Synthesis of Organo-Quartz from Lumajang Sea Sand Using Sodium Dodecyl Benzene Sulfonate (SDBS) Modifier for Adsorption of Fe$^{3+}$

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Received 09 March 2020; Accepted 14 April 2021

ABSTRACT

This study aims to determine the effect of sea sand modification with SDBS for adsorption of Fe$^{3+}$. Sea sand was treated with 0.1 M HCl solution at 25°C. Organo-quartz was prepared using various SDBS concentrations (below, equal, and above the CMC value) by shaking the mixture for 4 hours at 100 rpm. Characterization by FTIR spectrophotometry showed a change in the spectra pattern. The activation caused increasing of -OH silanol while modifications make the silanol group decrease. Characterization with SEM showed that the morphology of the sea sand was not uniform with irregular white chunks. The EDX results showed that the dominant elements were C (13.89 ± 10.86%), O (40.48 ± 6.58%), Si (16.51 ± 8.13%), and Fe (11.68 ± 14.38%). Adsorption was carried out using Fe$^{3+}$ at 50 ppm. The Fe$^{3+}$ analysis was conducted by AAS. Decreasing of Fe(III) adsorption was about 17% due to activation, but increasing of the adsorption was about 6% due to modification of sea sand by surfactant at below CMC relative to the activated sea sand. The low Fe$^{3+}$ adsorption is probably caused by the dissolved iron oxides in the sea sand during activation.

Keywords: sea sand, quartz, surfactant, SDBS, adsorption

INTRODUCTION

Industrial activities in Indonesia increases every year. However, the increasing industrial activity will certainly have a negative impact on the environment, as it generates hazardous waste during the production process. One of many hazardous waste is heavy metals that can pollute the environment especially water if it was not treated properly. Heavy metal waste will be dissolved in water and make the water quality decreased and within a certain time will be accumulated in the sediment.

For example, iron content (Fe), based on the study Putra (2014) [1] on the sample of batik waste is 1.9 mg/L. The value of Fe threshold, according to the Indonesian Regulation of PPRI No. 82 year 2001 [2] in drinking water, is allowed only 0.3 mg/L. In other words, the batik waste is in polluted criteria, in which excess iron in the waters can cause poisoning. This high concentration of iron in waters can be treated by adsorption using many options of natural and/or man-made adsorbents.

Sea sand is known to have quartz content that is abundant in nature and is often utilized as adsorbent. Quartz is composed of silicon dioxide (SiO$_2$) with a content above 90% [3]. According to Liu [4], some fine granular minerals including quartz, dolomite, calcite, and feldspar have low porosity characterized by high young modulus values. The low porosity
value caused the adsorption process of quartz sand was not optimal. Based on Widiharti’s work [5], sea sand adsorption ability can be increased by activation using acid solution to dissolve the impurities so that the pores and the active sites are not obstructed. At an acidic pH of around 4, the [H+] levels in the solution is quite high, thus the amount of Si-OH (silanol) formed is also higher. Widiarti [6] also reported that the activated sea sand has ability to reduce the content of Cu2+ in water by 99.53%.

Several methods are used to improve the adsorption capability of sea sand by sea sand surface modification. Quartz has a tetrahedral structure that makes its surface more negative charged. The negative charge of the quartz surface can be used to bind an organic group that can produce a catalytic centre for heavy metal ions interaction [7]. Gennaro, et al [8] reported a successfully modified clinoptilolite’s surface using HDTMA cationic surfactant.

The organic compound utilised in this study for sea sand surface modification is Sodium Dodecyl Benzene Sulfonate (SDBS) which belongs to the anionic surfactant group. Putriani [9] successfully modified the surface of zeolite using SDBS. The use of SDBS will provide more negative hydrophilic groups on the quartz surface, so that by this modification more heavy metal cations in water can be adsorbed. The effect of sea sand modification using SDBS is studied. Moreover, the effect of various concentration of SDBS toward the changes of surface functional groups, and the adsorption ability to reduce the concentration of Fe3+ in water were also investigated.

