

Preparation, Characterization and Methylene Blue Dye Adsorption Ability of Acid Activated-Natural Zeolite

O A Saputra, M D Prameswari, V T D Kinanti, O D Mayasari, Y D Sutarni, K Apriany and W W Lestari

Chemistry Department, Sebelas Maret University, Faculty of Mathematic and Natural Sciences, Jl. Ir Sutami 36A Surakarta, 57126 Indonesia.

Email: oziadisaputra@student.uns.ac.id

Abstract. The aim of this research was to prepare an acid-activated natural zeolite (Ac-Zeo) as a low-cost adsorbent material and to investigate their ability on methylene blue dye removal in aqueous solution. The natural zeolite was activated using hydrochloric acid and the final product was characterized using Fourier transform infra-red (FTIR), X-ray diffraction (XRD) and scanning electron microscopy (SEM). The adsorption process was carried out using the batch method. Some parameters like pH condition, contact time and varied dye initial concentration were studied to determine the adsorption ability of Ac-Zeo. In this study, kinetic adsorption was evaluated using pseudo-second order model approach and found that the kinetic adsorption rate constant (k) and adsorption capacity at equilibrium are $0.1872 \text{ mg.g}^{-1}.\text{min}^{-1}$ and 14.94 mg.g^{-1} , respectively. Moreover, Langmuir, Freundlich, and Dubinin-Kaganer-Radushkevich isotherm adsorption models as well as sorption mechanism were studied in this research.

1. Introduction

Zeolites are a class of microporous crystalline aluminosilicate material, widely available in Indonesia [1]. Zeolites have three-dimensional frameworks, consist of $[\text{SiO}_4]^{-4}$ and $[\text{AlO}_4]^{-5}$ tetrahedral [2, 3]. Beside of that, the zeolites also contain cations (i.e. Na^+ , Ca^+ and K^+) to balance the negative charge in its structure [2, 4]. The presence of negative charge in zeolite frameworks makes them have an adsorption capacity to some cationic compound like metal ion and basic dye [5-7]. In the past work, numerous researchers have studied about the applicability of zeolite in various purposes, i.e. catalyst [8], ion metal adsorption [9], gas purification [10], environmental engineering [11], and dye adsorption [7, 12]. However, the commercial synthetic zeolites with high purity are high cost [5]. Thus the using of natural zeolite is very necessary to utilize these minerals also to reduce the operating cost in waste water management in textile industry.

Synthetic dyes are commonly used in dyeing process than natural dyes due to its low-cost production, brighter colors, high resistance to the environment and application, thus the consumption of synthetic dye is higher than natural dyes even though highly toxic and carcinogenic [13]. The dye compound consists of chromophores groups which influence the dye color, and auxochromes group which determines the color intensity [14]. The rapid development of industries like textile, paper and pulp, leather, food, pharmaceutical and cosmetic, causes the increasing of colored effluent and



generates a considerable amount of polluted waste water [15, 16]. This pollution becomes a major concern in environmental problems, human health and marine lives [13].

It was noted that the removal dye in aqueous solution is difficult to be achieved due to the inert properties of synthetic dye and their low concentration in aqueous solution [17]. During the past decade, several methods were used for dye removal in aqueous solution, including photocatalytic degradation [18], ion exchange [19], electrochemical [20], coagulation [21], physicochemical treatment [22, 23] and adsorption [7, 12, 24]. Among all of these methods, the adsorption process is very suitable for dye removal due to its advantages such as low operational cost to remove the organic dye molecules, easy and relatively effective in dye removal and can be operated at low concentration of dyes [13, 25, 26].

