The Adsorption Effect of Pine Resin (*Pinus Merkusii*) in Reducing Hardness ($CaCO_3$) in Clean Water

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Abstract

Globally, the quantity of land and water resources on earth is relatively fixed, while the quality progressively decreased. One of the problems with clean water quality is the hardness level caused by valence cation ions of two metals such as Ca2 +, Mg2 +, Fe2 + and Mn2 +. The purpose of this study is to determine the effect of pine resin (*Pinus merkusii*) in reducing hardness (CaCO3) in clean water. This type of research is a quasi-experimental study by testing the treatment of hard water using pine resin media (*Pinus merkusii*) measuring ± 5 cm with variations in the thickness of the media that is 20 cm, 40 cm, and 60 cm by replicating 3 times. The results of this study found that the reduction in hardness at 20 cm media thickness by 42.14%, at 40 cm thickness by 51.58%, and a thickness of 60 cm 73.78%. And the one way ANOVA test results showed the value of the comparison between hardness after filtration was sig.0.00 ≤ 0.05 so that there was a significant difference between the thickness of the pine resin (*Pinus merkusii*) 20 cm, 40 cm, 60 cm. The conclusion from the study of water management through filtration using pine resin media (*Pinus merkusii*) meets the requirements according to the Health Ministry of Indonesia Regulation Number 32 of 2017. Water treatment with pine resin if used for the community should use a thickness of 60 cm. As for researchers, it can further use other variations such as the thickness of the pine resin used.

Keywords: *Adsorption, Pine Resin, Hardness, and Clean Water.*

Introduction

Water is the essence of life. With the presence of water, all living things on this earth can grow and develop properly. Water covers 75% of the earth's surface. The presence of water on this earth covers 97% in the ocean, 2% in ice sheets or glaciers, 0.6% in the soil, 0.3 is water vapor, 0.1 is in the soil surface. In living cells, 70% or more consists of water, including the human body. In the bones, there is water as much as 22% of the bone weight and 83% in the blood and kidneys.

The importance of water for health can be seen from the percent of the amount of water in the body's organs, which is 80% in the blood, 25% in the bones, 75% in the nerves, 80% in the kidneys, 70% in the liver, and 75% in the muscles.[1]

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Reducing 4% to 5% of the water in our body will be able to affect the decline in workability by 20% to 30% and greater water loss can be fatal for us.[2]

In addition to quantity, decreasing water quality is also very influential in human health, one of which is high hardness in some areas, especially in South Sulawesi.

Some areas surveyed by researchers regarding hardness levels in several areas in South Sulawesi showed that the level of hardness in clean water taken from community dug wells was 626 mg/L.[3] A survey in 2015 in Tonasa 1, Pangkep Subdistrict, the level of hardness obtained was 380.9 mg/L.[4] Another survey by in 2016 in Citta Subdistrict, Soppeng District, the level of hardness obtained was 323.83 mg/L.[5]

The hardness standard is 500 mg/L,[6] while other references stated that the hardness level> 300 mg/L is classified in very hard water.[7] To overcome this problem, it needs treatment efforts before the water is used so it will not interfere with health such as blockage of heart arteries and kidney stones or damage household cookware and household or industrial piping networks.

Hardness can be reduced by several ways such as heating to temporary hardness, adding chemicals to reduce pH in raw water such as the addition of lime soda (Na2CO3) or the addition of caustic soda (NaOH), the recarbonation process for pH stabilization, ion exchange using zeolites, or the use of resins both natural and synthetic resins.[8]

Resin is a hydrocarbon compound that can exchange ions so that the ions are often in drinking water treatment or wastewater treatment.[9] Natural resins can be obtained from plant sap such as pine trees (*Pine merkusii*) which are processed through the distillation process. This pine sap contains abietic acid (C20H30O2) and terpene acid (C5H8).[10] The use of this media only requires a relatively low cost, and is widely available in South Sulawesi and can be used many times.

Based on the description above, the authors are interested in examining how much the ability of pine resin adsorption in reducing hardness levels in clean water.

