POTENSIAL OF CARAMBOLA WULUH (*AVERRHOA BILIMBI*) FILTRATE ON REDUCING LEAD (*PB*) METAL LEVELS IN ANGSANA RIVER WATER, TANAH BUMBU

Syarifah Sitti Aisyah[1*], Tuti Alawiyah[1], Dede Mahdiyah[1] and Nur Hidayah[1]

[1]*Bachelor of Pharmacy Study Program, Faculty of Health, Sari Mulia University, Indonesia*

**Syarifahsittiaisyahh@gmail.com*

Abstract

The river in the Angsana area has been polluted by lead metal caused by oil palm plantations and mining so that the river in the Angsana area is positive for containing high lead compounds. This is quite dangerous for health if you often carry out activities related to rivers such as bathing, washing or other activities. Reducing lead metal levels in river water can be done in various ways, one of which is by using natural ingredients, namely belimbing wuluh fruit which contains citric acid which is used as a metal binder or binder.

To determine the potential of starfruit filtrate to reduce levels of lead (Pb) metal in river water in the Angsana Tanah Bumbu area, with time variations of 30 minutes, 60 minutes and 90 minutes.

The type of research was Pre-Experimental design, then the research design was carried out in the form of a Post test only and group design and data analysis using One way Anova and then using a sampling technique with Purposive Sampling.

The treatment used with a concentration of 75%, with a time of 30 minutes can reduce lead metal content by 24.45%, 60 minutes by 33.66%, and 90 minutes can reduce lead metal content by 37.29%. The results showed that belimbing wuluh filtrate had the potential to reduce lead metal content in river water in the Angsana area with an optimal time of 90 minutes.

Carambola wuluh filtrate has the potential to reduce lead levels in river water in the Angsana area with variations of 30 minutes, 60 minutes, 90 minutes. The optimal time for descent is 90 minutes.

Keywords: *Angsana River, Citric Acid, Carambola Wuluh, SSA*

Introduction

Rivers are one of the natural resources in Angsana Tanah Bumbu and are needed to support the lives of some residents. Rivers are water sources, they not only act as providers of water sources but also have a supporting function for natural tourism activities and traffic routes for small boats. The Angsana River is one of the rivers whose surrounding area is in the area of oil palm plantations and the mining industry, so the Angsana River area is polluted by these transportation activities.

According to (Kadarsah et al., 2020) the lead (Pb) content in the coal mining area in Setarap Village is smaller with a Pb range of 0.04 – 0.056 mg/L. This shows that lead (Pb) pollution is above the quality standard threshold which is around <0.002 mg/L based on Republic of Indonesia Government Regulation No. 22 of 2021.

Lead metal (Pb) has toxic effectiveness which can harm the human body, including causing damage to the nervous system if lead accumulates in soft tissue and bones over a long time. The impact of exposure to lead metal that exceeds the threshold value will have negative potential for health, because lead metal can disrupt the nervous system, reduce intelligence levels and affect children's growth. Exposure to lead metal can be reduced by the presence of citric acid compounds.

Contains citric acid compounds which can be used as chelating compounds for heavy metals such as lead (Pb). Citric acid content is an alternative way to reduce lead (Pb) metal levels. According to Latumeten et al (2013), the more citric acid content in a material, the more heavy metals it is possible to bind and remove during the washing process. (Saraswati, 2019)

Citric acid has a series of groups consisting of three carboxyl groups –COO (tricarboxylate), as well as a hydroxyl group –OH. The carboxyl group is released from citric acid and will bind to heavy metals.

Citric acid can be found in various types of fruit and vegetables such as pears, oranges, starfruit, lemons, passion fruit, tomatoes and others. One of the fruits containing citric acid is star fruit (Averrhoa Bilimbi). Starfruit (Averrhoa bilimbi) is a fruit that has many benefits, one of the beneficial ingredients is citric acid. The content of citric acid compounds contained in starfruit (Averrhoa Bilimbi) is around 44.6%. (Hatta et al., n.d.)

