these data, the concentration of cadmium and lead metals produced by PT PXI exceeded the quality standards of the Minister of Environment Regulation No. P12 of 2020 in Appendix III regarding wastewater quality standards in the water holding ponds in B3 waste storage facilities in the form of piles. Waste pile and impoundment are

0.1 mg/L (Menteri LHK, 2020). Therefore, there is a need for research that can contribute to helping PXI solve the problem of heavy metals in its wastewater.

On this occasion, the researchers tried to solve the research gap by utilizing adsorbents from chitosan by varying the mass of coffee grounds activated carbon added to reduce cadmium and lead metals in PXI industrial wastewater treatment, which exceeds the quality standard. The control variables controlled in this study were a pressure of 1 atm and a temperature of 25 °C with a contact time of 60 minutes. In addition, the use of chitosan and coffee grounds expect to reduce the negative impact of environmental pollution due to the use of chemical adsorbents and the presence of coffee grounds waste.

2. Methodology

2.1 Research Time and Place

This research was carried out at PXI while sample testing at the PT. TÜV NORD Indonesia loCated at Jl. Science Timur 1 bloCk B3-F1 Industrial area Jababeka 5 Cibatu Cikarang, Bekasi 17530 starting from the sample preparation stage to testing. This research was conducted for seven months, from February 2021 to September 2021.

2.2 Research Tools and Materials

The tools that used in this study consisted of a beaker, analytical balance, filter paper, volume pipette, funnel, porcelain dish, universal indicator, oven, spatula, acrylic plate, hot plate, sieve, furnace, desiccator, rubber bulb, aluminium foil, ball mill, magnetic stirrer, vacuum, atomic absorption spectrophotometer (SSA/AAS) with specifications Agilent Technologies 200 Series AA with Graphite Tube Atomizer (GTA) 120, Fourier Transform-Infra Red (FT-IR) and Scanning Electron Microscopy-Energy Dispersive X-Ray (SEM-EDX). The operating conditions of the AAS instrument used are as follows Table 1 as follows:

Table 1. Condition of the agilent technologies 200 series AA AAS instrument on the measurement of Cadmium and Lead metal concentrations

No	Parameter	Unit	Value
1	Wavelength	nm	228.8 (Cd); 283.3 (Pb)
2	Flame type	-	*Electrothermal (graphite furnace)*
3	Lamp type Burner gas flow rate	-	Hollow Cathode Lamps (HCL) Cd and Pb
4	Burner gas flow rate	L/menit	0.3
5	Slit width	nm	0.5
6	Highest temperature	oC	2600
7	Gas type	-	Argon

The materials used in this study were 12 grams of chitosan (Sigma Aldrich brand) and 100 grams of coffee grounds waste from a coffee shop in Cikarang. And the mother standard solution used was Pb^{2+} 1000 mg/L main solution (p.a. Merck) and Cd^{2+} 1000 mg/L (p.a. Merck) main solution.

2.3 Research Procedure

2.3.1 Wastewater Collection

The required sample was taken by grab sampling with the required volume and put into a container that has been washed thoroughly and rinsed using HNO3 1:1 and rinsed again using aquabidest. Then the sample is put into a filter with filter paper with a pore size of 0.45 µm and then accommodated into a container for analysis (SNI 6989.59: 2008).

2.3.2 Preliminary Test

This wastewater quality test is used to determine wastewater's initial content before going through a reduction treatment proCess using an adsorbent by the Minister of Environment and Forestry Regulation No. P12 of 2020 concerning Wastewater Quality Standards in Water Storage Ponds in Hazardous Waste Storage Facilities in the form of Waste Piles and Waste Impoundment.

The material used is PT. X as much as 100 mL. The preliminary study used Atomic Absorption Spectroscopy (AAS) with specifications Agilent Technologies 200 Series AA with Graphite Tube Atomizer (GTA) 120. After initial research, the results calculate based on equation 1 as follows (APHA 3113 B, 2017):

$$\text{Metal Grade (mg/L)} = C \times fp \qquad (1)$$

Description:

C = The concentration obtained from the measurement results

fp = Final volume of the test sample (mL)

2.3.3 Wastewater Sample Preparation

The homogenized test sample was pipetted 100 mL and put into a 250 mL beaker. Then 10 mL of concentrated HNO_3 was added and covered with a watch glass. It is heated on a hot plate until the remaining volume is 15-20 mL, then 5 mL of concentrated HNO_3 is added if the destruction is not complete (not apparent). The watch glass was rinsed using aquabidest. After that, the test sample was filtered and transferred into a 100 mL volumetric flask, then added aquabidest to the mark and homogenized (APHA 3113 B, 2017).

2.3.4 Synthesis Activated Carbon From Coffee Ground

The coffee grounds were dried in an oven at 100 oC for 24 hours to remove the moisture content. The tea dregs are put into a porcelain cup and burned with an electric stove until the temperature is ± 950 oC for 15 minutes for the carbonation proCess. After that, it was removed from the electric stove and cooled to room temperature. Then for the activation proCess, the carbon is immersed in a 30% ZnCl2 solution for 24 hours. Then washed with warm water at 80 oC for 20 minutes and washed with 0.1 N HCl for 20 minutes, washed again using warm water until there are no air bubbles (Nurhidayanti, 2020). Then calculate the moisture, ash, volatile matter, and bound carbon content (Sari, 2019).

