Desalination of Seawater to Reduce Ca^{2+} and Na^{+} using Natural Zeolite in Vertical Column

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ABSTRACT

Water is a source of life. The ocean contains enormous potential for daily life, especially for people who inhabitants near the sea. Around two-thirds of Indonesia's territory is the ocean. In certain conditions, seawater has been applied for some industrial processing such as in Gresik Petrochemical. This study aims to reduce the Ca^{2+} and Na^{+} content of seawater as part of desalination. In this study, zeolites were supplied from the Wonogiri region. The zeolite rocks were crushed and then sieved to the desired size. The zeolites were washed with distilled water and then dried for 4 hours at 400 °C in the furnace. Furthermore, the zeolites were activated using NaOH solution and heated at 90 °C. After that, the zeolite was neutralized and dried within four hours at 110 °C. Furthermore, the zeolite is ready to be applied as an adsorbent for separating Ca^{2+} and Na^{+}. In the experiment, the zeolite is placed in a vertical column pipe and seawater is poured from the bottom of the pipe continuously. After circulating for a certain time, the seawater coming out from the column was analyzed for Ca^{2+} and Na^{+} content. Based on observation, it was found that the decrease of Ca^{2+} and Na^{+} could reach 29.75% and 25.14%.

1. Introduction

Water is an important substance for human life. People use water for household needs such as cooking, drinking, bathing, washing, etc. Even water is also used in chemical industrial processes. However, water supplies, especially groundwater, are increasingly difficult to obtain due to the increase in human population and very rapid industrial growth.

Generally, seawater desalination is intended so that the water obtained meets certain requirements. People use desalination for removing salt content. Therefore, drinking water can also be obtained from seawater through desalination. Desalinated water can be drunk or used for other purposes. People who are living around the coast, especially in remote areas may have used desalinated water to meet their daily needs.

The salt-free water from seawater can be obtained in various ways such as distillation, membrane filtration, freezing, and ion exchange [1], [2]. The two most widely used methods for desalination are distillation by heating seawater and reverse osmosis [3]. Research on seawater desalination needs to be continued to find a more efficient method.

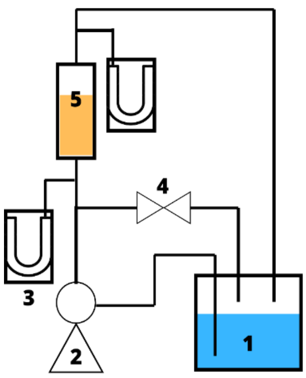
A method to do desalination is using zeolite [4]. This method works by exploiting the properties of zeolite. Some of the important properties of zeolite that can be applied to desalination are having exchangeable ions, having small cavities, high affinity, and so on. In general, the pore size of zeolite is less than 2 nm. The surface of the zeolite is surrounded by a negative charge so that it can be exchanged with positive ions [5]. Desalination using zeolite works with the mechanism of exchanging ions in the zeolite with adsorbate ions. Some of the main factors that affect the success of desalination are bed height, liquid flow rate, particle size [6], temperature, pH, and dissolved ion concentration [7].

Natural zeolite generally has a limited surface. To be more effective, the active surface of the zeolite needs to be enlarging of activation. Using the activation of the zeolite, it will be able to capture more ions from the adsorbate. A Chemical such as sodium hydroxide can be used as an activating agent for zeolite. Based on reports it is known that zeolite activated by the base tends to be more polar when compared to zeolite which is activated by acid [This research aimed was to study the reduction of Ca^{2+} and Na^{+} levels from seawater using natural zeolite bed. According to a report, the content of Ca^{2+} and Na^{+} in seawater is 0.4% and 10.56% respectively [9]. In this study, the variables studied were the character of the zeolite bed and its effect on reducing Ca^{2+} and Na^{+} from seawater.

2. Experiment

This study was conducted in several steps of the experiment. The first step was to set up the equipment to be used in the experiment. The equipment consists of a water container, pump, and a vertical column which assembled as shown in Fig. 1. The second step was to prepare the materials such as natural zeolite supplied from the Wonogiri region, sodium hydroxide, distilled water, and seawater. In the study, seawater was taken from Parangtritis beach, Yogyakarta. The zeolite was sieved into various sizes. Furthermore, the zeolite was washed with distilled water, followed by heating in a furnace at 400 ºC for 4 hours. After cleaning, the zeolite was activated using NaOH. Zeolite activation was carried out by placing the zeolite in a beaker containing 1 N sodium hydroxide solution. The solution was then stirred for one hour and then heated at 90 ºC. Then the zeolite was separated and neutralized using distilled water until a pH close to 7. Next, the zeolite was heated again in the oven at 110 ºC for 4 hours.

