Adsorption Capacity of Ca\(^{2+}\) by Hydrochloric Acid Activated Kaolin

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Abstract. A high concentration of calcium ions in water is a problem as it can cause blockages in engine pipes. Adsorption is a relatively cheap and straightforward method that can be used to reduce the calcium ion content in water. Kaolin is a mineral that has a potential as an adsorbent and whose adsorption capacity can be increased by activation. This research studied the adsorption capacity of activated kaolin by hydrochloric acid against Ca\(^{2+}\) ions. Kaolin was chemically activated using 6 M HCl solution for 24 hours. The adsorption contact time in batches was varied with time variations of 30, 90, 150, and 180 minutes. The maximum adsorption capacity of activated kaolin to the Ca\(^{2+}\) was determined by varying the initial concentrations of water samples, namely 4, 7, 10, and 13 mg/L. The concentration of Ca\(^{2+}\) was determined by a titration method using ethylene diamine tetraacetate (EDTA). The results showed that the activation of kaolin with 6 M HCl at the optimum contact time of adsorption, namely 150 minutes, increased the percentage of adsorbed Ca ions to 2 times of that of natural kaolin, from 33.3% to 68.3%. Based on the Langmuir equation, the maximum adsorption capacity of calcium ions by activated kaolin HCl 6 M increased 1.7 times from natural kaolin to 0.346 mg/g.

1. Introduction

Water is universally used as a major resource in production in a wide range of industries. However, it sometimes contains impurities, such as microorganisms, sediments, dissolved salts, dissolved gases, suspended solids, odor, metal ions, etc. that can be dangerous or reduce its capacity to perform a certain function[1]. Among these impurities, the amount of magnesium and calcium contained in the water is our main concern as it affects water’s performance and functions in many ways. High magnesium and calcium contents in water can cause water hardness, which can also fracture boiler pipes in plantations such as those in the oil palm fruit industry[2].

Adsorption is a general, cheap and straightforward method to reduce hardness in water using adsorbents made from organic [3], [4] or inorganic raw material [5], [6]. Kaolin (Figure 1) is a white or slightly whitish inorganic material mainly composed by kaolinite minerals with low iron content [7]. Figure 2 shows kaolinite structure based on molecular simulation represented by Awad et al. [8]. In this study we used local kaolin as raw material for adsorbent in an attempt to further reduce the price of adsorbent.
Activation or modification is also needed to improve the properties and adsorption capacity of the adsorbent. Wahyuni et al. [2] have activated natural kaolin from the Capkala region in West Kalimantan and used it as an adsorbent to reduce magnesium content in water. The results showed that kaolin activated by 6 M HCl could adsorb 68.9% of Mg$^{2+}$ at the optimum contact time of 150 minutes. This article is a continuation of this previous research paper. Here, we will report another application of acid-activated kaolin as adsorbent to remove calcium from water.

2. Methodology

2.1. Equipment
The equipment used in this research included standard glassware, 120 mesh sieve, magnetic stirrer, centrifuge, and furnace. The materials used in this research were distilled water, Hydrochloric Acid (HCl), pH 10 buffer, EBT indicator, methyl red indicator, calcium sulphate ($\text{CaSO}_4\cdot2\text{H}_2\text{O}$), $\text{Na}_2\text{H}_2\text{EDTA}$, silver nitrate ($\text{AgNO}_3$). Natural kaolin sample taken from Capkala Sub-district, Bengkayang Regency, West Kalimantan.

2.2. Determination of optimum contact time for adsorption of Ca$^{2+}$ by activated kaolin
Kaolin activated with 6 M HCl was prepared by Wahyuni et al [2]. Four water samples, 25 mL each, containing 10 mg/L of Ca$^{2+}$, were prepared. One gram of 6M HCl activated kaolin was added to each of the water samples. The four mixtures were stirred for 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.

2.3. Determination of Ca$^{2+}$ concentration by EDTA titration
The level of Ca$^{2+}$ was determined by complex titration using 5x10^{-4} M EDTA. 50 mL of EDTA was poured into the burette. 10 mL of water sample was poured into Erlenmeyer. The edges of the container was rinsed with some distilled water. 1 mL of buffer solution pH 10 and 5−10 mg of EBT indicator was added to the hard water sample. It was then titrated with EDTA until the burgundy solution turn light blue. The volume ($V$) of EDTA used was noted, and the concentration ($M$) of the ion was determined using equation (1).

$$M_{\text{Ca}^{2+}} \times V_{\text{Ca}^{2+}} = M_{\text{EDTA}} \times V_{\text{EDTA}}$$

(1)

