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# Adsorption of Manganese (MnII) from aqueous solutions by using modified Kaoline-surfactan as adsorbent

**A Putra[1], B Arifin[2], Marwan[3], Suhendrayatna[4], Syafruddin[5]**
[1,5]Department of Chemical Engineering, Lhokseumawe Polytechnic State
Jalan Medan Banda Aceh Km 280 Lhokseumawe, Indonesia
[2,3,4]Department of Chemical Engineering, Syiah Kuala University Darussalam Banda Aceh, Indonesia

[1]putraalf@yahoo.com

**Abstract.** The Study about, kaoline adsorbent modified with a surfactant (organokaoline) to absorb metal ions Mn (II) in aqueous solution. Modifications were used the 3 (three) types of surfactants, anionic, cationic and ampholitic with surfactant concentration were used 45%, 60% and 75% respectively of the total weight of 300 grams adsorbent. The contact time of variation between 10-90 minutes with stirring speed of 50, 70 and 90 rpm respectively. Mn metal concentration analysis done by Atomic Absorption Spectrometer (AAS) (Shimadzu UV-1800) whereas the determinations of the characteristics for wavelengths before and after treatment are used Spectrophotometer Fourier Transform Infra Red (FTIR) IR Prestige-2, and organokaoline surface morphology using SEM. The results of the study organokaoline successfully reduce Mn metal ions in water till 95% of the initial concentration of 10 mg/L. Testing FTIR spectra showed differences as well as the SEM test looks morphology before and after the absorption of the metal ion Mn.

## 1. Introduction

The metals ion present in the aquatic system through the rocks and soil, and of various human activities that could potentially produce the metal as waste [1], so that the water resources polluted by metal ions. In addition, many water companies take raw materials from groundwater and river water suspected to have been contaminated to be processed into clean water and drinking water. One of the ground water problem is the existence of heavy metals from [8] various industries such as the metal industry, manufacturing, electroplating, mineral and industrial battery. The existence of such metals in a number of large concentrations can cause health problems and damage to ecosystems [2]. Good water quality is essential to the lives of living beings, whereas a clean and healthy water is needed by humans for health and daily usage requirements. While the metal ions such as cadmium, chromium, zinc, manganese and iron are often encountered in water [3]. One of the dangerous heavy metals contained in the ground water is Manganese (Mn) in the form of ions.

The negative effect of human health is manganese can affect the respiratory tract and brain, in addition to the cause Parkinson, lung embolism, and bronchitis, for a long time due to the accumulation in the body causing impotence. Based on the United States Environmental Protection Agency (USEPA) [19]. The concentration of manganese in the water allowed a maximum of 0.05 mg / L and safe for consumption. The existence of manganese in the water due to the disposal of industrial waste will have an impact on the environmental damage therefore the need for proper processing before being discharged into the environment. Reduced levels of manganese in the water can be done by physical and chemical means such as adsorption, chemical precipitation, ion exchange, membrane infiltration and

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extraction solvent. Drop off all of the existing methods are not efficient because it is too expensive and generate new waste such as chemical use in detecting and eliminating levels of Mn, especially at low concentrations in living memory [7]. One alternative water treatment cost is to use natural materials as adsorbents like caolin use.

Kaolin itself has been widely used as adsorbent such as adsorption of lead, zinc and cadmium by modifying kaolin and polyphosphate [4], the impurity Gas Absorption [5], kaolin to absorb arsenic [6] and Modification Polyphosphate with kaolin to absorb ions Pb (Son, 2015). The process adsorbs itself very effective in absorbing metal Mn, using natural materials which have been modified such as the absorption of Pb in water solutions using kaolin, and metal kaolin , using the Natural zeolite [9], using clay as adsorbent [10], sulfate and Phosphatet [3], removal of Zn, Cd and Mn From aqueus solutions [20], Modified Bentonite with Titanium dioxide [11], the use of adsorbent orange peel in absorbing Cu and Fe [12], and the use of carbon nano adsorbent active in absorbing Cu (IV) [13].

