Optimization of Kaolin adsorbent to reduction iron metal ion using ultrasonic technology

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Abstract. This study was to adsorb of metal ion in water solution by modifying kaolin with anionic surfactant and ultrasonic irradiated. The purpose of this study was to optimize the absorption of metals more specific in absorbing Fe metals in water using modified kaolin with anionic surfactants and ultrasonic irradiated. The adsorption process was carried out using a surfactant modified kaolin modification and without surfactant modification with irradiation time variations of 5, 10, 15, 30, 50 and 80 min at 55 °C. Samples were analysed using Atomic Absorption Spectrophotometers (AAS), while their characteristics used Fourier Transform Infrared Spectroscopy (FTIR) and Scanning Electron Microscope (SEM). The results showed that the maximum removal efficiency of kaolin modification occurs faster than that of kaolin without modification. The maximum allowance for kaolin modified removal efficiency reached 72.81% at 30 minutes irradiation time, while for kaolin without modification the removal efficiency was 65.1% at 30 minutes irradiation time.

Keywords. Adsorption; modification kaolin; anionic surfactant; ultrasonic

1. Introduction
The presence of metals in water is often a problem for human health. Especially heavy metals that have difficult to degrade, toxic, and accumulative properties [1]. For removing metal, adsorption has been considered one of the most efficient and economical processes for the removal of pollutants from water, which stands out due to its low cost and operational limits [2]. One of the adsorbents that is often used in the adsorption process of metal ions is kaolin.

Kaolin is a 1:1 layer sheet of structured hydrated aluminum silicate with a very fine particle size with one silicon oxygen tetrahedral layer (SiO₄) and one alumina octahedral layer [3]. Kaolin contains granules that are very smooth, soft and less plastic when mixed with water. The minerals include kaolin group is kaolinat, nakrit, and pplyosite, with its main mineral kaolinat, often oxides such as Fe₂O₃, TiO₂, CaO, MgO, K₂O and Na₂O contained in the kaolin as impurities. The composition of pure kaolin is SiO₂ 46.54% Al₂O₃ 39.5% and H₂O 13.96% [4].

The most important property possessed by kaolin is the ability to perform low substitution, the charge on kaolin sheets is very minimal, and inert. These properties are very useful in applications in the industrial world. In the past, kaolin was used more widely as raw material for the manufacture of glass fibers or organo-clays and as a catalyst. However, the ability of kaolin as adsorbent is still very...
low compared to zeolite, activated charcoal and bentonite [5], so there needs to be an effort to increase kaolin absorption, one of which is by modifying using organic compounds such as surfactants.

Surfactants consist of two parts, namely the head and tail. The head is positively charged and hydrophilic, while the tail is not charged and hydrophobic [6]. Modification of kaolin using surfactants to increase its absorption has been carried out by several previous researchers. Modification of kaolin using anionic surfactants cationic surfactants [7] and ampholytic surfactants [8].

Increasing absorption ability of the adsorbent can be improved with the aid of ultrasonic technology. Ultrasonic technology has an advantage due to low operational costs and does not have a negative impact on the environment. According to Santi [9], the capacity of the adsorbent that has been activated and irradiated by ultrasonic waves has increased up to twice, because ultrasonic irradiation can specifically increase the surface area of the adsorbent.

The focus of this research is to study and learn about the optimization of the absorption of kaolin as an adsorbent by means of modification of kaolin with an anionic surfactant is alkyl benzene sulfonate (ABS) and irradiation ultrasonic in absorbing metal Fe in the water.

2. Methodology
The study was carried out using kaolin which has been mashed with a size of 100 mesh measurement is based on previous research where the best conditions are at that size (11). After that kaolin was carried out for 2 hours of physical activation with a temperature of 105 °C and chemical activation using 1 N HCl for 1 hour. Kaolin is then washed to pH 7, dried and stored in a desiccator. Activated Kaolin is modified with anionic surfactants with a surfactant use ratio of 45% of the total weight of 200 gr. The kaolin-surfactant mixture is stirred and allowed to stand for 2 hours. The kaolin precipitate is filtered and washed to pH 7, then dried and stored in a desiccator.

In the adsorption process, 5 grams of organokaolin and 100 ml of waste water artificially with a concentration of 100 mg/l were put into a 250 mL erlenmeyer, then covered with aluminum foil to avoid contact with outside air. Samples were contacted at 50 °C with ultrasonic irradiation times of 5, 15, 30, 50, 80 minutes. The samples were analyzed using Atomic Absorption Spectrophotometers (AAS), while the characteristics used were Fourier Transform Infrared Spectroscopy (FTIR) and Scanning Electron Microscope (SEM).

