Characterization of Hydrochloric Acid Activated Natural Kaolin and its application as adsorbent for Mg\textsuperscript{2+}

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Abstract. Hard water can form deposits (scale) on pipe walls and operating units in industrial machines. One way to soften hard water is by using adsorbents to reduce the number of ions causing hardness, one of which is Mg\textsuperscript{2+}. Kaolin is a natural mineral which has potential as an adsorbent. The ability of kaolin as an adsorbent can be enhanced utilizing activation. In this study, kaolin was chemically activated using HCl solution with varying concentrations, namely 4, 5, and 6 M. The activation was carried out by stirring kaolin with the activator solution for 24 hours. The adsorbent characterization was performed by the infrared spectrophotometer (FTIR) and the gravimetric method. The adsorption test for Mg\textsuperscript{2+} by activated kaolin was determined by adding 1 g of adsorbent to 25 mL of 10 ppm Mg\textsuperscript{2+} solution with stirring rate 150 rpm. Furthermore, the adsorption contact time was varied, namely 30, 90, 150, and 180 minutes. The concentration of Mg\textsuperscript{2+} was determined by a titration method using ethylenediaminetetraacetate (EDTA). The percentage of Mg\textsuperscript{2+} adsorbed was calculated as the concentration of Mg\textsuperscript{2+} adsorbed against the initial concentration. The results showed that kaolin activated by 6 M HCl could adsorb 68.9\% of Mg\textsuperscript{2+} at the optimum contact time of 150 minutes. Activation of kaolin with HCl 6M can release organic impurities present in natural kaolin, which is thought to affect increasing its adsorption capacity for Mg\textsuperscript{2+}.

Keywords: chemical activation, hydrochloric acid, kaolin, magnesium ion

1. Introduction

Advancement in industries, in line with that in science, is getting faster and more complex. Many industries, both small and large, use tools that require propulsion, one of which is by using steam produced in boilers [1,2]. One example is the oil palm industry, a common industry in West Kalimantan that uses steam as a driving source as well as a heat source for the process of boiling oil palm fruit.

Scale formation on pipe walls and operating units due to high water hardness is a serious problem often encountered in industries that use boilers. The formation of magnesium salts can act as an insulator that can inhibit heat conductivity and cause rupture of boiler pipes [2,3]. Hardness caused by calcium and magnesium ions is called permanent hardness. In this case, the magnesium sulfate formed will increase its solubility in water if the temperature is raised. As a result, the content of calcium and
magnesium cannot be reduced by heating. Hardness can only be reduced by incorporating softener materials using ion exchange principles [3].

Currently, the most common method of hard water treatment for the prevention of sediment formation is through ion exchange by using ion exchange resins. While proven to be effective, this method of treating boiler feed water, however, requires a large investment [1]. Other cheaper alternatives are thus decided to reduce the cost of water treatment. One potential alternative is by using adsorbents. Some researchers have studied the use of adsorbents from moringa oleifera seeds [4], coconut shell activated carbon [1], activated carbon from cashew nutshell [5], or synthetic zeolite [6].

Clay minerals are one of Indonesia’s abundant natural resources whose utilizations are still relatively limited. The structural framework of the clay is negative and it binds ionic bonds to neutralize the charge. Kaolin is among abundant minerals in the Province of West Kalimantan [7]. It is a type of 1:1 clay whose negative surface can be used as an adsorbent. Natural kaolin requires activation, either chemically and/or physically, to enhance its adsorption capacity. Activation of natural kaolin by using 6 M HCl can release metal impurities in kaolin [8]. Also, activation with acids can increase the interaction of bixin on kaolin and thus increase the photostability of this natural pigment [8].

This study aimed at examining the potential of natural kaolin from Bengkayang Regency, West Kalimantan to adsorb Mg$^{2+}$ ions. The kaolin was activated using HCl with a concentration variation of 4 to 6 M. Identification of the functional groups using infrared spectroscopy was carried out on the prepared kaolin and activated kaolin HCl 4-6 M. Determination of the SiO$_2$ and Al$_2$O$_3$ content in the prepared and activated kaolin was carried out gravimetrically.

2. Methodology

The equipment used in this research included common glassware, 120 mesh sieve, magnetic stirrer, centrifuge, furnace, XRD Philips X’Pert diffractometer, and infrared spectrophotometer (Shimadzu FTIR-8201 PC). The materials used in this research were distilled water, ammonium chloride (NH$_4$Cl), ammonium hydroxide (NH$_4$OH), hydrochloric acid (HCl), nitric acid (HNO$_3$), acid sulfate (H$_2$SO$_4$), pH 10 buffer, EBT indicator, methyl red indicator, calcium sulfate (CaSO$_4$.2H$_2$O), magnesium sulfate (MgSO$_4$.7H$_2$O), Na$_2$H$_2$EDTA, silver nitrate (AgNO$_3$) and natural kaolin sample taken from Capkala Sub-district, Bengkayang Regency, West Kalimantan.

