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RESEARCH ARTICLE

Potential Bioabsorbent Extract of Skin and Leaves Ananas Comosus on reduction of Copper, Mercury, and Lead in *Anadara granosa*

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ABSTRACT:
Kenjeran sea waters were polluted by several types of heavy metals such as copper (0.015mg/L), lead (0, 0036 mg/L), and mercury (0.001mg/L). Consuming *Anadara granosa* containing heavy metals exceeding the standard is very dangerous. The purpose of this study was to determine the effect of pineapple leaf and peel extract on reducing levels of copper, lead, and mercury in *Anadara granosa* in Kenjeran. Methods: Treatment without giving pineapple leaf and peel extract (Control) and treatment with pineapple leaf and peel extract using 0% and 3% concentrations. The results of heavy metal levels were in the form of numbers indicating the content of heavy metal levels in *Anadara granosa* determined in mg/kg using AAS. Results: The average copper concentration of 0% was 5.037mg/kg, and the 3% concentration was 2.563mg/kg, the average lead concentration at 0% concentration was 2.4333mg/kg and the concentration of 3% is 1.4433mg/kg, the average mercury concentration of 0% is 0.963mg/kg, and the concentration of 3% is 0.323mg/kg (4) Conclusion: there is an effect of pineapple peel and leaf extract on the decrease in copper levels by 50.88%, lead levels by 59%, and 33.54% decrease in mercury levels.

KEYWORDS: Pineapple leaf and peel extract, Copper, Lead, Mercury, Bioabsorbent.

INTRODUCTION:

Surabaya is the second largest city in Indonesia after the capital city of Jakarta, Surabaya has various supporting sectors which are the leading sectors, one of which is the industrial sector[1]. Surabaya has a well-known marine tourism object, namely Kenjeran beach. Kenjeran beach is one of the tourist objects located in the northeast of the city of Surabaya[2]. Many human activities around the coast of Kenjeran Beach can produce waste, both household waste, industrial waste, and waste originating from the activities of ships going in and out of the fishing port (TPI), so this can affect the quality of the waters around the coast Kenjeran Surabaya[3-5]. the increase in industrialization has an impact on environmental pollution with the disposal of waste, produced by human and industrial activities around the Kenjeran beach, Surabaya which is channeled to the beach[3].

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The results of the analysis of water quality based on the pollution index method on the east coast of Surabaya City show the results of water pollution index value on the Kenjeran coast currently reaching 4.6 which indicates the Kenjeran waters are in a lightly polluted state[6]. Based on the Decree of the Minister of the Environment of the Republic of Indonesia No. 51 of 2014 concerning seawater quality standards, it is explained that the maximum threshold for several metal pollutants in a row, namely zinc (Zn) 0.095mg/L; chromium (Cr) 0.002mg/L; mercury (Hg) 0.002mg/L; lead (Pb) 0.005mg/L; nickel (Ni) 0.075mg/L and cadmium (Cd) 0.002mg/L. Based on the Decree of the Ministry of Health of the Republic of Indonesia No.03725/B/SK/1989 for consumption biota on Cu metal, which is 20mg/kg.

The Indonesian National Standard (SNI) No. 7387: 2009 concerning the maximum limit of heavy metal contamination in food for lead (Pb) in shellfish is 1.5 mg/kg, the maximum limit for heavy metal contamination in food for mercury (Hg) in shellfish (bivalve) Molluscs and sea cucumbers are 1.0mg/kg and

if consumed will have an impact on health[7]. The Decree of the Minister of the Environment No. 51 of 2004 states that the content of heavy metal copper (Cu), and heavy metal copper (Pb) in Kenjeran Beach waters exceeds the maximum standard set[8,9]. Copper (Cu) can oxidize proteins and lipids, bind nucleic acids, and increase the formation of free radicals. When copper levels in the body exceed the normal limit (about 100mg) it can cause health problems. Acute poisoning causes heartburn and vomiting. Chronic toxicity results in Wilson's disease which is characterized by hemolytic anemia, chronic liver disorders, and neurological syndromes[10]. Several researchers have reported several effects of Lead (Pb) on human health[9-13], namely, Pb can interfere with the male reproductive system by reducing semen quality if the concentration is 5.29-7.25g/dl[14], if the concentration in the blood is greater than 20g/dl it can cause a decrease in hemoglobin and increase the risk of developing anemia[15]. Acute mercury (Hg) poisoning can cause damage to the digestive tract, cardiovascular disorders, acute renal failure, neurological disorders, and psychiatric disorders such as insomnia, nervousness, headaches, forgetfulness, tremors, and depression[9,16-18].

