The ultrasound effect of cationic surfactant on the preparation of natural bentonite Nisam, North Aceh.

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Abstract. The preparation of natural bentonite Nisam, North Aceh by cationic surfactant were investigated under ultrasound. A cationic surfactant, Cetyl trimethyl ammonium bromide (CTAB) were intercalated into natural bentonite from Nisam, North Aceh in aqueous solution. The solutions were exposed to 37 kHz ultrasound irradiation within 20 – 100 min. The modified bentonites were compared with raw bentonite. It was found that preparation with sonication has improved the interlayer spacing of bentonite by the intercalation of CTAB, and the improvement is getting higher with increasing of reaction time, as confirmed by the XRD patterns. FTIR measurements of modified bentonite indicate the incorporation of surfactants into bentonite. SEM analysis proved that increasing reaction time affect the morphology of bentonite.

1. Introduction

Bentonites consist essentially of clay minerals of the smectite groups. It widely used as industrial raw materials for many industries. Bentonite is generated from weathering of volcanic ash. Bentonite has been applied as drilling mud, the adsorption agent, medicine, carrier materials and fine chemicals [1].

The properties of natural bentonites consist of 2:1 layered aluminosilicate. The negative layers in bentonite balance electrically by equal charge cations. The clay layers are negatively charged as a consequence of an isomorphic distribution of exchangeable counterbalanced cations such as Na⁺ and Ca²⁺ in the interlayer. Because of the hydration of inorganic cations on the exchange site, the clay mineral surface is hydrophilic [2,3]. Thus, natural clays are ineffective for mixing with organic compounds.

Cationic surfactant can be used for improving and modifying the properties of natural clay due to the substitution of the hydrated inorganic cations by the organic cations in the interlayer [4]. Under suitable conditions, the inorganic ions on clay minerals can be replaced by organic ions, and then the interlayer spaces become hydrophobic. As a result, the sorption capacity of the modified clay minerals (i.e., organoclay) toward hydrophobic organic compounds can be significantly improved [5].

Organically modified layered silicates can be produced by modifying clays and clay minerals with various organic surfactant through intercalation process. Mechanical stirring is used by many researchers for preparing natural clay into organoclay. Most of the researcher need 2,5 h to 24 h for preparation of bentonite using mechanical stirring [4,5,6,7,8,9].

However, there is still lack of information about preparation of bentonite by ultrasound. A medium submitted to ultrasound can produce a number of physicochemical effects, such as increased reaction kinetics, changes in reaction mechanism, emulsification effects, crystallization, erosion, precipitation, etc[10]. Ultrasound effects are expected to shorten the preparation time of bentonite into organoclay.
The aim of this work is to prepare natural bentonite Nisam, North Aceh, by intercalation of cationic surfactant cetyl trimethyl ammonium bromide (CTAB) with ultrasound assisted. The effect of ultrasound on intercalation of cationic surfactant into bentonite were investigated by X-Ray diffraction (XRD), Fourier Transform Infrared (FTIR) and Scanning Electron Microscopy (SEM) analyses.

2. Materials and methods

2.1. Purification of bentonite

The raw bentonite was collected from Nisam region in North Aceh, Indonesia. The raw bentonites were purified before for removing the impurities. The purification of raw bentonite was prepared by the method of Gong et al [1]. The raw bentonite was ground firstly with a universal grinder. Then 3 gr grounded bentonite was suspended in 36 gr deionized water with sodium hexametaphosphate (2% of bentonite mass). The mixture then stirred magnetically for 24 hours. The supernatant of the dispersion was separated by centrifugation at a certain speed for 2 min. The purified bentonite was obtained by a centrifugation at 4500 r/min for 2 min, followed by drying the solid at 60°C in an oven.

2.2. Preparation of surfactant-modified bentonite by ultrasound

For organophilization process, 2 gr of purified bentonite was dispersed in 100 ml distilled water. Then a certain amount of surfactants with 2 CEC CTAB were added to the solution. The dispersions were sonicated for varying reaction time from 20 to 100 min at 70°C. Sonication process was performed with an Elmasonic ultrasonic liquid processor of 750 W output with a 37 kHz. All samples were centrifuged, washed with deionized water until free from bromide anions and dried at 60°C.

