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JCNaR
Journal of Chemical Natural Resources

Utilization Study of Nata De Soya from Soybean Wastewater As Adsorbent On Magnesium (Mg^{2+}) and Calcium (Ca^{2+}) Cations On Boiler Raw Water at PT. SMART Tbk

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Abstract. The use of Nata De Soya prepared from soybean wastewater as an adsorbent on magnesium (Mg^{2+}) and calcium(Ca^{2+}) cations caused hard water in the boiler raw water at PT. SMART Tbk has been studied. Nata De Soya has been activated with H_2SO_4 1N before use as an adsorbent for Mg^{2+} and Ca^{2+} cations in the boiler raw water. The study resulted demonstrated that the optimum mass of adsorbent to adsorb Ca^{2+}cation was 2.5 g with adsorption capacity at 60.64%. Meanwhile, the optimum mass of adsorbent to adsorb Mg^{2+}cation was 2.0 g with the adsorption capacity at 66.34%. The regenerated Nata De Soya adsorbent has been also studied to adsorb $Ca^{2+}$and Mg^{2+} cations. In other aspects, the percentage of Ca^{2+} and Mg^{2+} cations decrease by 9.27% and 9.47%, respectively after Nata De Soya treatment to the boiler raw water.

Keywords: Adsorbent, Hardness Water, Nata De Soya

Received [4 May 2020] | Revised [16 June 2020] | Accepted [27 July 2020]

1 Introduction

Water hardness is the main problem that must be eliminated in the process of industrial water treatment, especially in the process of producing water vapor or steam. The water used usually comes from groundwater, which is usually high in magnesium and calcium. The solubility of magnesium and calcium in water is inversely proportional to temperature, where the higher the temperature so they are more insoluble. The higher hardness levels in the water cause the formation of crust on the boiler piping system so resulting in the heat transfer process are not good, overheating can cause pipe and boiler furnace rupture (PT. Lonsum 2008).

Various methods have been applied to reduce calcium and magnesium levels including precipitation with chemicals such as sodium carbonate. With the addition of sodium carbonate

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so the hard water remains formed from the chloride and sulfate salts will be precipitated into calcium carbonate. Calcium will precipitate as calcium carbonate. The softening process is a fast way (1 to 2 hours) that can be concurrent with flocculation, a simple way, high efficiency, and low price, but has drawbacks namely the addition of a lot of chemicals that can damage the ecosystem environment.

Another method used is the ion exchange process, the medium used is resin. During the process of softening hard water with ion exchange resin, the ions dissolved in the water will absorb into the ion exchange resin and the resin will release other ions in equivalent equivalence. The nature of this process is very fast and can not coincide with other processes, the operation is complicated and requires very expensive costs. Due to the high cost required in lowering the hardness value, it is necessary new alternatives to reduce the hardness value of water.

Therefore, the authors are interested to research the utilization study of Nata de Soya from soybean wastewater as an adsorbent on calcium and magnesium cations that cause hard water in boiler raw water PT. SMART Tbk.

2 Materials and Methods

2.1 Equipments

In this study, the equipments used were glassware, burette, and Whatman filter paper.

2.2 Materials

The materials used were, boiler raw water was taken at PT. SMART Tbk. Soybean waste water was collected from Karang Sari village. *Acetobacter xylinum*, H_2SO_4, Ethanol, Na_2EDTA, Buffer pH 10, NaCl, Eriochrome Black T (EBT), and sodium hydroxide (NaOH) were purchased from Merck.

2.3 Fabrication of Nata De Soya

As much as 1 L of tofu wastewater was prepared. Then as much as 5 g of urea and 80 g of sugar were added to the tofu wastewater. This culture medium was heated to boil while stirring and left to room temperature. Next, CH3COOH was added until the medium reached a pH of 4. Finally, *Acetobacter xylinum* was added to the medium and it was inoculated for 14 days at room temperature.

2.4 Activation of Nata De Soya

The resulted nata was cut into small pieces and washed with water until the pH was neutral. Then washed with NaOH 2% solution and rinsed again with distilled water to pH 7. Then Nata De Soya was washed again with ethanol so that the trapped molecules in the pores of the bacterial cellulose of Nata De Soya did not return. As much as 1 kg of Nata was blended until smooth and activated with H2SO4 1N for 1 hour while stirring. Next, Nata was washed with distilled water to neutral pH and filtered. It was placed on a glass plate with a thickness of ± 5 mm and then heated at 95ºC for 6 hours (Sulistiyana, 2011).

2.5 Determination of Ca^{2+} and Mg^{2+} Concentration in Boiler Raw Water Before Addition of Nata De Soya Adsorbent

In order to determine the concentration of Mg^{2+}, as much as 50 mL of boiler raw water was taken dan put into 250 mL of Erlenmeyer glass, then added as 2 mL of buffer pH 10. Next, as much as 0.4 mg of EBT was added and titrated using Na_2EDTA 0.01 N until the color changed from burgundy to blue. In addition, as much as 100 mL boiler raw water was inserted into 250 mL of Erlenmeyer and as much as 4 mL NaOH 1N was added. After that, added murexid indicator, then titrated with Na_2EDTA 0.01 N until the color change from red to violet.