Lumajang seasand was used in this research because it has potency as source of minerals. Lumajang sea sand is known as iron sand due to its black color related to vulcanic minerals comming from Semeru and Bromo mountain activities [10]. Generally, the iron sand consists of iron oxides such as magnetite (Fe3O4), hematite (α-Fe2O3), and maghemite (γ-Fe2O3). Magnetite (Fe3O4) is black iron oxide and can be used as an adsorbent [11].

EXPERIMENT
Chemicals and instrumentation
Aldrich), hydrochloric acid 37% (Merck), iron (III) chloride hexahydrate (Merck), and distilled water. The instrumentsations used in this research were FTIR spectrometer (Shimadzu type 8400S), SEM-EDX (FEI type Inspect S50), and AAS (AA-6200).

Sea Sand Preparation
Sea sand was washed using the distilled water and dried at 110-120°C for 2 hours. The activation was done by placing 100 grams of the dry sea sand in a beaker, soaked it with 200 mL HCl 0.1 M and stirred 100 rpm at room temperature for 4 hours. Next, the sand was filtered off and washed with distilled water until the pH was neutral. The activated sand then dried in an oven at 110-120°C for 2 hours.

Synthesis of Organoquartz using SDBS
Each of 10 grams of the sea sand was placed in three separate beaker glass. Next, 100 mL of SDBS was added with a concentration of 0.5 mmol/L (< CMC); 2.58 mmol/L (∼ CMC); 30 mmol/L (> CMC), hereinafter referred to as OQ1, OQ2, and OQ3. The mixture was shaken by automated shaker machine at 100 rpm for 4 hours. Then the sand was filtered off and washed with distilled water, and dried at 110-120°C for 2 hours.

Characterization of Organoquartz
The activated sea sand of all three samples were characterized using FTIR and the spectra were compared to that of organoquartz sand (OQ1, OQ2, and OQ3). The analysis was performed using KBr pellet method in a range of 4000-400 cm⁻¹. The organoquartz sand was
also characterized using SEM-EDX instruments to determine the surface morphology and elemental composition contained in the sample.

**Adsorption by Organoquartz**

Standard solution of Fe\(^{3+}\) 50 ppm was made by dissolving 5 mg of FeCl\(_3\) anhydrous with 100 mL distilled water in a volumetric flask. 0.5 grams of adsorbent namely (sea sand without activation (QLMJ), activated sea sand (AQLMJ), and organoquartz (OQ1, OQ2, and OQ3)) was mixed with 20 mL of Fe\(^{3+}\) 50 ppm and the solution was shaken at 100 rpm for 60 minutes at room temperature. The solution was then filtered off and the filtrate was analysed by AAS (at 248.3 nm) for the Fe\(^{3+}\) concentration. As comparison, the initial Fe\(^{3+}\) solution 50 ppm was also measured by AAS. The adsorption test was repeated 3 times.

**Analysis of Fe (III) with AAS**

The absorbance value from the results of the analysis with AAS was used to calculate the Fe\(^{3+}\) concentration after the adsorption process. Using the Lambert-Beer equation, the concentration of absorbance values can be calculated with the equation:

\[
A = abc
\]

A = Absorbance  \quad a = \text{absorptivity (L mol}^{-1}\text{ cm}^{-1})
\quad b = \text{gap width (cm)}  \quad c = \text{concentration (mol L}^{-1})

The absorbance value of the standard metal with the metal after adsorption can be compared and calculated using this equation:

\[
\frac{A_1}{A_2} = \frac{abc_1}{abc_2}
\]

Equation (4) can be simplified because it had the same a and b values, an equation was obtained to calculate the concentration value after adsorption as follows:

\[
\frac{A_1}{A_2} = \frac{c_1}{c_2}
\]

The percentage of adsorbed metal was calculated using the following formula:

\[
\% \text{ metal ion adsorbed} = \frac{C_0 - C_s}{C_0} \times 100\%
\]