2.3. Characterization

The X-ray Diffraction scattering patterns were recorded using Shimadzu XRD 7000, operating at Cu Ka radiation at 40 kV and 30 mA. The samples were scanned in the range of 3 – 15° with a scan rate of 2.4°(2θ)/min. The Fourier Transform Infrared (FT-IR) spectra of the raw and modified bentonites were acquired using Shimadzu FTIR Prestige-2 spectrophotometer with a background calibration using the standard KBr pellet. The spectra were collected by accumulating 45 scans in the range 400-4000 cm⁻¹. The surface morphologies of raw clay and modified bentonites were examined using Scanning Electron Microscopy JEOL JSM.

3. Results and discussion

3.1. XRD analyses

The raw bentonite and modified bentonite by cationic surfactant with different time reaction of sonication were analyzed using X-ray diffraction (XRD) to compare the influence of ultrasound effect on the preparation of natural bentonite. XRD patterns of natural bentonite and a series of sonication time of modified bentonite by cationic surfactant are shown in Figure 1. It was observed a typical diffraction peak of raw bentonite was 5.09°, responding to an interlayer spacing 11.42 Å. After sonication with cationic surfactant under 37 kHz ultrasound irradiation, the interlayer spacing of modified bentonite had increased with increasing of sonication time on bentonite by the cationic surfactant. The interlayer spacing increased from 12.59 Å (2θ : 4.47°), 13.94 Å (2θ : 4.43°), 16.56 Å (2θ : 4.29°), 16.73 Å (2θ : 3.98°) and 16.87 Å (2θ : 3.84°) corresponding to sonication time 20 min, 40 min, 60 min, 80 min and 100 min, respectively. It can be seen that after 60 min exposed under ultrasound irradiation, the interlayer spacing of natural bentonite had increased 45% compared to initial interlayer spacing.
Ultrasound generated the microbubbles in the liquid medium. When the microbubbles collapsed, it leads sudden energy release and created local high temperatures, high pressures, and formation of strong shock waves. It helped to expand the interlayer of clay particles and make surfactant can intercalate into clay interlayer [11]. After the sonication of cationic surfactant, it can be seen that the position the XRD spectrum of the modified bentonite had changed compared to raw bentonite. It indicated that CTAB molecules had intercalated into the interlayer space of bentonite and enlarged the interlayer spacing of the bentonite. The results of this study are similar to Ocisly et al (2016) that used different quaternary ammonium salts for preparing organoclay [3].

### 3.2. FTIR analyses

The FTIR spectra of raw bentonite and modified bentonite by cationic surfactant under ultrasound irradiation with different time of sonication are shown in Figure 2. The band in the region 930-1100 cm⁻¹ for raw bentonite corresponding to the stretching vibration of Si-O group. The band at 3612 cm⁻¹ corresponding to structural OH stretching of water. After sonication, the band at 3612 cm⁻¹ decreased suggesting that the intercalation of cationic surfactants partially removed the interlayer water from the bentonite resulting an increased hydrophobicity. The new characteristic peaks appear at 2928 cm⁻¹ and 2851 cm⁻¹ corresponding to the –CH₂ asymmetric and –CH₂ symmetric stretching vibrations for CTAB. According to Acisli [1], the development of new peaks in modified bentonite could be attributed to the incorporation of the surfactant ions into interlayer galleries of bentonite.

![XRD patterns of raw bentonite (a) and with sonication time 20 min (b); 40 min (c); 60 min (d); 80 min (e); 100 min (f).](image-url)
3.3. SEM analyses

The SEM results of raw bentonite and modified bentonite by cationic surfactant using ultrasound irradiation provide important information about the morphology of the materials. The SEM photograph of raw bentonite shows the distinct structure compared with modified bentonite. Figure 3 shows that the particle size of modified bentonite is smaller than that of raw bentonite. Ultrasound irradiation had destroyed the structure of raw clay into the smaller size. According to Chattel et al [10], this phenomenon caused by the intense effects of ultrasound through the formation, growth and sudden collapse of gaseous microbubbles in the liquid phase. By imploding these bubbles create locally high pressures (1,000 bar) and temperatures (up to 5,000 K) that can lead to high energy radical mechanisms and also generate physical effects [10]. The collapse bubbles also help to disperse, expand and split the clay particles.

Figure 3. SEM images of raw bentonite and modified bentonite by cationic surfactant under ultrasound irradiated.
4. Conclusion
This study examined the ultrasound effect of cationic surfactant on the preparation of natural bentonite Nisam, North Aceh. The results show that ultrasound irradiation assists the cationic surfactant intercalating into interlayer of bentonite. The interlayer spacing of natural bentonite increases with increasing of ultrasound irradiated reaction time while the particle size of modified bentonite by cationic surfactant under ultrasound irradiation getting smaller than that of raw bentonite.

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