The elimination of metal ions using kaolin are based on ion exchange mechanism. The existence of negative ions due to the ratio between silica and alumina (Si/Al) which are relatively small and also the presence of oxygen and hydroxyl groups on the surface of the kaolin. Kaolin is still similar to the zeolite and betonite, zeolite and bentonite but better absorption rate or higher than the kaolin especially when compared with active carbon and therefore required an effort to improve the absorption of kaolin. One of the efforts to increase the absorptive capacity of kaolin as an adsorbent can be done by modifying the use of organic compounds such as surfactants. Surfactants have several types of anionic and cationic Surfactant a long chain organic compound that consists of two parts, namely the head and tail. The head is positively charged and hydrophilic, while the tail is not charged and hydrophobic. Surfactants can form micelles; monolayer or bilayer on a kaolin surface modification depends on the concentration of surfactant used.

Applications Kaolin modified with surfactants (Organokaolin) to absorb the metal ion Mn (II) the information is still limited. The aim of this study was to study the ability of absorption of kaolin and increase the absorption of kaolin modified with a surfactant in the metal absorb Mn (II) in water. Modification of kaolin with a surfactant intended to bind the surfactant to the surface of hydrophobic kaolin. Adsorption of the surfactant on the surface of kaolin to involve interaction with the surface of the molecule and between molecules. This interaction can affect surfactant material is formed, the material is determined by the concentration of surfactant. Higher concentration of surfactant then the greater the interaction between molecules so that the material is formed to be increased. The material is formed to determine the nature of the kaolin surface adsorbs anions bound and more [6].

## 2. Experiment method

### *2.1. Material*

In this research, the materials used are surfactants Alkyl Benzene Sulfonate (ABS) for the group which is negatively charged, distilled, MnCl2.4.H2O, KOH and HNO3 is used in the activation process using alkaline and acid to eliminate the levels of metals and organic compounds contained kaolin for increase the absorption rate as well, pure kaolin [14]. All the chemicals used were obtained commercially from Waco ltd and Aldrich. Manganese stock solution with a concentration of 50 mg/L, prepared using MnCl2.4.H2O dissolved into distilled water as much as 0.1802 gram, then dilution up to 10 mg/L

### *2.2. Instruments*

Analysis of Mn assays used Absorption Atomic Spectrometer (AAS) (Shimadzu UV-1800) whereas the determination of the characteristics for wavelengths before and after treatment are used Spectrophotometer Fourier Transform Infra Red (FTIR) IR Prestige-2. PH levels using a pH meter Hanna Instruments, while the stirring speed used Shaker Incubator Pyrex, to see the pores in the adsorbent used SEM JEOL JSM-6510 LA.

### *2.3. Preparation of adsorbent kaolin-surfactant modifications.*

Kaolin do physical activation for 2 hours with temp. 105OC, chemical activation using H2SO4 and KOH for 2-3 hours, neutralized to pH 7, dried and stored in a desiccators. Activation kaolin modified

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with an anionic surfactant with a surfactant usage ratio 45%, 60%, 75% of the total weight of 300 grams. Kaolin mixture of surfactants (Organokaolin stirred using Incubator Shaker for 2 hours with stirring speed of 90 rpm and 50.70 and the contact time between 10-90 minutes. The precipitate is filtered and washed kaolin to pH 7, then dried and stored in a desiccators. The precipitation is carried out during 4 hours before being stored in a desiccators before use.

*2.4. The process of adsorption*
The Metal Ion of Manganese (Mn) was adsorb using organokaoline do with variations and different conditions. Organokaoline used 2 grams, was not it water containing metal mn (II) of 200 ml and a concentration of 10 mg/L. The contact time varied from 30 to 90 min, pH 6.8 - 7.2 with the process occurs at room temperature (25$^0$C). Batch experiments performed using an 250-ml Erlenmeyer tube was closed using aluminum foil to avoid contact with air. All of the sample is inserted into the Shaker Incubator with a stirring speed of 90 rpm.

