Comparison Between Surfactant and Chitosan Organo-kaolin Adsorbents to Remove Metal and Organic Compound in Peat Water

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Abstract: This study compares adsorben ts to remove metal and organic compounds in peat water solution. The kaolin adsorbent was modified with organic compounds (organo-kaolin). Modifications used two types of organic compound namely surfactant and chitosan with the organic compound concentration used of 15%, 39% and 45% respectively from the total weight of 200 grams adsorbent. The contact time used was 30 minutes with stirring speed of 90 rpm. The concentration of metal ion Fe and organic compound was analyzed by Atomic Absorption Spectrometer (AAS) (Shimadzu UV-1800) and Total Organic Carbon (TOC), the determination of the characteristics for wavelengths before and after treatment used Spectrophotometer Fourier Transform Infra-Red (FTIR) IR Prestige-2, while organo-kaolin surface morphology used SEM. The results of the study show that organo-kaolin surfactant and chitosan successfully reduces Fe metal ion in water up to 91.8% and 88.2% of the initial concentration of 2.07 mg/L from peat water. Both organo-kaolin modification (surfactant and chitosan) ability to remove organic compound was 46.7% and 35.7%. The results of FTIR spectra testing and SEM test also show differences before and after the absorption of the metal ion Fe and organic compounds.

1. Introduction
Kaolin is one of natural adsorbents that is often to be used for lead, zinc and cadmium by modifying kaolin using organic materials such as polyphosphate and surfactants (Amer et.al, 2010). Kaolin is an inorganic polymer contains minerals as an inorganic ion exchanger, so that the outside ion exchange process with the help of water can be performed naturally. The negatively charged ion comes from relatively small ratio of silica and alumina (Si/Al), so that the kaolin surface raises oxygen and hydroxyl groups that is resulting in the appearance of negatively charged points. This charge has the potential to bind cations that can be exchanged by other cations and causing ion exchange. The positive charge due to modification and hydrophobicity in kaolin can improve kaolin efficiency in adsorbing other anions and cations and as an adsorbent of non-polar molecules. Using this reference then the modified kaolin was used in the water treatment in this research.

Many people have conducted the research on the absorption increase of adsorbents using organic compounds to increase the adsorbent performance. Zeolite modification uses cationic surfactant to absorb bicarbonate ion, where the research result on positively charged surfaces can be used as ion exchanger, so that it can reduce bicarbonate. [1]. Kaolin has been widely used as adsorbent for example is for lead, zinc and cadmium by modifying kaolin and polyphosphate [2], Absorption in Gas impurity [3], as well as the Modification of mineral surface by surfactant and zeolite-A [4] The ability of cationic surfactant in conducting high absorption especially in the ion exchanger of chromate [5], sulfate,
phosphate [6], and arsenic [4]. In addition, there is kaolin modification by anionic type surfactants in lowering metals in the water [7].

It is known in previous studies that kaolin modification by surfactant can increase metal absorption in water up to 2 (two) times higher than the adsorbent before being modified by kaolin [8]. Surfactants consist of several types namely anionic and cationic surfactants. Cationic surfactant is a long-chain organic compound consisting of head and tail. The head is positively charged and hydrophilic while the tail is not charged and hydrophobic. Surfactant can form micelles, monolayers, or bilayer on the modified kaolin surface depends on the used surfactant concentration. Moreover, research on the kaolin absorption increase has been conducted by modifying chitosan in absorbing organic compound and metal [9]. Chitosan is polycationic and hydrophilic natural biopolymer compound, in which the amino groups in chitosan are easier to be cation in acidic solution so that they can adsorb anion with electrostatic attraction.

Kaolin modification in this research was conducted with organic compound (organo-kaolin) using surfactant and chitosan with the same object in a peat water solution contains Fe metal. This research aims to see the effect of organic compound modification on the kaolin absorption in the water contains Fe metal. In addition, this process was conducted to compare the adsorbent performance that was modified by surfactant and chitosan compounds.