Acid Activation of kaolin. Acid activation of kaolin was carried out by following the method developed by Wahyuni et al [8]. Three samples of kaolin, 100 g each, were prepared along with 700 mL of 4, 5, and 6 M HCl. Acid activation was conducted at room temperature by slowly pouring the HCl solution into a beaker containing kaolin while stirring using a magnetic stirrer. After all the HCl was added, the activation process was allowed to continue for 24 hours. The solid was then filtered and washed with distilled water until it was free from Cl$^-$ ions, as shown by the AgNO$_3$ test. It was later dried in an oven at 80°C until a constant weight was reached. Then, it was crushed until smooth and sieved using a 120 mesh sieve. The activated kaolin which passed the 120 mesh sieve was ready to be used as Mg$^{2+}$ adsorbent.

Adsorption of Mg$^{2+}$ by activated kaolin with HCl 4-6 M. Three samples of kaolin, activated with 4, 5, and 6 M HCl, 1 g each, were prepared and poured into three different bottles. Then, 25 mL of hard water sample containing 10 mg/L Mg$^{2+}$ was added into each of the three bottles. The mixtures were stirred for 150 minutes at a stirring rate of 150 rpm. After that, each mixture was centrifuged and the resulting supernatant was titrated with EDTA.

Determination of optimum contact time for adsorption of Mg$^{2+}$ by activated kaolin. Four water samples, 25 mL each, containing 10 mg L of Mg$^{2+}$ were prepared. One gram of 6M HCl activated kaolin (HA6) was added to each of the water samples. The four mixtures were stirred with a variation of 30, 90, 150, and 180 minutes, respectively, with a stirring speed of 150 rpm, and then centrifuged. The
resulting supernatants were then titrated with EDTA. The same treatment was carried out for prepared kaolin (KP).

Determination of Mg$^{2+}$ concentration by titration with EDTA. The concentration of Mg$^{2+}$ was determined by complexometric titration using $5 \times 10^{-4}$ M EDTA. 50 mL of EDTA was poured into the burette. 10 mL of hard water sample was poured into erlenmeyer flask. Rinse the edges of the container with some distilled water. 1 mL of buffer solution pH 10 and 5–10 mg of EBT indicator were added to the hard water sample. It was then titrated with EDTA until the burgundy solution turns light blue. The volume (V) of EDTA used was noted and the concentration (M) of the ion was determined using equation (1).

$$M_{Mg^{2+}} \times V_{Mg^{2+}} = M_{EDTA} \times V_{EDTA}$$  (1)

The percentage of Mg$^{2+}$ adsorbed was calculated using the equation (2).

$$\% Mg^{2+} \text{adsorbed} = \frac{\text{Initial Concentration} - \text{Final concentration}}{\text{Initial concentration}} \times 100\%$$  (2)

3. Result and Discussions

The kaolin diffractogram is shown in figure 1. Natural kaolin used in this study is mostly composed of quartz minerals (83.8%), kaolinite (14.5%), and muscovite (1.6%). The purpose of the preparation was to separate the quartz and kaolinite fractions and this can be carried out by centrifugation [9,10].

As figure 1 shows, after preparation, the quartz fraction is no longer identified. Prepared kaolin contains 78.8% kaolinite and 21.2% muscovite.

Although activation of kaolin using hydrochloric acid destroyed the structure of kaolinite, it did not significantly change the functional groups (figure 2). As figure 2 shows, the absorption peak in the area around 3600 cm$^{-1}$ was identified as corresponding to the stretching vibration of internal hydroxyl bonds (Al-O-H) in the octahedral sheet identified as kaolinite. The wavenumber at 3400 cm$^{-1}$ corresponds to the stretching vibration for the –OH bond of H$_2$O [9]. Three bands at 1100 cm$^{-1}$-1000 cm$^{-1}$ were assigned to Si-O stretching. Al-OH deformation bands were identified at two peaks at 900 cm$^{-1}$ and 750 cm$^{-1}$. Al-O-Si deformation was detected at approximately 530 cm$^{-1}$ [11,12].

