1. INTRODUCTION

A reservoir is a place for waste disposal originating from city buildings, be it from hospitals, government agencies, and also from households in urban areas. This reservoir is also located in the city, so it is often a tourist destination, but the waste that flows into this reservoir based on testing from the local environmental service contains dangerous metals, which if these metals touch humans will have a bad impact. for humans. The dangers of heavy metal mercury to humans if exposed to high levels can permanently damage the brain, kidneys, and developing fetus. Adhinugroho (2018) Effects on brain function cause irritability, shyness, tremors, vision or hearing changes, and memory problems. Meanwhile, short-term exposure to high levels of mercury vapor causes lung damage, nausea, vomiting, diarrhea, increased blood pressure or heart rate, skin rashes, and eye irritation. This waste can be handled using several conventional methods such as chemical deposition of membranes, filtration, coagulation, chemical extraction, ion exchange, etc. However, this conventional technique has several disadvantages such as high energy requirements, sensitive operating conditions, and low efficiency. Putri et al. (2022)

To overcome this drawback, the adsorption method is considered as one of the most economical and efficient processes for removing harmful metal ions, due to its availability, low cost, and operation. Estrada et al. (2016) Mahmoodi et al. (2019) Mahmoodi, N. M. (2014). This process involves separating a substance from one phase and collecting it on another surface. This method is effective in removing toxic pollutants, even at low concentrations, and is easy to operate. Udin (2017), Siyal et al. (2018) Adsorption is often accompanied by an inversion-desorption process, which represents the transfer of adsorbate ions to solution from the adsorbent surface. The reversibility of adsorption can depend on the amount of adsorbate that is adsorbed from the adsorbent, the more adsorbate is adsorbed, the more reversible the adsorption process. Ridwan (2018), Singh (2016) Kaolin is one of the adsorbents that is often used in the metal ion adsorption process. Leal et al. (2017).

Kaolin (Al₂Si₂H₄[OH]) or kaolinite is an alternative material that can be used as an adsorbent. Kaolin has a low expansion, high chemical stability, and cation exchange capacity. Kaolin is classified into trioctahedral and dioctahedral minerals. Nugraha and Kulsum (2017), Coelho et al. (2014). Kaolin has potential as an adsorbent because it is cheap, safe, and easy to obtain, and is available worldwide in rock as a crystalline structure. Santhosh et al. (2016), Rao et al. (2014). However,
the absorption ability of kaolin as an adsorbent is still low when compared to zeolite, activated charcoal., and bentonite. Mishra (2014), Efforts need to be made to increase the adsorption ability of kaolin, namely by using surfactants as modifying agents.

The weathering process in the formation of kaolin occurs at or near the soil surface, which mostly occurs in igneous rocks. Gupta et al. (2016), Emam et al. (2017). The hydrothermal alteration process occurs because hydrothermal solution flows through fractures, faults, and other permeable areas while converting limestone into kaolin deposits. Gupta et al. (2016), Mouni et al. (2018), Mustapha et al. (2019) Kaolin deposits consist of two kinds, namely residues and sediments. Residual kaolin, this type is found where it forms with the parent rock, has not undergone displacement, is crystal regular, and ion substitution is rare. Safitri et al. (2020), Mudzielwana et al. (2019) Kaolin sediments, have been displaced by water, wind, glaciers, deposited in basins, and irregular crystals. The structure of kaolin can be seen in Figure 2.

The surface of the kaolinite crystal has a constant negative charge and does not depend on pH (permanent charge). The negative charge comes from atomic substitution in the crystal structure which does not affect the crystal structure, for example, the presence of an Al atom with a +3 charge replacing a Si atom with a +4 charge causes the kaolinite skeleton to be less. positive charge or excess negative charge. Sodeifian and Ali (2018), Roosta et al. (2017), Suryani et al. (2020).