In the adsorption process, 2 g organokaoline and 200 ml of water the peat with the initial conditions, especially the content of Fe, Mn and organic compounds known included in a 250 ml flask, is contacted for 90 minutes with a stirring speed of 90 rpm using the Shaker Incubator. The samples were analyzed using Atomic Absorption Spectrophotometer (AAS) before and after treatment. Sample covered with aluminum foil to avoid contact with the outside air. The supernatant was then collected and examined using Atomic Absorption Spectrometer (AAS) (Shimadzu UV-1800). Testing is done by triple (repetition 3 times) and taken the average price. Differences in initial and final conditions are calculated, so that the efficiency obtained Mn decreased levels of metal ions in water. The percentage of allowance for metals Mn (R) in a solution of water and the amount of ion Mn (II absorbed in the adsorbent (qe) was calculated with the following equation:.

$$R = \frac{Co-Ct}{Co} X\ 100 \ \ldots\ldots\ldots\ldots\ldots\ldots..(1)$$

$$Q_e = \frac{Co-Ct}{} X\ V \ \ldots\ldots\ldots\ldots\ldots\ldots\ldots..(2)$$

Where Qe is the number of ion Mn (II) was absorbed by organokaolin adsorbent (mg/g). and C0 and Ct is the ion concentration of Mn (II) (mg/L) prior to the beginning of the adsorbent and after absorption. V is the solution volume (ml) and m is the weight of adsorbent (g) [15].

## 3. Result and Discuss

*3.1. FTIR spectra analysis*
In this study, the spectra of FTIR for organokolin that have been activated and organokaolin that has absorbed Mn metal ions can be seen in Figure 1. This tool can also distinguish various functional groups, due to the vibration of functional groups have bonding in the molecule different [16]. Infrared spectrophotometer analysis was done to evaluate the characteristics in kaolin adsorbent modified with a surfactant. Changes in the structure of the Si-O-Al stretching organokaolin kaolin which has been activated or before the adsorption loss of the peak at 750-752 nm indicating the changes due to the presence of metal Mn and the emergence of the O-H vibration deformation. The existence of Mn metal influence on spectra, organokaolin containing Mn metal ion spectra generated more noisy (more wavy) compared with organokaolin that have not absorb metal. This indicates that the metal ion Mn affect organokaolin wave, because the spectra are very sensitive if conditions change e.g. temperature, concentration and the presence of other compounds that change in spectra can be detected using FTIR. These results are consistent with research conducted by Prof. Tsenkova, where the presence of metal in the water provides water spectra changes significantly. [16]. Changes others that happened was in the structure of Si-O deformation at a wavelength of 850 nm, 970 nm and 1100 nm where changes occur very significantly with the presence of the metal manganese in the adsorbent organokaolin, that alter the structure of vibration in organokaolin that has absorbed metals Mn into O-H octahedral. The results of

this used FTIR nearly equal to that produced by Fairoos who adsorbs Ni ions in solution using a nano-composite [18].

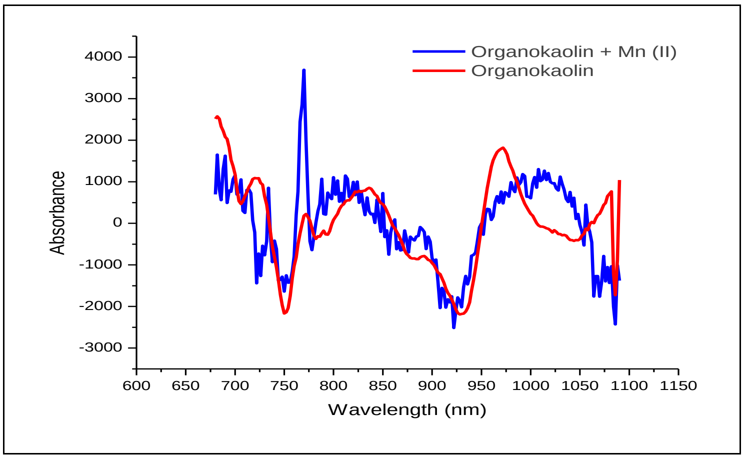


**Figure 1.** Spectra of Organokaolin + Mn and Organokaolin

*3.2. Effect of contact time*

Decreasing the concentration of Mn using kaolin modified adsorbent with a surfactant indicates allowance Mn metal in the water after the adsorption process. This process is greatly influenced by the contact time between organokaolin and Mn metal ions in water, the behavior of metals decrease with contact time can be seen from figure 2 below.

