

SORPTION CAPACITY OF SURFACTANT–MODIFIED ZEOLITE NANOPARTICLES: EFFECT OF ZEOLITE–HEXADECYLTRIMETHYLAMMONIUM–BROMIDE RATIOS AND CONTACT TIME

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ABSTRACT

Natural zeolites, crystalline-hydrated tectoaluminosilicates, with their high cation exchange capacity (CEC) are widely used in the process removing of heavy metal cations from aqueous solution. However, natural zeolite has very low affinity for inorganic anions or nonpolar particles due to the presence of uncompensated negative charge of zeolites crystal lattice. Therefore, treatments are required to modify chemical surface properties of zeolite for improving the anion exchange capacity. This research aimed to quantify the effect of zeolite-hexadecyl trimethylammonium bromide (HDTMABr) ratios and contact time on the sorption capacity of surfactant-modified zeolite nanoparticles. Different ratios of zeolite-HDTMABr (1:500, 1:1000, 1:1500, and 1:2000) and contact times (6, 12, 18, 24, and 48 hours) were applied for the preparation of surfactant-modified zeolite nanoparticles (SMZ). The sorption capacity of SMZ was quantified by the measurement of adsorbed HDTMABr onto zeolite surface using bromophenol blue (BPB) method. Results of this research showed that contact time between zeolite and HDTMABr did not influence the sorption of HDTMABr onto zeolite. The amount of adsorbed HDTMABr onto zeolite with a contact time of 6 hours was in the range of 0.083–0.269 me g⁻¹, and the amount of adsorbed HDTMABr was relatively unchanged (0.073–0.261 me g⁻¹) when the contact time increased to 48 hours. However, variation in the amounts of adsorbed HDTMABr onto zeolite was observed with differences in the ratios of zeolite–HDTMABr. Ratio of 1:500 (zeolite:HDTMABr) resulted in optimum sorption of HDTMABr onto zeolite. Result of this study demonstrates that the ratios of zeolite nanoparticle–HDTMABr play an important role in the modification of zeolite chemical surface properties.

Keywords: zeolite nanoparticles, adsorption, chemical surface properties, surfactant, HDTMABr

INTRODUCTION

Sorption process is a very important in a variety of natural environment. For example, sorption of natural organic carbon (OC) onto soil minerals plays important role in the maintenance of soil fertility (Bento et al., 2019; Cusack and Turner, 2021) and reducing emission of carbon dioxide from soil systems (Liu et al., 2019; Ramesh et al., 2019). The sorption process is also reported to be the most factor influence the transport and availability of nutrients and contaminants in soils and waters (Fu et al., 2018; F. Wang et al., 2020). This suggests sorption process influence the accumulation and mobilization of nutrients and contaminants in soil-water systems.

Zeolites are hydrated aluminosilicate minerals with cage-like framework structure, consists of AlO_4^{5-} and SiO_4^{4-} tetrahedra units, which are linked to each other by the sharing of oxygen atoms (Li et al., 2019; Rožek et al., 2019). Substitution of each Al^{3+} to Si^{4+} in the tetrahedra framework introduces a net negative charge (Samanta et al., 2021; H. Wang et al., 2020), therefore, natural zeolite with their relatively high cation exchangeable capacity (CEC) are extensively used in the process removing of cationic ions from aqueous solution. Several studies have been shown the successfulness of natural zeolite application for removal of some heavy metals from wastewater (Elboughdiri, 2020; Irannajad and Kamran Haghghi, 2021; Isawi, 2020). However, these zeolites with the presence of uncompensated negative charge of zeolites crystal lattice are unable to remove anions for aqueous solutions and usually have little affinity for anions (Yan et al., 2019; Zekavat et al., 2020). Therefore, special treatments are required to modify chemical surface properties of zeolite to be used for sorption of anionic ions in the remediation of pollutants and wastes.