This modification enhances anion absorption through ion exchange. Based on research18, natural kaolin was successfully modified through surfactant intercalation Alkyl Benzene Sulfonate (ABS) to the interlayers. The modified adsorbent showed a maximum adsorption capacity of 2.3 and 2.88 m2/g. That is, the help of ultrasonic technology can significantly improve the adsorption ability of the adsorbent. Ultrasonic has proven to be a very useful tool in breaking the relationship between adsorbent and adsorbate and intensifying the mass transfer process. Raya and Zakir (2014), Jeeva et al. (2019), Wu et al. (2015).

Ultrasonic technology has the advantages of low operating costs and no negative impact on the environment. This technique has the effect of increasing the adsorption capacity of the adsorbent up to two times with the help of ultrasonic speed which in the process increases the surface area of the adsorbent. II). Later, the wastewater to be adsorbed will be tested for TDS and PH to see the effectiveness of the adsorbent. Suryani et al. (2018), Pakaya (2020).
2. METHODOLOGY AND CHARACTERIZATION

2.1. MATERIALS

Kaolin is taken from Nisam, North Aceh. N-Methyl-2-pyrrolidone (NMP) was purchased from Merck and Polyethersulfone (PESf) as a binder was purchased by Amoco Chemicals and Article 135 (CRODA). Raw kaolin and PESf were heated to 100 °C in an oven to remove the adsorbed moisture and used without purification. Then, kaolin was activated using 1N HCl for one hour, then washed and dried in an oven at 85 °C, sieved through a 110 mesh sieve, and then stored in a desiccator before use. Alkyl Benzene Sulfonate (ABS) purchased from Merck was used as a surfactant. The wastewater used in this study was taken from the Lhokseumawe City Reservoir Waste. A sampling of the reservoir waste water on the edge and the reservoir water has been tested to contain mercury and several other metals. Wastewater samples were filtered using filter paper to remove suspended solids before testing.

2.2. METHODOLOGY

2.2.1. KAOLIN SYNTHESIS WITH ABS SURFACTANT

Before being synthesized, kaolin was activated with 1 M HCl, 120 g of activated kaolin was added to a surfactant solution of Alkyl Benzene Sulfonate (ABS) (80 mL) and the mixture was put into a shaker incubator at 35 oC and 150 rpm for 24 hours. The resulting residue was washed with distilled water several times to remove excess surfactant. The residue obtained was then dried in an oven at a temperature of 60 oC for 12 hours and then ground using a mortar and pestle to pass a 115 mesh sieve. KM modification used as much as 1.8 g, as well as PK, weighed as much as 1.8 g. Each adsorbent was irradiated by ultrasonic with a 100 ml reservoir waste sample.

2.3. CHARACTERIZATION

Modified kaolin was characterized by SEM before and after the adsorption process. The physicochemical properties of the samples were determined by Fourier to transform infrared spectroscopy (FT-IR), pH measurements were performed using a pH meter every 10 minutes and TDS measurements were performed using a TDS instrument. The ultrasonic device used is a heating system (Elmasonic, Italy) at a frequency of 60 Hz and a power of 130 W is used for ultrasound-assisted adsorption procedures. The adsorption of metal ions Hg(II) from water with modified kaolin using the ultrasonic technique was studied to find the optimal adsorbent dose, pH, TDS, and sonication time as well as the initial concentration of Hg (II). The solution containing the metal ion Hg2+ was mixed with natural kaolin and modified kaolin adsorbent at a certain pH (adjusted with acetate buffer) in an ultrasonic bath for varying times. Then the adsorbent was immediately separated from the solution and the remaining concentration of Hg(II) ion was measured by atomic absorption spectrophotometer. Mathematically the number of Hg (II) ions adsorbed at equilibrium conditions (Qe, mg g-1) is obtained by using Equation 1:

\[ Qe = \frac{(C_0 - C_e)V}{M} \]

Equation 1
Where, Co and Ce are the initial and equilibrium concentrations of Hg (II) (mg L\(^{-1}\)), and V and M are the volume of solution (ml) and mass of adsorbent (g). Roosta et al. (2017).