The third step was to carry out the seawater desalination to remove Ca^{2+} and Na^{+}. The activated zeolite of a certain size was put inside a vertical column with a diameter of 2 inches at various of heights. Furthermore, seawater flowed through the zeolite bed. The seawater flowing through the zeolite bed was in continuous circulation for a certain time. Then the fourth step was to observe the quantity of Ca^{2+} and Na^{+} in seawater that has passed through the bed within a period. Observation of the amount of Ca^{2+} and Na^{+} was carried out using an Atomic Absorption Spectrophotometer (AAS) in which the Ca^{2+} at a wavelength of 422.7 nm and for Na^{+} at 589 nm.



1. Seawater container
2. Pump
3. Manometer
4. Valve
5. Vertical column

Fig. 1. Experimental equipment set-up

3. Results and Discussion

The study of the reduction of Ca^{2+} and Na^{+} ions from seawater could be used to observe desalination for other ions in seawater. The contents of Ca^{2+} and Na^{+} in seawater are relatively more than other ions. To remove the ions more efficiently, the desalination was carried out in continuous circulation. The use of particles bed for continuous adsorption has been reported as reported by [10].

The sizes of the zeolite used in this study were -10+20, -20+30, and -30+50 mesh with zeolite masses of 150, 200, and 250 grams. The contact time between zeolite and seawater was 30, 60, 120, and 180 minutes. The following presents the data obtained during the study.

3.1. Zeolite Bed Characteristics

To study the ability of zeolite to adsorb Ca^{2+} and Na^{+}, it is needed the density and height of the zeolite in the column. The results of observation of both the density and height of the natural zeolite bed in this study are shown in Table 1.

Table 1. The density of natural zeolite used in this study before activation

Particle size	Density (g/mL)
-10+20	3.47
-20+30	5.09
-30+50	5.36

Natural zeolites are formed from volcanic rocks through natural processes over millions of years. Natural zeolite has various colors with a density between 2.0-2.3 g/cm^3, smooth and soft [11]. Generally, natural zeolites contain mineral compounds such as Al_2O_3, SiO_2, CaO, MgO, Na_2O, and K_2O. The compound content in a kind of zeolite will determine its density. Besides, the density is also influenced by the pores and the size of the solid. Generally, particles with large density will have small porosity. Particles with large size will have large distance between the particles. So that there are empty spaces between the particles and consequently the particle density decreases. On the other hand, at smaller particle sizes the density is higher because the free space is less.

When removing certain components from a liquid using a zeolite bed, the character of the height must be considered. This is due to the nature of the zeolite at a relatively smaller size which easily forms cakes. The formation of a very thick cake can make a difficulty for the liquid to pass through, creating back pressure and blocking the flow. Table 2 describes the relationship between the mass and height of the zeolite particles.

Table 2. Relationship between bed height and activated zeolite mass at Zeolite size = -10+20 mesh

Zeolite Mass (g)	Height of Zeolite (cm)
150	7.4
200	9.3
250	13.5

From Table 2, it can be seen that the height of the bed is correlated with the mass of the zeolite. When the mass is greater, the bed will be higher. This altitude character is needed to see how far desalination can be carried out. As will be explained in another section, the size of the zeolite also influences the success of desalination.

Fig. 2 explains the effect of the amount of zeolite mass on the pressure drop. The more mass of zeolite or the higher the bed the more difficult for liquid to pass through. This is characterized by a decrease in flow rate after passing through the bed. As contact time increases, the pressure drop tends to increase even though the decrease is not significant.