Lately, a low-cost adsorbent by utilizing the natural resources, such as chitosan [27], cellulose from waste product [24], clay minerals [28], and natural zeolite [7, 29-31] has been developed. Due to their porosity, the zeolite has a good ability to be used as adsorbent material in dye removal. Han et al. [7, 29] has been successfully utilized natural zeolite in particle form for methylene blue dye removal in aqueous solution. Alpat et al. [30] also used Turkish natural zeolite with the structure like-clinoptilolite for cationic dye removal, Toluidine Blue O, and gave the best adsorption condition at pH 11 with an adsorption maximum capacity of $2.1 \times 10^{-4} \text{ mol.g}^{-1}$. Another work has been reported that an enhancement of maximum adsorption capacity could be achieved by modifying the natural zeolite [32]. The adsorption ability of zeolite is determined by their porous structure. Elaiopoulus et al. [2] reported that by the dealuminated process using acid treatment (HCl) was able to reform the pore structure and removed the amorphous Al-species. This caused the crystallinity of zeolite increased as well as influenced in their porosity. Based on the literature review, in this research was tested the effect of acid treatment in natural zeolite on the methylene blue dye removal. Furthermore, the characteristic of natural zeolite after treatment was analyzed through FTIR (Fourier transform infrared), XRD (X-ray diffraction) and SEM (scanning electron microscopy).

2. Experimental

2.1. Materials

Natural zeolite was collected from Klaten, Indonesia. Hydrochloric acid (HCl), sodium hydroxide (NaOH) and ammonium chloride (NH_4Cl) were purchased from Merck. The methylene blue dye was commercially available from Surakarta, Indonesia. The distilled water was supplied from Chemistry Laboratory of Sebelas Maret University.

2.2. Preparation of Acid-Activated Natural Zeolite (Ac-Zeo)

Natural zeolite was crushed into powder form and sieved to obtain ± 200 mesh of particle size. The zeolite powder was refluxed with hydrochloric acid 50% at 50°C for 1 hour. Afterward, the material was filtered and washed with distilled water until pH 7. The sample was recorded as acid activated-natural zeolite (Ac-Zeo). The Ac-Zeo was then immersed in 1 M ammonium chloride solution for five days. Then, the Ac-Zeo was washed several times using distilled water and dried at 60°C for 24 hours. The Ac-Zeo was stored in vacuum desiccator before used.

2.3. Characterization of Ac-Zeo

The Ac-Zeo was characterized using Fourier transform infra-red (FTIR) spectroscopy IR Prestige 21 SHIMADZU. The sample was prepared in pellet form and recorded in the range of $400\text{-}4000 \text{ cm}^{-1}$ wave number. The scan number was set up to 45 times with resolution 2 cm^{-1} . The crystallinity of Ac-Zeo was studied using X-Ray Diffraction (XRD) model Shimadzu XRD Lab-X 6000. The morphology of Ac-Zeolite was observed using Scanning Electron Microscopy (SEM) model Phenom FEI.

2.4. Methylene Blue Adsorption

2.4.1. Effect of pH. A Methylene blue solution was prepared into 30 mg.L⁻¹ of concentration by dissolving 30 mg dye with 1 L distilled water. About 0.02 g of Ac-Zeo was added into 10 mL methylene blue solution with various pH (3, 5, 7, 9, and 11). Then, the mixture was shaken about 30 minutes at room temperature. The dye solution was filtered immediately and analyzed using UV-Vis Perkin Elmer Lambda 25 Spectroscopy.

2.4.2. Effect of Contact Time. Methylene blue solution was adjusted at optimum pH. About 0.02 g of Ac-Zeo was added into methylene blue solution (10 mL, 30 mg.L⁻¹) and shaken for 10, 20, 30, 40 and 60 minutes. After adsorption process, the dye solution was filtered immediately. The Adsorbed dye was calculated using UV-Vis PerkinElmer Lambda 25 spectroscopy.

2.4.3. Effect of Initial Dye Concentration. Methylene blue solution was prepared at 10, 20, 30, 40 and 50 mg.L⁻¹ and conditioned at optimum pH condition. About 10 mL of dye solution was added into an erlenmeyer containing 0.02 g of Ac-Zeo and shaken for 30 minutes. The solution was filtered and analyzed using UV-Vis PerkinElmer Lambda 25 spectroscopy.