2.3.5 Synthesis and Characterization Adsorbent

Activated carbon from coffee grounds was conducted by determining the moisture, ash, volatile, and bound carbon content. Characterization of physical and chemical properties in the form of surface morphology of the adsorbent and components of coffee grounds activated carbon and coffee grounds chitosan-activated carbon was carried out using SEM EDX instrument, while chemical characterization to determine the functional groups of the adsorbent was carried out using FTIR methods (Sharma and Bhardwaj, 2019; Yurdakal et al., 2019) at the UPT laboratory Integrated Diponegoro University. 1.2 grams of chitosan was weighed, then dissolved in 60 mL of 3% acetic acid, added 0.6 grams of coffee grounds carbon, stirred until homogeneous. Poured into an acrylic glass, dried in an oven at 60°C for 24 hours. The resulting product was immerged with 1 M NaOH for 24 hours. Then, removed from the acrylic glass and washed with distilled water until neutral. It was dried at room temperature stored in a desiccator. The same thing was complete with variations by weight of the addition of carbon as much as 0.8; 1; 1.2, and 1.4 grams (Sari, 2019). Chitosan-activated carbon adsorbent of coffee grounds with a weight variation of 0.6 g; 0.8 g; 1g; 1.2 g; and 1.4 g introduce into the column. Pipette 50 mL of prepared wastewater into the queue. Then the wastewater is passed through the column with a vacuum pump and collected for analysis, and the wastewater is ready to be measured using AAS (Sari, 2019).

2.3.6 Data Analysis Method

The data proCessing proCess in this study was calculated the effectiveness of reducing the concentration of PT. X with the adsorption method using chitosan-activated carbon from coffee grounds as the adsorbent. Comparisons were made for each parameter by comparing the initial concentration (Ci) with the final concentration (Ce). Calculation of effectiveness using equation 2 as follows (Cherdcoo et al., 2019):

$$\% \text{ Effectiveness} = (Ci-Ce)/Ci \times 100\% \quad \text{.....................(2)}$$

Keterangan :
% Effectiveness = Percentage of decrease in heavy metal concentration
Ci = Initial heavy metal concentration
Ce = Final heavy metal concentration

3. Results and Discussion

3.1 Preliminary Test

The waste used is the textile industry wastewater of PT. X. This wastewater quality test is used to determine wastewater's initial content before going through the reduction treatment proCess using an adsorbent by PerMenLHK No. P12 of 2020 concerning Wastewater Quality Standards in Water Storage Ponds at Hazardous Waste Storage Facilities in the Form of Waste Pile and Waste Impoundment. The results of the preliminary test can be seen in Table 2 as follows:

Table 2. PXI industrial wastewaterquality preliminary test results

No.	Parameter	Unit	Test Results	Quality standards
1.	Lead (Pb)	mg/L	1.02	0.10
2.	Cadmium (Cd)	mg/L	1.15	0.05

Based on the preliminary test results, the Pb concentration value was 1.02 mg/L, and Cd was 1.15 mg/L. Therefore, it concluded that the three parameters still exceed the quality standard requirements of PerMenLHK No. P12 of 2020 concerning Wastewater Quality Standards in Water Storage Ponds at Hazardous Waste Storage Facilities in the Form of Waste Pile and Waste Impoundment (Menteri LHK, 2020).

3.2 Characterization of Coffee Ground Activated Carbon and Chitosan-Activated Carbon

3.2.1 Characterization of Coffee Ground Activated Carbon

The characterization of activated carbon aims to determine the ability of activated carbon to absorb wastewater containing heavy metals. The results of the description of the coffee grounds triggered carbon obtained are presented in Table 3 as follows:

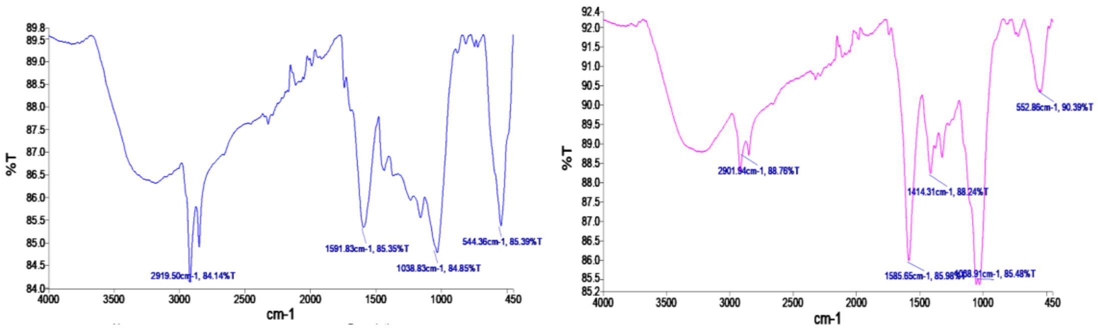
Table 3. Results of characterization of coffee ground activated carbon

