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HARDNESS WATER REMOVAL BY USING CELLULOSE PAPYRUS FIBERS (Borrasus flabelifer L) FROM EAST NUSA TENGGARA MODIFIED WITH CITRIC ACID

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ABSTRACT

Hardness water removal using adsorbent ester cellulose citrate from Papyrus Fibers (Borrasus flabelifer L) from East Nusa Tenggara modified with citric acid has been done. The Adsorbent was modified with 0.6 mol/L citric acid at 120º C for one-half hour. The Adsorbent ester cellulose citrate from papyrus fibers (Borassus flabelifer L) has an ester carbonyl functional group (C=O) and O-H alcohol active group (O-H), which react to Ca^{2+} and Mg^{2+} from hardness water. The effects of adsorption conditions, such as contact time, pH, and hardness water concentrations were studied. The result shows that ester cellulose citrate from Papyrus Fibers (Borrasus flabelifer L) can remove hard water. The best condition for adsorption hardness water using ester cellulose citrate adsorbent from papyrus fibers in 6 h contact time with pH 6 and 250 mg/L as CaCO3 hardness water. The hardness of water removal is up to 71%.

Key words: *adsorbent; agricultural waste; citric modified; estererification; hardness water*

INTRODUCTION

Water containing large amounts of insoluble divalent metal, predominantly calcium and magnesium and other cation including aluminum, barium and iron, is called hardness water. Hardness water is expressed as milligrams of calcium carbonate equivalent per liter (Meena et al., 2011). Natural activities produce hard water through the hydrological cycle. In the hydrological cycle, rainwater will be absorbed into the ground and flow on the soil layer. When the water flows, Carbonic acid (HCO3-) will be produced by reactions between the water and CO_2 produced by microbial respiration. Carbonic acid can dissolve calcium and magnesium on calcareous rocks in soils such as limestone and dolomite. The dissolved calcium and magnesium are expressed as Calcium bicarbonate ($Ca(HCO_3)_2$) and Magnesium Carbonate ($Mg(HCO_3)_2$).

Kupang City is an area dominated by limestone that can lead to the highest hardness water. The water source for drinking water and hygiene sanitation in Kupang City comes from well water and PAM water. Several PAM water sources for Kupang City come from the Namosain and Baumata water springs (Sarifudin 2022). Based on a previous study, Namosain spring water in Kupang city contain 606 mg $CaCO_3$/L hardness water (Manulangga, 2011), and Baumata water springs contain 412 mg $CaCO_3$/L hardness water (Sarifudin, 2021). Depending on the Minister Of Health Regulation Number 492/MENKES/PER/IV/2010 and 32/MENKES/PER/2017, the water required for drinking water and hygienes sanitation contains hardness water with a maximum concentration of 500 mg $CaCO_3$/L. Hardness water with a higher concentration than the maximum concentration can cause environmental and health problems. Environmental problems include water becoming turbid, difficulty with soap foam, and corrosion of water pipes, washing machines and cooking utensils (Seo, 2010). Hardness water causes several health problems such as acute (anemia and diarrhea) as well as some chronic diseases such as kidney stones, cardiovascular, gastric, muscle weakness, and bowel and breast cancers (Rolance, 2014) (Mustapha, 2016). Therefore, removing hardness in water is essential to prevent health and environmental problems for humans, especially in Kupang City.

Hardness water removal by adsorption method is one of the methods developed recently. The adsorption method based on adsorption the adsorbed on the surface of the adsorbent through chemical bonds. It has several advantages, such as the adsorbed agent is easily removed and the raw materials are abundant in nature. In recent decades, agricultural waste is widely used as low cost and eco-friendly adsorbent. Agriculture waste contained several carbohydrate components, including cellulose, lingo cellulose, hemi cellulose and lignin which have the potential as a functional group to bind divalent metals in the aquatic environment. One of the agricultural waste that can be used as an adsorbent is papyrus fiber. Papyrus fiber contains 68.94% cellulose, 5.37% lignin, 14.03% hemicellulose and 0.6% wax (Boopathi, 2012). Based on previous study (Solo, 2014), the papyrus fibers from east nusa tengga activated by 1.5 mol/L sodium hydroxide was used to decreasing the concentration of Pb^{2+} in water.