3. Results and Discussion

3.1. Material Characterization

Quantitative analysis of natural zeolite and the activated product was conducted using XRD. The result showed that natural zeolite was classified as zeolite mordenite. Figure 1 describes the comparison of natural zeolite and Ac-zeo with the standard diffraction pattern of zeolite mordenite (Zeo-mordenite) from the International Zeolite Association [40]. As we can see in Figure 1, there is no significant effect on the pattern of natural zeolite after the acid activation. However, natural zeolite has broad peak at 2θ 5.40 which indicates the amorphous phase. After acid treatment, the pattern shows that broad peak has vanished. According to Elaiopoulus et al. [2], the acid treatment will eliminate the amorphous Al³⁺-species in natural zeolite structure. The eliminating of amorphous Al-species (dealumination) could increase the crystallinity of zeolite. Consequently, it will increase the pore in zeolite and it can be used as an active site for organic dye molecules binding.

Chemical analysis of zeolite and its modification was conducted using FTIR. This technique is very important to analyze the functional group of each material. Moreover, it was also used by the researcher for proving the chemical interaction in compounding, to analysis the material structure and to obtain information about the ions substitution in the material like zeolite [2, 33]. The FTIR spectra of the natural zeolite and acid-treated zeolite are shown in figure 2. It showed that natural zeolite which has classified as mordenite generally consists of Si-O tetrahedral layer and Al-OH octahedral layer. It was proven by the absorption band appeared at 1042 cm⁻¹ which correspond to the stretching vibration band of Si (Al)-O [34, 35]. After acid treatment, the effect can be seen as a shift in the vibration position at 1042 cm⁻¹ to 1086 cm⁻¹. The shifting was due to dealumination process [8]. It also confirmed by X-ray diffractogram (figure 1). The adsorption peak at 798 cm⁻¹ is characteristic vibration of -OH deformation in Al-OH. The vibration of Si-O-Al deformation observed as a band at 530 cm⁻¹, while the vibration of Si-O-Si deformation is also found at 456 cm⁻¹. A broad peak appearing at 3438 cm⁻¹ is assigned to hydrogen bonding of OH in zeolite framework. Moreover, the peaks at 3630 cm⁻¹ and 1637 cm⁻¹ are typical adsorption band of the water molecules in the zeolite. As we know, the presence of water could poison the active sites of zeolite. Adding acid into zeolite could make the pore wide open and clean from impurities. It was proven after acid treatment intensity at 3630 cm⁻¹ and 1637 cm⁻¹ decreased. The Infrared spectrum of Ac-Zeo has absorbance band at 3156 cm⁻¹ and 1400 cm⁻¹, which characteristic of NH stretching and bending vibration which generated from NH₄⁺ ion exchange. The presence of NH₄⁺ ions could increase the acid site of zeolite.

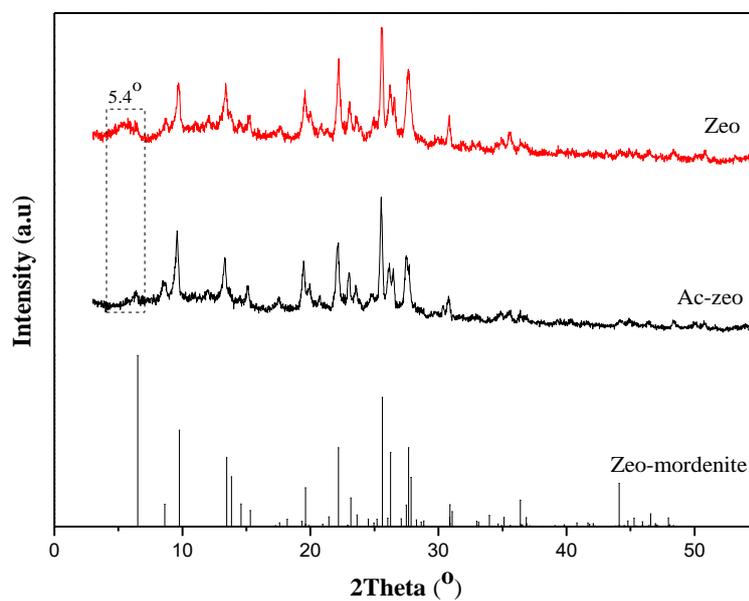


Figure 1. XRD pattern of Zeolite and Ac-Zeo.