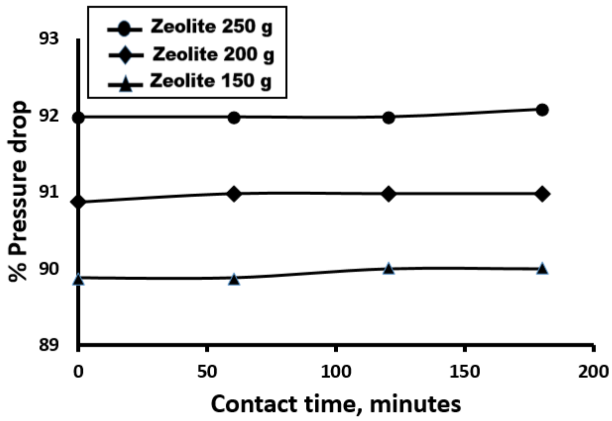


Fig. 2. Pressure drop of fluid within desalination time

3.2. Effect of Debit

The particle size affects the density of the particles. The smaller the size, the greater the density of the zeolite. With the same amount of mass, the smaller the size results in a lower height of the zeolite bed. As a result, it affects the flow pressure as shown in Table 3. It is shown that the smaller the size of the zeolite, the greater the resistance to flow. The condition will result in decreasing the pressure of the liquid leaving the bed. The smaller size of the zeolite causes a greater density so it is more difficult for seawater to pass through the bed. In addition, at a smaller particle size, it is easier to coagulate so that it restrains the flow rate. When an experiment was carried out using 100 mesh particles, the liquid did not flow due to the resistance of the bed being very high.

Table 3. Relationship between bed height and size of activated zeolite 250-gram mass of zeolite

Zeolite Size (mesh)	Zeolit Bed Height (cm)	Average pressure drop ΔP, mmHg
-10+20	13.5	68.091
-20+30	12	89.632
-30+50	11.5	100.90

The smaller the size of the zeolite will re insult slower the flow rate, however when the condition occurs the desalination will be better. Slow flow rates result better mass transfer because the interactions occur more intensively overall on bed surfaces. Therefore, more ions could be removed from seawater.

In the study of debit character which is affected by particle size, an experiment was carried out using particles of the same size within 3 hours. The results are shown in Fig. 3 explaining that the flow rate decreases over time. This is caused by the formation of physical bonds between particles in the bed since the beginning of the flow resulting slower flow rate. The results show that for a long time, the initial height of the bed affects the decrease of flow pressure. The initially higher zeolite bed has more flow resistance resulting greater decrease in discharge.

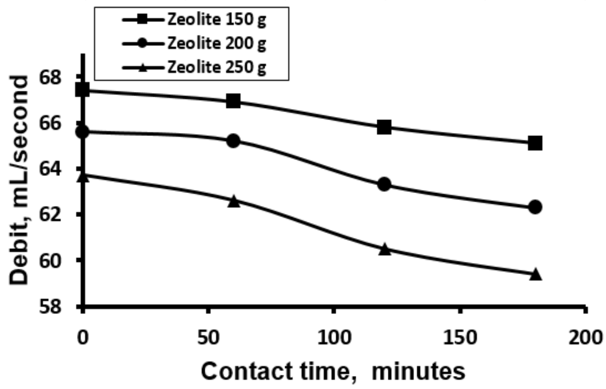


Fig. 3. The relationship between contact time and seawater flow rate

3.3. Effect of contact time, amount of zeolite, and zeolite size

1) Effect of contact time

To study the effect of time, experiments were carried out using a mass of 250-gram zeolite with a size of -10+20 mesh. The results of the observation of seawater that has been passed over the zeolite bed are shown in Figure 4.

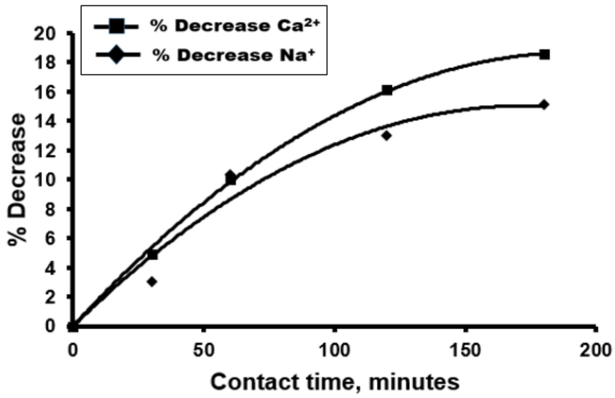


Fig. 4. Decreasing Ca^{2+} and Na^{+} amounts within circulation time

Fig. 4 shows that the rate of decrease of Ca^{2+} and Na^{+} is greater as well as time. At the longest time, which was 180 minutes, the level of Ca^{2+} in desalinated seawater decreased by 18.55% while Na^{+} decreased by 15.14%.

2) Effect of mass ratio

Based on the report [12], the greater the amount of zeolite used, the higher the percentage of adsorption produced. This is strongly influenced by the concentration of the zeolite activator solution. It is known that the entrapment of waste using zeolite reaches 82.31% [12]. In the study of desalination of brackish well water using zeolite by [13] it is known that the optimum mass ratio of zeolite to adsorbate sample is 3:10. In this experiment for three hours, the results were obtained as shown in Fig. 5.