Materials and Method

This type of research is a quasi-experimental study by testing the treatment of hard water using pine resin media (*Pinus merkusii*) measuring ± 5 cm with a variation of media thickness of 20 cm, 40 cm, and 60 cm by replicating 3 times.

In this study, the sample used was clean water from residents' dug wells in the Citta Subdistrict, Soppeng Regency which had a high level of hardness. This research was conducted at the Makassar Health Polytechnic College precisely at the College Workshop on Environmental Health and laboratory analysis testing was conducted at the Chemical Laboratory majoring in environmental health Makassar Health Polytechnic.

The time of this study was divided into two stages, namely the preparatory stage, which includes the collection of secondary data that took place from February to March 2019, and the implementation phase, including research activities that took place from May to August 2019.

The sample in the study was clean water from a community dug well in Citta Subdistrict, Soppeng Regency which had a high level of hardness. Primary data using data obtained based on the results of processing with pine resin (*Pine merkusii*) in reducing hardness in clean water. Secondary data was data obtained from various references both articles, books, and other literature that were considered to be able to support existing theories, and were considered to have a relationship with this research.

The data analysis technique was carried out with the ANOVA test from observations obtained at the time of the implementation of the experiment and described in tabular form. The results of the study were accompanied by descriptions based on supporting theories.

Results

Large Decreased Hardness in Thickness of Pine Resin Media (Pinus merkusii) 20 cm. Based on research activities and examination of clean water samples in the laboratory, the average results can be described in Table 1:

Table 1: Average Hardness After Through Pine Resin Media Filtration Thickness of 20 cm in the 2019 Dug Well Water Sample

Before Treatment	Repetition	Hardness Level (mg/l)		Effectiveness of Decrease (%)
		After Treatment		
		Control	The thickness of 20 cm	
660.96	1	579,36	380.26	42.47
	2	628.32	391.68	40.74
	3	595.68	375.36	43.21
Average		601.12	382.43	42,14

Based on Table 1. above was the average yield of hardness before and after treatment with pine resin media thickness of 20 cm used in water samples from the first repetition to the third repetition. The results for hardness before treatment were 660.96 mg/l with three times repetition to control the average yield of 601.12 mg/l, after treatment on pine resin media thickness of 20 cm obtained an average result of 382.43 mg/l with the effectiveness of 42.14%.

Large Decreased Hardness in Thickness of Pine Resin Media (*Pinus merkusii*) 40cm. Based on research activities and examination of clean water samples in the laboratory, the average results can be described in Table 2:

Table 2: Average Hardness After Filtration Through Pine Resin Media Thickness of 40 cm in 2019 Dug Well Water Samples

Before Treatment	Repetition	Hardness Level (mg/l)		Effectiveness of Decrease (%)
		After Treatment		
		Control	The thickness of 40 cm	
660.96	1	652.80	328.03	50.37
	2	612.00	313.75	52.53
	3	542.64	318.24	51.85
Average		602.48	320.01	51.58

Based on Table 2 above was the average yield of hardness before and after treatment with pine resin media thickness of 40 cm used in water samples from the first repetition to the third repetition. The results for hardness before treatment were 660.96 mg/L with three times repetition to control the average yield of 602.48 mg/L, after treatment on pine resin media thickness of 40 cm obtained an average result of 320.01 mg/l with the effectiveness of 51.58%.

Large Decreased Hardness in Thickness of Pine Resin media (Pinus merkusii) 60cm. Based on research activities and examination of clean water samples in the laboratory, the average results can be described in Table 3:

Table 3: Average Hardness After Filtration of Pine Resin Media Thickness of 60 cm in 2019 Dug Well Water Samples

Before Treatment	Repetition	Hardness Level (mg/l)		Effectiveness of Decrease (%)
		After Treatment		
		Control	The thickness of 60 cm	
660.96	1	652.80	181.97	72.46
	2	530.40	178.70	72.96
	3	593.64	159.12	75.93
Average		592.28	173.26	73.78

Based on Table 3 above was the average yield of hardness before and after treatment with pine resin media thickness of 60 cm used in water samples from the first repetition to the third repetition. The results for hardness before treatment were 660.96 mg/L with three times repetition to control the average yield of 592.28 mg/L, after treatment on pine resin media thickness of 60 cm obtained an average result of 173.26 mg/L with the effectiveness of 73.78%.