The capacity of the adsorption can increase by modification. The purpose of the modification is to increasing the functional groups of the adsorbent surface. Cellulose has active sites that allow to the occurrence of chemical reactions. Oxygen rings from glycosidic linkages in cellulose may undergo intermolecular interactions. While three hydroxyl groups in each glucose unit can interact with other compounds. This is why cellulose has the potential to be modified (Perez, 2010). Modified cellulose has been utilized to adsorb divalent ions in aquatic environment. Modified soybean peels with 0.6 mol/L citric acid at 120ºC for 90 minutes were able to adsorb Cu^{2+} ions with adsorption capacity 1.76±0.03 mmol/g (Marshall, 1999). Based on previous study (Solo, 2018), modified cellulose of papyrus fiber from east nusa tenggara with 0.6 mol/L citric acid can add the carbonil functional group with 1.147 DS value that can be used to adsorb the hardness water.

Therefore, in this research will be investigated about the utilization of papyrus fiber from east nusa tenggara modified with citric acid to hardness water removal. The observed adsorption conditions include contact time, pH and adsorbed initial concentration were studied using hardness water synthetic and the application of the adsorbent for remove hardness water in was studied.

RESEARCH METHOD

Chemicals and instrumentation

The adsorbent powder was prepared from papyrus fibers collected from Oesapa district, Kupang City, East Nusa Tenggara, Indonesia. All Chemicals used for this research include Citric acid, NaOH, HCl, Erichrome Black T, CaCl2, MgCl2.6H2O, Na2EDTA.2H2O, NH4Cl, NH4OH, Whatman Filter Paper 41 pore size, glassware, digital scales, 120 mesh sieve, magnetic stirrer, FT-IR and pH meter.

Procedure reaction

Adsorbent

In this research, The Adsorbent was cellulose isolated from Papurus Fibers (*Borrasus flabelifer* L). The papyrus fiber cellulose was modified using esterification method using 0.6 mol/L citric acid (1:7) at 120ºC.

Adsorbed

Synthetic hardness water was prepared with dissolved 3 grams $CaCl_2$ and 1.67 gram $MgCl_2.8H_2O$ in 3L distilled water to make synthetic hardness water with concentration 1173.98 mg/L as $CaCO_3$.

The effect of contact time for hardness water removal

Each 0.3 grams adsorbent were added to 100 mL synthetic hardness water 1000 mg/L as $CaCO_3$. Samples were mixed in 200 rpm at various contact time (3, 4, 5, 6, 7 and 9 h). Then sample were filtered by using whatman filter paper and filtrates were collected to analysis using complexity titration method.

The effect of pH for hardness water removal

Each 0.3 grams adsorbent were added to 100 mL synthetic hardness water 1000 mg/L as $CaCO_3$ at various pH (3, 4, 5, 6, 7 and 8). The pH of the solution was adjusted using a solution of 0.1 mol/L HCl or 0.1 mol/L NaOH. The sample was mixed at 6 h in 200 rpm. Then sample were filtered by using whatman filter paper and filtrates were collected to analysis using complexity titration method.

The effect of initial concentration for hardness water removal

Each 0.3 grams adsorbent were added to 100 mL synthetic hardness water at various concentration (100, 250, 500, 750, 1000, 2000 and 3000 mg/L) and mixed in 200 rpm at 6 h. Then sample were filtered by using whatman filters and filtrates were collected to analysis using complexity titration method.