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

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

(2)
2.4. The maximum adsorption capacity of activated kaolin

The maximum adsorption capacity of activated kaolin to the Ca\(^{2+}\) was determined by varying the initial concentrations of water samples, namely 4, 7, 10, and 13 mg/L. The mixture was stirred for 150 minutes for optimum adsorption time with a stirring speed of 150 rpm at a constant temperature of 27\(^{\circ}\)C, and then centrifuged. The resulting supernatant was then titrated with EDTA. The final concentration data obtained from the measurement using EDTA was the concentration of calcium ions that were not adsorbed or the concentration of residual or final concentration or concentration at equilibrium \((C_{eq})\). The value of \(C_{eq}\) was used to calculate the adsorption capacity \((q_e)\) [7] according to equation 3 below:

\[
q_e = \frac{(C_0 - C_{eq})}{m} V \tag{3}
\]

where \(q_e\) is the adsorption capacity (mg/g), \(C_0\) is the initial concentration of Ca\(^{2+}\) (mg/L); \(C_{eq}\) is the equilibrium concentration of Ca\(^{2+}\) (mg/L); \(V\) is the volume of solution (L), and \(m\) is the mass of adsorbent (g).

The data obtained were then entered into a graph plot according to the Langmuir adsorption isotherm equation (equation 4) and the Freundlich isotherm equation (equation 5) [8]. Hence by plotting \(C_{eq}/q_e\) against \(C_{eq}\) it is possible to obtain the value of the Langmuir constant \(K_L\) and \(q\); by plotting \(\log (q_e)\) against \(\log (C_e)\), the Freundlich constant of \(K_F\) and \(n\) can be determined.

\[
\frac{C_{eq}}{q_e} = \frac{1}{q_mK_L} + \frac{C_{eq}}{q_m} \tag{4}
\]

\[
\log q_e = \log K_F + \frac{1}{n} \log C_{eq} \tag{5}
\]

where \(q_m\) is the adsorption capacity maximum (mg/g), \(K_L\) is Langmuir adsorption equilibrium constant, \(K_F\) is the adsorption equilibrium constant Freundlich.

3. Result and discussions

The contact time of the adsorbent and adsorbate in the adsorption is related to the time given to the sample solution containing calcium ions to interact with the kaolin surface. In general, the longer the adsorption contact time, the more magnesium ion is absorbed (Table 1). The highest percentages of Ca\(^{2+}\) for prepared kaolin and kaolin activated by 6 M HCl were achieved at the stirring time of 150 min, namely 33.3% and 68.3%, respectively. The activation process can increase the ability to absorb calcium ions more than two times that of kaolin. Increasing stirring time to 180 minutes, however, causes the number of calcium ions absorbed to decrease due to the interaction of calcium ions with the kaolin surface through weak interactions and due to repulsive forces between the adsorbent present in solid and bulk phases[9][10].

Table 1. Determination of Contact Time for Optimal Adsorption Ca\(^{2+}\)

| Contact time (min) | % adsorption |
|-------------------|--------------|
|                   | Kaolin       | Activated kaolin |
| 30                | 29.0         | 52.7             |
| 90                | 31.5         | 59.2             |
| 150               | 33.3         | 68.3             |
| 180               | 30.9         | 61.5             |

The adsorption capacity of kaolin and activated kaolin with various initial concentrations of Ca\(^{2+}\) is presented in Figure 3. The isotherm for the adsorption of calcium ions on kaolin and activated kaolin represents the formation of a monolayer [10]. Data obtained from these studies have been tested with the Langmuir and Freundlich linearized equations. These results are summarized in Table 2.
Figure 3. Adsorption isotherms for Ca\textsuperscript{2+} on kaolin and activated kaolin at ions concentrations from 4 to 13 mg/L, an adsorbent dose of 40 g/L, an agitation speed of 150 rpm, a temperature of 27°C, and a contact time of 150 min.

The adsorption parameters in Table 2 show that kaolin and activated kaolin fit the Langmuir isotherm equation by comparing the R\textsuperscript{2}[6]. The q\textsubscript{m} values obtained for kaolin and activated kaolin is 0.180 mg/g and 0.346 mg/g, respectively. Activation of kaolin with HCl can increase its adsorption capacity to the Ca\textsuperscript{2+} due to the release of a number of impurities on the surface of kaolin[2].

| Adsorbent                  | Langmuir Model | Freundlich Model |
|----------------------------|----------------|------------------|
|                            | q\textsubscript{m} | K\textsubscript{L} | b    | R\textsuperscript{2} | K\textsubscript{F} | n   | R\textsuperscript{2} |
| Kaolin                     | 0.180           | 0.334            | 16.632 | 0.9719   | 3.591         | 2.226 | 0.9261             |
| Acid activated kaolin      | 0.346           | 0.423            | 6.816  | 0.9722   | 2.663         | 1.798  | 0.9467              |

4. Conclusions
Activation of kaolin using 6 M hydrochloric acid enhances the adsorption capacity of calcium ions. Base on the Langmuir model isotherm adsorption (adsorbent dose of 40 g/L, an agitation speed of 150 rpm, a temperature of 27°C, and a contact time of 150 min), each gram of activated kaolin can adsorb 0.346 mg of Ca\textsuperscript{2+}.

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