Activation of Natural Zeolite and Its Application for Adsorbents in Domestic Wastewater Treatment in Tembalang District, Semarang City

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1. Introduction

Management of water resources and the environment requires multidisciplinary science to understand groundwater-surface water (GW-SW) interactions. This interaction forms a close relationship between terrestrial ecosystems, aquatic ecosystems, and the integrity of water resources [1]. The amount of land that is fixed, and the population that is always increasing, causes the problem of clean water sources and wastewater to be interesting to study. The problem of clean water and domestic wastewater is very much felt in big cities in the world, including in Indonesia [2]. This is compounded by the presence of active chemicals that are used directly in the household (such as detergents, shampoo, toothpaste, cooking oil), which are directly discharged into sewers without being treated first. Then the carrying capacity of the environment is reduced due to increasing waste disposal [3]. Therefore, domestic wastewater and hospital wastewater treatment before disposal in the sewer is absolutely necessary, as was done in Doha, Qatar [4]. This
is somewhat different from the habits of the people in Indonesia. Indonesian people generally do not treat their domestic wastewater but are directly discharged into the surrounding water gutters.

Tembalang is one of the districts in the city of Semarang whose economic growth is rapid. There are 12 sub-districts in the Tembalang district, and the Tembalang sub-district is the location of the Diponegoro University campus, as shown in Figure 1. Thus, the need for clean water and disposal of domestic wastewater becomes quite complicated, so it is interesting to study. Domestic wastewater, in addition to causing environmental pollution, can cause discomfort and even health problems. One way to reduce the impact of domestic wastewater is to treat domestic wastewater before it is discharged into the environment.

![Figure 1. Map of Tembalang district](image)

Previous studies of communal domestic wastewater treatment used a stratified screening process and water hyacinth bioremediation [5]. The results were quite satisfying but required a long time and a reasonably large area. Another way is to combine an Anaerobic Baffled Reactor (ABR), Anaerobic Filter (AF), and Upflow anaerobic sludge blanket (UASB). The combination of the three methods gave excellent results (removal above 80%) but required a long time, expensive cost, and large area[6]. Another cheaper and easier way to do this was by adsorption using zeolites. The results were unsatisfactory if done only once (25%), but if replicated up to 3 times, it obtained significant results (74.5%). Whereas, if it was combined with iron sand and zeolite, it gave very satisfying results (96.6%) [7].

The material for treating domestic wastewater by adsorption (with zeolite as an adsorbent) is still wide open. In Indonesia, zeolite deposits are very abundant [8]. Zeolite is a hydrated aluminosilicate crystal that has attractive properties and mesoporous structures. Some names of natural zeolites that are well known are mordenite, analcime, phillipite, chabazite, heulandite, clinoptilolite, erionite, ferrierite, and laumontite [9]. Zeolites are usually used as adsorbents and catalysts in an industry or company. Natural zeolites, in general, have low thermal stability, non-uniform pore size, and low adsorption and catalytic activity. Therefore, it is necessary to modify zeolites to improve the adsorption and catalytic properties[10, 11].

Zeolite modifications made can be used by chemical modification methods such as dealumination with acids or cation exchange with metals. The addition of acid causes the aluminum to come out of the zeolite framework and increase the ratio of silica to alumina[10, 11, 12, 13, 14]. In this study, natural zeolites were used using HCl and H2SO4 to be further used to improve the quality of domestic wastewater in the Tembalang sub-district, Tembalang district, through the adsorption process. Previously we had done zeolite dealumination for biodiesel synthesis purposes [15]. Measurement parameters observed were chemical oxygen demand (COD), pH, biological oxygen demand (BOD), and total suspended solids (TSS) in the domestic wastewater. Also, to compare the parameters of wastewater with applicable regulations (Minister of Environment and Forestry Regulation No: 68 of 2016). Samples of domestic wastewater were taken from 3 sub-districts, Kramas, Tembalang, and Meteseh. Natural zeolites and activated zeolites HCl and H2SO4 were characterized by FTIR spectroscopy, while the Si/Al ratio was analyzed using Atomic Absorption Spectrophotometry (AAS).

2. Methodology

2.1. Materials and Equipment

The materials used were domestic wastewater (as much as 1 liter taken from three different sub-districts in Tembalang district as a sample), 250 g natural zeolite, hydrochloric acid (HCl) 6 M, sulfuric acid (H2SO4) 6 M, potassium permanganate (KMnO4) 0.5 M, distilled water and silver nitrate (AgNO3). While the equipment used was a pH meter, FTIR spectrometer, Atomic Absorption Spectrophotometry (AAS), 100–200 mesh sifter, some glassware, furnace, magnetic stirrer, water bath, a set of reflux apparatus, electric scales and hot plates.