**RESULT AND DISCUSSION**

**Characterization Using FTIR**

The effect of SDBS concentration toward the functional groups on activated sea sand was studied by using spectrophotometer FTIR. The concentration used is 0.5 mmol/L (< CMC) for OQ1, 2.58 mmol/L (= CMC) for OQ2, and 30 mmol/L (> CMC) for OQ3. The concentrations used were 0.5 mmol/L (< CMC) for OQ1, 2.58 mmol/L (=CMC) for OQ2, and 30 mmol/L (> CMC) for OQ3. The IR spectra are shown in Figure 1, while IR spectra sinterpretation are shown in Table 1.
Figure 1. IR spectra of activated sea sand (AQLMJ) and as-synthesis with SDBS in various concentrations of 0.5 mmol/L (OQ1), 2.58 mmol/L (OQ2), and 30 mmol/L (OQ3).

Table 1. IR interpretation of activated sea sand (AQLMJ) and modified sea sand with SDBS

| Sample                  | Literature                        |
|-------------------------|-----------------------------------|
| AQLMJ (Activated Sand)  |                                   |
| 3750                    | -OH stretch from Si-OH            |
| 3620.90                 | -OH stretch                      |
| 1700                    | C=O stretch                       |
| 1645.93                 | -OH bending from Si-OH and C=C stretch (SDBS) |
| 1001.75                 | Si-O-Si stretch asymmetry         |
| 768.38                  | Si-O-Si stretch symmetry          |
| 581.30                  | Si-O-Fe bending                   |
| 467.50                  | Si-O-Si or O-Si-O bending         |

Activation process and modification by SDBS affect the functional groups on the surface of the sea sand as observed in Figure 1. Activation of sea sand caused the absorption intensity
of the -OH silanol on the 3750 cm\(^{-1}\) increases, due to the substitution of metal cation with H\(^+\) from acid solution [17]. Variations of SDBS concentration affect the generated IR spectrum. The interaction that occurred at the concentration at <CMC (OQ1) was between the hydrophobic group of SDBS which lead to Si-O-Si on the surface of the sea sand through the interaction of Van der Waals forces. This interaction lowers the absorption intensity of -OH silanol.

The wavenumber around 3500 cm\(^{-1}\) indicates that the addition of SDBS caused the absorption intensity -OH functional group to increase in OQ1, which is due to the ion-dipole forces interaction between the hydrophilic groups of SDBS with surrounding water molecules, thus increasing the absorption intensity of the -OH functional group. Higher concentrations of SDBS lead to lower absorption intensity. This was compliant with the IR spectra. Interaction that occurred on the surface of the sea sand with SDBS concentrations at < CMC (OQ1) is illustrated in Figure 2.

The addition of SDBS with concentration at \(\approx\) CMC (OQ2) began to form micelles. The formation of micelles caused the absence of Van der Waals interactions. The interaction was ion-dipole between the hydrophilic groups from the micelles with the -OH silanol on sea sand surface as predicted in Figure 3.

SDBS concentration at > CMC (OQ3) caused change in the shape of micelles, resulting in large and complex formation. As a result, the absorption intensity of -OH silanol group was lower because the ion-dipole forces that occur between the hydrophilic groups on micelles with the surface of the sea sand are increasing. The large form of micelles also causes the hydrophobic SDBS groups to gather more, hence reducing the water content that resulted in lower absorption intensity of the -OH functional group. The interactions is predicted in Figure 4.

Figure 2. Prediction of Van der Waals forces between sea sand surfaces with SDBS.
Figure 3. Prediction of ion-dipole forces between sea sand surfaces and micelles at SDBS concentration ≈CMC (OQ2).

Figure 4. Prediction of ion-dipole forces between sea sand surfaces and micelles at SDBS concentration > CMC (OQ3).

Characterization with SEM-EDX

Characterization with SEM-EDX was conducted at magnifications of 700, 4000, and 20000 times. Surface morphology of the sea sand shows a non-uniform surface, in white chunks that indicate the presence of SDBS on synthesized sea sand was also observed. White lumps spread on the surface in different sizes. The results of characterization of OQ2 sample is shown in Figure 5. Based on the EDX analysis the content of the main elements in the OQ2 sample can be identified. The average percentage of the main elements in the sample is shown in Figure 6.