The following are the results of data analysis using one way ANOVA statistical tests to determine whether there are differences in filter media used as interventions/treatments:

Table 4: Statistical Analysis Results Using One Way Anova Test Difference in Decreased Hardness Levels After Filtration Using Pine Resin Media with Thicknesses of 20 cm, 40 cm, and 60 cm in 2019

	Sum of Squares	df	Mean Square	F	Sig.
Between Groups	492731,292	5	98546.258	76,328	0.00
Within Groups	15493,054	12	1291,088		
Total	**508224,346**	**17**			

One way ANOVA test results based on Table 4 showed the comparison value between hardness levels after going through filtration where filtration results at thicknesses of 20 cm, 40 cm, and 60 cm were obtained from the One Way ANOVA statistical test results using SPSS results of Sig. if ≤ 0.05 then it showed that there was a difference but if the Sig. ≥ 0.05, it is showed that there was no difference.

The results above indicated a difference because of the Sig. 0.00. Or $0.00 \leq 0.05$ so the hypothesis was accepted this showed that for the decrease in hardness there was a significant difference between the thickness of the pine resin media 20 cm, 40 cm, and 60 cm.

Discussion

Water is one of the natural resources that have a very important function for human life and life, as well as to advance public welfare so that it is the basic capital and the main factor of development. Water is also an environmental component that is important for the survival of humans and other living things. That can be seen from the fact that 70 percent of the earth's surface is covered with water and two-thirds of the human body consists of water.[11]

Groundwater is a part of the water in nature that is below the surface of the land. The formation of groundwater follows the cycle of water circulation on earth called the hydrological cycle, which is a natural process that takes place in water in nature that undergoes a sequential and continuous displacement.[12]

The hardness standard in Indonesia Regulation is 500 mg/L[6] but another literature[7] stated that the hardness level>300 mg/L is classified in very hard water. To overcome this problem, it needs treatment efforts before the water is used so it will not interfere with health such asblockage of heart arteries and kidney stones or damage household cookware and household or industrial piping networks.

Hardness can be reduced by several ways such as heating to temporary hardness, adding chemicals to reduce pH in raw water such as the addition of lime soda (Na2CO3) or the addition of caustic soda (NaOH), the recarbonation process for pH stabilization, ion exchange using zeolites, or the use of resins both natural and synthetic resins.[8]

Hardness is classified in two ways, namely based on metal ions and based on anions associated with metal ions. Based on metal ions, hardness is divided into calcium hardness and magnesium hardness. Based on anions associated with metal ions, hardness is divided into carbonate hardness and non-carbonate hardness.[5]

Hardness is caused by excessive amounts of mineral-containing metal cations with two-dimensional cations. Usually what often causes hardness is the Ca ++ and Mg ++ cations. Total hardness is hardness caused by Ca ++ and Mg ++ together.[5]

Resin is a hydrocarbon compound that can exchange ions so that the ions are often in drinking water treatment or wastewater treatment.[9] Natural resins can be obtained from plant sap such as pine trees (*Pine merkusii*) which are processed through the distillation process. This pine sap contains abietic acid (C20H30O2) and terpene acid (C5H8).[10] The use of this media only requires a relatively low cost, and is widely available in South Sulawesi and can be used many times.

The hardness of water is different from the acidity of water, even though the two are closely related. Both can be easily distinguished. Acidic water usually shows a soft reaction. Therefore, the hardness of water is often called the hardness of the water.[13] Hardness is the nature of water caused by the presence of valence metal ions. Such ions can react with soap to form lumps. The main cause of hardness is cation Ca^{2+}, Mg^{2+}, Fe^{2+} and Mn^{2+}.[14]

Hardness in groundwater is caused by contact between groundwater and the layers of rocks. Rainwater that falls to earth cannot dissolve the large amounts of solid material contained in water. That ability can only be achieved if it has reached the soil where CO_2 is released by the reaction of bacteria, this CO_2 in the soil is in equilibrium with carbonic acid.