According to research (Budi Agustin et al., n.d.), reducing the lead (Pb) content of Bader fish meat (Barbonymus gonionotus), namely by using starfruit (Averrhoa bilimbi) filtrate, has an influence on the concentration of starfruit filtrate, the length of soaking time and a combination of the two on reduction of lead metal levels in bader fish meat. The combination of the length of soaking time and the concentration of the starfruit filtrate showed a significant reduction which occurred at a concentration of 75% with a soaking time of 60 minutes by reducing the lead metal content by approximately 40% or 40.580%

Materials and Methods

Objective

Looking at the potential content of starfruit (averrhoa bilimbi) filtrate to reduce lead (Pb) metal levels in river water in the Angsana area with time variations of 30 minutes, 60 minutes, 90 minutes.

Method

The research method used in this study was true experimental with a posttest only control group design and data analysis using one way ANOVA and then using a purposive sampling technique. This research was intended to see the decrease in lead (Pb) levels after being treated with a concentration of 75% starfruit filtrate with time variations of 30 minutes, 60 minutes, 90 minutes.

Sample

The sample that will be used in this research is river water in the Angsana Tanah Bumbu area. Samples were taken from 100 ml of river water. The samples that have been taken are stored in a glass bottle.

Tools and materials

The tools that will be used in this research are the Atomic Absorption Spectrophotometer (SSA), glassware, blender, measuring cup, volume pipette, filter paper, Erlenmeyer, funnel and stirring rod, knife, tissue. The materials that will be used in this research are starfruit, samples (river water), Pb(NO3), HNO3 1 M and distilled water.

Work procedures

The first working procedure is to make wuluh starfruit filtrate, namely by washing the wuluh starfruit, then blending it and squeezing it with a clean cloth then filtering it to get the wuluh starfruit fruit filtrate, you get a filtered result of 250 ml with a concentration of tration 100% (pure). Next, a 75% concentration was made using a mixture of starfruit filtrate and distilled water in a volume of 100 ml, 75 ml of starfruit filtrate used was mixed with 25 ml of distilled water.

The second procedure is preparation of Angsana River water samples. Sample preparation was carried out by carrying out a wet digestion process using a hot plate. River water samples that had been added with starfruit filtrate at varying times of 30 minutes, 60 minutes and 90 minutes were then filtered using Whatman filter paper no.41. Then the mixture was heated and 2.5ml of HNO3 was added. After that, wait until 10 ml of the sample remains, then add distilled water to 50 ml.

The third procedure is quantitative testing. Preparation of standard lead (Pb) solution Preparation of 1000 ppm Pb main solution, weigh 100 mg of diluted Pb(NO3)2 and add 10 ml of HNO3 and put it in a 100 ml measuring flask, then add distilled water to the mark. To make 1000 ppm of mother liquor, 100 mg/100 ppm is needed.

Making a 100 ppm Pb standard solution, take 100 ml of the 1000 ppm stock solution using a pipette then put it in a 100 ml measuring flask. And the solution that has been taken is diluted by adding HNO3 in a volumetric flask to the limit mark.

The Pb Standard Series was made by making a 0.1 ppm series; 0.5ppm; 1 ppm; 2 ppm; and 4 ppm pipetted as much as 0.05 ml; 0.25 ml; 0.5 ml; 1ml; and 2 ml is put into a 25 ml measuring flask, after which it is diluted with distilled water to the limit mark, then a Pb standard solution is obtained for the standard curve of 0.1 ppm; 0.5ppm; 1 ppm; 2 ppm; and 4 ppm.

Results and Discussion

Results

Lead Calibration Curve

The lead calibration curve was determined using a series of series, namely 0.1 ppm, 0.5 ppm, 1 ppm, 2 ppm, 4 ppm, then measured using atomic absorption spectrophotometry at a wavelength of 217 nm. The results of absorbance measurements in this study can be seen in the table below:

Table 1. Results of Absorbance Measurement of Lead Standard Solutions

Concentration	Absorbance
0,1	0,0019
0,5	0,0135
1	0,0304
2	0,0659
4	0,1273

The results of measuring standard lead solutions with several concentrations will produce absorbance, namely a: -0.0015 b: 0.0325 r: 0.9995. Based on the table above: the resulting lead standard curve can be seen in the image below:

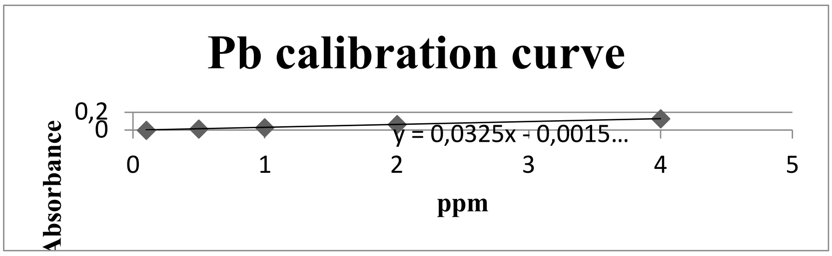

Figure 1 Lead Standard Solution Curve

Measurement of Lead Heavy Metal Levels in Samples

Measurement of the levels of the heavy metal lead in river water, where the control group samples were treated without exposure to starfruit filtrate at 0 minutes and with exposure to starfruit filtrate treatment at 30 minutes, 60 minutes, 90 minutes. To find out and calculate the concentration of this sample, use the formula y= bx + a. The results of measuring the lead samples showed the concentration results listed on the following label:

Table 2. Measurement results on samples

Time	Absorbance	Pb levels
0	0,012	0,413
30	0,009	0,312
60	0,007	0,274
90	0,007	0,259

Percentage reduction in Lead Metal Levels

The results of calculating the percentage reduction in the concentration of the heavy metal lead (Pb) in river water samples after adding starfruit filtrate using the formula calculation:

%= (C0-C1)/C0 X 100%

Information :

C0 = initial concentration of solution (mg/ml)

C1 = final concentration of solution (mg/ml)

Table 3. Percentage reduction in lead metal content

No	Time	%Reduction in Pb
1	30	24,45%
2	60	33,66%
3	90	37,29%

Validation and Reliability Results

The results of the LOD and LOQ test calculations were carried out statistically using the Pb standard curve. Then several criteria are determined, namely LOD and LOQ, in the following table:

Table 4. Calculation of SD, LOD and LOQ

LoD & LoQ				
Concentration (ppm)	Absorbance	Xi	(X-Xi)	$(X\text{-}Xi)^2$
0,1	0,0019	0,00175	0,2378	0,0565
0,5	0,0135	0,01475	0,2248	0,0505
1	0,0304	0,031	0,2085	0,0435
2	0,0659	0,0635	0,1760	0,0310
4	0,1273	0,1285	0,1110	0,0123
LOD				0,2346
LOQ				0,7821

The results of precision test calculations were carried out statistically using the Pb standard curve and samples. Then several criteria are determined, namely standard deviation and precision test in the following table:

Table 5. Precision Calculation

Replikasi	Absobance	X
1	0,105	3,277
2	0,106	3,3077
3	0,106	3,3077
4	0,105	3,2769
5	0,107	3,3385
6	0,105	3,2769
7	0,106	3,3077
8	0,108	3,3692
9	0,106	3,3077
10	0,105	3,2769
$\sum(X\text{-}Xbar)^{\wedge 2}$		0,00842
SD		0,0306
RSD%		0,9252

Data Analysis Results

Normality test

Table 6. Normality Test Results

Tests of Normality

		Kolmogorov-Smirnov[a]			Shapiro-Wilk		
	Waktu	Statistic	df	Sig.	Statistic	Df	Sig.
Conentration_filtrate_carambola wuluh	0	.213	3	.	.990	3	.806
	30	.253	3	.	.964	3	.637
	60	.333	3	.	.862	3	.274
	90	.219	3	.	.987	3	.780

Based on table 6, it shows that the significance value for the 0 minute time is 0.806, the 30 minute time is 0.637, the 60 minute time is 0.274, and the 90th time is 0.780, which means it is greater than 0.05 so it can be concluded that the data that has been tested is declared to be normally distributed.

Homogeneity Test

Table 7. Homogeneity Test Results

Test of Homogeneity of Variances

		Levene Statistic	df1	df2	Sig.
Conentration_filtrate_carambola wuluh	Based on Mean	1.506	3	8	.286
	Based on Median	.624	3	8	.619
	Based on Median and with adjusted df	.624	3	5.906	.626
	Based on trimmed mean	1.434	3	8	.303

Based on table 7, it shows that the significance value is greater than 0.05, so it can be concluded that the data tested is declared homogeneous.