2.2. Sample Preparation

Bayat natural zeolite was washed and soaked with distilled water overnight and dried at 110°C and then crushed until smooth and sieved with a size of 100–200 mesh.

2.3. Dealumination of natural zeolites

To 50 g of natural zeolite, 100 mL HCl 6 M and 100 mL KMnO4 0.5 M were added. The mixture was heated at 80°C for 4 hours, then allowed to stand for one night (48 hours) at room temperature. The obtained mixture is then filtered and washed with distilled water until it was neutral (tested with AgNO3 solution until no white precipitate occurs) and dried at 110°C for 5 hours and calcined for 3 hours at 500°C. The sample obtained was coded ZT1. The same thing was done using H2SO4 instead of HCl, and the sample was given a ZT2 code.
2.4. Characterization of natural zeolites, HCl-activated zeolites, and H_2SO_4-activated zeolites

Characterization of Si/Al ratio was performed on natural zeolites, HCl activated zeolites, and H_2SO_4 activated zeolites using Atomic Absorption Spectrophotometry (AAS). While the analysis of functional groups was carried out using Fourier-transform infrared spectroscopy (FTIR) spectrometers.

2.5. Adsorption Performance Test
2.5.1. Collection and treatment of Domestic Waste Water Samples

Before conducting the activity test, three sub-districts were taken in the Tembalang district, namely Kramas, Tembalang, and Meteseh. A total of 100 mL samples of domestic wastewater, AgNO_3 added to remove chloride ions. A total of 1 gram of natural zeolite adsorbent was mixed into the sample and then heated at 40°C in a three-neck flask that was equipped with a thermometer and stirrer, then refluxed for 60 minutes. The same thing was done on zeolite, which was realized as H_2SO_4 and HCl.

2.5.2. Separation of Residues and Filtrates

A mixture of adsorbed domestic wastewater, then filtered with filter paper to separate the filtrate and residue. The filtrate was wastewater that has been adsorbed while the residue is zeolite adsorbent. The filtrate was allowed to sit for a day and then for later analyzed.

2.6. Analysis of waste that has been adsorbed

Next, an analysis is performed on the sample solution, with Chemical oxygen demand (COD), pH, biological oxygen demand (BOD) and Total suspended solids (TSS). Measuring for each process was carried out three times.

3. Results and Discussion

Zeolites used are zeolites from the Klaten (Bayat) region. The clean and dry natural zeolite was crushed with porcelain mortal until smooth and sieved with a 100-200 mesh size sieve. Destruction was conducted to enlarge the surface area of natural zeolite so that the adsorption ability could be more optimal and could interact maximally with reactants. In zeolite that has been free of organic matter and impurities, a dealumination process was carried out by acidification with H_2SO_4 and HCl accompanied by the addition of KMnO_4. The addition of KMnO_4 was intended to oxidize existing organic impurities and metals. With the activation process carried out for 4 hours at 80°C and overnight at room temperature, it was expected that alumina coming out of the zeolite framework could be optimized. The addition of acid aimed to exchange cations to form zeolite-H where the cations in zeolite exchange with H+. Ion exchange between cations in zeolites with H+ was intended to replace all the cations in zeolites because in zeolites; there are alkaline or alkaline earth cations such as Na+, Ca++, Mg++ which act as balancing charges [10, 11, 12].

As a result of acid addition, an interaction between the acid and zeolite results in the release of alumina species from the zeolite. H+ ions derived from acids interact with free electrons in O atoms to form coordination bonds. Al-O groups will lack electrons so that they are more polar and weaker, so Al will break from the bonds [10, 11, 12, 13, 14].

3.1. FTIR analysis

Figure 2 presents the FTIR spectrum of natural zeolites and zeolite dealumination using HCl and H_2SO_4, which displays characteristics of zeolite. The zeolite framework is shown in the range of wave numbers 300-1300 cm⁻¹ originating from O-Si-O and O-Al-O tetrahedral bonds. The band 900-1250 cm⁻¹ is an asymmetrical range, while the symmetrical range is shown in the band 650-850 cm⁻¹, the bending of Si-O-Al-O (TO) internally appears in the region of 420-500 cm⁻¹ while for the external it appears at 700-780 cm⁻¹ [7, 9, 10, 11, 12, 13, 14, 16].