Because it is negatively charged, it is necessary to modify the zeolite to increase the positive charge on the zeolite surface in order to be capable of sorbing anionic nutrients and wastes. Modification of negatively charged zeolite surface generally includes the application of specific materials for forming layers of adsorbed cationic surfactant on the zeolite surface by adding surfactants such as hexadecyltrimethylammonium-bromide (HDTMA-Br) (Aloulou et al., 2021; Tran et al., 2018) and hexadecyl pyridinium bromide (HDP-Br) (Bagherifam et al., 2021). The addition of this surfactant is reported to be able to modify the chemical surface properties of zeolite so that it has the ability to adsorb anionic ions. Several previous studies showed a high ability of surfactant-modified zeolite in the removal of pertechnetate ($^{99}\text{TcO}_4^-$) from nuclear waste streams (Dickson et al., 2020), pesticide (Alvarez-García et al., 2020; Pukcothanung et al., 2018), and volatile organic compounds (VOCs) and polycyclic aromatic hydrocarbons (PAHs) from aqueous solutions (Hedayati et al., 2021; Wołowiec et al., 2017). The results of this study indicate the high effectiveness of surfactant-modified zeolite in absorbing anionic ions.

The capability of surfactant-modified zeolite to adsorb anionic ions is controlled by several factors in the process of making the association of surfactant-zeolite. Matusik et al. (2022) reported that the surfactant to CEC ratio close to 1.0 is optimal to achieve the highest adsorption. Several important parameters such as adsorbent dosage, pH, temperature, contact time and initial pollutant concentrations play an important role in determining the sorption capacity of surfactant-modified zeolite (Hailu et al., 2017). Dimas Rivera et al. (2021) suggests that the presence of CH_2^- groups after the modification play a key role for the anion attraction to the surfactant-modified zeolite. Results of these studies demonstrate the importance of changes in chemical properties of zeolite surface for increasing the amounts of anionic ions sorbed onto surfactant-modified zeolite. This study aimed to determine the effect of HDTMABr-zeolite ratios and contact time on the amounts of adsorbed HDTAMBR onto zeolite.

MATERIALS AND METHODS

Natural Zeolite

The natural zeolite used for this study originated from Klaten Regency, Central Java Province. Zeolite is obtained in the form of powder from conventional milling to meet the needs of waste treatment, and others. The types of minerals contained in the zeolite were analyzed using an X-ray diffraction microscope (XRD), and the results of the XRD analysis showed that the types of zeolite consisted of: 29.4% modernite, 13.2% Ca-clinoptiolite, 12.1%

heulandite, 6.1% Ca-heulandite, and another 14.7%. The natural zeolite milling process to nanoscale is carried out using planetary ball milling where the zeolite is ground in a wet state. Milling was carried out using a ball per ratio (BPR), 1:50, ball size of 5 mm, milled for 24 hours.

