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The influence of Cetyltrimethylammonium Bromide Surfactant on The Ability of Natural Zeolite as An Adsorbent for Indigo Carmine Dye

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Abstract: *In the textile industry, indigo carmine is a synthetic dye used to produce blue. Disposal of these dyes in waters can disrupt the water ecosystem, therefore efforts need to be made to reduce the concentration or degrade these dyes. This research aims to obtain natural zeolite modified by cetyltrimethylammonium bromide (CTAB) as an adsorbent for indigo carmine dye. The research procedure consisted of (i) natural zeolite activation, (ii) modification with CTAB at concentrations of 20, 40 and 60 mM, (iii) adsorption of indigo carmine dye at varying concentrations of 40, 60, 80, 100 and 120 ppm and varying contact times of 3, 5, 10, 15, 30, 45 and 60 minutes, (iv) The activated and CTAB-modified zeolites were characterized by FTIR, while the adsorption results were analyzed by UV-vis spectroscopy. The results show that the adsorption of indigo carmine tends to increase with increasing adsorbate concentration and contact time. At indigo carmine concentrations of 40, 60, 80, 100 and 120 ppm, adsorption reached 99% when the concentration was 40 ppm with an optimum contact time of 45 minutes from variations of 3, 5, 10, 15, 30, 45 and 60 minutes. The presence of CTAB in zeolite is very effective in increasing the adsorption performance of indigo carmine dye.*

Keywords—natural zeolite; CTAB; cationic surfactant; indigo carmine dye, adsorption

1. INTRODUCTION

Synthetic dyes are suspended solids and organic substances that are often found in textile industry waste. Textile dyes are generally made from azo compounds and their derivatives which are benzene, toluene, anthracene functional groups, which are difficult to degrade naturally. One of them is indigo carmine.

Industrial development in Indonesia is increasing, and regulations regarding industrial waste are becoming increasingly stringent to realize environmentally sound development, so effective and efficient waste processing is very important. The rapid growth of industry not only has positive impacts but also negative impacts. One of them is producing dangerous waste, such as indigo carmine waste, because this waste tends to tends to reduce water quality. The presence of this waste causes changes in colour, smell and taste water; obstruction and loss of aquatic biological activity; land pollution and groundwater; as well as physical changes in plants.

Several methods for handling of indigo carmine waste is carried out by degradation such as biodegradation using micro-bacteria (Adnan et al., 2024), photocatalytic degradation by graphene nanodots (Jamil et al., 2024), photo-adsorption by CeO_2 (Majani et al., 2024), degradation by Cu-TiO_2/WO_3 (Buddiga et al., 2023) by TiO_2/zeolite (Ansori et al., 2016), or adsorption (Hor et al., 2016).

Adsorption is a popular and easy method for reducing the concentration of dye from wastewater. One substance that can be used as an adsorbent is zeolite. Zeolite is an inorganic polymer with a structure containing a framework of $(SiO_4)^{4-}$ and $(AlO_4)^{5-}$. Adsorption by zeolite can occur through pores or zeolite surface interactions. Indigo carmine dye has a larger size than natural zeolite pores which 3-15 Å (Ates & Akgül, 2016). So, the adsorption mechanism for indigo carmine dye could possibly occur through interaction on the zeolite surface. The increasing of the adsorption capacity, surface modification was carried out with cationic surfactants.

The overall surface structure of zeolite has a negative charge, while indigo carmine is anionic in solution. For this reason, it is necessary to modify the zeolite surface to increase the adsorption capacity of indigo carmine, namely using cationic surfactants such as cetyltrimethylammonium bromide (CTAB).

In the research of (Komariah et al., 2017) CTAB surfactant modified natural zeolite as adsorbent for Alkyl Benzene Sulfonate compounds. The adsorption performance of ZMS (zeolite modified surfactant) tends to increase with increasing CTAB. The use of TiO2 modified zeolite can increase the degradation of indigo carmine under acidic conditions (Ansori et al., 2016).

Previous studies have shown that the surfactant cetyltrimethylammonium bromide can be used to modify the zeolite surface. This paper reports the modification of natural zeolite using the surfactant cetyltrimethylammonium bromide as an adsorbent for indigo carmine dye. Factors that influence the adsorption of indigo carmine dye include concentration and contact time, which are studied in this paper.

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2. METHODOLOGY

2.1 Materials and equipment

The materials used are natural zeolite from Klaten, Central Java, HF 40% (Merck), NH_4Cl (p.a, Merck), cetyltrimethylammonium bromide/CTAB powder (p.a, Merck), Indigo carmine (p.a, Merck), Aquades.

