Nitrate (NO$^{3-}$) removal from wastewater by adsorption using modified kaolin

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Abstract. This study aims to determine the effect of the initial concentration and pH conditions of the nitrate solution on the removal of nitrate in water, which was carried out in batch. The raw material used is kaolin, which is firstly mashed and sieved with a size of 120 mesh, then activated by immersing it in a 0.5 M HCl solution for 24 hours, followed by modification of the surfactant by immersion in a 0.5 M cetyltrimethylammonium bromide (CTABr) solution for 120 minutes, and accompanied by stirring using a magnetic stirrer at a speed of 150 rpm. Before being used as an adsorbent, kaolin CTABr-modified was analyzed using a scanning electron microscope (SEM) to determine the surface morphology of the material. Batch adsorption test was carried out by adding 1 gram of kaolin CTABr-modified to 100 mL of a solution containing nitrate with various concentrations of 10; 20; 30 mg/L and the pH of the solution is 5; 7; 8. The experiment was carried out for 180 minutes, where every 30 minutes the solution was sampled and analyzed for nitrate content using a spectrophotometer UV-Vis. The conclusion of this study is that kaolin CTABr-modified can be used as an adsorbent, where the SEM test results show that the surface morphology of kaolin CTABr-modified is denser and more compact than the prepared kaolin and kaolin HCl-activated. Based on the experimental results according to the Langmuir isotherm equation, the constant value was 0.78. The mechanism of nitrate removal includes ion exchange, hydrogen bonding, and intermolecular interactions. The maximum adsorption capacity was 0.72 mg/g, found under acidic conditions (pH 5) and with a contact time of 180 minutes.

1. Introduction

Water is very important for living things, and thus the cleanliness of the water is maintained from various pollutants. However, in reality, water pollution is one of the main problems in life. Water containing high concentrations of biogenic causes eutrophication. Over the last few years, eutrophication has become a serious threat because it triggers the growth of algae and cyanobacteria, thereby reducing water quality. This results in limited biodiversity, lack of dissolved oxygen, reduced fish populations, and complicates the water purification process [1].

Nitrate is the main form of nitrogen which is very soluble in water and is stable. Excess nitrate causes water quality to decrease, lower dissolved oxygen and causes bad smell and taste [2]. In Hendrawati, Government Regulation no. 81 (2001) has set the maximum permissible level for nitrate, which is 20 mg/L. One of the water purification methods that can be used is the adsorption method. This method is widely used because it is safe, the equipment used is simple and inexpensive, easy to work with, can be recycled, and is efficient and economical [3]. Absorbent materials or adsorbents commonly used in the adsorption process are carbon, metal oxides, minerals, and waste materials [4].

Kaolin is a mineral found in sedimentary rocks [5] which has porous material, is chemically and mechanically stable, and has a high cation exchange capacity [6], and thus it can naturally carry out ion exchange processes that come from outside with the help of water. Negatively charged ions come from
the relatively small ratio of silica and alumina (Si/Al), so that the surface of kaolin gives rise to oxygen and hydroxyl groups. At the same time, the positively charged ions that exist due to modifications and the hydrophobic nature of kaolin can increase the efficiency of kaolin in adsorbing other anions and cations [7]. The minerals found in kaolin are kaolinite, nacrite, discrete, and halloysite, with kaolinite as the main mineral. Kaolin also has a hydrous composition of aluminum silicate \((\text{Al}_2\text{SiO}_5)\) [8].

One of the efforts to increase the adsorption of kaolin as an adsorbent can be done by modifying the surfactant, which aims to bind the surfactant to the hydrophobic surface of kaolin. Adsorption of surfactants on the surface of kaolin involves the interaction of molecules with the surface and between molecules. The material formed can determine the surface properties of the bonded kaolin and will adsorb more anions [7].

2. Materials and methods
The equipment used includes a 120 mesh sieve, glassware from the laboratory, shaker, pH meter, digital oven, analytical balance, hot plate, magnetic stirrer, and UV-Vis spectrometer. The materials used were kaolin from Belitung, hydrochloric acid, CTABr surfactant, distilled water, and filter paper.

2.1 Kaolin activation
Activation was carried out with 100 grams of 120 mesh kaolin material into 300 mL of 0.5 M HCl solution and stirred using a magnetic stirrer at 150 rpm for 30 minutes, then set aside for 24 hours. Washing was carried out with distilled water until the pH was neutral. Drying was carried out using an oven at a temperature of 105°C for 5 hours.

2.2 Kaolin modification
Modifications were made with 100 grams of activated kaolin material into 300 mL of 0.5 M CTABr solution and stirred using a magnetic stirrer at 150 rpm for 2 hours, then set aside for 24 hours. Washing was carried out with distilled water until the pH was neutral. Drying was carried out using an oven at a temperature of 105°C for 5 hours. Analysis of activated kaolin was performed using an Electron Microscope (SEM) to determine the shape or morphology of kaolin.