2. Research Method
The sample used was peat water from Geuredong Pase Village, North Aceh Regency. The sample's color and metal content that were in sample and organic compound level was tested for the initial performance. The material used in this research was amphoteric CH type surfactant CH$_{11}$H$_{23}$CONH(CH$_2$)$_3$N$^+$ (CH$_3$)$_2$CH$_3$COO$^-$ (Zwitterionic Surfactant), which positively and negatively charged. Commercial standard chitosan was used as an adsorbent for the kaolin activating modification process. The Aquades KOH and HNO$_3$ was used in activating modification process using base and acid to remove metal content and organic compound contained in kaolin to increase the absorption. All used chemicals were commercially obtained from Waco Ltd and Aldrich. Modification was performed by mixing the kaolin and surfactant (organo-kaolin). The organo-kaolin's total weight was 200 grams, the modification was performed by comparing the percentage between kaolin and organic compounds (surfactant and chitosan), which was 0%; 15%; 39%; and 45% of surfactants from organo-kaolin's total weight. Shaker incubator was used for the absorption process with a speed of 90 rpm, and 30 minutes contact time. Precipitation was conducted for 4 hours before being stored in a desiccator before it was used. Analysis was conducted for each sample to find the concentration by using AAS, the organic content used TOC, the surface morphology used SEM, and the wavelength characteristic used FTIR.

3. Results and Discussion

3.1. Organo-kaolin Comparison in Absorbing Loam Fe (II)
The use of peat water as water source by the public has an effect on health related to the peat water containing humic acid, Fe, Mn and organic compounds that exceed the threshold of clean water standard. Therefore, the modified kaolin adsorbent with organic compounds was used to reduce Fe and organic compounds level in peat water. The removal of Fe metal and organic compounds by using modified kaolin adsorbent with amphoteric surfactant indicates the changing in Fe and organic compounds concentration in peat water after the absorption process. To determine the initial conditions of peat water, a performance test of peat water comes from Geuredong Pase Village, North Aceh Regency was conducted. The result of peat water performance test can be seen in Table 1. This initial condition serves as a reference point in conducting research by looking how far the kaolin adsorbent can reduce Fe level in peat water.
Table 1. The initial condition of peat water as sample

| No | Peat water composition | Initial concentration (ppm) |
|----|------------------------|-----------------------------|
| 1  | Metal Fe               | 2.07                        |
| 2  | Mn Metal               | 1.007                       |
| 3  | Organic Compound      | 20.32                       |

Figure 1 shows the efficiency of Fe metal removal in peat water, and the increase between non-activation, activation and modification. This process proves that the addition of chitosan can improve the adsorbent performance. The use of NaOH solution in organo-kaolin aims to harden the organo-kaolin so that chitosan repolymerization occurs and the addition of methanol will also help organo-kaolin compaction. In addition, the iron metal ions in the peat water also has decreased significantly. This occurs due to the anionic surfactant on the adsorbent surface resulting in molecular interaction with intermolecular surface that affects the adsorbent speed in conducting the movement. These interactions can affect surfactant material, and the condition will last until equilibrium condition occurs (4). The performance improvement is also caused by the negatively charged surfactant tail, so that it can capture the positively charged metal ion, which in this case is Fe ion in peat water. However, when the modified organo-kaolin, surfactant and chitosan are compared, then the obtained results are slightly better by using organo-kaolin surfactant. It is caused by surfactant molecules that have polar (hydrophilic) parts containing hydroxyl group and appear as surfactant heads that are negatively charged, so that they can bind Fe metal that has a positive group. Furthermore, organo-kaolin chitosan will cover the kaolin active cluster by chitosan so that the most active cluster is chitosan. The more the chitosan, the higher the absorption percentage, as the number of chitosan active cluster increases and competes with chitosan active cluster that plays a role in binding Fe metal ions. As a result, the chitosan active cluster can adsorb more than the blocked active kaolin cluster and the absorption percentage decreases.