Meanwhile, the equipment and instruments used were glassware, sieves, Merck pH indicator, analytical balances (Ohaus), magnetic stirrers, BINDER oven, Vulcan 3-130 Furnace, MAXQ 2000 shaker, FTIR spectrophotometer 8201PC Shimadzu, UV-vis spectrophotometer Shimadzu.

2.2 Synthesis of CTAB-zeolite

A total of 30 grams of natural zeolite powder measuring 100 mesh was soaked in 1% HF, then filtered using a vacuum, then the residue was neutralized and dried at 110°C for 4 hours. Next, the zeolite was soaked in 100 mL of 2 M NH_4Cl solution for 24 hours, then washed until neutral. After drying, it is calcined using a furnace at a temperature of 350°C for 4 hours. The activated zeolite was characterized by FTIR.

A total of 10 grams of activated zeolite was mixed with 100 mL of CTAB surfactant at concentrations of 20 mM, 40 mM and 60 mM for 24 hours (Mirzaei et al., 2016). Then the mixture was filtered, and the solid was dried in an oven at 70°C overnight. CTAB surfactant modified zeolite (CTAB-zeolite) was characterized by FTIR.

2.3 CTAB-Zeolite Adsorption Test on Indigo carmine

A total of 0.1 gram of CTAB-zeolite was contacted with indigo carmine 40, 60, 80, 100, 120 ppm, varying contact times 3, 5, 10, 15, 30, 45, and 60 minutes. Interaction and stirring of CTAB-zeolite - indigo carmine using a shaker speed of 150 rpm. After filtering, the concentration of remaining indigo carmine contained in the filtrate was analyzed by UV-Vis spectrophotometer at a maximum wavelenght of 610 nm (Zolgharnein et al., 2014).

3. RESULTS AND DISCUSSIONS

The activation of natural zeolite aims to clean pores and remove impurities by modifying its properties, such as increasing surface area and acidity. Activation can be done physically and chemically. Physical activation takes the form of heating at high temperatures and reducing the grain size. The purpose of physical activation is to expand the surface and enlarge the pores. Meanwhile, chemical activation consists of adding chemicals which aim to remove inorganic impurities.

Chemical activation with 1% HF aims to dissolve impurity oxides. The active zeolite undergoes an ion exchange process with ammonium ions using NH_4Cl 2 M. During chemical activation, cations from zeolite (Na^+, K^+, Ca^{2+} and Mg^{2+}) are exchanged with NH_4^+ cations, resulting in zeolite-NH_4. The cation exchange process can be accelerated by stirring. This stirring will cause the cation exchange active groups on the surface of the zeolite to move more actively so that the intensity of collisions between cations from the zeolite and NH_4^+ will increase. This is because with stirring, the irregularities in the solution increase and cause the kinetic energy in the solution to become greater, thereby accelerating the achievement of activation energy.

After obtaining zeolite-NH_4 with a neutral pH and free from Cl- ions, the zeolite was calcined at 350°C for 4 hours. The aim of the calcination process at a temperature of 350°C is to release NH_3 to obtain activated zeolite-H. The reaction that occurs in the process of activating natural zeolite with NH_4Cl to form activated zeolite-H can be seen in Figure 1.

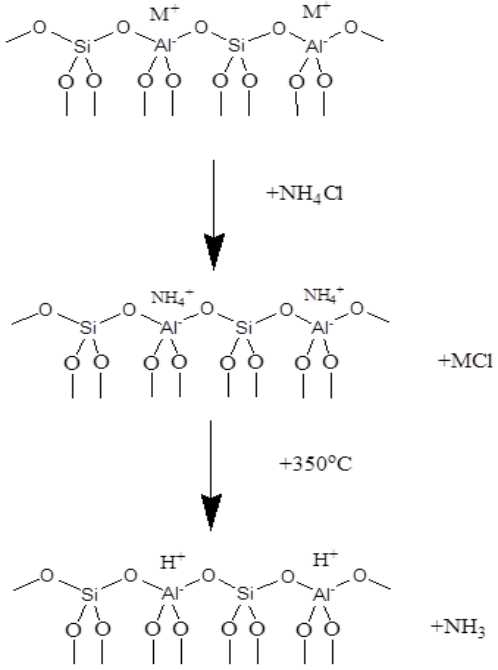

Fig. 1 *Activation process of natural zeolite using NH_4Cl*

Based on previous research, natural zeolite from the Klaten, Central Java consists of the minerals mordenite, quartz and clinoptilolite (Sriatun et al., 2024). Usually, this type of mineral has a medium Si/Al ratio so it is suitable for cation exchange between the cations in the zeolite and the CTAB cations.