2.6 Adsorption of Ca^{2+} and Mg^{2+} Cations with Nata De Soya Adsorbent

As much as 200 boiler raw water was inserted into 250 mL of Erlenmeyer. Then, 0.5 g Nata De Soya was added and stirred by a mechanical stirrer for 1 hour and filtered. The obtained filtrate determined Ca^{2+} and Mg^{2+} contents. The same procedure was carried out for the weight of Nata De Soya 1.0; 1.5; 2.0; 2.5; 3.0; and 3.5 g.

2.7 Regeneration of Nata De Soya

Nata already used in adsorption Ca^{2+} and Mg^{2+} were regenerated with reactivated treatment with H2SO4 1N and stirred for 1 hour. Nata that was regenerated was the most optimum mass of adsorbent to adsorb Ca^{2+} and Mg^{2+} cations. This regenerated Nata was reused to adsorb the Ca^{2+} and Mg^{2+} cations in the boiler raw water and then determined again the concentration of Ca^{2+} and Mg^{2+} cations in the same way as the above method.

2.8 Determination of Ca and Mg Levels In Nata De Soya Adsorbent

Soybean wastewater contains Ca^{2+} and Mg^{2+} cations so it is necessary to measure Ca^{2+} and Mg^{2+} cations in the adsorbent. In the process, Nata De Soya adsorbent was inserted into the porcelain cup, then destructed using a furnace at 500ºC for 4 hours. Then, the porcelain cup was removed from the furnace and placed into the desiccator, left to cool. As much as 1 g of destructed Nata De Soya was put into 250 mL of Erlenmeyer, then added as 10 mL of HCl 37% and heated to boil. Next, as much as 150 mL of aquabidest and heated the solution for 30 minutes. The solution was removed and cooled, then the solution was transferred into a 500 mL of a graduated cylinder while rinsing with aquabidest to the marked line, homogenized, and filtered using filter paper The concentration of Ca^{2+} and Mg^{2+} cations were measured by the same procedure as the above method (Rio, 2011).

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3 RESULT AND DISCUSSION

The measurement of Ca^{2+} and Mg^{2+} concentration on boiler water samples were done by complexometric titration method. From the resulted study, the optimum mass of adsorbent treatment is presented in Table 1.

Tabel 1. Adsorption data of Ca^{2+} and Mg^{2+} cations with Nata De Soya adsorbent

No	Mass of adsorbent (g)	Cation Total (mg/L)	Ca^{2+} Cation (mg/L)	Mg^{2+} Cation (mg/L)
1	0.0	59.46	18.04	41.42
2	0.5	47.01	13.39	33.62
3	1.0	40.45	11.75	28.70
4	1.5	24.05	7.10	16.95
5	2.0	24.60	10.38	14.30
6	2.5	25.14	11.20	13.94
7	3.0	25.69	11.20	14.49
8	3.5	26.24	12.02	14.22

For adsorption treatment with regenerated Nata De Soya can be seen in Table 2:

Tabel 2. The calcium and magnesium cations adsorption data with regenerated adsorbent

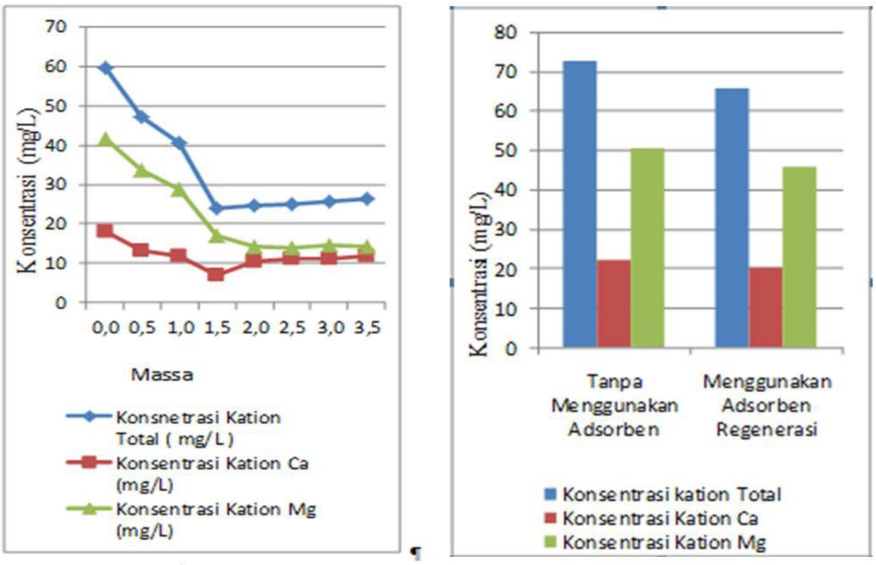
Concentration of Total Cation (mg/L)	Concentration of Calsium Cation (mg/L)	Concentration of Magnesium Cation (mg/L)
66.13	20.15	45.98

Before the raw water sample was adsorbed with the regenerated Nata De soya adsorbent. The concentration of calcium and magnesium cations was determined in the boiler raw water. The resulted data is indicated in Tabel 3.