![Figure 1. Efficiency of Fe (II) metal ion concentration decrease in peat water](image-url)
a. Organic Compound Decrease in Peat Water

Organic compounds found in peat water were 20.32 mg/L, measured using organic content devices namely Total Organic Carbon (TOC). From the absorption result using modified kaolin adsorbent with surfactant and chitosan, the results are depicted in Figure 2.

![Figure 2. Organic Compound Decrease in Peat Water](image)

The Figure 2 also shows the ability of modified kaolin adsorbent with chitosan that is only able to remove the organic compounds up to 35.5%. In the organic compound removal, organo-kaolin is not very efficient because the chitosan content contains organic compounds so the ability of modified kaolin with surfactant is more efficient in reducing organic compounds. This state occurs because the organo-kaolin active cluster has been covered by samples in the form of organic compounds (Putra, 2016). In other hand, the surfactants that cover a part of kaolin adsorbent surface form a multilayer, which allow the absorption of organic ions in peat water. As shown in Figure 2, the process of organic compound removal is affected by organic compounds modified by kaolin, where the higher the dose of organic compounds, the higher the organic compound removal. This occurs because organic compounds containing inside the peat water have been absorbed as a whole in organo-kaolin pores, and the organic compound is capable to bind the organic compounds with different ions. This fact indicates that the ability of organo-kaolin that has negative group is more efficient in absorbing organic compounds due to the dispersion force that occurs because the presence of two clusters in organic compounds.

b. Characteristic Test using Fourier Transform Infrared

TIR analysis in this research aims to view the adsorbent characteristics. Figure 3 is the result of kaolin IR spectra of organo-kaolin activation with surfactant and chitosan organo-kaolin. Changes in the Si-O-Al structure of non-activated kaolin stretches are proven at the loss of vibrational region of OH and Si-O deformation, which is in wave numbers of 754.2 cm\(^{-1}\) and 884.4 cm\(^{-1}\) and the increase in spectrum peak area in the wave numbers of 913.33 cm\(^{-1}\). These changes occur due to the different metals and organic compounds absorbed by each adsorbent. Significant changes occur in the surfactant organo-kaolin, and this process indicates that surfactant is greatly affecting kaolin's wavelength. In the kaolin peak activation of 912.37 cm\(^{-1}\), it indicates the emergence of O-H deformation vibration. It is supported by
the loss of peak in the wave numbers of 1007.85 and 1042.57 cm\(^{-1}\), which is the vibration region of Si-O strain and the spectrum peak area increase in the numbers of 1112.97 cm\(^{-1}\). Vibration differences in both spectra occur due to kaolin that is activated using HNO\(_3\) and KOH so the vibration changes. However, the last peak of two spectra indicates the same vibration, namely octahedral O-H with a wavelength of 3694.81 cm\(^{-1}\).

![Figure 3. Characteristics of activated kaolin, surfactant kaolin and chitosan kaolin](image)

Organo-kaolin vibration changes also occur in the organo-kaolin modified from surfactants and chitosan. It can be seen from the changes in IR spectrum in the vibration region of Si-O deformation on the wavelength of 797.6 cm\(^{-1}\) that becomes the vibration region of Si-O strain and the increase in the spectrum peak area at 1114.9 cm\(^{-1}\) wave numbers. Organo-kaolin faces change in Si-O deformation vibration that becomes O-H deformation vibration in 910.44 cm\(^{-1}\) wave number. This spectrum change occurs due to the absorption process of Fe metal in organo-kaolin.

4. conclusion

As a conclusion, the use of organic compounds of chitosan and surfactant improves the performance of kaolin adsorbent in absorbing Fe metal and organic compounds in peat water. Moreover, ability of surfactant Organo-kaolin absorption is better when compared to organo-kaolin absorption using chitosan. The surfactant and chitosan compounds affect the spectra change in kaolin as well as the presence of Fe and organic metal compounds and they also form their own characteristics. As a result, each change according to the presence of each compound can be identified.
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