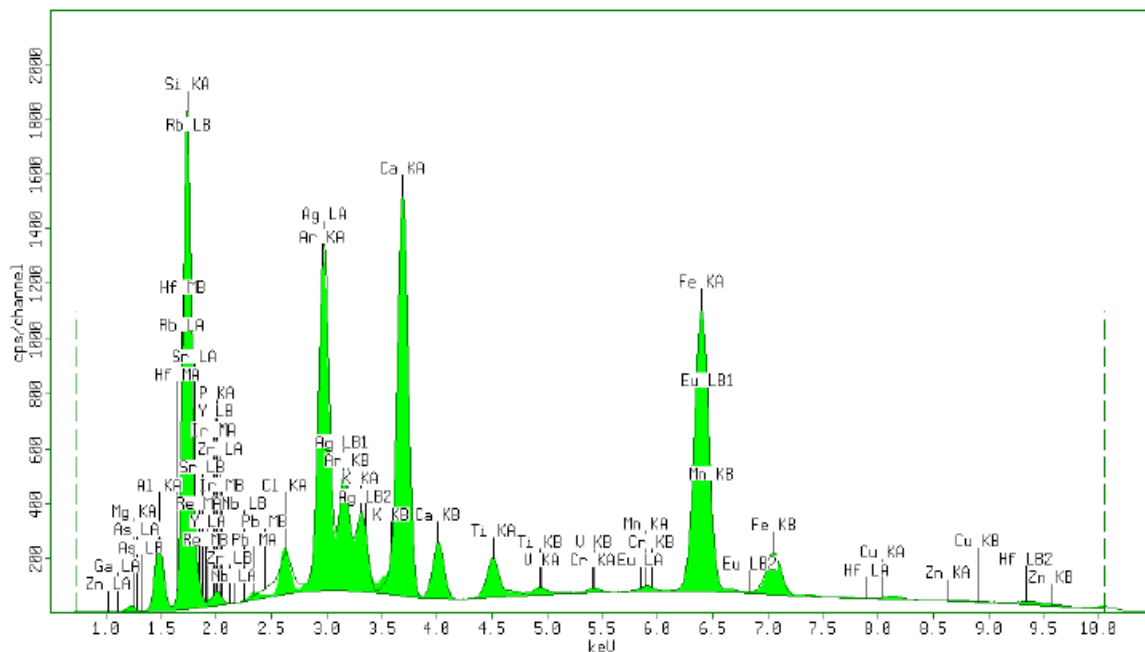


Figure 1. The XRF pattern of nanozeolite particles

Preparation of Surfactant Modified Zeolite

Measurement of cation exchange capacity (CEC) of zeolite was carried out before modification of zeolite surface using HDTMABr using the method for measuring soil CEC. Preparation of surfactant modified zeolite was carried out by adding 5 g of nano-zeolite into an Erlenmeyer and given enough water, then adding 125 mL of HDTMABr solution with a concentration of twice the amount of CEC nano-zeolite. The ratios of zeolite:HDTMABr tested were 1:500, 1:1000; 1: 1500, and 1:2000, while the contact times used were 6, 12, 18, 24, and 48 hours. The mixtures of zeolite and HDTMABr according to the treatment tested were then shaken using an orbital shaker and filtered, and the HDTMABr filtrate was accommodated in an Erlenmeyer flask to measure the amount of HDTMABr adsorbed onto the zeolite. The funnel containing the HTMABr–zeolite association was then rinsed with distilled water until the filtrate was free of Br which was tested with AgNO_3 solution. The solids on filter paper were then dried in an oven at 80 °C for 24 hours.

Measurement of Non-adsorbed HDTMABr

A total of 4.0 mL of 0.03 mM bromophenol blue (BPB) solution in 0.01 M NaOH was added to 4.0 mL of filtrate containing HDTMABr in a test tube. The solution in the tube was then adjusted to pH 8.0 using 0.1 M buffer phosphate solution, and the volume of solution was adjusted to 10.0 mL. A total of 5.0 mL of the solution was transferred to another tube and then mixed 5.0 mL of chloroform and then allowed to stand for 20 minutes. The complex of (HDTMA)₂BPB was quantified using UV-Vis spectrophotometer at 605 nm.

RESULTS AND DISCUSSION

Characteristics of Zeolite Nanoparticles and Surfactant-Modified Nanoparticles

The results of XRF analysis of zeolite nanoparticles showed that the dominant elements in zeolite nanoparticles include Si_2O , Si_2O_3 , CaO , Fe_2O_3 , P_2O_5 , K_2O and CaO . The amounts of these elements reached to 97.98% of the total elements present in zeolite nanoparticles. Details of the XRF analysis of zeolite nanoparticles was described in Table 1. Table 1 also shown that the ratio of $\text{SiO}_2/\text{Al}_2\text{O}_3$ of this zeolite nanoparticle was 2.85.

Table 1. The XRF analysis results for nanozeolite particles

SiO_2	Al_2O_3	CaO	Fe_2O_3	P_2O_5	K_2O	MgO	$\text{SiO}_2/\text{Al}_2\text{O}_3$
60.73	21.29	7.41	5.20	1.05	1.34	0.90	2.85

Fourier-transform infrared spectroscopy (FTIR) analysis was conducted to determine changes in chemical surface of zeolite nanoparticles with the addition of HDTMABr surfactant. Results of FTIR analysis was shown in Figure 2. Due to the fact that HDTMABr sorption process occurs only on the surface of zeolite nanoparticles, the bands connected with the internal Si–O(Si) and Si–O(Al) vibrations in tetrahedra or alumin- and silico-oxygen (in the range of $400\text{--}1200\text{ cm}^{-1}$) were relatively unchanged. However, changes in chemical surface of zeolite nanoparticles causes that in the spectra of zeolites bands associated with the presence of HDTMABr appear. The adsorbed HDTMABr onto zeolite nanoparticles was confirmed by the adsorption peaks of the N–H stretching at bands of 3042 cm^{-1} and 3383 cm^{-1} and by N–H bending at band of 1619 cm^{-1} (Figure 2).

