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Adsorption of Methylene Blue Dye using Fe_3O_4 Magnetized Natural Zeolite Adsorbent

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Abstract

Preparation and characterization of Fe_3O_4 magnetized natural zeolite adsorbent for adsorption of methylene blue dye have been carried out. Natural zeolite/Fe_3O_4 adsorbent preparation was carried out using coprecipitation of Fe^{2+} and Fe^{3+} ions (1: 2 mol ratio) on the natural zeolite surface. Characterization was carried out using X-Ray Diffraction (XRD), Fourier Transform Infra-Red (FTIR), and Scanning Electron Microscopy (SEM) to determine the effect of Fe_3O_4 on the natural zeolite surface. UV-Vis spectroscopy was used to determine the concentration of methylene blue after the adsorption process. The characterization results showed that Fe_3O_4 was successfully embedded in the natural zeolite without damaging the natural zeolite's crystallinity. Natural zeolite/Fe_3O_4 adsorbent showed easy separation from water medium after the adsorption process. The optimum conditions for adsorption were achieved at the contact time of 60 minutes, and the initial concentration of methylene blue was 30 ppm with an adsorbent mass of 25 mg. Adsorption kinetics followed pseudo-second-order reaction kinetics, and adsorption isotherm followed Langmuir isotherm with an adsorption capacity of 32.258 mg/g.

1. Introduction

Methylene blue is a synthetic dye widely used because it is easy to obtain and relatively cheap. Methylene blue dye is commonly used in textile dyeings such as cotton, silk, acrylic, cotton cloth, wool, and various dyeing processes [1]. Accumulation of methylene blue in the body that is too high can increase heart rate, vomiting, cyanosis, and tissue necrosis in humans [2].

Various methods of handling dyestuff waste have been carried out, including biodegradation, oxidation, coagulation-flocculation, photodegradation, and adsorption. Among these methods, adsorption is a method that is considered more attractive because the process is simple, effective, environmentally friendly, and the price is relatively low. One of the low-cost materials that have great potential as an adsorbent and its abundant availability in nature is natural zeolite.

Natural zeolite is a silica-alumina mineral with a porous skeleton structure, forms a channel, and is constructed by the primary tetrahedral units of $[SiO_4]^{4+}$ and $[AlO_4]^{3+}$. Each replacement of the central atom of the Si^{4+} ion with the Al^{3+} ion results in a negative charge on the zeolite framework, which is neutralized by the monovalent or divalent cations located in the pores of the zeolite along with water molecules [3]. The monovalent and divalent cations can be used as cation exchangers in the adsorption process. The porous natural zeolite structure produces a large surface area, so the zeolite has a high adsorption capacity [4].

The separation of natural zeolite adsorbents from the water medium after the adsorption process is generally carried out through precipitation and filtering. This method becomes less practical if applied in large-scale waste treatment, as it requires a long time for the adsorbent deposition process or a high cost for the adsorbent filtering process. To overcome this problem, research on the magnetization of natural zeolites using iron oxide (Fe_3O_4) has been carried out to produce adsorbents that contain magnetic properties [5]. The magnetization of natural zeolites aims to facilitate the separation of zeolites after the adsorption process by

using an external magnetic field. It is hoped that the separation of the adsorbent from the external magnetic field can save time and cost. Modification of natural zeolite using Fe_3O_4 has also been carried out to absorb heavy metal ions [6] and waste organic compounds [7] with very effective adsorption results. Many studies have been carried out in modifying zeolites for handling heavy metal waste and organic compounds so far. However, no studies have reported the handling of methylene blue dye waste using Fe_3O_4 magnetized natural zeolite. Therefore, it is necessary to research the handling of methylene blue dye waste using Fe_3O_4 magnetized natural zeolite adsorbent.

2. Methodology

2.1. Materials and tools

The natural zeolite used in this study was taken from Gunung Kidul, Wonosari, Yogyakarta. While other materials are Whatman 42 filter paper, distilled water, N_2 gas (CV. Perkasa), HF 38% (Merck), Na_2EDTA (Merck), $FeCl_2{\cdot}4H_2O$ (Merck), $FeCl_3{\cdot}6H_2O$ (Merck), NH_4OH 25% (Merck), NaOH (Merck), methylene blue (Merck), all chemicals are of a pro-analysis quality.

The instruments used in this study were X-ray diffractometer (Rigaku JICA Multiflex 2kW) for analysis of the crystallinity of the adsorbent, FTIR spectrophotometer (Shimadzu Prestige 21) for analysis of functional groups of adsorbents, Scanning Electron Microscope (JEOL JED-2300) for analysis of the surface morphology of the adsorbent, and Spectrophotometer UV-Vis (Shimadzu UV-1700) to analyze the concentration of methylene blue.