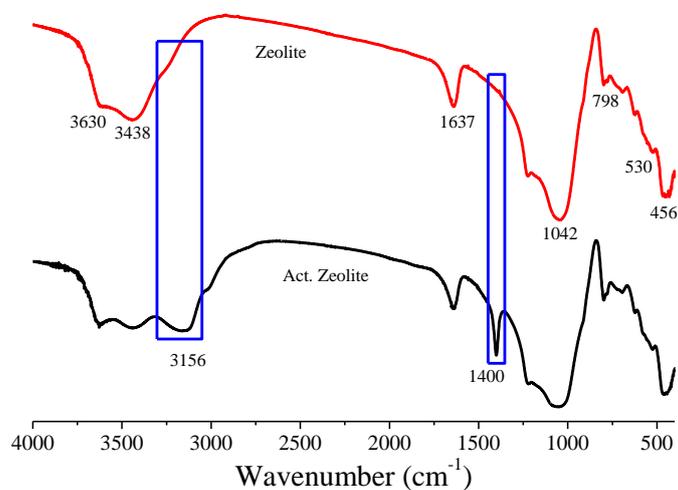


Figure 2. Infra-red spectrum of zeolite and Ac-Zeo.

Morphological study of Ac-Zeo surface was examined using scanning electron microscopy (SEM). Figure 3 showed the morphology of the Ac-Zeo with 40000 times magnification. Based on the SEM image, it was clearly seen that the physical structure of the Ac-Zeo like a tubular rod.

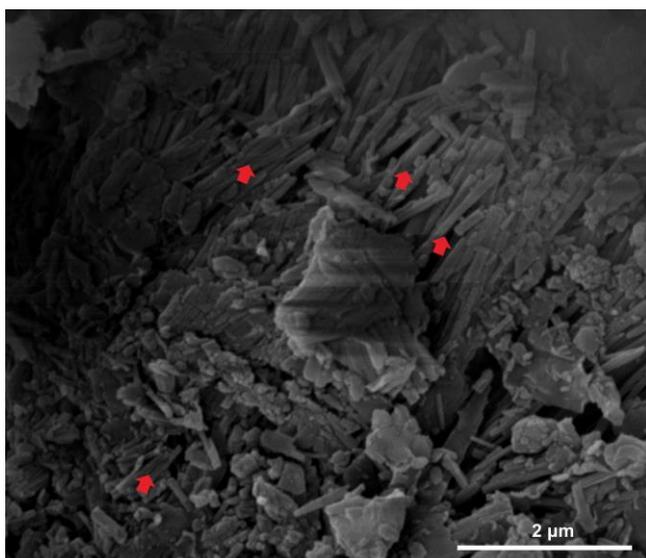


Figure 3. Morphology of Acid-activated Zeolite with 40000x magnification

3.2. Effect of pH

The pH played an important role in the adsorption process [34]. However, in our study, the dye removal percentages at various pH condition were not significantly different, where at acid or basic condition, it has high dye removal percentages which are more than 90%. Figure 4 shows the dye removal in various pH condition with the best condition is achieved in acid condition (pH 3). In the pH range of 3-5, the methylene blue dye removal slightly decreases, where at pH 3 the dye removal is 97.9% while at pH 5 reach 97.6%. The dye removal of methylene blue decreases gradually at pH 7, which is 15.6% compared to the condition at pH 3. At basic condition (pH 9 and 11), the dye removal increases compared to at pH 7, but lower than at acid condition (pH 3 and 5). The other investigation [7, 36], the increasing of pH led the adsorbed methylene blue onto zeolite increased because at lower pH the presence of H^+ ions competed with MB in the adsorption process. However, based on this data, the lower of pH gave the best condition. It was noted that the presence of a porous structure of zeolite also played an important part in the adsorption process [31, 37]. By the acid treatment, the negative charge in zeolite surface was neutralized by the positive charge of H^+ . Moreover, the addition of ammonium chloride compound in the zeolite increased the acid site of zeolite. Thus, at acid condition, the MB is possible to be more basic and make it easy to attach at the acid site of zeolite.