Copper, lead, and mercury that settle in the waters sea could undergo a process of deposition and accumulation in sediment, especially in sedentary marine biota and metals heavy will be concentrated in body creature life with method meaningful bioaccumulation enhancement concentration element chemical in body creature life and biomagnification as a bioindicator Examples of marine biota that can use as bioindicator. *Anadara granosa*. *Anadara granosa* also have properties that can stay in one place because of their slow movement and can filter water to get their food so that they are susceptible to water pollution, namely the heavy metals copper, lead, and mercury, which are accumulative in nature and cause the growth of blood clams to accumulate heavy metals in their bodies if the waters are contaminated with heavy metals[19-24], people eat the vegetables with heavy metals content can have a negative impact on health[25].

Based on interviews that have done on January 2022 on the seller shellfish in the beach area kenjeran Surabaya stated that *Anadara granosa* is the type the most clams sold. Consuming *Anadara granosa* that contains rate metal heavy copper *(Cu*), lead (Pb) and Mercury (Hg) exceed standard is very dangerous, then required effort for lower rate copper *(Cu*), lead (Pb), and Mercury (Hg) the use compound chemistry that can tie metal (adsorbent)[16]. The adsorbent that can use, comes from ingredient natural[26-28], which are waste of pineapple leaves and skin which not enough utilized properly. Based on the results study about the utilization of waste pineapple leaves (*Ananas comosus*) as adsorbent metal heavy copper (Cu) indicates results the content of cellulose from pineapple leaves as much as 25.33% which is enough tall could be utilized as adsorbent through the delignification process or lignin removal, and time optimum contact adsorption on Cu metal is 90 minutes[29]. However, several organisms also showed their potential for remediation of a polluted environment, such as fish[30] and *Scenedesmus* sp[31]. Pineapple leaves content cellulose contained in fiber pineapple leaves as much as 69.5% - 71.5%[32]. On cellulose there is group hydroxyl, Interaction Among group hydroxyl (OH) with metal the more lot, the amount adsorbate on adsorbent or substance absorbent will the more increase so that reach point fed up result in the desorption process or release adsorbate or absorbed metal return cause the adsorption process becomes reduce[33].

Besides the content of cellulose in pineapple leaves which can lower metal weight, utilization of Pineapple skin can also be used as effort drop metal heavy, another plant from the genus *Sagiitaria*, namely *S. montevidensis* was subsequently detected as presenting a natural phytoextraction ability for elements potassium and calcium and also exhibiting rhizofiltration potential for phosphorus, manganese, aluminum, vanadium, sulfur, iron, arsenic, copper, magnesium, zinc, sodium, lead, cadmium, nickel, chromium[34].

Pineapples (*Ananas comosus)* a lot contain compound sour citrate. The citric acid in pineapple skin is 78% of the total acid it contains[35-36]. Acid citric character for tie metal (*chelating agen*) so that could liberate lost ionic properties of metal ions the with three groups functional its conditioned carboxyl (COOH) in concentration and time contact certain will could experience deprotonation or destruction. The release of potential H^+ which has a big ionization could enter to lattice and able replace the position with metal ions and the occurrence of chelation which is equilibrium between metal ions with agent characterized fastener formation more from one bond Among metal with molecule agent binder that causes formation structure ring that surrounds metal[37].

The synthesis of cellulose citrate and succinate from cellulose Durian skin (*Durio Zibethius murr*) and its use as metal ion adsorber Pb^{2+}, show results ability of cellulose citric as adsorbent or substance absorbent far better than the ability cellulose. Because there is group carbonyl (C=O) in acid citrate, and besides group hydroxyl (OH) of interacting cellulose against metal ions that cause increased reactivity distant chemistry higher than cellulose[38], the synergy between cellulose and citric acid contained in pineapple leaf and peel extracts is more effective in reducing heavy metal levels.

Research purposes For knowing the influence of gift extract pineapple (Ananas comosus) leaves and skin drop rate metal heavy copper (Cu), lead (Pb), and mercury (Hg) in shellfish blood (Anadara granosa) in the region coast beach Kenjeran, Surabaya.