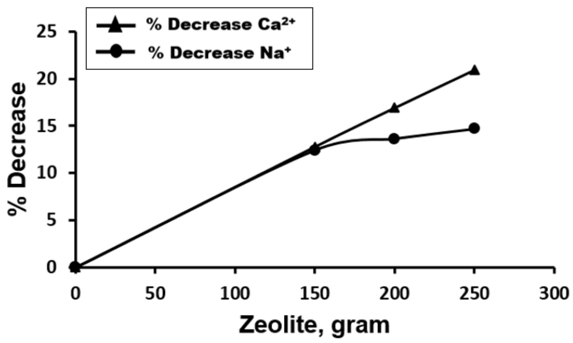


Fig. 5. The influence of zeolite mass on decreasing Ca^{2+} dan Na^{+}

Fig. 5 explains the correlation of the amount of zeolite against the decrease of Ca^{2+} and Na^{+} of seawater processed. It can be seen that more zeolite is used, the better the process for removing Ca^{2+} and Na^{+} ions. This is because the more amount of zeolite used the greater capacity for desalination.

3) Effect of zeolite size

The various size of zeolite has been applied for the study of removing ions from liquids. The desalination seawater using natural zeolite-activated was reported that a 40 mesh zeolite activated in 0.2 N HCl solution could reduce contaminants up to 1.66% [9]. Several reports explained that zeolite sizes of more than 50 mesh have been successfully carried out using the batch method. The batch method study was carried out by [14] using 80 mesh, while [13] [12] used a zeolite size of 100 mesh, and the researcher [15] used 60 mesh. However, reports of continuous desalination using zeolite sizes of more than 50 mesh on vertical columns have not been found. The use of particles that are too small causes the formation of a zeolite slurry which easily solidifies like a cake and resists the flow of liquid causing back pressure. As a result, the flow of liquid to be filtered cannot pass through the zeolite cake. When the back pressure is large enough, the flow becomes small and gradually stops. In this study, the continuous flow desalination process worked well when it was carried out with a maximum particle size of -30+50 mesh with an initial flow rate of 140.98 ml/s. Within these conditions, operations have been running well and the contact between the zeolite particles and seawater is also very good so that the process of reducing ions will be better. The comparison of the results for removing Ca^{2+} and Na^{+} based on particle size can be seen in Fig. 6.

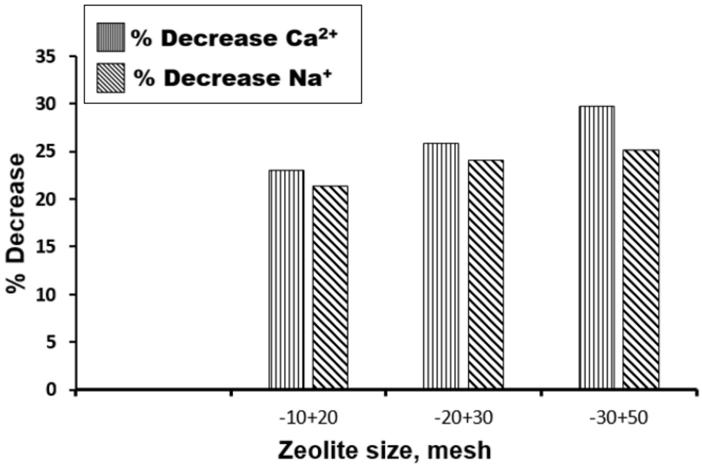


Fig. 6. Decreasing of Ca^{2+} and Na^{+} from seawater based on particle size

Based on Fig. 6 it can be seen that the smaller the particle size, the greater the decrease in Ca^{2+} and Na^{+} content. Reducing the particle size has increased the surface area. The reduction of Ca^{2+} and Na^{+} levels reached 29.75% and 25.14%, respectively. These results were obtained at relatively smaller particle sizes.

4. Conclusion

From the experiment conducted, it can be concluded that the reduction of Ca^{2+} and Na^{+} was successfully applied using zeolite. The desalination of the ions from seawater using a natural zeolite bed for 180 minutes reached 29.75% and 25.14% respectively for Ca^{2+} and Na^{+}. The effective size of the zeolite in the study is -30+50 mesh with an amount of zeolite mass of 250 grams and an initial height of 13.5 cm.

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