![FTIR spectrum of (a) H_2SO_4-activated zeolite, (b) HCl-activated zeolite, and (c) natural zeolite](image)

Interpretation of the IR spectrum can be obtained from several absorption bands. Dealumination occurs when internal stretching vibrations ascend, and external stretching vibrations decrease in wavenumbers. The shift in the region 420-300 cm⁻¹ in the direction of the lower wavenumber indicates the pore opening. Natural zeolite shows a peak at wave number 322.13 cm⁻¹, natural H_2SO_4-activated zeolite is 313.45 cm⁻¹, and that of HCl is 316.34 cm⁻¹. This indicates that the pore opening occurs due to the dealumination process [7, 9, 10, 11, 12]. These results also show that dealumination with H_2SO_4 gives a greater pore opening than HCl. It was further explained that internal vibrations related to TOₕ(T = Si, Al) tetrahedral, which is the main structural unit in the region of 950-1250 cm⁻¹. These wavenumbers represent the internal interwoven of tetrahedral asymmetrical stretching vibration and the external interwoven of asymmetric...
stretching vibration. Absorption in this area shows a shift in the wavenumber, in which natural zeolite by 1042.57 cm\(^{-1}\) to 1072.47 cm\(^{-1}\) on H\(_2\)SO\(_4\)-activated zeolite and 1064.75 cm\(^{-1}\) on HCl-activated zeolite. A greater shift occurred in zeolite activated H\(_2\)SO\(_4\) compared to HCl. This shows that H\(_2\)SO\(_4\) dealumination is more effective compared to HCl.

This shift is due to the dealumination of natural zeolites so that the tetrahedral stretching vibration of the T-O bond (T = Si, Al) is more common in Si-O bonds than Al-O. At wave numbers between 3400–3500 cm\(^{-1}\), peaks show the presence of water (hydrates) or free OH groups possessed by zeolite crystals [7, 9, 10, 11, 12]. The peak occurred at wavenumbers 3450.80 cm\(^{-1}\) for natural zeolites, 3417.04 cm\(^{-1}\) for H\(_2\)SO\(_4\)-activated zeolites, and 3455.62 cm\(^{-1}\) for HCl-activated zeolites.

3.2. Si/Al ratio analysis

Table 1 presents the Si/Al ratio of natural zeolite, activated zeolite H\(_2\)SO\(_4\), and HCl.

| No | Sample                | Si/Al ratio |
|----|-----------------------|-------------|
| 1  | Natural zeolite       | 4.5662      |
| 2  | HCl-activated zeolites| 5.4098      |
| 3  | H\(_2\)SO\(_4\)-activated zeolites | 6.4159 |

Natural zeolite, which has not been dealuminated, has the lowest Si/Al ratio of 4.5662. While the ratio of Si/Al to zeolite activated H\(_2\)SO\(_4\) was the highest at 6.4159, compared to HCl of 5.4098. This indicates that H\(_2\)SO\(_4\) does dealumination more effectively than HCl. These results have been similar to the study of Srijatiha and Darmawan [17], where dealumination with H\(_2\)SO\(_4\) was more effective compared to HCl.

3.3. Wastewater adsorption test

Tests of the activity of adsorption of domestic wastewater by natural zeolites and acid-activated zeolites were carried out by mixing 100 mL of 100 mL domestic wastewater samples with 1 g of zeolite. This process was carried out at 40 °C in a three-neck flask equipped with a thermometer and stirrer. It is expected that the intensity of the collision between the adsorbent and the adsorbate reaches its optimum point.

The results of the measurement of domestic wastewater from the three sub-districts located in Tembalang District (Kramas sub-district, Tembalang sub-district, and Metese sub-district) and the effectiveness of adsorption performance of natural zeolites (ZA), HCl-activated zeolites (ZT 1) and H\(_2\)SO\(_4\)-activated zeolite (ZT 2) can be seen in table 2. The results of the analysis of domestic wastewater are compared with the Standard Quality Standards (Minister of Environment and Forestry Regulation No: 68 of 2016).