Water that contains high hardness will result in high use of soap, due to the chemical relationship between hardness ions and soap molecules, causing detergent properties of soap to disappear. Excess Ca^{2+} ions and CO_3 ions (one of the alkalinity ions) result in the formation of scale on the pipe and pan walls caused by the deposition of calcium carbonate $CaCO_3$.

The processing used in this research was processing with filtration which has a basis as physical, chemical, and biological filtering to separate/filter out particles that were not deposited in the sedimentation process through porous media. The filtering process was needed to separate the small/fine-sized flocks that cannot be deposited by the deposition process.[11]

One effort to overcome hardness is by softening hard water. Softening is the removal of certain ions that are in water and can react with other substances until the water distribution and use are disrupted. Theoretically, the reduction or softening of water hardness consists of various processes that exist in the process of softening hard water, namely using an ion-exchange system where water treatment uses resin or zeolite to replace unwanted ions in water such as Ca^{2+} and Mg^{2+} and replace them with N^{+} ions and K^{+}.[15]

This process is very fast (20-30 minutes), cannot take place with other reactions and raw water must not be turbid, installation and operation are complicated, high efficiency, price is relatively expensive (suitable for the industry). This process can be used for processing permanent and temporary hardness by separating unwanted ions contained in hard water. The material used in this process is in the form of activated carbon and or synthetic resin which is put into a column where water can already flow through the compounds.[16]

Adsorption is the capture or binding of free ions in water by adsorbents. Examples of substances used for the adsorption process are zeolites and resins which are the polymerization of polyhydric phenols with formaldehyde. For example, the binding of Ca^{2+} and Na^{2+} ions. Each gram of resin can adsorb 4-9 MeV (milliequivalent). The amount of adsorbent needed depends on the concentration of the solution. The higher the concentration of the solution, the greater the adsorbent needed to purify water.[9]

Pine resin has been through the distillation process produced by the merkusii pine tree classified as oleoresin which is a liquid resinous acid in turpentine that trickles out when the resin channel on wood or needle bark is cut or broken. The name oleoresin is used to differentiate pine resin from natural resin that appears on the skin or is contained in cavities in wood tissue as a genus of members of the *Dipterocarpaceae*, *Leguminoceae*, and *Caesalpiniaceae* families.[10]

The sap that comes from the pine tree is dark yellow and sticky, which consists of a complex mixture of chemicals. The most important elements that makeup pine resin are terpene acids and abietic acids. The mixture is dissolved in alcohol, gasoline, ether, and some other organic solvents, but it is not soluble in water. Besides, from the results of the distillation of *Pinus merkusii* sap produced an average of 64% gondorukem, 22.5% turpentine, and 12.5% impurities. The resin canal is not a part of the wood, but a cavity surrounded by parenchymal cells or epithelial cells. All layers surrounding the resin channel are called epitellium.[10]

Distilled pine sap will produce gondorukem (gum rosin) and turpentine (gum turpentine). The color is pale, clear, and sticky and when evaporated becomes brittle, it states that pine resin is composed of 66% resinous acid (resin), 25% turpentine (monoterpene), 7% neutral non-volatile material, and 2% water.[17]

Gondorukem or resinis a hydrocarbon compound that can exchange ions so that it is often used in drinking water treatment or wastewater treatment. At present, there are two types of resins, natural resins, and synthetic resins. Natural resins are processed from pine wood sap taken specifically, usually in the industry used for lacquer. Synthetic resins are made from hydrocarbons through chemical processes. This synthesis resin is widely used in the plastics industry, household appliances, toys, and decoration.[9]

The use of resin is one method to treat water by passing water to the resin media. Water treatment with this resin is one method of separation according to chemical changes by exchanging ions. The principle of water treatment with resins is to replace or exchange ions bound to the polymer filling resin with the ions that are passed. There are two kinds of ion exchange resins.