No.	Parameter	Unit	Test Results	Quality standards
1.	Water content	%	7.35	Max. 15
2.	Ash Level	%	4.09	Max. 10
3.	Volatile Substance Level	%	20.83	Max. 25
4.	Bonded Carbon Content	%	75.08	Min. 65

Based on the results of testing the water content, ash content, volatile matter content and bound carbon content in the activated carbon of coffee grounds, it has met the carbon quality requirements of SNI No. 06-3730-1995. The water content that meets SNI indicates that there are still activated carbon pores that can be occupied by the adsorbate so that the adsorption takes place optimally (Ghafarunnisa et al., 2017). Ash content with SNI indicates the number of metal oxides or inorganic materials in coffee grounds' activated carbon (Solihat et al., 2021). The level of volatile substances shows the decomposition results of the substances that make up charcoal due to the heating proCess during the preparation of coffee grounds, resulting from the interaction between carbon and water vapour (Wardani, 2018). The bound carbon content obtained was 75.08%, indicating the large fraction of carbon bound in the charcoal in addition to the fraction of water, volatile matter, and ash after the carbonation and activation proCess (Erawati et al., 2018).

3.2.2 Biosorbent Characterization Using FT-IR and SEM-EDX

The results of the characterization of the chitosan-activated carbon biosorbent functional group of coffee grounds using FT-IR are presented in Figure 1 as follows:



a) b)

Figure 1. Results of FT-IR spectrum from biosorbent a) Activated carbon of coffee grounds and b) Chitosan-activated carbon of coffee grounds

Based on Figure 1 above, it can be determined several functional groups contained in the bioadsorbent combination of chitosan-activated carbon coffee grounds based on the reference according to Table 4 as follows:

Tabel 4. FT-IR data analysis of coffee grounds activated carbon and chitosan-activated carbon of coffee grounds

Peak	Wavelength (cm^{-1})			Functional groups
	Coffee grounds activated carbon	**Combination of chitosan-coffee grounds activated carbon**	**Reference (Mohamed et al., 2017)**	
1	2919.50	2901.94	3000-2850 (alkana stretch)	C-H
2	1591.83	1585.65	1640-1550 (primary, secondary amines and amides: bend)	N-H
3	-	1414.31	1550 - 1350 (nitro: R-NO_2)	N=O
4	1038.83	1038.91	1300-1000 (alcohol, ethers, esters, carboxylic acids, anhydrides)	C-O
			1350-1000 (amines)	C-N
5	544.46	552.86	785-540 (chloride)	C-Cl

Based on table 4 above shows that the results of the FT-IR spectrum analysis on coffee grounds activated carbon there are several absorption peaks, including indicating the presence of functional groups CH (as alkanes), NH (possibly as secondary/primary amines and amides), CO (possibly as alcohols). / ether/ ester/ carboxylic acid/anhydride), CN (amine) and C-Cl (chloride). While the results of the FT-IR spectrum analysis on chitosan-activated carbon of coffee grounds, there were several absorption peaks, including indicating the presence of functional groups CH (as alkanes), NH (possibly as secondary/primary amines and amides), N=O (nitro), CO (possibly as alcohol/ ether/ ester/ carboxylic acid/ anhydride), CN (amine) and C-Cl (chloride) (Mohamed et al., 2017). Based on the results of the FT-IR analysis, it shows that there is an addition of a functional group N=O on the adsorbent of chitosan – coffee grounds activated carbon compared to coffee grounds activated carbon. It shows that the interaction that oCcurs between the activated carbon of coffee grounds and chitosan is a physical interaction (Sari, 2019) and a chemical interaction in the form of a nitrogen oxidation reaction that causes the formation of a nitro group (NO_2) in the chitosan bio adsorbent – coffee grounds activated carbon. The addition of a nitro group to the adsorbent of chitosan-activated carbon coffee grounds increases the adsorption ability due to the electrostatic interaction between the nitro functional group and the metal cations of cadmium and lead. The results of the characterization of chitosan biosorbent and activated carbon of tea pulp using SEM EDX are presented in Table 5, and Figure 2 is as follows:

Table 5. Results of chemical element characterization of biosorbents using SEM EDX

No	Element	Coffee grounds activated carbon	Combination of chitosan-coffee grounds activated carbon
1	Carbon	69.26%	74.30%
2	Oxygen	19.53%	18.29%
3	Aluminium	-	0.06%
4	Sodium	-	0.88%
5	Magnesium	0.32%	0.34%
6	Phosphor	0.52%	0.34%
7	Chlorine	2.46%	0.46%
8	Potassium	-	0.42%
9	Calcium	-	0.27%
10	Copper	0.27%	0.53%
11	Lead	-	2.99%
12	Indian	2.08%	-
13	Silicone	-	0.15%
14	zinc	-	0.46%
15	Zirconium	-	0.51%