2.2. Adsorbent preparation

The research was started by doing the natural zeolite size uniformity by grinding and sieving using a 250 mesh sieve. Furthermore, natural zeolite was activated by a multilevel washing method using HF and Na_2EDTA solutions [8]. As much as 1 gram of sieved natural zeolite was put into 25 mL of HF solution (0.05% v/v) and stirred for 3 hours, then filtered and dried at 100°C. The natural zeolite was washed with HF solution, then put in 200 mL of Na_2EDTA (0.075 M) solution, stirred for 50 hours, and then filtered and dried at 100°C.

Activated natural zeolite was subsequently used to prepare natural zeolite/Fe_3O_4 adsorbent by the coprecipitation method, with the deposition of Fe^{2+} ions and Fe^{3+} ions (1: 2 mol ratio) using NH_4OH solution [9]. The coprecipitation process began by heating 50 mL of 2 M NH_4OH solution, to which 3 grams of natural zeolite were added at 70°C while N_2 gas flowed. N_2 gas flow aimed to remove oxygen in the solution and prevent the oxidation of Fe^{2+} to Fe^{3+} when adding $FeCl_2{\cdot}4H_2O$ solution [10, 11]. The solution was added dropwise 100 mL of a mixture of $FeCl_2{\cdot}4H_2O$ (1.988 g) and $FeCl_3{\cdot}6H_2O$ (5.406 g). This reaction is carried out for 30 minutes. The natural zeolite/Fe_3O_4 precipitate formed was then washed with distilled water until a neutral pH was obtained and separated with a bar magnet's assistance. The same procedure was also used to synthesize Fe_3O_4 by not adding natural zeolite to the NH_4OH solution. Activated natural zeolite, natural zeolite/Fe_3O_4, and Fe_3O_4 adsorbents obtained were characterized using XRD, FTIR, and SEM.

2.3. Methylene blue adsorption

The adsorption process was carried out to determine the kinetics and adsorption capacity of methylene blue using natural zeolite/Fe_3O_4 adsorbent. The determination of adsorption kinetics was carried out by using the pseudo-first-order, and pseudo-second-order kinetics model approaches. 25 mg of natural zeolite/Fe_3O_4 adsorbent was added to 40 mL of methylene blue solution (10 ppm), then added with NaOH solution (0.05 M) dropwise until pH 9 was obtained. The reaction was carried out by varying the contact time for 5; 10; 15; 30; 45; 60; 90; 120 and 180 minutes. After the adsorption process, the natural zeolite/Fe_3O_4 adsorbent was separated from the water medium using an external magnetic field for 5 minutes by attaching a magnetic rod to the container's wall to pull the natural zeolite/Fe_3O_4 adsorbent. The magnetic field continued to be applied during the process of transferring the solution to another container.

The determination of the adsorption capacity was carried out using the Freundlich and Langmuir isotherm model approach. The adsorption process was carried out by adding 25 mg of natural zeolite/Fe_3O_4 adsorbent into each of 40 mL of methylene blue solution with various concentrations: 5; 10; 15; 20; 25; 30; 35, and 40 ppm. Each solution was added with NaOH solution (0.05 M) dropwise until pH 9, and the reaction was carried out for 60 minutes (the optimum time for determining the adsorption kinetics). The process of separating the adsorbent from the water medium was carried out to determine the optimum time.

The concentration of methylene blue in each solution, after the adsorbent separation process, was measured using a UV-Vis spectrophotometer at a wavelength of 664 nm. The equation determined the adsorption percentage of methylene blue:

$$\%adsorption = \frac{C_i - C_s}{C_i} \times 100\% \quad (1)$$

Where Ci is the initial methylene blue concentration and Cs the residual methylene blue concentration

3. Results and Discussion

3.1. Crystal Structure, Functional Groups, and Morphology of the Adsorbents

The XRD diffraction patterns of Fe_3O_4, natural zeolite, and natural zeolite/Fe_3O_4 adsorbent are presented in Figure 1. Figure 1a shows the peaks of 2θ = 30.06°; 35.56°; 43.16°; 53.85°; 57.28° and 62.88° are the diffractogram patterns of Fe_3O_4 particles [7]. The diffractogram peaks of natural zeolite (Figure 1b) after being compared with the standard show that the zeolite type is mordenite, and there is little quartz (SiO_2) as an impurity, the same result was also reported by Wahyuni and Mudasir [8]. The diffractogram peaks of natural zeolite/Fe_3O_4 adsorbent (Figure 1c) show the similarity and combination between the diffractogram peaks of Fe_3O_4 (Figure 1a) and natural zeolite (Figure 1b). These

results indicate that Fe_3O_4 is successfully embedded in the natural zeolite surface.