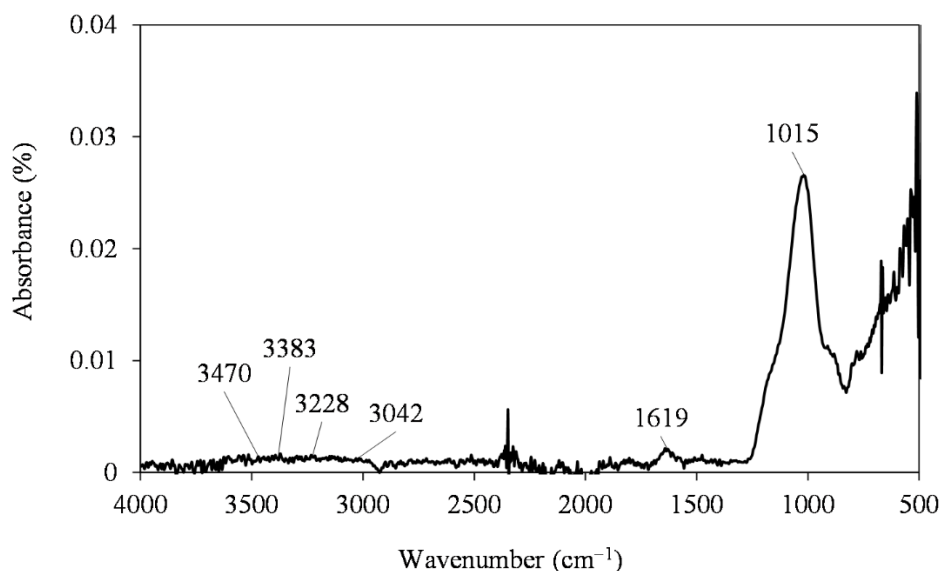


Figure 2. The FTIR pattern of surfactant-modified zeolite-nanoparticles

Effect of Zeolite Nanoparticles-HDTMABr Ratio and Contact Time

Natural zeolite has a cavity dimension $4.2\text{--}7.2\text{ \AA}$ and HDTMA-Br surfactant has head around 7.0 \AA , therefore, HDTMA^+ was adsorbed on the surface of zeolite. The critical micelle concentration (cmc) of HDTMABr surfactant is 0.9 mmol L^{-1} (Wibowo et al., 2011), and the zeolite modification was conducted using HDTMABr concentrations above its cmc value. Therefore, a layer of surfactant molecules was formed on the zeolite surface.

Previous research conducted by Thanos et al. (2012) showed that the results of the measurement of the zeta potential of surfactant-modified zeolite particles have positive zeta values, which indicates that surfactant-modified zeolite nanoparticles have the ability to adsorb anionic species. The main mechanism of this process is the creation of tail–tail hydrophobic interactions and the affinity between the positively charged surfactant head groups and counter ions. Wen et al. (2018) suggests that the main mechanisms of anionic species adsorption onto zeolite involves at least three types of interactions, a cation-exchange interaction, adsorption of ion pairs, and tail–tail interactions. In the zeolite modification process, HDTMA species initially penetrate into the interlayer by the cation exchange mechanism and then the excess of surfactant species are adsorbed onto the external surfaces via hydrophobic bonding, causing finally positive charge development on surfaces (Hailu et al., 2017). The results of this study imply a huge potential in the utilization of surfactant-modified zeolite nanoparticles in the management of water wastes and slow release of nutrients.