One Way Anova Test

Table 8. One Way Anova Test Results

ANOVA

Concentration_filtrate_carambola wuluh

	Sum of Squares	Df	Mean Square	F	Sig.
Between Groups	43278.000	3	14426.000	318.221	.000
Within Groups	362.667	8	45.333		
Total	43640.667	11			

Based on the test results in table 8, a significant value of 0.000 is obtained, which means the Ha value is <0.05, so there is an effect of varying the length of time (30, 60 and 90 minutes) with starfruit (averrhoa bilimbi) filtrate on reducing levels of lead metal (Pb).) in river water in the Angsana Tanah Bumbu area.

Discussion

This research was carried out by analyzing the reduction in lead metal levels in addition to knowing the lead metal content in river water. The aim of this research was also to carry out a quantitative test using the atomic absorption spectrophotometry (SSA) method to determine the level of lead metal by exposure to the concentration of starfruit filtrate with certain time variations.

In this study, river water samples that had previously been taken from river water in the Angsana Tanah Bumbu area were subjected to a wet destruction process on the samples. Digestion is carried out first to remove or separate the other ion content. (Murtini et al., 2017). Wet digestion is digestion that uses acid reagents to decompose the sample or transform the sample with strong acids, either alone or in a mixture. There are several solvents that can be used, one of which is nitric acid (HNO3), which is effective when hot and oxidizes metal, so that the metal can dissolve with nitric acid. (Sri Asmorowati & Susilogati Sumarti, 2020)

Furthermore, this research was carried out to analyze the reduction in levels of lead metal Pb in river water by exposure to starfruit filtrate at different time variations and using river water samples taken from the area around Angsana Tanah Bumbu. Star fruit has the ability to bind heavy metals derived from citric acid with tricarboxylic groups. (Priyadi et al., 2013)

The star fruit in this study was taken from the Banjarmasin area with the fruit still fresh green in color, then wet sorting was carried out which aims to separate foreign materials that are not useful in making the filtrate. After carrying out wet sorting, the next stage is washing. The fruit that has been washed is then cut into pieces to make it easier to collect the filtrate. After that, filtration is carried out so that the filtrate and fruit dregs are separated so that you get 250 ml of pure filtrate from the star fruit. (Agun, 2022)

This research focuses on citric acid. Citric acid in the filtrate of star fruit has the ability to chelate metals, therefore citric acid can bind heavy metals which will act with metal ions to form complex ions that are easily soluble in water (Suparyanto and Rosad (2015, 2020).

Chelating agents are compounds that have –COOH, phenol and alcohol groups that can bind to metal ions and form complexes. Citric acid consists of three carboxyl groups –COO (tricarboxylate), as well as a hydroxyl group –OH. The carboxyl group is released from citric acid and will bind to heavy metals. (Priyadi et al., 2013).

In this study, a qualitative test was carried out to determine the metal content of lead (Pb) using an atomic absorption spectrophotometer with a wavelength of 217 nm for Pb. Next, the absorbance of the Pb standard solution was measured using SSA and a calibration curve was created between absorbance and concentration. Based on Figure 1, the results of measuring the calibration values from the standard solution curve of 0.1 ppm, 0.5 ppm, 1 ppm, 2 ppm, 4 ppm, a correlation coefficient (r) of 0.9995 is obtained, which means that the correlation coefficient value meets the regulatory requirements. stipulated by SNI that the correlation coefficient value must be ≥ 0.995 (Lusiana et al., 2008).

Based on calculations using the linear equation formula $y=0.0325\ x - 0.0015$, the results show that the standard concentration curve forms a straight line equation in Figure 1. This shows that the greater the concentration of a substance, the greater the absorbance of free atomic radiation (Romsiah et al. ., 2017).