Determination of Hardness Using the Complexometric Titration Method

Total water hardness was determined based on SNI 06-6989.13-2004 standard. A total of 25 mL of the filtrate was put into a 250 mL Erlenmeyer flask, then diluted with 50 mL of distilled water. Then 1 mL of buffer solution (Buffer) pH 10 and a spatula tip (30 mg) EBT indicator were added. The titration was carried out slowly with 0.01 M Na_2EDTA standard solution until the color changed from purplish red to blue. The volume of the Na_2EDTA solution used was recorded to calculate the hardness water after the adsorption process.

Data Analysis

Water Hardness Calculation

The data obtained in the complexometric titration method is the volume of EDTA used to reach the endpoint of the titration. These results are used to calculate total water hardness as $CaCO_3$ in mg $CaCO_3$/L with the following equation:

$$\text{Hardness Water}\left(mg\frac{CaCO_3}{L}\right) = \frac{1000}{V_{Cu}} \times V_{EDTA} \times M_{EDTA} \times 100\ gr/mol$$

Where:

V_{CU} = Volume of sample solution (mL)

V_{EDTA} = Average volume of Na_2EDTA standard solution for titration (mL)

M_{EDTA} = Molarity of Na_2EDTA standard solution for titration (mmol/mL)

100 gr/mol = Mr $CaCO_3$

Adsorbed Water Hardness

$$W = \frac{C_1 - C_2}{1000} \times V \times \frac{1}{B}$$

Where :

W = Weight of water hardness as adsorbed $CaCO_3$ per gram of adsorbent (mg/g)

C1 = Initial hardness water concentration (mg/L $CaCO_3$)

C2 = Concentration of Hardness Water after adsorption process (mg/L $CaCO_3$)

V = volume of synthetic hard water (mL)
B = grams of adsorbent used (g)

Efisiensi Penyisihan Kesadahan Air

The efficiency of hardness water removal is calculated using the following equation:

$$\%\text{Removal Efficiency} = \frac{\text{Initial Hardness} - \text{Final Hardness}}{\text{Initial Hardness}} \times 100\%$$

RESULT AND DISCUSSION

1. *Characterization of Adsorbent*

Modification of adsorbent that contain cellulose used esterification method produce the ester cellulose citrate based on the previous studied. Ester cellulose citrate that product from cellulose from papyrus fibers with citric acid 0.6 mol/L peak at 1740.43 cm^{-1} probably corresponds to bending of ester carbonyl functional group (C=O) and the board absorption band at 3406.82cm^{-1} show the present of O-H functional group. The carbonyl (C=O) and hydroxyl functional groups (O-H) can interact with Ca^{2+} and Mg^{2+} from hardness water.

2. *Effect of contact time on hardness water removal*

The contact time indicates the time required to interact between the active groups in citric acid-modified cellulose with Ca^{2+} and Mg^{2+} metals. The optimum contact time is determined based on the most significant percentage of total hardness removal. The results of calculations and analysis of water hardness on contact time variations can be seen in Table 1.