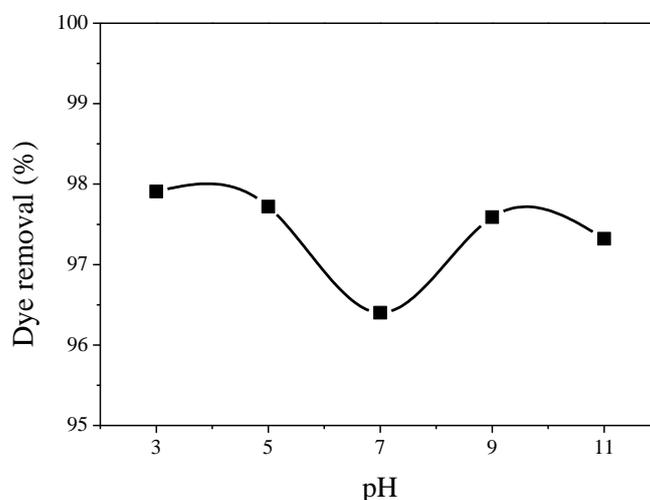


Figure 4. Effect of pH condition on dye removal.

3.3. Adsorption Kinetic

The effect of contact time on methylene blue adsorption onto zeolite can be seen in figure 5. In the beginning, the dye removal reaches more than 90%, and it quickly increases after 20 minutes of applied contact time by 98.6%. The mechanism of methylene blue adsorption follows two phases. At the first stage, the methylene blue adsorption is fast due to high chemical and physical contact through the zeolite pores. At second phase, the adsorption is slow because the methylene blue adsorbed onto zeolite reached an equilibrium or the concentration of methylene blue was relatively small [7,38]. The adsorption of methylene blue onto zeolite has reached an equilibrium state at 40-60 minutes. By acid treatment, the ability of zeolite to adsorb methylene blue increased, compared to Han *et al.* [7] work, which reached equilibrium state at 820 minutes.

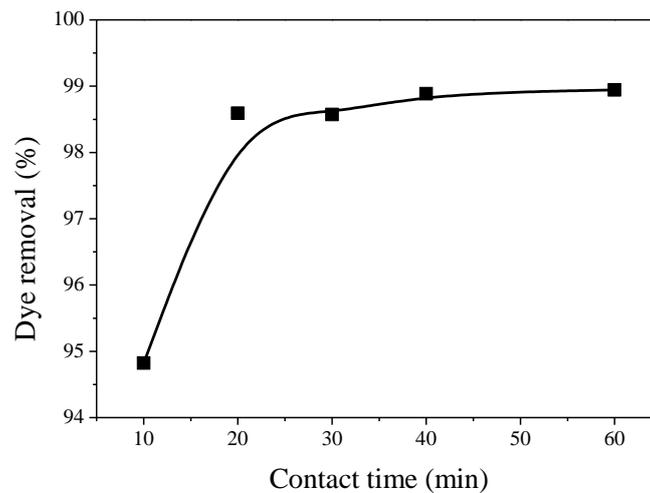


Figure 5. Effect of contact time on dye removal.

A simple kinetic adsorption can be described using a linear form of pseudo-second order using equation 1 [31]:

$$\frac{t}{Q_t} = \frac{1}{k \cdot Q_{et}^2} + \frac{1}{Q_{et}} t \quad (1)$$

where, t is the contact time (min), Q_t is the adsorption capacity at t time ($\text{mg} \cdot \text{g}^{-1}$), k is the rate constant of pseudo-second order ($\text{g} \cdot \text{mg}^{-1} \cdot \text{min}^{-1}$) and the Q_{et} is adsorption capacity at equilibrium ($\text{mg} \cdot \text{g}^{-1}$).

Figure 6 shows the linear form of the second-order kinetic of methylene blue dye adsorbed onto zeolite. From t versus t/Q_t plot pseudo second order model, it can be obtained the kinetic rate constant (k) and the adsorption capacity at equilibrium (Q_{et}). The k and Q_{et} of methylene blue adsorbed onto Ac-Zeo are $0.1872 \text{ mg} \cdot \text{g}^{-1} \cdot \text{min}^{-1}$ and $14.94 \text{ mg} \cdot \text{g}^{-1}$, respectively. The correlation coefficients (R^2) obtained by using the linear form of pseudo-second order model is closed in 0.99995, indicating the models is applicable for the adsorption. A similar result has been found by Wang *et al.* [31] on methylene blue dye adsorbed onto zeolite.