3.1 RESULTS OF ZEOLITE MODIFICATION WITH CTAB

The purpose of the activated zeolite is modified by CTAB to increase the adsorption capacity of the zeolite. The presence of CTAB on the zeolite surface, it is hoped that it will have the ability to absorb anionic dye compounds.

The mechanism that occurs in this modification, in general, the adsorption of ionic surfactants on solid surfaces is the formation of a monolayer or hemicelle and this formation occurs below the CMC (critical micelle point). The process takes place through the stages of surfactant cation exchange so that a monolayer is formed between the zeolite and the surfactant on the zeolite surface. If the surfactant concentration is above the CMC, chemical interactions will

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occur between the hydrophobic ends of the surfactant and the other hydrophobic ends to form a double layer or admicelle.

One characterization to identify the compound content, functional group analysis was carried out using an FT-IR spectrophotometer. Qualitative analysis is obtained by looking at the spectral character where typical peaks will be seen which can be read as groups contained in the compound being analyzed and quantitative analysis is by reading the value of the wave number peaks.

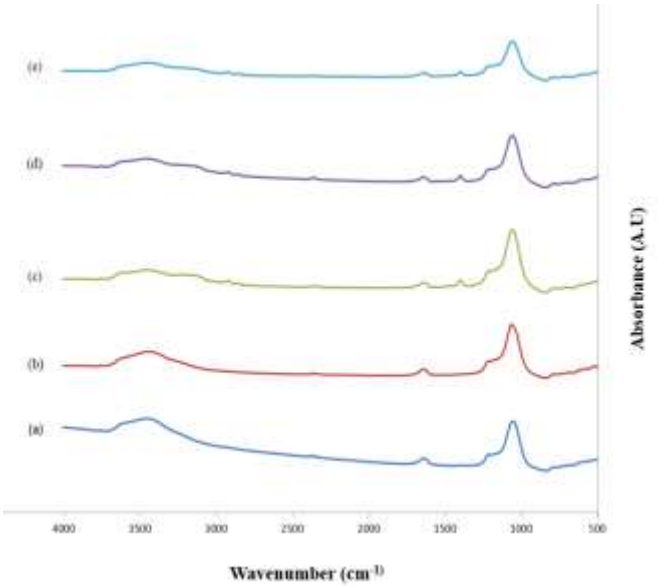

Fig. 2 *FTIR spectra of (a) Natural Zeolite (b) Activated Zeolite (c) 20 mM CTAB modified Zeolite (d) 40 mM CTAB modified Zeolite and (e) 60 mM CTAB modified Zeolite*.

In Figure 2, the zeolite framework structure is shown at wavenumbers 300-1300 cm^{-1}, these wavenumbers indicate the presence of tetrahedral bonds $(SiO_4)^{4-}$ and $(AlO_4)^{5-}$. The wavenumber 420-500 cm^{-1} is the internal bending vibration of Si-O/Al-O (T-O). Meanwhile, the wave number 700-780 cm^{-1} is the external bending vibration of Si-O/Al-O (T-O). The symmetry range is shown at wave numbers 650-850 cm^{-1} while the asymmetry range is shown at wave numbers 900-1250 cm^{-1}.

Natural zeolite has two bond groups, namely (1) wavenumber 1630-1640 cm^{-1}, related to the bond vibration of adsorbed water molecules (1635.64 cm^{-1}), (2) the wavenumber 3000-3700 cm^{-1}, related with overlapping symmetric (3448.72 cm^{-1}) and asymmetric (3749.62 cm^{-1}) stretching vibrations of the -OH group in H_2O (Stuart, 2000). Protonation of ammonium molecules and coordinatively bound ammonia can be distinguished spectroscopically by -NH deformation and stretching vibrations. Ammonium ions showed absorption at 1450 and 3300 cm^{-1}, coordinatively bound ammonia at 1250, 1630 and 3330 cm^{-1}. Vibrational deformations at 1450 and 1630 cm^{-1} were used as accurate indicators for the presence of protonated and coordinatively bound ammonia. The CTAB surfactant in zeolite can be identified from the vibration of the trimethylammonium head group and methylene tail of the CTAB surfactant. The presence of the trimethylammonium head group in CTAB is shown at the wavenumber 1404.18 cm^{-1} which is the bending vibration of N^+-$(CH_3)_3$. Vibrations of the methylene tail appear at wavenumbers 2800-2900 cm^{-1} which are symmetric (2854.65 and 2862.36 cm^{-1}) and asymmetric (2931.80 and 2924.09 cm^{-1}) stretching vibrations of the CH_3-R group. In the range 2800-3000 cm^{-1} there are asymmetric stretching vibrations CH_2 (2924.09 cm^{-1}) and symmetric stretching vibrations CH_2 (2862.36 and 2854.65 cm^{-1}). The peak shift at the wave number 2800-3000 cm^{-1} occurs due to a different conformation of CH_2. The conformation that occurs depends on the concentration added to the zeolite. At high concentrations CH_2 is in the all-trans conformation, while at low concentrations CH_2 is in the gauche conformation and the wave number shifts to a higher direction (Larkin, 2018).