The capacity of kaolin activated by hydrochloric acid to adsorb magnesium ions is shown in table 1. The highest percentage of magnesium ions adsorbed by activated kaolin was achieved by that activated using 6 M HCL, i.e. 68.9%. The activation process can release organic matter impurities and other metal impurities, and thus it can have an impact on the ability of the adsorbent to bind magnesium ions [8]. Besides, activation also increases the Si / Al ratio, which is thought to have a role in increasing the number of absorbed magnesium ions. A higher percentage of SiO$_2$ can be used to reduce the permanent hardness of water [13]. Based on the gravimetric analysis, the content of Al$_2$O$_3$ and SiO$_2$ in the prepared kaolin and activated kaolin by 6 M HCL were 56.8% and 28.1 (KP), 56.4% and 30.9% (HA6), respectively.

| HCl concentration (M) | Initial concentration (ppm) | Final concentration (ppm) | Mg$^{2+}$ adsorbed (ppm) | % of adsorption |
|-----------------------|----------------------------|----------------------------|--------------------------|-----------------|
| 4                     | 9.98                       | 3.65                       | 6.33                     | 63.5            |
| 5                     | 9.98                       | 4.53                       | 5.45                     | 54.6            |
| 6                     | 9.98                       | 3.11                       | 6.88                     | 68.9            |
Figure 1. XRD pattern of natural kaolin and prepared kaolin
Figure 2. Infrared spectra of prepared kaolin (KP)
Figure 3 Infrared spectra of activated kaolin using 4 M HCl (HA4)
Figure 4. Infrared spectra of activated kaolin using 5 M HCl (HA5)
Figure 5. Infrared spectra of activated kaolin using 6 M HCl (HA6).
Table 2. Determination of Contact Time for Optimal Adsorption Mg$^{2+}$.

| Contact time (min) | Kaolin (KP) | Activated kaolin (HA6) |
|-------------------|-------------|------------------------|
| 30                | 15.0        | 55.6                   |
| 90                | 15.0        | 62.0                   |
| 150               | 25.5        | 68.9                   |
| 180               | 18.6        | 63.1                   |

4. Conclusions
Conditions for optimum adsorption of Mg$^{2+}$ ions by activated kaolin are as follows: HCl concentration for the activation procedure is 6 M and contact time between activated kaolin and Mg$^{2+}$ is 150 minutes. The concentration of Mg$^{2+}$ ions adsorbed by activated kaolin at its optimal conditions is 68.9%. Hydrochloric acid activated kaolin is a potential adsorbent that can be used to reduce total hardness in water.

5. References
[1] Rolence C 2014 Water Hardness Removal by Coconut Shell Activated Carbon Int. J. Sci. Technol. Soc. 2 97
[2] Lestari A Y D, Malik A, Sukirman, Ilmi M I and Sidiq M 2018 Removal of calcium and magnesium ions from hard water using modified Amorphophallus campanulatus skin as a low-cost adsorbent MATEC Web Conf. 154 4–7
[3] Ahn M K, Chilikala R, Han C and Thenepalli T 2018 Removal of hardness from water samples by a carbonation process with a closed pressure reactor Water (Switzerland)10 1–10
[4] Muyibi S A and Evison L M 1995 Moringa oleifera seeds for softening hard water Water Res.29 1099–104
[5] Varada V K 2018 Adsorption studies on water hardness removal by using moringa oleifera seed pod husk activated carbon as an adsorbent Int. J. Life Sci. 1–8
[6] Sepehr M N, Zarrabi M, Kazemian H, Amrane A, Yaghmaian K and Ghaffari H R 2013 Removal of hardness agents, calcium, and magnesium, by natural and alkaline modified pumice stones in single and binary systems Appl. Surf. Sci. 274 295–305
[7] Sasri R, Wahyuni N and Utomo K P 2017 Filtration treatment of processing Kapuas river’s water by coral sands/kaolinite/activated carbon AIP Conf. Proc. 1823
[8] Wahyuni N, Hs I, Arryanto Y, Zupriadi Y, Kimia J, Matematika F, Alam P, Kimia J, Matematika F, Alam P, Mada U G, Yani J A and Fax T 2008 Konsentrasi Larutan Asam Klorida 7 12–21
[9] Wahyuni N, Zissis G, and Mouloungui Z 2018 Prepublication: Photostability of B-Carotene/Modified Kaolinite Appl. Surf. Sci. 274 295–305
[10] Wahyuni N, Zissis G and Mouloungui Z 2018 Characterization of acid sites on modified kaolinite by FTIR spectra of pyridine adsorbed AIP Conf. Proc. 2026
[11] Saikia B J and Parthasarathy G 2010 Fourier Transform Infrared Spectroscopic Characterization of Kaolinite from Assam and Meghalaya, Northeastern India J. Mod. Phys.01 206–10
[12] Kumar S, Panda A K and Singh R K 2013 Preparation and characterization of acids and alkali treated kaolin clay Bull. Chem. React. Eng. Catal.8 61–9
[13] Aragaw T A and Ayalew A A 2019 Removal of water hardness using zeolite synthesized from Ethiopian kaolin by hydrothermal method Water Pract. Technol.14 145–59
[14] Mustapha S, Ndamitso M M, Abdulkareem A S, Tijani J O, Mohammed A K and Shuaib D T 2019 Potential of using kaolin as a natural adsorbent for the removal of pollutants from tannery wastewater Heliyon5 e02923