3. RESULTS AND DISCUSSION
3.1. ADSORBENT CHARACTERIZATION
3.1.1. CHARACTERIZATION OF THE SCREENING ELECTRON MICROSCOPE (SEM)

Table 1 presents the surface area of BET, pore diameter, and pore volume of PK and KM. The analysis revealed that after modification with ABS surfactant, the total surface area of kaolin clay minerals decreased drastically from 19.12 m\(^2\)/g to 9.32 m\(^2\)/g. On the other hand, the pore diameter and pore volume increased from 0.04 cc/g to 0.08 cc/g and 9.47 to 24.30 nm, respectively. The increase in pore diameter and pore volume as well as a decrease in the surface area caused by surfactants that fill most of the space on the clay surface results in an increase in pore volume and pore diameter. The result obtained in this study is twice the surface area of 4.3 m\(^2\)/g reported by Lee et al., Rihayat et al. (2019), Safitri et al. (2020), Mudzielwana et al. (2019).

Table 1

<table>
<thead>
<tr>
<th>BET surface area (m(^2)/g)</th>
<th>Pore volume (cc/g)</th>
<th>Pore diameter (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PK</td>
<td>19.12</td>
<td>0.04</td>
</tr>
<tr>
<td>KM</td>
<td>9.32</td>
<td>0.08</td>
</tr>
</tbody>
</table>

The morphology observed by SEM for the kaolin-modified surfactant (SMK) produced by Ultrasonic-assisted is shown in Figure 3. It was found that the kaolin-modified ABS surfactant was essentially homodisperse without aggregation and the nanocomposite had a cubic structure with an average diameter of about 100 nm. KM before the Hg (II) metal adsorption process showed that the KM surface still had many large pores Figure 3(a). Meanwhile, in the observation of KM after the Hg (II) metal adsorption process Figure 3(b), the cavities that have been crushed have small pores. These cavities and pores are formed due to the absorption of Hg (II) metal in KM.

Figure 3
3.1.2. FOURIER TRANSFORM INFRA-RED (FTIR) CHARACTERIZATION

The FTIR spectrum of the material was used to determine the composition and pattern of functional groups. The FTIR spectra of natural kaolin (PK) and surfactant-modified kaolin (KM) are presented in Figure 4. For PK, the absorption bands at 3663.23 cm⁻¹ and 1626.17 cm⁻¹ show the -OH stretching vibration in water which is adsorbed by physics. The bands at 1012.50 cm⁻¹ and 961.54 cm⁻¹ were associated with the vibrations of the Si-OH and Al-OH bonds. The band at 1509.46 cm⁻¹ shows the vibration of the CC–C flex vibration associated with the methylene group. Bands at lower wavelengths show vibrations of Al-O-Si and Si-O-Si networks.

The spectrum of Alkyl Benzene Sulfonate shows a stronger absorption band in the region of 2893.51 and 2944.05 cm⁻¹, which is bound to the CH stretching bond in the -CH₃ and -CH₂ groups. The bands at 925.72 cm⁻¹ and 946.4 cm⁻¹ correspond to CN bond vibrations. It can be seen at the wavelengths of 2847.25 and 2975.31 cm⁻¹ that the kaolinite adsorbent was successfully modified which was assumed to be derived from the vibration of the CH bond. After mercury adsorption, no changes were observed in the modified kaolin spectrum. However, there is an increase in the transmission intensity of the band. This could be an indication that Hg(II) can result in higher adsorption affinity for contaminants.

3.2. EFFECT OF CONTACT TIME

3.2.1. EFFECT OF CONTACT TIME ON NATURAL KAOLIN AND MODIFIED KAOLIN ON Hg(II) ABSORPTION

Batch experiments were conducted to determine the adsorption efficiency and ultrasonic-assisted adsorption process to remove Hg (II) ions in the Lhokseumawe city dam waste. The contact time required to effectively remove the metal by the adsorbent is important to determine when the equilibrium time is reached. The effect of contact time on metal adsorption on KM and PK kaolin is shown in Figure 4. The results showed a very significant difference between KM adsorbent and PK adsorbent, KM was more efficient in the adsorption of Hg (II) compared to PK adsorbent.