Table 1 The FTIR interpretation of natural zeolite, activated natural zeolite and CTAB modified zeolite (Larkin, 2018)

Wavenumber (cm^{-1})					vibration range	Interpretation
Natural zeolite	Activated Zeolite	20 mM CTAB Modified zeolite	40 mM CTAB Modified zeolite	60 mM CTAB Modified zeolite		
462.92	462.92	447.49	462.92	424.34	420-500	internal bending vibration of T-O Si-O/Al-O
-	601.79	-	671.23	717.52	680-850	external bending vibration of T-O Si-O/Al-O
779.24	694.37	794.67	794.67			
1056.99	1064.71	1056.99	1056.99	1056.99	900-1250	asymmetric range trimethylammonium head group
-	-	1404.18	1404.18	1404.18		
1635.64	1635.64	1635.64	1635.64	1635.64	1630-1640	vibration of water molecules
-	2862.36	2854.65	2854.65	2854.65	2800-2900	symmetric stretching vibration of the methylene tail
-	-	2924.09	2924.09	2924.09		asymmetric stretching vibration of the methylene tail
3448.72	3448.72	3224.98	3448.72	3448.72	3000-3700	-OH stretching vibration in H_2O
	3749.62	3448.72 3749.62	3749.62	3749.62		

3.2 Performance of Cetyltrimethylammonium Bromide (CTAB) modified zeolite as an adsorbent for Indigo carmine dye

The adsorption process of indigo carmine dye by CTAB modified zeolite was carried out by varying the concentration of adsorbate (indigo carmine) and contact time. The remaining indigo carmine concentration in the filtrate was analyzed using a UV-vis spectrophotometer at a maximum wavelength of 610 nm (Zolgharnein et al., 2014).

Effect of adsorbate concentration on the adsorption performance of CTAB modified zeolite

The aim of varying the concentration of indigo carmine is to determine the maximum concentration of adsorbate that can be absorbed by 20 mM, 40 mM and 60 mM CTAB surfactant modified zeolite. Meanwhile, the indigo carmine adsorbate concentration was 40 ppm, 60 ppm, 80 ppm, 100 ppm, 120 ppm with a contact time of 30 minutes. The filtrate was analyzed using a UV-Vis spectrophotometer at a maximum wavelength of 610 nm.

Adsorption is an event where a solid substance, usually called an adsorbent, has a tendency to absorb molecules of gas or liquid adsorbate. Apart from contact time, the adsorbate concentration is another factor influencing adsorption. The higher the adsorbate concentration, the more adsorbed it will be. The adsorbent and indigo carmine used were 0.1 g of adsorbent in 10 mL of adsorbate. The more adsorbent, the greater the amount of adsorbate that is adsorbed into the adsorbent. This is because by increasing the ratio it is possible for the adsorbate to move more freely, so that it binds more quickly to the surface of the adsorbent.

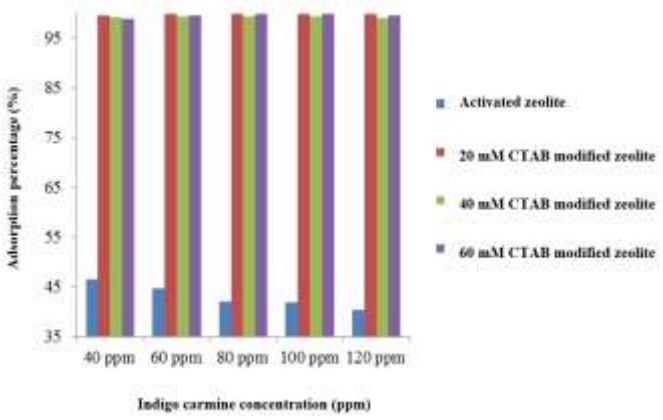

Fig. 3 *Percentage of indigo carmine adsorption using activated and CTAB-modified zeolite*

Fig. 3 shows that CTAB-modified natural zeolite can adsorb indigo carmine. If we look at the results obtained, the order of zeolite's ability to adsorb from the lowest is activated zeolite, 40 mM CTAB modified zeolite, 60 mM, and 20 mM. From the various concentrations of indigo carmine, it showed that almost 99% of the results at a concentration of 40 ppm have occurred. Indigo carmine concentrations of more than 40 ppm produce relatively the same adsorption percentage, this showed that the adsorbent can no longer adsorb or can be said to have reached its saturation point.