Cation exchange resin is a resin that will exchange or take cations from the solution. For example, if the water contains Fe (iron) ions the Fe ions will be bound by resin into R-Fe ions. However, the bond is not permanent so when it is saturated, the resin used for water filters can be washed with warm water that is given salt (NaCl). Furthermore, the resin will be pure again and can be reused. The resin takes the role of taking cations from the solution. Cation exchange resins take cations from the solution. Cation exchange resins contain carboxylic, sulfonic, phenolate or other groups and several equivalent cations.[9]

Anion exchange resins are used using separation based on the charge held by the solute. One example is the ion group containing sodium.[9] Ion exchange that occurs in the filtration process is also influenced by the thickness and height of the water sample when jetting thicker the pine resin media used, the higher the decrease in hardness levels in water through the filtration process with pine resin media.

The basic principle of filtration is physical, chemical, and biological particle filtering to separate/filter out particles that are not deposited in the sedimentation process through porous media.[18] The most influential filtration principle in this research is the deposition process that occurs on slow filters or filters with flow direction from the bottom up. The space between the grains of sand media functions as small sedimentation. Even small particles, as well as colloids and some bacteria, will settle in the space between the grains and adhere to the physical effect (adsorption) grains.

Filtration in a clean water treatment system is the process of removing fine particles/flocks that pass through the sedimentation unit, where the particles/flocks will be retained on the filtering media as long as the water passes through the media. The design of the research that has been made by using a filtering device from PVC pipe that is designed so that it becomes a simple filtering device using media, the filtration process used is in the direction of up-flow which is a water treatment system by passing through a media filter with direction flow from the bottom up so that if the media used is dirty the washing process will be very easy.

Upstream flow direction requires a lot of water samples because water samples will be flowed gravity and also use pressure so that water samples will flow through the media that has been prepared.

When viewed from the effectiveness of the thickness of the filter media, filtration with a thickness of pine resin 60 cm is the most effective in reducing hardness in water samples, from 660.96 mg/L down to an average of 173.26 mg/L with the effectiveness of 73.78% compared to the thickness of pine resin 20 cm which dropped to an average of 382.43 mg/L with the effectiveness of 42.14%, and the thickness of a 40 cm pine resin dropped to an average of 320.01 mg/L with the effectiveness of 51.58%.

Based on the results of statistical tests using one way ANOVA test to determine the differences in more than two interventions with replication. On the results of hardness inspection using variations in the thickness of the pine resin media 20 cm, 40 cm, and 60 cm, the Sig. the value was obtained. $0.00<0.05$ so that the hypothesis was accepted, this showed that for hardness there was a significant difference in the intervention by using variations in the thickness of the pine resin media 20 cm, 40 cm, and 60 cm.

However, if compared with Health Ministry of Health Regulation Number 32 in 2017 concerning Environmental Health Standard Quality and Water Health Requirements for Sanitary Hygiene, Swimming Pools, Solus Per Aqua and Public Baths, especially on water health requirements for sanitary hygiene requirements from total samples for hardness levels ($CaCO_3$) nothing has passed the established quality standard of 500 mg/L, on the results of sample water that has been through filtration treatment.

Conclusion

Based on the results of research that has been done can be concluded that there was a decrease in hardness of an average of 42.14% and qualify for water through filtration treatment with the media at a thickness of pine resin (*Pinus merkusii*) 20 cm. The average hardness reduction of 51.58% and qualify for water through filtration treatment with media at a thickness of pine resin (*Pinus merkusii*) media of 40 cm. This research found a significant decrease in hardness of an average of 73.78%, the most effective and eligible for water through filtration treatment with media at a thickness of pine resin (*Pinus merkusii*) 60 cm. The significant value between the difference in thickness of the pine resin media 20 cm, 40 cm, 60 cm is sig. $0.00<0.05$.

Based on the conclusions above, the authors suggest for the Community that people who want to use this processing, preferably using a thickness of 60 cm or more so that the results of more optimal processing. Besides, if the processing is used continuously for household needs, then the filter media should be cleaned for a certain period. Other researchers can then try to do filtration by comparing variations by adding different thicknesses.

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