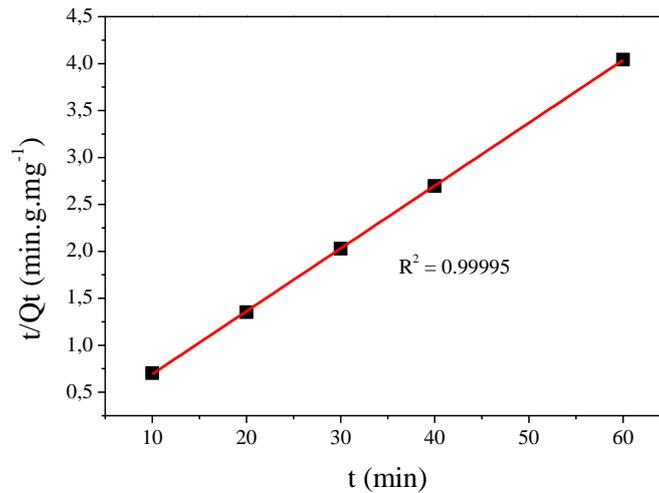


Figure 6. Effect of contact time on dye removal.

3.4. Adsorption Isotherm

To study the adsorption isotherm, the Langmuir and Freundlich models were applied in this research. Moreover, the Dubinin–Kaganer–Radushkevich (DKR) model was also studied to clarify the energy sorption in methylene blue adsorbed onto Ac-Zeo. The linear form of Langmuir, Freundlich, and Dubinin–Kaganer–Radushkevich Models equation are described in equation 2 [7], 3 [31], and 4 [39].

$$\frac{C_o}{q_e} = \frac{1}{K_L \cdot Q_m} + \frac{1}{Q_m} C_o \quad (2)$$

$$\ln q_e = \ln K_F + \frac{1}{n} \ln C_o \quad (3)$$

$$\ln Q_e = \ln Q_s - \beta \epsilon^2 \quad (4)$$

Where, C_o is initial dye concentration (mg.L^{-1}), q_e and Q_m is adsorption capacity (mg.g^{-1}) at equilibrium and maximum, respectively. Q_e is the amount of methylene blue dye adsorbed in mmol.Kg^{-1} . Q_s is the DKR monolayer capacity (mmol.Kg^{-1}), β is energy sorption constant ($\text{mol}^2.\text{J}^{-2}$), and ϵ is Polanyi potential which calculated using Equation 5.

$$\epsilon = RT \ln \frac{1}{C_o} \quad (5)$$

Energy sorption can be calculated following equation 6.

$$E = \frac{1}{\sqrt{2\beta}} \quad (6)$$

Figure 7, 8 and 9 shows the linearized Langmuir, Freundlich, and Dubinin–Kaganer–Radushkevich adsorption isotherms of methylene blue on Ac-Zeo. The parameters of all models, such as the

adsorption maximum capacity, n value, energy sorption, the isotherm constants and correlation coefficients are presented in Table 1. The R^2 of Freundlich model is higher than other models, which is 0.999. It means that the adsorption process well fit to Freundlich model. Thus it followed the Freundlich mechanism, similar to Alpat *et al.* [30] works.

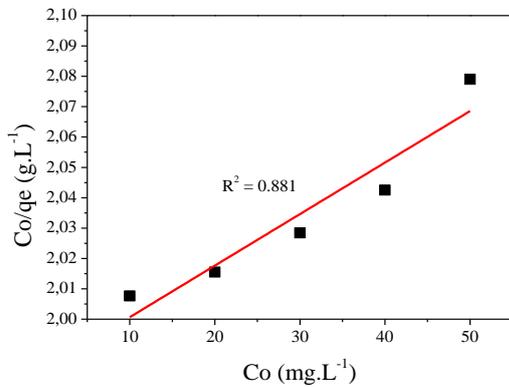


Figure 7. Langmuir isotherm model Co versus Ce/qe.