Table 3. Calcium and magnesium cation concentration data in the boiler raw water samples prior to treatment with adsorbent of regenerated Nata De Soya.

Concentration of Total Cation (mg/L)	Concentration of Calsium Cation (mg/L)	Concentration of Magnesium Cation (mg/L)
73.0	22.21	50.79

Based on the obtained study results show that the optimum mass of Nata De Soya adsorbent which was the most optimum in the adsorption of calcium cation at 2.5g where there was a decrease in the concentration of about 60.64 % from the initial concentration of 18.04 mg/L to 7.10 mg/L. In addition, the optimum mass Nata de Soya adsorbent to adsorb the magnesium cation was obtained at a mass of 2 g where there is a decrease in the concentration of about 66.34 % from the initial concentration of 41.42 mg/L to 13.94 mg / L. Meanwhile, in the adsorption process with the adsorbent of regenerated Nata De Soya, there was only a decrease that was not significant for the two cations. In calcium cations using regenerated adsorbents, the concentration of calcium cations decreased about 9.27 % from the initial concentration of 22.21 mg/L to 20.15 mg/L. In contrast, with magnesium cations with the use of regenerated adsorbent Nata De Soya, there was a decrease of about 9.47% from the initial concentration of 50.79 mg/L to 45.98 mg/L which is displayed in figure 1.



a) **b)**

Figure 1. Ca^{2+} and Mg^{2+} cations adsorption a). with Nata De Soya adsorbent, b). before and after regenerated Nata De Soya adsorbent treatments

The activation process on Nata De Soya was conducted with the addition of H_2SO_4 1N where the purpose of this activation process was to break the glycosidic bonds of cellulose from Nata De Soya, due to this activation will form more OH groups because cellulose will be hydrolyzed into D-glucose. The molecular mechanism of hydrolysis with acid catalyst on β-1-4-glycosidic bonding begins with a proton of acid that interacts rapidly with oxygen from the glycosidic bonds that connects the two D-glucose units, thus forming the acidic bond conjugation. The splitting of the C-O bonds and conjugate acid on the cyclic carbonium ion then broke into D-free glucose and unstable carbonyl group, after the addition of water, the intermediate compound of carbonium was converted into D-glucose, and along with the acid group again released H^+ and so on (Xiang et al., 2003).

According to Badger (2002), the chemical hydrolysis reaction can be done using dilute acid or concentrated acid. The use of dilute acid in the hydrolysis process was performed at high temperatures and pressure with a fast reaction time. The temperature used was up to 200ºC. In this study, activation time was carried out using the addition of H_2SO_4 1N for 1 hour. This was possible cause the adsorbent's ability to absorb magnesium and calcium cations was not significant, due to it was not the perfect formation of OH groups during the hydrolysis process.

The absorption of cations in the regenerated adsorbent was also insignificant. This may be due to the H^+ ions of sulfuric acid at the reactivation time were not able to replace the metal ions which bind to the OH groups with cellulose.

Furthermore, Yefrida (2008) reported that the type of adsorption that occurs was chemical adsorption where the type of interaction that occurs was the ionic interaction between metal cations with functional groups of cellulose macromolecules, and similar to the interaction in cation exchange resins whose specific strength depended on the radius and charge of metal ions, and competition from certain positive charges with polymers. The Ca^{2+} cation will interact with the OH groups from the cellulose Nata De Soya adsorbent or with the CO groups of the cellulose Nata De Soya adsorbent, as well as the Mg^{2+} ion process will interact with the groups of the cellulose adsorbent.

In addition, Munaf (1998) also said that the adsorption process on cellulose or lignin involved functional groups of hydroxy and carboxylate in bio adsorbent. The ions in the solution will be bound to the bio adsorbent and displace the ions of the same sign. When the ion solution flowed on an adsorbent, hydrogen ions from the adsorbent will exchange with cations and hydroxyl ions will exchange with anions.

4 Conclusion

In conclusion, Nata De Soya adsorbent can adsorb calcium cation with the optimum mass of adsorbent about 2.5 g and adsorption capacity of about 60.64% of the initial concentration of 18.04 mg/L to 7.10 mg/ L. Meanwhile, the magnesium cation can be adsorbed with Nata De Soya adsorbent with an optimum mass of about 2.0 g and an absorption capacity of about 66.34% with an initial concentration of 41.42 mg/L to 13.94 mg/L. Nata De Soya adsorbent that has been regenerated can still absorb calcium and magnesium cations with the adsorption capacity were 9.27% and 9.47%, respectively. The initial concentration of calcium cation was 22.21 mg/L to 20.15 mg/L, while the initial concentration of magnesium cation was 50.79 mg/L to 45.98 mg/L.

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