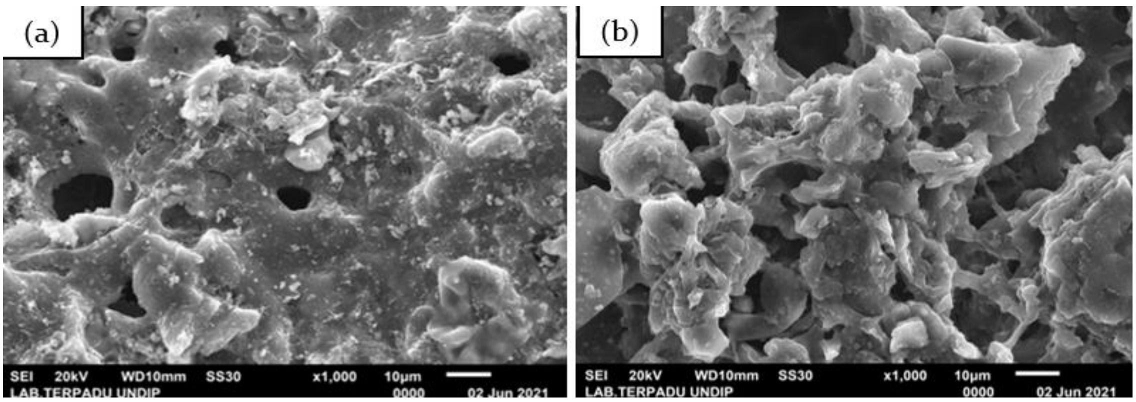


Figure 2. Results of biosorbent characterization using SEM-EDS (a) Activated carbon of coffee grounds and (b) Chitosan-activated carbon of coffee grounds with 1000 times magnification

Based on Table 2, the dominant element in the biosorbent of chitosan and activated carbon of coffee grounds is the C atom. Chitosan is a polysaccharide polymer, while coffee grounds are polymers in cellulose chains. The table shows an increase in the carbon element (C) of coffee grounds activated carbon by 69.26% to 74.30% after combining with chitosan. The cellulose-based coffee grounds polymer structure indicates a relatively strong chemical adsorption ability on metal ions and organic bases. The increase in % the mass of carbon atoms in chitosan-coffee grounds suggests an increase in the adsorbent's performance (Suwazan et al., 2022). Figure 2a shows the surface of the coffee grounds activated carbon, and Figure 3b shows the character of the chitosan-activated carbon coffee grounds biosorbent. Figures 3a and 3b show that the pores of the chitosan-activated carbon of coffee grounds are irregular with more significant and more profound cavities.

In contrast, the pores of the activated carbon of coffee grounds have an almost flat surface with several round holes with large pore sizes. Smaller than coffee grounds started carbon chitosan. It shows that adding coffee grounds activated carbon to chitosan can enlarge the surface pores and increase the biosorbent active site to increase the absorption of cadmium and lead metals in PXI industrial wastewater (Sari, 2019; Sahu et al., 2021). The increase in pore size and quality of the adsorbent causes the combination of chitosan-coffee grounds activated carbon to be more effectively used as an adsorbent compared to chitosan adsorbent or coffee grounds activated carbon. The larger the surface area of the adsorbent, the higher the adsorption ability (Pranoto et al., 2020).

3.3 Lead Metal Reduction Effectiveness

The results of measuring the concentration of lead metal in PT PXI wastewater samples after the adsorption proCess can be seen in Table 6 below:

Table 6. Absorption and effectiveness of lead metal adsorption during adsorption process

No.	Sample	Pb concentration before adsorption (mg/L)	Pb concentration after adsorption (mg/L)	Lead metal absorption (mg/L)	Metal Absorption Effectiveness (%)
1	Chitosan-Coffee 0.6 g	1.02	0.26	0.76	74.24
2	Chitosan-Coffee 0.8 g		0.22	0.80	78.31
3	Chitosan-Coffee 1.0 g		0.18	0.84	82.38
4	Chitosan-Coffee 1.2 g		0.12	0.90	88.21
5	Chitosan-Coffee 1.4 g		0.09	0.93	90.86

The table above shows that the maximum absorption of lead metal in the combination of chitosan with the addition of 1.4 grams of activated carbon is 0.93 mg/L, while the lowest absorption is in the variety of chitosan with the addition of 0.6 grams of activated carbon which is only capable of absorbs the concentration of Pb metal to 0.76 mg/L. That shows that the higher the dose of activated carbon added will increase the absorption of lead metal in the biosorbent. Chitosan has active amino and hydroxyl groups and can chelate several metals, including lead. The active site of chitosan with the addition of coffee grounds activated carbon either in the form of NH2 or in a protonated state NH3+ can increase the absorption of lead metal through chemical interactions by forming chelates electrostatic interactions in the presence of ion-exchange or the formation of electron pairs. Increase the adsorption ability of the adsorbent (Sari, 2019). The graph of the effectiveness of the preparation of lead metal concentrations is presented in Figure 3 as follows:

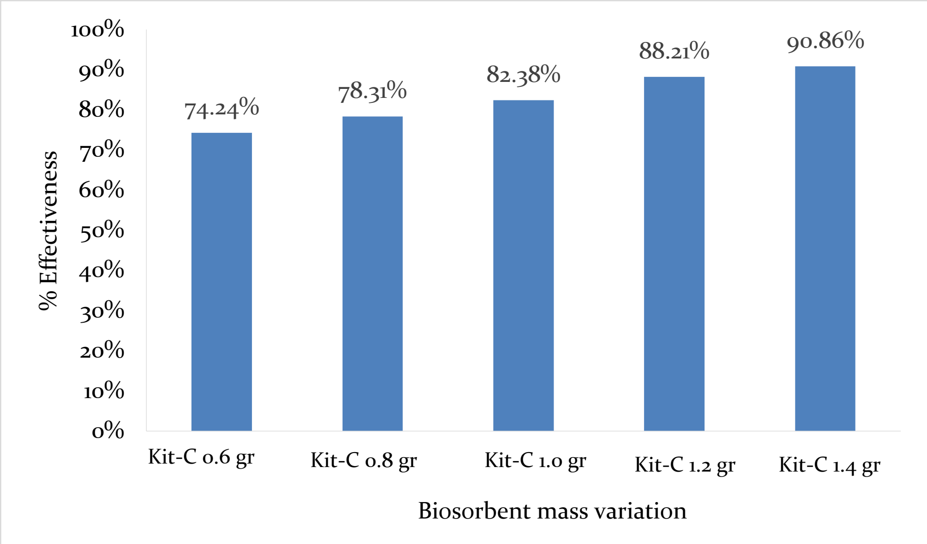


Figure 3. Graph of the effectiveness of lead metal concentration reduction during the adsorption process

The graph shows that the effectiveness of reducing the lowest concentration of lead metal in the use of chitosan activated carbon coffee grounds is 0.6 grams, which is 74.24%. It has an increase in the use of chitosan activated carbon coffee grounds as much as 0.8 grams, which is 78.31%, then experienced a continuous increase in the addition of 1.0-gram coffee grounds activated carbon; 1.2 grams and 1.4 grams, the effectiveness of reducing the maximum metal concentration of lead on the use of 1.4 grams of activated carbon coffee grounds chitosan is 90.86%. This shows that the energy of lowering the lead concentration increases with the increase in the mass of activated carbon added to coffee grounds (Lessa et al., 2018). Previous research stated that chitosan-coated with activated carbon could increase the percentage of lead and other heavy metals absorption. Activated carbon is a very effective adsorbent to absorb metals in wastewater due to the high number of micropores and mesopores, large surface area, and functional groups on the activated carbon surface that interact with heavy metal ions (Rodriguez et al., 2017). Lead metal ions will be attracted to the surface of the activated carbon pores and are trapped in these pores. The more activated carbon, the more metal is absorbed in the carbon pores so that the decrease in metal content in chitosan with the addition of carbon is higher (Sari, 2019). The addition of coffee shell waste with a concentration of 10% in chitosan for 120 minutes can reduce the concentration of lead metal with an efficiency of 92.26 (Ayunda et al., 2019). Based on the results of the study showed that the use of a combination of chitosan-activated carbon from 1.4 grams of coffee grounds could reduce the concentration of lead metal with an efficiency of 90.86% to 0.09 mg/L so that it could meet the quality standard of the Minister of Environment and Forestry Regulation No. P12 of 2020.

3.4 Cadmium Lead Metal Reduction Effectiveness

The results of measuring the concentration of lead metal in PT PXI wastewater samples after the adsorption proCess can be seen in Table 7 below:

Table 6. Absorption and effectiveness of lead metal adsorption during adsorption process

No.	Sample	Pb concentration before adsorption (mg/L)	Pb concentration after adsorption (mg/L)	Lead metal absorption (mg/L)	Metal Absorption Effectiveness (%)
1	Chitosan-Coffee 0.6 g	1.15	0.29	0.86	74.57
2	Chitosan-Coffee 0.8 g		0.21	0.94	81.87
3	Chitosan-Coffee 1.0 g		0.17	0.98	85.54
4	Chitosan-Coffee 1.2 g		0.09	1.06	91.85
5	Chitosan-Coffee 1.4 g		0.07	1.08	94.35

The table above shows that the maximum absorption of cadmium metal in the combination of chitosan with the addition of 1.4 grams of activated carbon is 1.08 mg/L, while the lowest absorption is in the variety of chitosan with the addition of 0.6 grams of activated carbon which is only able to absorb the concentration of Pb metal to be 0.86 mg/L. That shows that the higher the dose of activated carbon added will increase the absorption of cadmium metal in the biosorbent. Chitosan combined with coffee grounds activated carbon will increase the pore surface capacity to absorb cadmium metal. The higher the mass of activated carbon added will increase the number of active carbon pore surface active sites. The ability to absorb cadmium and other heavy metals will increase (Ayunda et al., 2019; Cherdcoo et al., 2019). The graph of the effectiveness of reducing the concentration of cadmium metal is presented in Figure 4 as follows:

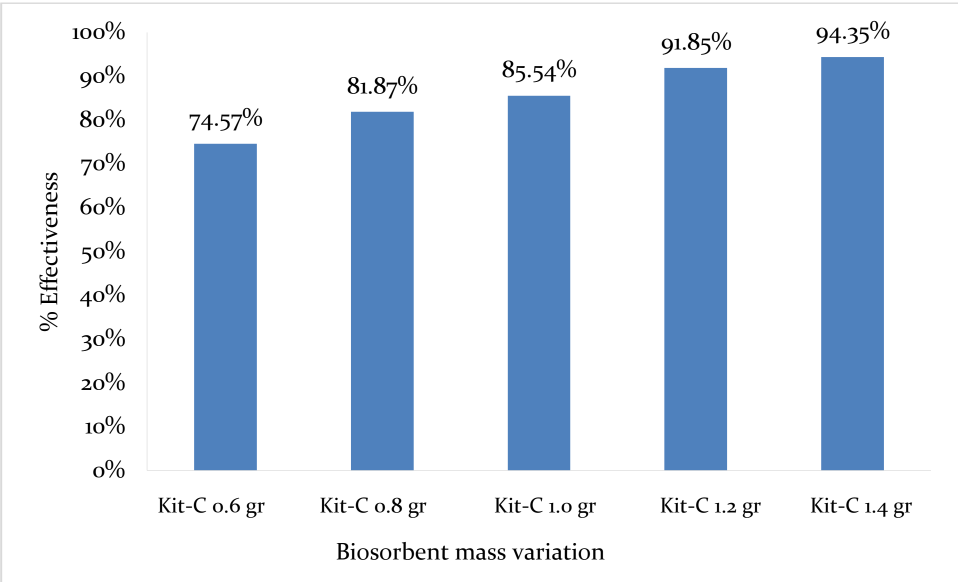


Figure 3. Graph of the effectiveness of cadmium metal concentration reduction during the adsorption process

Figure 3 shows the effectiveness of decreasing the lowest concentration of cadmium metal on the use of coffee grounds activated carbon chitosan as much as 0.6 grams, which is 74.57%. An increase in the use of coffee grounds triggered carbon chitosan by 0.8 grams, which is 81.87%, then there is a continuous increase. On the addition of 1.0 grams of coffee grounds activated carbon, 1.2 grams and 1.4 grams, the effectiveness of reducing the maximum concentration of cadmium metal on the use of 1.4

grams of activated carbon coffee grounds chitosan is 94.35%. That shows that reducing the concentration of cadmium metal increases with the increase in the mass of activated carbon added to coffee grounds (Lessa et al., 2018). Previous research states that chitosan-coated with activated carbon can increase the percentage of absorption of cadmium metal and other heavy metals (Park et al., 2019). Activated carbon is a very effective adsorbent to absorb metals in wastewater due to the high number of micropores and mesopores, large surface area, and functional groups on the activated carbon surface that interact with heavy metal ions (Rodriguez et al., 2017; Rodrigues et al., 2019). Cadmium metal ions will be attracted to the surface of the activated carbon pores and are retained in these pores. The more activated carbon, the more heavy metals are absorbed in the carbon pores. The decrease in cadmium metal content in chitosan with the addition of carbon is higher. Adding 0.6 grams of coffee grounds activated carbon in chitosan can reduce cadmium metal levels by 74.54% and nickel-metal by 73.43% (Sari, 2019). Based on the study results, it was shown that the use of a combination of chitosan-activated carbon from 1.4 grams of coffee grounds could reduce the concentration of cadmium metal with an efficiency of 94.35% 0.07 mg/L. P12 in 2020 is 0.05 mg/L. Further research needs to be completed by increasing the mass of coffee grounds activated carbon added to the adsorbent.

4. Conclusion

Based on the results, it can be concluded that using a combination of chitosan-activated carbon 1.4 grams of coffee grounds result in the absorption of lead metal of 1.08 mg/L with the effectiveness of reducing the concentration of lead metal by 90.86% and the absorption of lead metal of 0.93 mg/L with the effectiveness of reducing the concentration of lead metal is 94.35%. The combination of chitosan-activated carbon coffee grounds effectively reduces cadmium and lead metals. It has complied with the quality standard for metal concentrations of a lead according to PerMenLHK No. P12 in 2020. However, further research needs to be done by increasing the mass of coffee grounds activated carbon used so that cadmium metal can meet the expected quality standards. After proCessing PT, PXI wastewater does not pollute the environment.

Acknowledgment

The Research Team would like to thank DIPA of the Directorate General of Higher Education, Ministry of Education, Culture, Research, and Technology for the 2021 Fiscal Year for the research funding support that has been provided and Pelita Bangsa University for facilitating the submission of basic research proposals and coaching/capacity on research contract No. 036/KP/7.NA/UPB/VII/2021 so that the research can be carried out properly.