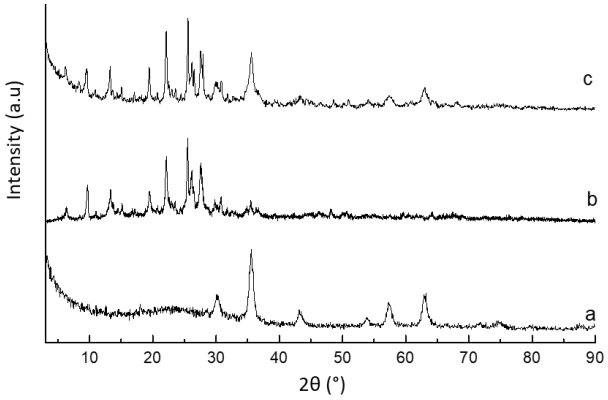

Figure 1. Diffractogram of (a) Fe_3O_4; (b) natural zeolite; (c) natural zeolite/Fe_3O_4

The functional group characterization of the zeolite/Fe_3O_4 adsorbent is presented in Figure 2. Figure 2a indicates the absorption at wave number 570 cm^{-1} which is the Fe-O group's stretching vibration in the spinel structure of Fe_3O_4 [12]. Absorption also appears at the wavenumbers 3426 cm^{-1} and 1628 cm^{-1} which characterizes O-H stretching and bending vibrations from Fe-OH groups or water molecules adsorbed on the surface of Fe_3O_4 [13]. In the FTIR spectra for natural zeolites (Figure 2b), it can be seen that the absorption appears in the area of wave number 1049 cm^{-1}; 795 cm^{-1}, and 463 cm^{-1}, which are the characteristics of the stretching and bending vibrations of the O-Si-O or O-Al-O groups in the activated zeolite structure. The absorption in the area of wave numbers 3448 cm^{-1} and 1636 cm^{-1} is a characterization of stretching vibration and bending vibration of O-H both from the Si-OH/Al-OH groups and from water molecules adsorbed on the activated zeolite surface [14, 15].

The FTIR spectra for natural zeolite/Fe_3O_4 adsorbent in Figure 2c show similar uptakes with Fe_3O_4 and natural zeolite. However, there is a shift in the absorption of wave number 463 cm^{-1} (Si-O/Al-O) from natural zeolite to 447 cm^{-1} and a shift in absorption at wave number 570 cm^{-1} (Fe-O) from Fe_3O_4 to 578 cm^{-1}. These results indicate an interaction between the Si-O group from natural zeolite and the Fe-O group from Fe_3O_4. Khodadadi *et al.* [16] stated that the absorption at the wave number 578 cm^{-1} is characteristic of the Fe-O-Si bond vibrations.

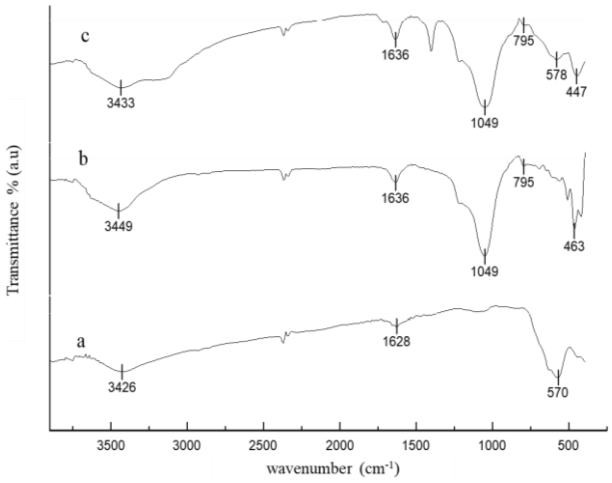

Figure 2. FTIR Spectra (a) Fe_3O_4 (a); (b) natural zeolite; (c) natural zeolite/Fe_3O_4

The SEM image shows a very significant morphological change from natural zeolite (Figure 3a) after embedding it with Fe_3O_4. In Figure 3b, it can be seen that some of the natural zeolite surfaces have been covered by Fe_3O_4. The distribution of Fe_3O_4 on the zeolite/Fe_3O_4 adsorbent is not uniform in shape and size due to the agglomeration process of Fe_3O_4 on the natural zeolite surface.

3.2. Adsorption of Methylene Blue

3.2.1. Separation of the adsorbent from the water medium

Figure 4 shows that the natural zeolite/Fe_3O_4 adsorbent can adsorb methylene blue dye well. After the adsorption process, the natural zeolite/Fe_3O_4 adsorbent was separated from the water medium using an external magnet for 5 minutes (Figure 4c). The adsorbent is very quickly attracted to the walls of the container where the magnet is placed. Figure 4c also shows that there is no adsorbent at the bottom of the container. This shows that the natural zeolite/Fe_3O_4 adsorbent is easily separated from the water medium after the adsorption process. These results indicate that the natural zeolite adsorbent separation process with Fe_3O_4 magnetized is more straightforward compared to the zeolite, in which Fe3O4 does not magnetize.