MATERIALS AND METHODS:

Materials:

The tools used in this research are a blender, sieve or sieve, analytical balance, filter paper, aluminum foil, Soxhlet chamber, distillation flask, condenser, 250ml, 500ml, and 1000ml beaker glass, watch glass, 100 measurings flask. ml, Erlenmeyer 250ml, spatula, tongs, hot plate, acid chamber, Atomic Absorption Spectrophotometry (AAS). The materials used in this study were *Anadara granosa*, 96% ethanol solution, aqua dest, Cu solution, Pb solution, mercury (Hg) solution, pineapple peel and leaf extract, HNO_3 + $HClO_4$ solution, HNO_3, H_2SO_4, HCl,

Methods:

A. Making Simplicia Leaves and peels of Pineapple (*Ananas comosus*) is as follows Separating the leaves and peels of the pineapple (*Ananas comosus*) from impurity or object foreign. Leaves and peels Pineapple (*Ananas comosus*) is cleaned by washing it with running water to remove dirt that sticks, then drain. Leaves and peels of pineapple (*Ananas comosus)* have been drained and then cut to speed up the drying process. Leaves and peels of pineapple (Ananas comosus) dried under the ray sun. The dried pineapple (Ananas comosus) leaves and skin were weighed 500 g each and mashed using a blender and filtered. use sieve. Simple then weighed again as much as 500 grams each and put in a container or plastic[39-40].

B. Making Pineapple (Ananas comosus) Leaf and Peel Extract is as follows Powder simplicia The leaves and skin of the pineapple are weighed 50 grams then wrapped in filter paper and put in the Soxhlet chamber, attach the pumpkin distillation in the bottom. Enter solvent 2x circulation of 96% ethanol (± 300 ml), then install the cooler return/condenser above it. Distillation flask heated to start the soxhletation process. The soxhletation process is carried out until the solvent in the soxhlet chamber is visibly clear. Extract in pumpkin distillation accommodated and evaporated to remove ethanol 96%

C. Preparation of Treatment of Blood Shellfish (Anadara granosa) Samples. Is as follows Clean shell blood (Anadara granosa) by washing using running water, then drain using paper strain. Soak shell blood (Anadara granosa) with Pb reagent with a concentration of 1.5 ppm for 1 hour. Drain shell blood (Anadara granosa) using filter paper, then weighed as much as. of each as much as 125 grams amount sample treatment. Add extract pineapple (Ananas comosus) leaves and skin with a concentration of 3% in each sample treat and shut up for 180 minutes. Label each sample.

D. Examination using Atomic Absorption Spectrophotometry (AAS) (17,41–43)

RESULT:

Based on the results of the study obtained data on the levels of heavy metals copper (Cu), lead (Pb), and Mercury (Hg) in blood mussels (*Anadara granosa)* after immersion in pineapple peel and leaf extract with a concentration of 3% shown in table 1.

Table 1: Results of laboratory tests for mercury (Hg) levels in *Anadara granosa* in the concentration of leaves and peels pineapple extract (mg/kg) for 180 minutes.

Sample	Copper levels of *Anadara granosa* (mg/kg).		lead levels of *Anadara granosa* (mg/kg)		Mercury levels of *Anadara granosa* (mg/kg)	
	0%	3%	0%	3%	0%	3%
1	5.05	2.87	2.26	1.47	1.190	0.610
2	5.86	2.27	2.46	1.52	1.040	0.260
3	4.20	2.55	2.58	1.34	0.660	0.100
Amount	15.11	7.69	7.3	4.33	2,890	0.970
Average	5.037	2,563	2.4333	1.4433	0.963	0.323
Standard Deviation	0.830	0.300	0.1616	0.0929	0.273	0.260

Furthermore, the average level of copper, lead, and mercury in *Anadara granosa* is shown in Figure 1

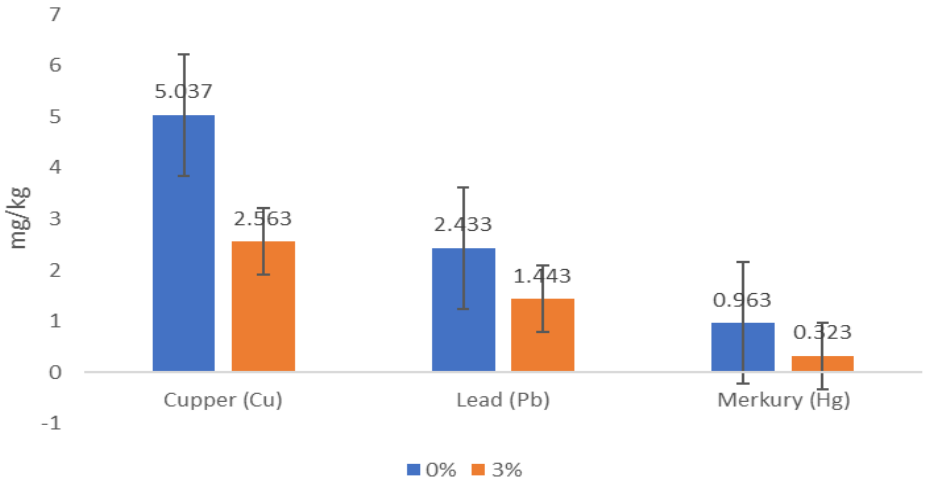

Figure 1: average levels of copper, lead, and mercury (mg/kg)