In the next research stage, determining the lead (Pb) content obtained initial results without filtrate, the lead metal content in the river water was 0.413 in the sample. The results of the decrease in lead metal levels after exposure to starfruit filtrate with a concentration of 75% at different times can be seen in table 2 which shows that the lead metal content in the 30th minute sample lead level was 0.312, at 60 minutes the lead level decreased by 0.274 and at 60 minutes 90 lead levels decreased by 0.259.

The results of reducing lead levels show that the longer the soaking time with starfruit filtrate with a concentration of 75%, the greater the lead levels that can be reduced. It can be seen from the table for reducing lead (Pb) levels that the optimal treatment for reducing lead levels using starfruit filtrate is at a concentration of 75% with a time of 90 minutes. (Budi Agustin et al., n.d.)

Next, a validity method test is carried out which includes LoD and LoQ tests, precision tests and accuracy tests. Determining the LoD and LoQ tests is used to determine the ability of a tool to detect analytes that will be analyzed using that tool. If the resulting LoD and LoQ results are small, then the tool's detection is still good and can provide appropriate analyte analysis results. The detection limit and quantitation limit cannot be separated from each other because there is a very strong relationship between the two. According to Harmita (2004), determining LoD and LoQ values to determine tool performance can be done using a calibration curve. The detection limit can be obtained from three times the standard deviation (x/y) divided by the slope obtained from the linear regression equation. Meanwhile, the quantitation limit can be obtained from ten times the standard deviation (x/y) divided by the slope. Based on table 4, it can be seen from the value for determining the concentration of the heavy metal lead in the sample, the LOD value was obtained at 0.2346 mg/L, which is unacceptable or does not meet the requirements, namely the value must be smaller than the smallest concentration value of 0.1 ppm with a value concentration is 0.105, while the LOQ value is 0.7821 mg/L, where the value meets the requirements or is acceptable, namely the value must be smaller than the largest concentration value of 4 ppm with a concentration value of 3.963. (Ratnawati et al., 2019)

Precision testing can be defined as the level of accuracy of the values of several measurement results at the same concentration repeatedly (Apridamayanti & Kurniawan, 2023). Precision values can be obtained from the standard deviation (SD) value approach and the calibration curve. The results of calculating the RSD% value with 10 replications were found to be around 0.9257%, which meets the acceptance requirements for the RSD% test below 2% (Harmita, 2004) (Apridamayanti & Kurniawan, 2023).

The accuracy test is a measure that shows the degree of closeness of the analysis results to the actual levels of the analyte. In this study, researchers did not carry out any accuracy tests at the Center for Standardization and Industrial Services Laboratory (BSPJI).

The results of the test samples obtained were then entered into the SPSS (Statistical Package for the Social Sciences) system to see the relationship between the differences in the filtrate of star fruit and the decrease in levels of lead metal (Pb), so it is necessary to analyze the data, namely by means of normality tests, homogeneity tests and anova.

According to (Siregar, 2015) the normality test aims to test whether in the regression model, confounding or residual variables have a normal distribution or not. If the significance value is > 0.05, then it is declared that the data is normally distributed, whereas if the significance value is < 0.05, then it is declared that the data is not normally distributed. Based on table 6, it shows that the significance value for the 0 minute time is 0.806, the 30 minute time is 0.637, the 60 minute time is 0.274, and the 90th time is 0.780, which means it is greater than 0.05 so it can be concluded that the data that has been tested is declared to be normally distributed. .

The homogeneity test is used as a reference material to determine statistical test decisions. According to (Widiyanto, 2010) the basis or guideline for decision making in the homogeneity test is if the value is significant or sig. < 0.05, then it is said that the variance of two or more population data groups is not the same (not homogeneous) and if the value is significant or sig. > 0.05, then it is said that the variance of two or more population data groups is the same (homogene). Based on table 7, it shows that the significance value is greater than 0.05, so it can be concluded that the data tested is declared homogeneous.