The results show that the elements of O, Si, and Fe were the main components of Lumajang sea sand with an average percentage of O (40.48±6.58%), Si (16.51±8.13%), and Fe (11.68±14.38%). In the sample, there is also carbon content (13.89±10.86%) which originated from the hydrophobic SDBS group. The elements of Na and S in the analysed sample were also found in the sample, with an average percentage of Na of 4.97±2.47% and S of 0.117%±0.10, which also originated from the SDBS.
Figure 5. SEM-EDX characterization results with magnification of (a) 700 times, (b) 4000 times and (c) 20000 times.

Figure 6. The average content of the main element in the OQ2 sample.
Effect of Sea Sand Modification with SDBS on Metal Ion Adsorption

The concentration of Fe\(^{3+}\) after adsorption process can be calculated using the absorbance value, using equation (6) the metal concentration can be calculated after the adsorption process. The absorbance value of Fe\(^{3+}\) 50 ppm standard solution was 0.0596. The adsorption value of original sea sand (QLMJ) was 70.46 ± 5.54%, while the activated sea sand (AQLMJ) was 58.22 ± 7.23%. The modified sea sands (OQ1, OQ2, and OQ3) were able to adsorb Fe\(^{3+}\) by 61.52 ± 7.95%, 53.24 ± 4.86%, and 59.90 ± 11.04%, respectively. The adsorption percentage of Fe\(^{3+}\) is presented in Figure 7.

Figure 7. Adsorption percentage of Fe (III) by original, activated, and modified sea sands.

The activation of sea sand increases the -OH silanol group. With an increase in the silanol group, the adsorption percentage on Fe\(^{3+}\) should be better. However, from the results obtained, the ability of activated sea sand (AQLMJ) adsorption was lower than that of sea sand without treatment (QLMJ). This is probably caused by the high iron content in the Lumajang sea sands, in which characterization by Mu’ida showed that instead of quartz, magnetite was also found [18]. Decrease on the adsorption percentage of Fe\(^{3+}\) after activation occurred due to the loss of magnetite in acid solution [19]. In this activation process, magnetite is likely to suffer damage thereby reducing the ability of adsorption.

The addition of SDBS with concentration below CMC value (OQ1) leads to Van der Waals forces formation, such as the interactions shown Figure 2. Existence of SDBS on the surface of sea sand can enhances ion attraction force between the negative SDBS head and Fe\(^{3+}\) cation. This make the modified sea sand (OQ1) adsorption was higher than that of active sea sand. The addition of SDBS with concentration close to CMC value (OQ2) make the adsorption percentage decrease compared to that of OQ1. At this concentration, micelles began to form in a ball shape. Ion-dipole forces occurred between some of the SDBS hydrophilic groups with the surface of the sea sand as shown in Figure 3. The interactions that occurred reduces the contact surface area, as a result, the hydrophilic groups available for adsorption of Fe\(^{3+}\) become less. Moreover, the addition of higher concentrations above CMC value (OQ3) had a higher adsorption percentage compared to that of. Higher SDBS concentrations forms larger micelles.
and more complex shapes, as illustrated in Figure 4. Changes in the shape of the micelles increases the contact surface area, which is due to the number of available hydrophilic groups was higher than that of OQ2 thus eventually gives higher percentage of Fe$^{3+}$ adsorption.

CONCLUSION
The change in the functional groups of Lumajang sea sand was affected by SDBS, resulting in a lower absorption intensity of -OH silanol. The variation of SDBS concentration affect the Fe$^{3+}$ adsorption which relates to different micelles formation. The adsorption percentage of untreated, activated, and modified Lumajang sea sand with organoquartz in SDBS various concentration of <CMC, ≈CMC, and >CMC were 70.46± 5.54%, 58.22 ± 7.23%, 61.52 ± 11.83%, 53.24 ± 4.86%, and 59.90 ± 20.04%, respectively.

ACKNOWLEDGMENT
Authors thank to Department of Chemistry, Brawijaya University for access to the laboratory facilities and instrumentations. We also thank to PUPT 2017 funding belong to Dr. Tutik Setianingsih, M.Si for supporting of chemicals, characterizations, and publication.

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