DISCUSSION:

Based on the results of laboratory tests using Atomic Absorption Spectrophotometry (AAS), the average copper (Cu) concentration of 0% was 5,037mg/kg, and the 3% concentration was 2,563mg/kg, the average level of lead (Pb) at a concentration of 0% was 2.4333 mg/kg and 3% concentration of 1.4433mg/kg, the average mercury (Hg) concentration of 0% was 0.963 mg/kg, and 3% concentration was 0.323mg/kg. Based on statistical data analysis with the ANOVA test and Tukey HSD test, it was found results with different averages by significance. which means that there is an effect of pineapple peel and leaf extract on the results of copper (Cu), lead (Pb) mercury (Hg) levels in *Anadara granosa*. Pineapple skin contains citric acid 78% of the total acid it contains. Citric acid itself is capable of forming complex compounds with metal ions, citric acid can also act as a metal binder (chelating agent) because it has three carboxyl functional groups (COOH) which are conditioned at a certain concentration and contact time so that the atom (H) is deprotonated or deprotonated. destruction.

The release of proton ions H^+ which has a large ionization potential will enter the lattice so that it can replace the position of metal ions and a chelation process occurs. is a balance between metal ions and binding agents which is characterized by the formation of more than one bond between the metal and the binding agent molecule which results in the formation of a ring structure that surrounds the metal [37]. Citric acid is a metal binding agent and is a stabilizer in food processing [44]. The citric acid in pineapple peel contains hydroxyl (OH) and functional carboxyl (COOH) groups causing citrate ions or binders, which can react with metal ions and form citrate salts. These citrate ions will bind to metals so that they can remove metal ions that accumulate or collect in organisms as complex compounds that are easily soluble in water[24,44,45]. Pineapple leaves contain a chemical composition of fiber, namely cellulose, lignin, pectin, fat, and other substances. The cellulose content in pineapple leaf fiber is 69.5% - 71.5% (27). This is because the cellulose in pineapple leaves can potentially be used as an alternative source of the adsorbent base material. Cellulose is an organic compound that contains a hydroxyl group in pineapple leaves.

The interaction between the hydroxyl group (OH) with metal increases, the amount of adsorbate on the adsorbent will increase so that it reaches a saturation point which results in the desorption process or the release of adsorbate or metal being reabsorbed causing the adsorption process to decrease[46]. The decrease in copper (Cu), lead (Pb) and mercury (Hg) levels in blood clams in this study was due to the presence of pineapple peel and leaf extract, which has the ability of citric acid (organic acid compounds) found in pineapple peels and the ability of cellulose (organic compounds) found in pineapple leaves so that With the binding of heavy metal ions of mercury with the incorporation of citric acid and cellulose[47], it can increase the adsorbent power and reduce the levels and also the toxicity of copper (Cu), lead (Pb) and mercury (Hg) in Anadara granosa. According to A. F. M Afifudin and R. Irawanto (2022), the concentration of copper before treatment was not measured, it assumed that the concentration of Cu in media was the same with concentration variations of experimental treatment, there were 0 mg/L, 1mg/L, 2mg/L, and 3 mg/L. This proves that the spear leaf plant can still absorb Cu metal well even though it has been exposed to the metal for an extended period [48-50]. Imron, et al (2019), L. minor has the potential as a phytoremediation agent to remove dyes from wastewater[51]. Based on research conducted by Al-Ajalin, et al (2020) that it was suggested that future

related research should accommodate the importance of several environmental conditions to the interaction between pollutants, plants, medium, and microbes as well as the impact of those interactions on the pollutant removal efficiency[52]. According to Hardani, et al (2021) chitosan and BSD had shown the potential to remove copper, cadmium, and lead with adsorption percentage up to 95%, The removal efficiency of jackfruit peel has showed 60% of lead removal[53]. The potential phytobase entity will appear in future scaffolds for medicinal chemists to increase potency while reducing toxicity[54]. The development of the results of this study can then be carried out in vivo testing to see the effectiveness of pineapple leaf and peel extracts in reducing heavy metal toxicity in Ratus novergicus exposed to heavy metals with various test parameters such as SGOT, SGPT, protein profile, lipid profile, and others. others, so that it can be potentially a candidate for the treatment of diseases caused by exposure to heavy metals.

CONCLUSION:

There was an effect of pineapple peel and leaf extract on the decrease in copper (Cu) heavy metal levels in blood clams by 50.88%, and a decrease in the lead (Pb) heavy metal levels in blood clams by 59%. , decreased mercury levels by 33.54%.

CONFLICT OF INTEREST:

The authors have no conflicts of interest regarding this investigation.

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