References

Ahsan, A.M,. et al. 2018. Biosorption of bisphenol A and sulfamethoxazole from water using sulfonated coffee waste: Isotherm, kinetic and thermodynamic studies. Journal of Environmental Chemical Engineering 6, 6602–6611.

American Public Health AssoCiation (APHA). 2017. Electrothermal atomic absorption spectrometric method. Part. 3113 B. Washington, DC.

Arifin, Karlina, A. & Khair, A. 2017. Pengaruh dosis kitosan terhadap kadar warna limbah cair home industri sasirangan " oriens handicraft" landasan ulin. Journal Health Sci. Preven. 1(2):58-67.

Ayunda, S., Nurmala,L. & Ramadhana., 2019. Adsorpsi Logam Cd^{2+} menggunakan bioadsorben berbasis komposit film kitosan - limbah cangkang kopi. Journal Sci. Technology. vol. 17, no. 2, pp. 13–21.

Badan Pusat Statistik. 2015. Produksi kopi di indonesia. Badan Pusat Statistik. Jakarta.

Badan Standardisasi Nasional. 1995. SNI 06-3730-1995: Arang aktif teknis. Jakarta : Badan Standardisasi Nasional.

Badan Standardisasi Nasional. 2008. SNI 6989-59-2008: Metoda pengambilan contoh air limbah. Jakarta : Badan Standardisasi Nasional.

Botahala L., 2019. Perbandingan efektivitas daya adsorpsi sekam padi dan cangkang kemiri terhadap logam besi (Fe) pada air sumur gali, cetakan pertama. Yogyakarta. Deepublish.

Cherdchoo, W., Nithettham, S. and Charoenpanich, J. 2019. Removal of Cr(VI) from synthetic wastewater by adsorption onto coffee ground and mixed waste tea, Chemosphere, vol. 221, pp. 758–767.

Erawati, E., & Helmy, E. R. 2018. Pembuatan karbon aktif dari serbuk gergaji kayu jati (tectona grandis l.f.) suhu dan waktu karbonasi. Urecol (University Research Colloquium). 105–112.

Ghafarunnisa, D., Rauf, A., & Rukmana, B. T. S. 2017. Pemanfaatan batubara menjadi karbon aktif dengan proses karbonisasi dan aktivasi menggunakan reagen asam fosfat (H_3PO_4) dan ammonium bikarbonat (NH_4HCO_3). Proseding Seminar Nasional XII. 1(1), 36–41.

Irmanto, Suyata. 2009. Penurunan kadar amonia, nitrit dan nitrat limbah cair industri tahu menggunakan arang aktif dari ampas kopi. Molekul. 4 No. 2: 105-114.

Iqbal, M., Dyah Uly Parwati, Wiwin., Ginting, Chandra. 2018. pengaruh ampas kopi sebagai pupuk organik dan dosis dolomit terhadap pertumbuhan bibit kelapa sawit di pre – nursery. Jurnal Agromast , Vol.3, No.2.

Liao, B., Sun, W., Guo, N., Ding, S., Su, S. 2016. Equilibriums and kinetics studies for adsorption of Ni(II) ion on chitosan and its triethylenetetramine derivative. Colloids Surf. PhysicoChem. Eng. Asp. 501, 32–41.

Lessa, E. F., Nunes, M. L. and Fajardo, A. R. 2018. Chitosan/waste coffee-grounds composite: an efficient and eco-friendly adsorbent for removal of pharmaceutical contaminants from water, Carbohydrate Polymer, vol. 189, pp. 257–266.

Menteri Lingkungan Hidup dan Kehutanan (LHK). 2020. Peraturan menteri lingkungan hidup dan kehutanan nomor P12 Tahun 2020 tentang penyimpanan limbah bahan berbahaya dan beracun. Jakarta.

Mohamed, M.A., Jaafar,J., Ismail, A.F., Othman, M.H.D. & Rahman, M.A. 2017. Chapter 1 - fourier transform infrared (FTIR) spectroscopy. Membrane Characterization 2017, 3-29.

Mosivand, S., Kazeminezhad,I. & Fathabad, S.P. 2019. Easy, fast, and efficient removal of heavy metals from laboratory and real wastewater using electroCrystalized iron nanostructures. MicroChemical Journal. 146. 534-543

Naushad, M., Ahamad, T., Al-Maswari, B.M., Alqadami, A.A., Alshehri, S.M. 2017. Nickel ferrite bearing nitrogen-doped mesoporous carbon as efficient adsorbent for the removal of highly toxic metal ion from aqueous medium,Chem.Eng.J.330, 1351–1360.

Nurhidayanti, N., & Ardiatma, D. 2020. efektivitas hidroponik tanaman bunga kana, kayu apu serta ampas kopi dalam pengoiahan air limbah greywater domestik. JurnaI Presipitasi: Media Komunikasi dan Pengembangan Teknik Lingkungan, 17(3), 272-283.