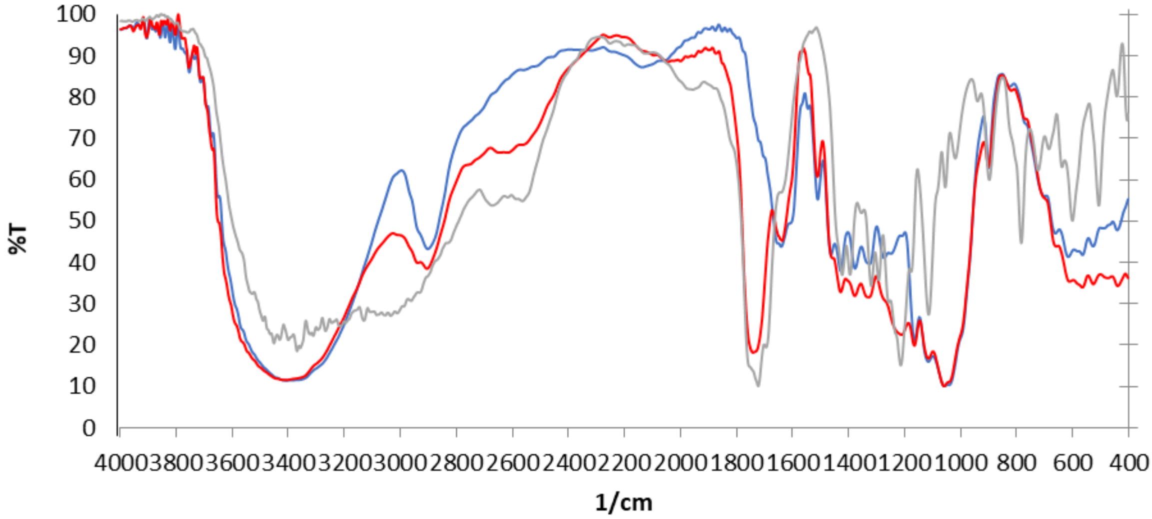

Figure 1. FTIR Spectrum of (a) Cellulose (blue line), Citric Acid (green line) and Ester Cellulose(red line)..

Table 1. Optimum Contact Time Analysis Results.

Contact Time (Hourse)	Total Hardness				Removal Efficiency (%)
	Initial Concentration (mg $CaCO_3$/L)	Final Concentration (mg $CaCO_3$/L)	Adsorbed Hardness Concentration (mg $CaCO_3$/L)	Adsorbed Hardness Concentration (mg $CaCO_3$/mg adsorben)	
3	1000	820.0	180	58.9	18.00
4	1000	742.5	257.5	85.7	25.75
5	1000	592.5	407.5	135.83	40.75
6	1000	527.5	472.5	157.2	47.25
7	1000	555.0	445	148.3	44.50
9	1000	590	410	136.2	41.00

The concentration of the adsorbate adsorbed on the surface of the adsorbent will increase with the addition of contact time and decrease after the optimum contact time. It can be seen from the increase in hardness adsorbed concentration in 3-6 hours of contact time. The increase in adsorbed hardness is due to the interaction between the functional groups in citric acid-modified papyrus fiber adsorbents (ester cellulose citrate) and Ca^{2+} and Mg^{2+} ions. The increase in contact time will cause increasing interaction between cation Ca dan Mg with the hydroxyl groups (OH) and carbonyl groups (C=O) present in the ester cellulose citrate. Based on the research results, the optimum contact time was 6 hours, with a hardness adsorbed concentration of much as 157.2 mg $CaCO_3$/mg adsorbent with a removal efficiency of 47.25%. After the optimum contact time (contact time > 6 hours), the release of adsorbate will occur due to desorption. This process occurs because of the electrostatic interaction between Ca^{2+} and Mg^{2+} cations with the functional groups (OH and C=O). It is possible to release the adsorbate if the contact time is increased due to the saturated condition of the adsorbent.

3. ***Effect of pH on hardness water removal***

In the adsorption process, the effect of pH can determine the amount of adsorbate adsorbed on the surface of the adsorbent. In this adsorption process, the pH affects the surface charge of the cellulose citrate ester adsorbent and the Ca2+ and Mg2+ cation species. The hydroxyl (OH) and carbonyl (C=O) functional groups in the cellulose citrate ester adsorbents from palm coir fibers can undergo protonation and deprotonation. It can increase the positive or negative charge on the surface of the adsorbent. In addition, pH can affect the Ca2+ and Mg2+ cation species which can cause an increase or decrease in the affinity of the cation for the functional group (Amalia, 2015).