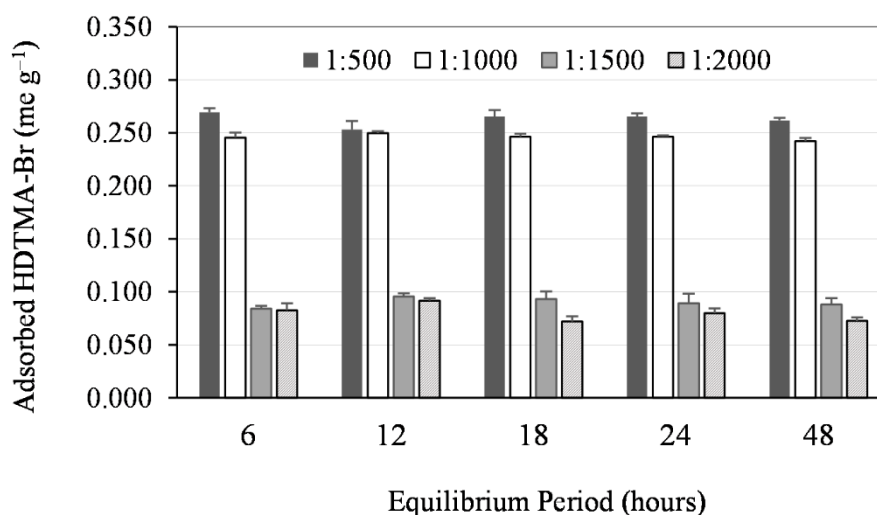


Figure 1. Effect of zeolite nanoparticles-hexadecyltrimethylammonium-bromide ratio and equilibrium period on the amount of sorbed hexadecyltrimethylammonium-bromide (HDTMA–Br). Lines above the bars represent the standard deviation of mean (n=3).

Contact time between zeolite dan HDTMABr did not affect the sorption capability of HDTMABr onto zeolite. For example, the amount of HDTMABr sorbed onto zeolite with a contact time of 6 hours was in the range of 0.083–0.269 me g⁻¹, and the amounts of adsorbed HDTMABr was relatively unchanged (0.073–0.261 me g⁻¹) when the contact time was increased to 48 hours (Figure 1). The results of this study indicate that the use of contact time of 6 hours has been able to produce optimal sorption of surfactant-modified zeolite nanoparticles.

Variations in the amounts of adsorbed HDTMABr occur with different ratios between zeolite nanoparticles-HDTMABr in the preparation of surfactant-modified zeolite nanoparticles. The use of a ratio of 1:500 (zeolite nanoparticles: HDTMABr) resulted in a relatively high amount of adsorbed HDTMABr, namely 0.263 me g⁻¹ (Figure 1). The amount of adsorbed HDTMABr onto zeolite nanoparticles decreased significantly to 0.080 me g⁻¹ when a ratio of 1:2000 (zeolite nanoparticles: HDTMABr) was used in the preparation of surfactant-modified zeolite nanoparticles. This result implies that the combination of 6 hours-equilibrium time

and the ratio of 1:500 (zeolite nanoparticles: HDTMA–Br) produces maximum sorption of surfactant-modified zeolite nanoparticles.

Variations in the amounts of adsorbed HDTMABr occur with the effect of the ratio of zeolite nanoparticles–HDTMABr were also reported in previous studies. For example, Szala et al. (2015) studied the effect of the amount of HDTMABr (0.2, 0.4, 0.6, 0.8 and 1.0 of external cation exchange capacity (ECEC)) applied to the development of surfactant–modified zeolite and found that the application of 1.0 of ECEC result in optimum sorption for this compound. At low HDTMABr concentrations, the sorption capacity of surfactant-modified zeolite is limited due to the lower amount of HDTMA Br attached on minerals (Hailu et al., 2017). Therefore, the amounts of HDTMBr are not adequately modified to form a full bilayer at the external surface of zeolite. When the amounts of added HDTMABr exceeds the critical micelle concentration (cmc), value at which the solution property of the molecule shows an abrupt change, a bilayer at the external surface of minerals with positive charges is formed. Several previous studies have shown that a layer of surfactant molecules was formed on the zeolite surface when the amounts of added HDTMABr exceeds the value of cmc (Jiménez-Castañeda and Medina, 2017; Pukcothanung et al., 2018; Reeve and Fallowfield, 2018).

CONSLUSION

Results of this study showed that contact time between zeolite dan HDTMABr did not result in differences in the sorption capability of HDTMABr onto zeolite. Contact time of 6 hours produces optimal sorption of surfactant-modified zeolite nanoparticles. On the other hand, ratios of zeolite nanoparticles-HDTMABr in the preparation of surfactant-modified zeolite nanoparticles influence the amounts of adsorbed HDTMABr onto zeolite. Increasing the ratios of zeolite nanoparticles-HDTMABr from 1:500 to ratio of 1:2000 decrease the amount of sorbed HDTMABr onto zeolite. The combination of 6 hours-contact time and the ratio of 1:500 (zeolite nanoparticles: HDTMABr) results in maximum sorption of surfactant-modified zeolite nanoparticles.

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