Table 2 shows that in Tembalang Sub-district, the pH, COD, BOD, and TSS values are relatively higher when compared to the other two sub-districts (Kramas and Metese). This can be understood because the population density in Tembalang Sub-district is indeed higher. The presence of Diponegoro University students, Semarang State Polytechnic, Dental Care Academy, Pandanaran University, and the presence of food and beverage stalls adjacent to the college campuses affect the population density in the Tembalang Sub-district. With a dense population, it is inevitable that wastewater from washing and bathroom waste is also increasing.

The degree of acidity (pH) represents the acidic or basic state of a solution. If the pH of the solution < 7 means acid, whereas if the pH of the solution > 7 means that the solution is basic [1, 3, 18]. The pH values in the three sub-districts (Tembalang, Kramas, and Metese) still meet the standards of the Quality Standards (Minister of Environment and Forestry Regulation No: 68 of 2016). However, the pH of domestic wastewater in Tembalang Sub-district is relatively higher. This might be due to the presence of a bath and washing wastewater, which is not processed and discharged directly into the environment.
Chemical Oxygen Demand (COD) is the amount of oxygen needed by material to neutralize organic compounds dissolved in water. The measurement result of Chemical Oxygen Demand (COD) for the Tembalang sub-district is 86.7 ppm, higher than the Kramas sub-district of 70.6 ppm, and the Meteseh sub-district of 71.2 ppm. This is due to the higher population density in Tembalang Sub-district so that the discharge of wastewater from the MCK and several food/beverage stalls is also higher. The higher the COD price in water indicates, the worse the quality of the water. Usually, excessive organic matter content in water, resulting in turbidity, odor, and color of the solution is no longer clear if the value of COD in water exceeds the specified threshold value. This can result in the destruction of ecosystems in the waters; even if this is not addressed correctly, it can damage the aquatic environment. To avoid this kind of thing, it is necessary to treat domestic wastewater before being discharged into sewers, so as not to pollute the environment [19, 20].

Biological Oxygen Demand (BOD) is the amount of oxygen needed by microorganisms to neutralize organic compounds dissolved in water. The measurement result of Biological Oxygen Demand in Tembalang Sub-district (BOD) is 59.6 (mg/L) which is higher than Kramas Sub-district of 47.8 mg/L and Meteseh Sub-district of 49.1 mg/L. The higher the BOD value in a solution, the worse the quality of the water. Usually, excessive organic matter content in water, resulting in turbidity, odor, and color of the solution is no longer clear [5]. Microorganisms with sufficient oxygen conditions are able to degrade organic compounds (proteins, fats, carbohydrates, etc.) dissolved in domestic wastewater into simpler molecules. If the BOD price in water exceeds the specified threshold value, this could result in damage to the ecosystem in the waters. Waters that contain many plants will have a higher oxygen content because plants function to increase or increase oxygen levels. The primary source of oxygen is from plant synthesis through roots in the soil. Then oxygen through running water or rainwater causes oxygen to dissolve in water [19, 21].

Total Suspended Solid (TSS) is derived from natural sources, garbage, agricultural runoff water, fisheries, urban areas, and industry. In the Tembalang sub-district, the total Suspended Solid (TSS) measurement result was 56.8 mg/L, which is higher than Kramas Sub-district 38.8 mg/L and Meteseh Sub-district 46.6 mg/L. If wastewater that is channeled into drains/gutters contains high TSS levels, then the water becomes turbid and increases the temperature in the water. The result is reducing the oxygen dissolved in water and disrupting the life of aquatic habitats. High TSS levels result in the blocking of sunlight to the body of water so that the photosynthesis process of plants in these waters becomes disturbed [20].

4. Conclusion

The results of the IR spectrogram and zeolite Si/Al ratio show that zeolite, which is activated by acid, shows a shift in wavenumber and different Si/Al ratio. The Si/Al ratio in natural zeolites was 4.57 and rose to 5.41 in HCl activated zeolites and increased again to 6.42 in HSO₄ activated zeolites. By using natural zeolite adsorbents, HCl activated zeolites and HSO₄ activated zeolites, a decrease in the value of water quality chemical parameters such as COD, pH, BOD, and TSS is as follows: Natural zeolite resulted in a decrease in COD of 21.8%, pH of 11.5%, BOD of 9.2% and TSS of 10.8%. Whereas HCl activated zeolite reduced COD by 78.9%, pH 16.2%, BOD 11.8% and TSS 44.4%. Moreover, HSO₄-activated zeolite succeeded in reducing COD by 85.5%, pH 17.9%, BOD 12.6%, and TSS 49.7%. From these results, it can be concluded that HSO₄-activated zeolite provides the best adsorption results.

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