The interaction between the zeolite surface charge and the CTAB surfactant head is an electrostatic interaction, where the zeolite surface is negatively charged and the CTAB surfactant head is positively charged. Hydrophobic interactions between surfactant tails, which are obtained from adding a concentration of cationic surfactant CTAB above CMC on the zeolite surface. This is possible because when adding surfactant to the zeolite surface the interaction that takes place will be different from the character of the surfactant itself in a solvent (for example: water). Where by adding surfactant to the surface of the zeolite, the electrostatic interactions that take place also influence the arrangement of the surfactant on the surface of the zeolite and there is also additional surface tension, moreover the zeolite has a charge on its surface. Meanwhile, in the nature of the surfactant character of the solvent (for example: water), the interaction that occurs is only between the solvent and the surfactant, so that if the concentration of the given surfactant is increased above the CMC, surfactant micelles will form and there will be no arrangement of the surfactant as in the arrangement of the surfactant on the surface of the zeolite (Komariah et al., 2017).

Effect of contact time on the adsorption performance of CTAB modified zeolite

Contact time greatly influences the diffusion and attachment processes of adsorbate molecules to the adsorbent. Contact time aims to determine whether the adsorbent has reached a saturation point. The results of the previous stage showed that the optimum concentration of indigo carmine adsorbate was 40 ppm. This concentration is used for the next process, namely variation of contact time concentration. The aim is to determine the optimum contact time for adsorption of indigo carmine using CTAB surfactant modified zeolite 20 mM, 40 mM, and 60 mM. The contact times used were 3, 5, 10, 15, 30, 45, and 60 minutes. This data is shown in Fig. 4.

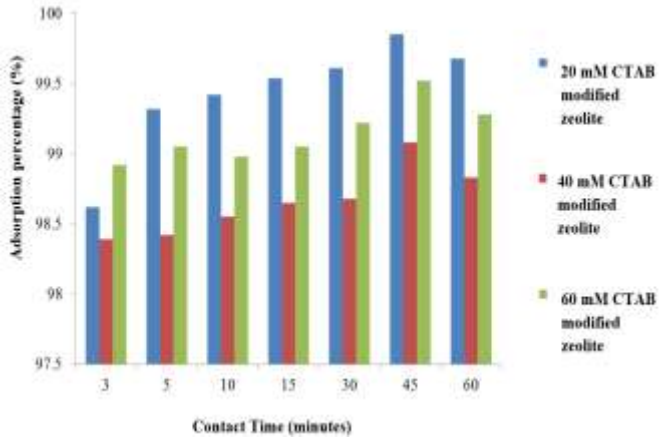

Fig. 4 *Percentage of indigo carmine adsorption using and CTAB-modified zeolite*

Fig. 4 shows that at a contact time of 3 to 45 minutes there was an increase in adsorption by the CTAB modified zeolite. This is because the surface of the zeolite is still slightly covered by indigo carmine adsorbate, so the adsorption capacity is high. At contact times above 45 minutes, there was a decrease in indigo carmine adsorbed by the zeolite. The decrease in adsorption capacity was caused by the zeolite surface being covered with indigo carmine adsorbate so that the adsorption capacity decreased. In the adsorption process, the adsorbate will be adsorbed on the surface of the zeolite until it covers the entire surface, so that at equilibrium the adsorption power will tend to be constant (Mirzaei et al., 2016).

4. CONCLUSIONS

Based on the results and discussion, it can be concluded that natural zeolite has been successfully modified with Cetiltrimethylammonium bromide. The presence of CTAB in zeolite is very effective in increasing the adsorption performance of indigo carmine dye, within 3 minutes the adsorption performance increased more than two times (113%) compared to zeolite without CTAB. The CTAB concentration did not have much effect on the adsorption performance. So, this material is highly recommended as an anionic dye adsorbent.

5. ACKNOWLEDGMENT

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