The optimum pH is determined based on the most significant percentage of total hardness removal. The optimum pH in hardness water adsorption using ester cellulose citrate from papyrus fiber was carried out using the optimum contact time of 6 hours. The results showed that the concentration of the hardness water adsorbed on the ester cellulose citrate surface would decrease with decreased pH. The decrease of hardness water occurs due to the presence of excess hydrogen in the environment (pH <6), causing protonation of the hydroxyl (OH) and carbonyl (C=O) functional groups through the interaction between oxygen atoms (O) in the adsorbent and hydrogen (H) present in the environment to form intra- and intermolecular hydrogen bonds. It causes the charge on the surface of the ester cellulose citrate to be more positive (Oh, 2005) (Pitsari, 2013), and the calcium and magnesium species will become Ca(OH)+ and Mg(OH)+, thereby reducing the electrostatic interaction with the existing positive charge on the surface of the ester cellulose citrate.

Based on the analysis results in Table 2, it can be seen that the optimum pH in hardness water adsorption using ester cellulose citrate is at pH 6 with the amount of hardness adsorbed as much as 130.8 mg CaCO3/mg adsorbent with a removal efficiency of 39.50%. At pH 6, the surface of the ester cellulose citrate was deprotonated, due to the interaction between hydrogen atoms (H) on the surface of the adsorbent with hydroxyl ions (OH) in the environment, so the surface charge of the adsorbent tended to be more negatively. In this case, the calcium and magnesium species will become Ca^{2+} and Mg^{2+} species which can increase the affinity of the cation for the functional group, which causes an interaction between the positive charge of the cation with the negative charge of the adsorbent surface, so that more calcium and magnesium in the hardness water are adsorbed.

After optimum conditions occur (pH>6), there will be a decrease in the amount of hardness adsorbed. Alkaline environmental conditions will cause deprotonation of the hydroxyl (OH) functional groups on the adsorbent's surface so that the adsorbent's surface charge becomes increasingly negative. Calcium and magnesium species will become $Ca(OH)_2$ and $Mg(OH)_2$ because of the interaction between Ca^{2+} dan Mg^{2+} with OH. It caused the affinity of the cation for the functional group to be decreased (Amalia, 2015) and the amount of hardness adsorbed to be relatively small.

Table 2. Optimum pH Analysis Results.

pH	Total Hardness				Removal Efficiency (%)
	Initial Concentration (mg $CaCO_3$/L)	Final Concentration (mg $CaCO_3$/L)	Adsorbed Hardness Concentration (mg $CaCO_3$/L)	Adsorbed Hardness Concentration (mg $CaCO_3$/mg adsorben)	
3	1000	792.5	207.5	69.2	20.75
4	1000	697.5	302.5	100.8	30.35
5	1000	642.5	357.5	118.6	35.75
6	1000	605.0	395.0	130.8	39.50
7	1000	667.5	332.5	110.1	33.35
8	1000	672.5	327.5	108.6	32.75

Based on the results of the FT-IR analysis in Figure 1, it can be seen that after the adsorption process using ester cellulose citrate from papyrus fiber for 6 hours at pH 6, there was no significant difference in functional groups. This shows that the adsorption of Ca2+ and Mg2+ ions is the physical adsorption.

4. Effect of initial concentration of hardness water removal

The adsorbate concentration can affect the adsorption process, where the amount of adsorbate on the adsorbent surface indicates the adsorbent's ability to adsorbent adsorbate. In this study, ester cellulose citrate was reacted with hardness water at various concentrations of 100, 250, 500, 750, 1000, 2000, and 3000 mg $CaCO_3$/L at pH 6 for 6 hours. Based on the results (Table 3), increasing the hardness water concentration will increase the amount of Ca^{2+} and Mg^{2+} adsorbed on the surface of the adsorbent. At a concentration of 100 mg/L, the number of moles of Ca^{2+} and Mg^{2+} cations in hardness water is relatively small compared to the number of active sites in the adsorbent. Therefore, at low concentrations, the amount of adsorption that occurs is affected by the low initial hardness of the adsorbate (Yu, 2003). Suppose the initial hardness increases; adsorbed Ca^{2+} and Mg^{2+} will increase. From table 3, it can be seen that the SSLA adsorbent is still able to absorb $CaCO_3$ up to a maximum initial hardness concentration of 3000 mg $CaCO_3$/L with an adsorbed hardness concentration of 430 mg $CaCO_3$/L. Although the ester cellulose citrate can adsorb water with a hardness of up to 3000 mg $CaCO_3$/L, the optimum hardness reduction efficiency is obtained at a hardness concentration of 250 mg $CaCO_3$/L with a removal efficiency of 71%.