The test results obtained a significant value of <0.000, which means the Ha value is <0.05, so there is an effect of varying the length of time (30, 60, and 90 minutes) with carambola wuluh (averrhoa bilimbi) filtrate on reducing lead (Pb) levels in river water in the Angsana Tanah Bumbu area. In accordance with the theory that the longer the soaking time, the more the lead metal content will be reduced. (Ondu & Jayadipraja, 2019)

Conclusion

Carambola wuluh filtrate has the potential to reduce lead metal levels in river water taken in the Angsana Tanah Bumbu area, this can be said to be due to the citric acid content in carambola wuluh filtrate. The percentage reduction in lead metal levels found in samples with a time of 30 minutes had a result of 24.45%, a time of 60 minutes had a result of 33.66%, a time of 90 minutes had a result of

37.29%. Based on the results above, it can be seen that the longer the soaking, the greater the decrease in levels of lead (Pb) in the river water in the Angsana Tanah Bumbu area.

Acknowledgements

The author would like to thank apt. Tuti Alawiyah, S. Farm., MM; Dr. Dede Mahdiyah, M.Si and Nur Hidayah, MT who have provided direction and guidance in completing this research.

References

Agun, Femmy Kristiani Kartina. (2022). Potential of Starfruit Fruit Filtrate (Avverhoa Bilimbi L.) in Reducing Ammonia Levels in Patin Fish (Pangasius Pangasius).

Apridamayanti, P., & Kurniawan, H. (2023). Analysis of Calcium Levels in Ambon and Raja Banana Skins using the Atomic Absorption Spectrophotometry Method. 3(2),247–255. https://doi.org/10.37311/ijpe.v3i2.19905

Budi Agustin, S., Rachmadiarti, F., Department of Biology, R., & Mathematics and Natural Sciences, Surabaya State University, F. (n.d.). Effect of Various Soaking Times and Concentration of Starfruit (Averrhoa bilimbi) Filtrate on Reducing Lead (Pb) Levels of Bader Fish (Barbonymus gonionotus) Meat from the Surabaya River. http://ejournal.unesa.ac.id/index.php/lenterabio

Hatta, M. H., Idayanti, R. W., & Hidayah, N. (n.d.). Organoleptic of Magelang Duck Thigh with Soaking Bilimbi fruit juice (Averrhoa bilimbi L.) at different concentrations.

Kadarsah, A., Salim, D., Husain, S., & Dinata, M. (2020). Species Density and Lead (Pb) Pollution in Mangrove Ecosystem, South Kalimantan. Biodjati Journal, 5(1), 70–81. https://doi.org/10.15575/biodjati.v5i1.7411

Ondu, A. F., & Jayadipraja, E. A. (2019). Effectiveness of Citrus aurantifolia swingle and Averrhoa bilimbi in reducing lead concentrations in Kalandue clams (Polymesoda sp) from Kendari Bay | Ondu | HYGIENE: Journal of Environmental Health. Hygiene, 5(1), 1–13. http://103.55.216.56/index.php/higiene/article/view/9760%0Ahttp://journal.uin-alauddin.ac.id/index.php/higiene/article/view/9760/6774

Priyadi, S., Darmaji, P., Santoso, U., & Hastuti, P. (2013). Chelation of Lead (Pb) and Cadmium (Cd) Using Citric Acid in Soybean Seeds. Agritech, 33(4),407–414. https://jurnal.ugm.ac.id/agritech/article/view/9536/7111

Ratnawati, N. A., Prasetya, A. T., & Rahayu, F. (2019). Indonesian Journal of Chemical Science Validation of the Heavy Metal Lead (Pb) Testing Method with Wet Destruction Using FAAS in West Semarang Canal Flood River Sediment. 8(1).

Saraswati, C. D. (2019). Description of lead (pb) levels in snakehead fish (Channa striata) soaked using starfruit extract (Averrhoa bilimbi). Repository of STIKES for Jombang Medical Scholars.

Sri Asmorowati, D., & Susilogati Sumarti, S. (2020). Comparison of Wet Digestion and Dry Digestion Methods for Analysis of Lead in Soil Around the FMIPA UNNES Chemistry Laboratory. Indonesian Journal of Chemical Science, 09(03),02–05. http://journal.unnes.ac.id/sju/index.php/ijcs

Suparyanto and Rosad (2015. (2020). Analysis of the Heavy Metal Pb in Tomato Sauce and Cavbai Sauce Circulating in the City of Surkarta Using Atomic Absorption Spectrophotometry. Suparyanto and Rosad (2015, 5(3), 248–253.