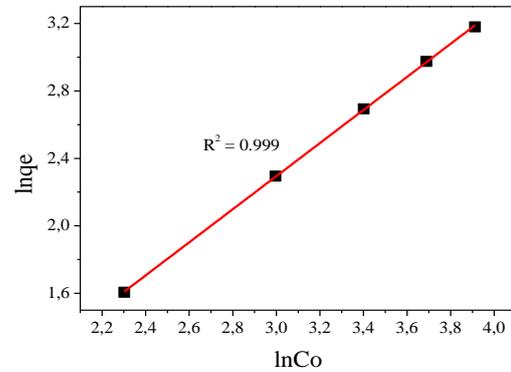


Figure 8. Freundlich isotherm model lnCo versus lnqe.

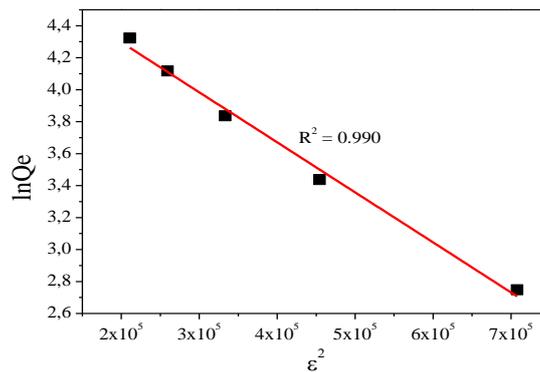


Figure 9. Dubinin–Kaganer–Radushkevich isotherm model ϵ^2 versus lnQe.

From the Langmuir model, it can be obtained the adsorption maximum capacity by plotting Co versus Co/qe [7, 30, 31]. The adsorption capacity maximum is 588.24 mg.g⁻¹. The Freundlich model was generated by the heterogeneity factor of adsorption sites (n). The 1/n value of methylene blue adsorbed onto Ac-Zeo is 0.98 (0<1/n<1), indicating favorability and higher adsorption ability of methylene blue on zeolite [7]. The DKR monolayer adsorption capacity is 137.36 mmol.Kg⁻¹, while the energy sorption of methylene blue is 0.399 KJ.mol⁻¹, indicating physical sorption [39].

Table 1. Some parameters on Isotherm adsorption.

Isotherm	Parameters	Value
Langmuir	Qm (mg.g ⁻¹)	588.24
	K _L (L.mg ⁻¹)	8.57 x 10 ⁻⁴
	R ²	0.881
Freundlich	1/n	0.98

	$K_F((\text{mg}\cdot\text{g}^{-1})(\text{mg}\cdot\text{L}^{-1})^n)$	0.52
	R^2	0.999
Dubinin–Kaganer–Radushkevich	$Q_s(\text{mmol}\cdot\text{Kg}^{-1})$	137.36
	$\beta(\text{mol}^2\cdot\text{J}^{-2})$	3.13×10^{-6}
	$E(\text{kJ}\cdot\text{mol}^{-1})$	0.399
	R^2	0.990

4. Conclusions

The acid treatment of zeolite has been conducted and caused an increasing of zeolite crystallinity. The Ac-Zeo has the porous structure and acts as an active site for methylene blue dye adsorption. The pH condition did not significantly influence the methylene blue dye removal. However, the best condition was given at acid condition (pH 3). The adsorption equilibrium was reached at range 40-60 minutes with dye removal was more than 90%. The rate constant of pseudo-second order (k) is $0.1872 \text{ mg}\cdot\text{g}^{-1}\cdot\text{min}^{-1}$. The isotherm study and adsorption mechanism followed the Freundlich model with a favorable mechanism. The maximum and DKR monolayer adsorption capacities are $588.24 \text{ mg}\cdot\text{g}^{-1}$ and $137.36 \text{ mmol}\cdot\text{Kg}^{-1}$, respectively. The adsorption mechanism is physical adsorption with energy sorption of $0.399 \text{ kJ}\cdot\text{mol}^{-1}$.

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