The results of PK adsorption efficiency obtained the best results at a contact time of 80 minutes at 62.74%, while the best results of KM at a contact time of 45
minutes was 84.21%. This is because Hg (II) has been adsorbed on the pores of the KM adsorbent. After all, the molecules in the wastewater move faster so that the interaction between the KM adsorbent and metal ions occurs more frequently, the longer the ultrasonic contact time, the lower the absorption efficiency due to saturation. The adsorbent in adsorption of metal Hg(II).29

Figure 5

![Figure 5](image)

**Figure 5** Effect of Contact Time on Hg (II) adsorption on KM and PK

### 3.2.2. EFFECT OF TIME ON PH AND TDS OF WASTEWATER

The mechanism for increasing the adsorption of kaolin adsorbents with the addition of surfactants is that the metal attaches to the surface of the kaolin forming interactions between the molecules on the kaolin and the surfactant. This interaction causes the formation of a new layer, thus forming a bilayer group which results in a lot of metal ions being adsorbed. In addition, the presence of surfactants also increases the number of ions present on the surface of the surfactant, so that the modified adsorbent captures more of the surrounding ions in the wastewater.

According to a study conducted by 31, adsorbed metal Cr(IV) using anionic surfactant-modified kaolin obtained an absorption efficiency of 95.08% at an optimal contact time of 180 minutes. the effect of using the high-speed ultrasonic technique in the adsorption process increases the surface area. This accelerates the movement of molecules so that the adsorption process occurs faster.32 This phenomenon is caused by cavitation (nucleation, growth, and collapse of small gas bubbles) and high-pressure variations induced during ultrasonic irradiation.33

**Table 2**

<table>
<thead>
<tr>
<th>No</th>
<th>Processing Time (minutes)</th>
<th>PH</th>
<th>TDS (mg/L)</th>
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<tr>
<td>1</td>
<td>10</td>
<td>4.5</td>
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<td>6</td>
<td>570</td>
</tr>
<tr>
<td>4</td>
<td>40</td>
<td>7</td>
<td>437</td>
</tr>
<tr>
<td>5</td>
<td>50</td>
<td>7.3</td>
<td>421</td>
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</table>
The contact time of the KM adsorbent with waste also affects its PH and TDS, from Table 2 it can be seen that the PH and TDS recording time is every 10 minutes, the longer the contact time, the PH of the wastewater to its normal PH as well as the lower TDS value, this is because the longer the ultrasonic contact time, the efficiency of metal absorption decreases due to saturation of the adsorbent in adsorption of Hg(II) metal and causes the metals to be sedimented.

4. CONCLUSION

In this study, natural kaolin clay (PK) was successfully modified through intercalation of ABS surfactant to the interlayers and ultrasonic assistance to remove Hg2+ metal ions in water. The synthesized adsorbent showed the maximum adsorption efficiency of KM and PK were 84.21% and 62.74%, respectively. In this study, it was also proved that the ultrasonic adsorption method became a very useful tool in intensifying the mass transfer process and breaking the relationship
between the adsorbate and the adsorbent. In comparison, ultrasonic adsorption is higher and faster than the adsorption process. Also, the efficiency of the adsorbent can be modified, which can be seen from the results of the PH and TDS testing of wastewater, which the longer the contact time the value decreases. Also, kinetic studies show that the adsorption process follows a pseudo-second order.

**CONFLICT OF INTERESTS**

None.

**ACKNOWLEDGMENTS**

None.

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Ultrasound-Assisted Adsorption Hg (II) Using Kaolin Adsorbents Modified with Anionic Surfactant


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