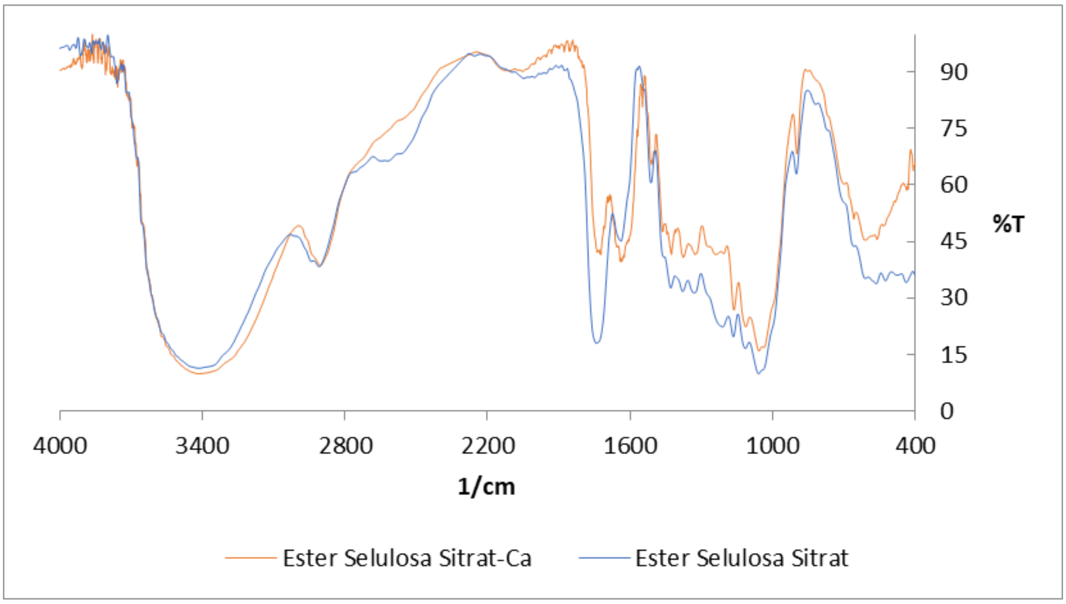

Figure 1. Results of FT-IR Spectra Analysis of Adsorbents Before and After the Adsorption Process of Ca^{2+} and Mg^{2+} in Hardness Water.

Table 3. Optimum Concentration Analysis Results.

Total Hardness				Removal Efficiency (%)
Initial Concentration (mg $CaCO_3$/L)	Final Concentration (mg $CaCO_3$/L)	Adsorbed Hardness Concentration (mg $CaCO_3$/L)	Adsorbed Hardness Concentration (mg $CaCO_3$/mg adsorben)	
100	72.5	27.5	9.2	27.50
250	72.5	177.5	57	71
500	252.5	247.5	82.2	49.50
750	460	290	96.5	38.67
1000	605	395	130.8	39.50
2000	1595	405	135	20.25
3000	2570	430	143.1	14.33

CONCLUSION

Based on the research results, ester cellulose citrate derived from papyrus fiber (Borassus flabellifer L) from East Nusa Tenggara can be used as an adsorbent to remove hardness water. Optimum adsorption conditions of hardness water removal in pH 6 with 6 hours contact time. The resulting removal efficiency is 71% with an optimum hardness concentration of 250 mg CaCO3/L with a total adsorbed hardness of 57 mg CaCO3/mg adsorbent.

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