Obaid, S.S., Gaikwad, D.K., Sayyed, M.I., AL-Rashdi,K. & Pawar, P.P. 2018. Heavy metal ions removal from waste water by the natural zeolites, Material Today 5, 17930–17934

Park, M. H. Et al. 2019. Removal of aqueous-phase Pb(II), Cd(II), As(III), and As(V) by nanoscale zero-valent iron supported on exhausted coffee grounds, Waste Management, vol. 92, pp. 49–58.

Panigrahi, T., Santhoskumar, A. U. 2020. Adsorption process for reducing heavy metals in Textile Industrial Effluent with low cost adsorbents, Prog. Chem. BioChem. Res. 2020, 3(2), 135-139.

Pietrelli, L. Et al. 2020. Chromium(III) removal from wastewater by chitosan flakes. Applied Science, 10, 1925.

Pranoto, P.,Martini, T., & Maharditya, W. 2020. Uji efektivitas dan karakterisasi komposit tanah andisol/arang tempurung kelapa untuk adsorpsi logam berat besi (Fe). ALCHEMY Jurnal Penelitian Kimia, Vol 16 (1), 50-66.

Prathna, T.C. et al., 2018 Nanoparticles in household level water treatment: an overview, Sep. Purif. Technol. 199, 260–270.

Pratiwi, R., Prinajati, D.P.S. 2018. Adsorption for lead removal by chitosan from shrimp shells.Indonesian Journal of Urban and Environmental Technology. 2(1): 35-46.

Rahardjo, P. 2012. Panduan budidaya dan pengolahan kopi arabika dan robusta. Penebar Swadaya, Jakarta.

Rengganis, A., P., Yulianto, A., Yulianti. 2017. Pengaruh variasi konsentrasi arang ampas kopi terhadap sifat fisika tinta spidol whiteboard. Jurnal MIPA 40(2) : 92 – 96.

Rodriguez et al., 2017. Adsorption Of Ni(II) On Spent Coffee And Coffee Husk Based Activated Carbon. Enviromental Chemical Engineering. Vol 6 : 1161 – 1170.

Rodrigues, F.H.A. et al. 2019. Hydrogel composites containing nanoCellulose as adsorbents for aqueous removal of heavy metals: design, optimization, and application. Cellulose 26, 9119–9133.

Sahu, N., Saigh,J. & Koduru, J.R. 2021. Removal of arsenic from aqueous solution by novel iron and iron–zirconium modified activated carbon derived from chemical carbonization of Tectona grandis sawdust: Isotherm, kinetic, thermodynamic and breakthrough curve modelling. Environmental Research 200, 111431.

Sari, Fitri Purnama. 2019. Pembuatan dan karakterisasi kitosan-karbon aktif dari ampas kopi sebagai adsorben untuk menurunkan kadar logam kadmium dan nikel. Tesis. Universitas Sumatera Utara.

Sembiring, M. T. dan T. S. Sinaga. 2003. Arang aktif (pengenalan dan proses pembuatannya). USU Digital Library. Sumatra Utara.

Seyedmohammadi, et al. 2016. Application of nanochitosan and chitosan particles for adsorption of Zn(II) ions pollutant from aqueous solution to protect environment. Model. Earth Syst. Environ. 2, 165.

Sharma, V., and Bhardwaj, A. 2019. Scanning electron microscopy (SEM) in food quality evaluation. Evaluation Technologies for Food Quality. Woodhead Publishing Series in Food Science, Technology and Nutrition, New Delhi, India, pp. 743–761.

Solihat, I., Setyowati, A. D., Pamulang, D. U. 2021. Penggunaan limbah kulit singkong pada filter air sederhana skala rumah tangga. Jurnal Ilmiah Teknik Kimia. 5(1), 61–70.

Supriyantini, et al. 2018. Pemanfaatan chitosan dari limbah cangkang rajungan (portunus pelagicus) sebagai Adsorben Logam Timbal (Pb). Jurnal Kelautan Tropis. ISSN 0853-7291. Vol. 21(1):23-28.

Suwazan, D., & Nurhidayanti, N. 2022. Efektivitas kombinasi kitosan dan ampas teh sebagai adsorben alami dalam menurunkan konsentrasi timbal pada limbah cair PT PXI. Jurnal Ilmu Lingkungan, 20(1), 37-44.

Velusamy S., Roy , A., Sundaram, S., Mallick, T.K. 2021. A Review on heavy metal ions and containing dyes removal through graphene oxide-based adsorption strategies for textile wastewater treatment. The Chemical Record, Vol 21, Issue 7, p. 1570-1610.

Wardani, S., & Rosa, E. 2018. potensi limbah tulang kambing sebagai arang aktif yang teraktivasi asam sulfat. Jurnal Serambi Engineering, 3(2), 308–315.

Yurdakal, S., et al. 2019. PhotoCatalyst characterization techniques: adsorption isotherms and BET, SEM, FTIR, UV–Vis, photoluminescence, and electroChemical characterizations. In: Marcì, G., Palmisano, L. (Eds.), Heterogeneous PhotoCatalysis: Relationships With Heterogeneous Catalysis and Perspectives. Joseph P. Hayton, Palermo, Italy, pp. 87–152.