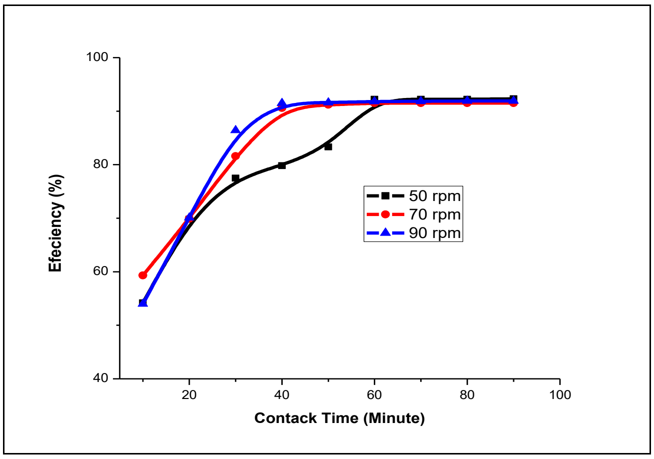


**Figure 2.** The effect of contact time on the absorption of Mn (II) using Organokaolin

From Figure 2 shows that the increase in efficiency of metal uptake Mn (II) in water or a decrease in metal content of Mn (II) increased with increasing contact time. This indicates that Mn metal contained in the effluent are absorbed gradually increases with increasing contact time. Increasing contact time affect the increased efficiency of the allowance for Mn metal in the waste water. Increasing the efficiency of an adsorbent is attributable to the performance of the GCC work longer so that more metal ion Mn belt adsorbent stretcher, while the influence of stirring speed very significant increase in the allowance for metals occur in adsorbent which has not been activated. This shows that the performance of the adsorbent is highly dependent on the movement of molecules around it, so that with the

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acceleration of stirring it easier for adsorbent (organokaolin) in the capture or bind metal ions Mn in water. At the contact time reached 60 minutes, visible uptake of metal ions in water has a maximum Mn, from chart 3 shows that after maximal conditions despite the addition of up to 90 minutes when done has been a constant condition,. This condition shows that organokaolin when contacts between 60-90 minutes can no longer absorb metal ions Mn due to the adsorbent has been experiencing burnout. Similar results were also obtained by Rachel, et.al who get the optimum time in absorption of Mg metal (II) by using activated carbon [15] and Fairoos using nano composites absorb metal ions Ni [18].

*3.3. Effect of surfactant concentration*

Modification of kaolin and surfactant aims to bind the surfactant to the surface of hydrophobic kaolin. Adsorption of the surfactant on the surface of kaolin to involve interaction with the surface of the molecule and between molecules. This interaction can affect surfactant material is formed, and the material is determined by the concentration of surfactant [6]. To determine the type of surfactant and the doses used in lowering the concentration of Mn ions in the water can be seen in Figure 3 below:

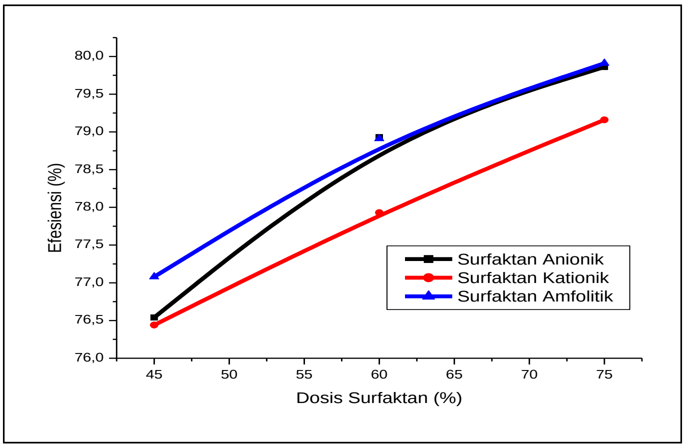


**Figure 3.** Effect dosis and types of surfactant on performance organokaoline

Surfactants are used there are three types of each anionic, cationic and ampholytic. Modification or adding of numbers of surfactant doses of 45, 55 and 75% respectively have a significant influence on the absorption of Mn metal in water. Increasing the number of surfactant doses proportional to the increase in efficiency or absorption organokaolin absorb metal ions Mn. This is caused by the ability of the surfactant to interact on the surface of the adsorbent, thereby increasing porosities adsorbent to absorb metals Mn, besides surfactant also layers (multilayer) a lot and capture metal ions Mn through ionic bonds contained in that layer. From Figure 4 shows that the type of surfactant on the performance of organokaolin in lowering levels of Mn metal, where the presence of ampholytic better when compared to the other two types of surfactant. The ability of surfactant higher aggregation number, that number when forming micelle surfactant. Micelle surfactant if this is soluble in water, the hydrophobic portion facing the micelle core and the hydrophilic part draw water phase. The presence of positive and negative charges on the surface of the adsorbent will affect disepersi when the surfactant is attached to the kaolin. This dispersion of power will be stronger / faster when both ions are owned by active amphoteric surfactants perform movements, resulting attract each other hydrophobic moieties are also great. These attractive forces tend to be owned by the amphoteric surfactant that is if we compare with cationic and anionic surfactants.

*3.4. Scanning Electron Microscope (SEM)*

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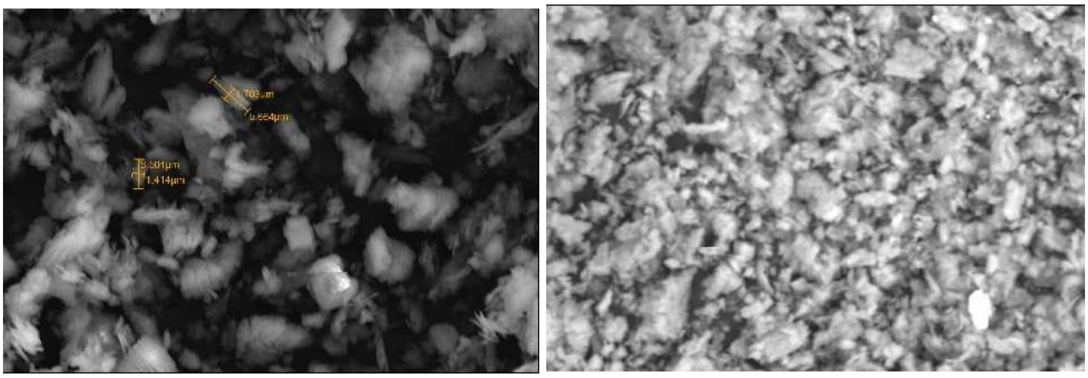
To see the morphology of the surface of the adsorbent organokaolin before and after the process of the adsorbent can be seen in Figure 4 below.




(a) (b)

**Figure 4.** Organokaoline (a) prior to the adsorption process (b) after the process of adsorption

Organokaolin surface before the adsorption process is done seen a lot of pore cavities. Meanwhile, on the observation organokaolin after Mn metal adsorption process the cavities are already squeezed and have small pores. Voids and pores are formed due to the absorption of Mn metal in this organokaolin.Hal indicate that the ability of the adsorbent organokaolin absorb Mn metal ions in water.

## 4. Conclusion

As a conclusion of this study, Organokaolin which is a modification of kaolin with a surfactant managed to increase absorption of the adsorbent and reduces the Mn ions in aqueous solutions up to 95%. FTIR analysis showed a significant difference between the spectra before and after the adsorption process Mn, seen the transfer of spectra and spectral locations that contain metal ions Mn more noisy. Tests using SEM showed morphological changes on the surface organokaolin before and after the absorption of Mn metal surface denser and disappearance of cavities in organokaolin prior to the adsorption process.

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