3. Results and discussions
Before modification with surfactant, performance adsorption test for kaolin is carried out on conditions before and after the activation process. Data from the measurement of the efficiency of decreasing Fe metal content in water can be seen in figure 1, it can be seen that the rate of Fe metal reduction efficiency is increased before the activation process is carried out and after activation.

![Kaolin structure](image)

This show that increased absorption due to the opening of kaolin pores after activation by using 1 NHCl for 1 hour. The condition of the new adsorbent and its pores are still many cavities that are able to capture Fe metal ions in water, thus increasing the performance of kaolin adsorbents in reducing Fe
metal ions in water. The activation process of kaolin using acid will produce kaolin which has a larger active site and greater surface acidity, so that adsorbents will be produced with higher adsorption capability than before activation while heating by calcination on clay will cause an increase in size. Pores with better crystal form. Heating with high temperature and long time, clay tends to recrystallize so as to produce better crystals with larger pores [9].

![Figure 2](image_url)

**Figure 2.** Comparison of Fe metal removal efficiency on adsorbents before and after modification.

From figure 2, the maximum removal of ferrous metal (Fe) for kaolin without modification occurs at 30 minutes irradiation time with an allowance of 61.28%. However, at 50 and 80 minutes irradiation time the removal efficiency decreased. Removal efficiency at 50 minutes irradiation time was 61.23% and at 80 minutes irradiation time was 60.47%. This is because artificial waste in Fe metal has been absorbed as a whole in Kaolin, so the pores are saturated and unable to absorb maximally Fe in water. For kaolin modification, the maximum removal of Fe metal anionic surfactant occurred at 30 minutes irradiation time with an allowance of 72.81%. The surfactant modified kaolin removal value is greater than unmodified kaolin, this is because the surfactant attaches to the kaolin surface, thus forming interactions between molecules on kaolin and surfactants. Interaction causes modification of kaolin adsorbent to absorb more Fe metal while in the research conducted by Putra [10], that is, the adsorption using modified kaolin anionic surfactant can get maximum Pb metal removal at 90 minutes at 78%. The time difference for maximum removal in absorbing metal is because according to Santi [9], the use of ultrasonic technology in the adsorption process can increase the surface area and accelerate the movement of molecules so that the adsorption process occurs faster.

In figure 3, it is an FTIR analysis that aims to look at the characteristics of adsorbents. The results of the IR spectra of kaolin modification of anionic surfactant before adsorption showed that there was a vibration change in O-H deformation (840.96 cm⁻¹) to Si-O strain at wavelengths 1049.13 cm⁻¹ and 1126.4 cm⁻¹. In the anionic surfactant spectra after Fe metal adsorption, the vibration of Si-O deformation (699.23 cm⁻¹) changes to a vibration of O-H deformation with a wavelength of 894.58 cm⁻¹ and 911.4 cm⁻¹. The increase in spectrum area at wave number 1113.94 cm⁻¹ indicates that the appearance of Si-O vibration is strain. This spectrum change occurs due to the absorption of Fe metal on kaolin which is modified by anionic surfactant. The last peak in both spectra shows the octahedral O-H vibration with a value of 3644.5 cm⁻¹.

Figure 4 shows SEM of for surfactant kaolin modification. From figure 4, SEM observation data on modified kaolin material with surfactant before Fe metal adsorption process shows that the organo-kaolin surface still has many large pores and empty cavities (figure 4a), Whereas the surfactant modification of kaolin after Fe metal adsorption process (figure 4b) shows the cavities that have been filled and coincide and have smaller pores. This is due to the absorption of Fe and Mg metals so that the cavities and pores that form are reduced.
After adsorptions

Before Adsorptions

Wave Number (cm⁻¹)

Absorbance (%)

Figure 3. Changes in the adsorbent structure of kaolin modification before and after adsorption.

Figure 4. SEM test results for surfactant kaolin modification before (a) and after (b) absorption in artificial waste.

4. Conclusion
From the results of this study some conclusions can be drawn: (1) kaolin adsorbent has been shown to reduce iron content in water, kaolin is able to improve its performance with the initial modification conditions of 61.28% at 30 minutes to 72.8% at the time 30 minutes after modification with anionic surfactant. (2) The use of ultrasonic irradiation affects the removal of Fe metal, where the adsorption time to achieve maximum absorption occurs faster than those without ultrasonic irradiation.
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