2.3 Adsorption
2.3.1 Effect of pH and Initial Concentration
Adsorption was carried out by adding 1 gram of adsorbent into Erlenmeyer, then adding 100 mL of adsorbate solution with a concentration of 10; 20; 30 mg/L at each pH (5; 7; 8), stirred for 3 hours, then filtered and filtrated for analysis using a UV-Vis spectrometer.

2.3.2 Contact time
Adsorption was carried out by adding 1 gram of adsorbent into Erlenmeyer, then adding 100 mL of adsorbate solution with a concentration of 10; 20; 30 mg/L at optimum pH, rotated for 3 hours while sampling with 30 time intervals; 60; 90; 120; 150; 180 minutes, then filtered and filtrated for analysis using a UV-Vis spectrometer.

3. Result and discussion
3.1 Characterization of kaolin
The SEM images of the adsorbent with 15,000 magnification are shown in figure 1. Kaolin with the activation + modification indicated more pores on surface particles. This is due to the process of releasing water and also metal oxidation [9].
3.1.1 Effect of pH

Figure 1. a) SEM micrograph of kaolin b) kaolin modified CTABr.

Figure 2. Effect of pH on nitrate adsorption.

The results of the analysis of the pH conditions of the nitrate solution against the adsorbed nitrate in figure 2 show that the greater the pH of the solution is, the lower the nitrate adsorbed is. This happens because the amount of OH\(^-\) increases along with the increase in the pH of the solution. Thus, in the adsorption process there is a competition between nitrate and OH\(^-\) on the surface of the adsorbent, which causes the adsorption capacity to decrease [1]. At a nitrate solution concentration of 10 mg/L, the adsorbed nitrate decreased as the pH of the nitrate solution increased, each of which was 8.40; 7.38; 7.31 mg. At a nitrate solution concentration of 20 mg/L; it is 8.08; 7.59; 6.81 mg. At the concentration of nitrate solution 30 mg/L; it is 7.40; 7.23; 7.19 mg.

This is in accordance with research (Ouardi et al., 2015) [10] which has conducted research using clay to adsorb nitrate. The results of this study indicate that the percentage of nitrate decreases from a solution pH of 2 to 10. The effect of variations in the pH of the solution on the adsorption process can be explained by the electrostatic interaction between the adsorbent and the adsorbate, which results in
high adsorption capacity at low pH solutions. Meanwhile, at the pH of the alkaline solution, the decreased nitrate absorption can be attributed to OH\(^-\) competing with pollutants.

### 3.1.2 Effect of contact time

![Figure 3. Effect of contact time on nitrate adsorption.](image)

The results in figure 3 above show that the adsorption capacity increased along with increasing contact time. However, at the 180th minute, the adsorbent became too saturated to absorb. This was due to the longer contact time is, the more adsorbent particles would collide with the adsorbate solution until it reached the saturation point [11]. The initial concentration is also a very decisive factor in the adsorption process. However, if the adsorbent is saturated, the concentration would have no effect [12].

This is in accordance with research [9] who has conducted research using CTABr modified zeolite to absorb phosphate. The results of the study showed that the amount of phosphate adsorbed increased significantly along with increasing contact time until it reached the optimum time. After reaching the optimum time and equilibrium, the amount of phosphate adsorbed becomes constant.

### 3.1.3 Batch isotherms

![Figure 4 a) Isotherm Curve in Langmuir and b) Freundlich Models.](image)

From figure 4(a), it can be seen that the Langmuir adsorption equation test is proven by a good linearization graph and has a coefficient of determination R\(^2\) 0.9. The adsorption properties can be either unfavorable (RL > 1), linear (RL = 1), favorable (0<RL <1) or non-reversible ((RL = 0) [13].
Table 1. Results of adsorption isotherm analysis in Langmuir and Freundlich Models.

| Model  | $R^2$ | $Q_{\text{max}}$ (mg/g) | $K_L$ (mg/g)$^{1}$ | n | $K_F$ (mg/g)$^{1}$ |
|--------|-------|-------------------------|---------------------|---|------------------|
| Langmuir | 0.990 | 0.813 | 0.784 | - | 0.004 |
| Freundlich | 0.975 | - | - | 0.073 | 0.610 |

From table 1 above, it is clear that $R^2$ that is close to 1 is the Langmuir method, namely $R^2 = 0.99$.

4. Conclusion
Based on the research, it can be concluded that the optimum pH at nitrate concentration of 10; 20; 30 mg/L is 5, which is 7.40374 respectively; 8.088016; 8.40076 mg/L. And the optimum contact time at a nitrate concentration of 10; 20; 30 mg/L is the 180th minute which is 7.23; 7.59; 7.31 mg/L.

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