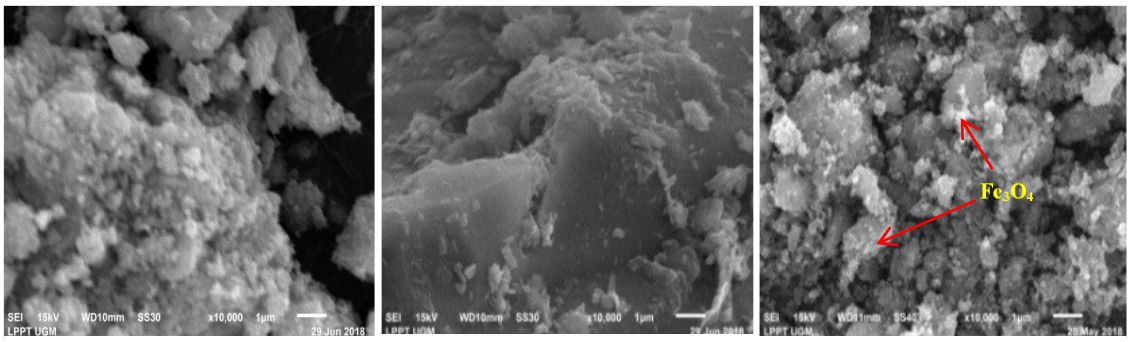

Figure 3. SEM images of (a) Fe_3O_4; (b) natural zeolite; (c) natural zeolite/Fe_3O_4

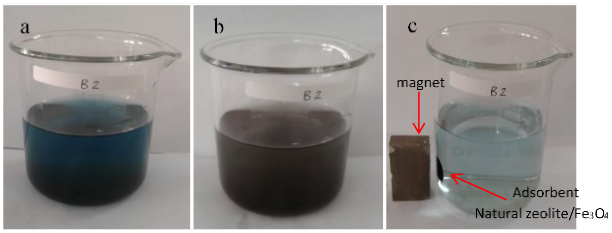

Figure 4. Adsorption of methylene blue: (a) at the beginning; (b) after 5 minutes; (c) after separating the adsorbent using an external magnetic field

3.2.2. Effect of contact time

The effect of contact time on the methylene blue adsorption process was studied by reacting 25 mg of adsorbent with 40 mL of methylene blue (10 mg/L) at a solution pH of 9 with a variation of the reaction time from 5 to 180 minutes. The pH of the solution is adjusted to pH 9 because, in alkaline conditions, most of the methylene blue molecules are in the form of cations. It will accelerate the cation exchange process during the adsorption process [17]. The adsorption results are presented in Figure 5.

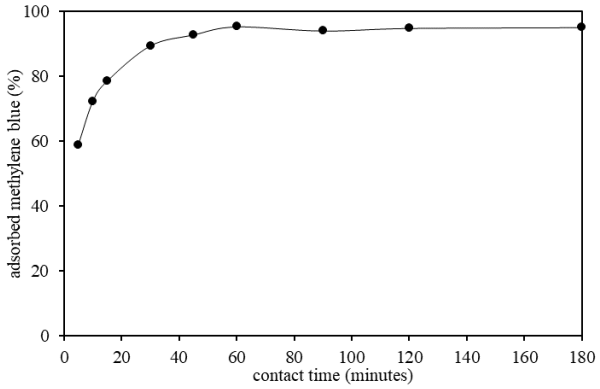

Figure 5. Effect of contact time on methylene blue adsorption

Figure 5 shows that the adsorption process of methylene blue on natural zeolite/Fe_3O_4 adsorbent increased sharply from the contact time of 5 to 30 minutes. The increase in methylene blue adsorption was since, at the initial time, there were still many active sites on natural zeolites, so that the adsorption of methylene blue was effective. At the contact time of 30-60 minutes, the increase of methylene blue adsorption on natural zeolite/Fe_3O_4 adsorbent was slow. This indicates that most monovalent and divalent cations as a counterweight to $[Al(OH_4]^-$ which is the active site of natural zeolites have been occupied by methylene blue cations; therefore, the subsequent adsorption process is inhibited. At 60 to 180 minutes, the increase of methylene blue adsorption on natural zeolite/Fe_3O_4 adsorbent has been constant. This indicates that all the active sites $[Al(OH)_4]^-$ in natural zeolites have been occupied by cations of methylene blue molecules, even though the longer the contact time is given, the adsorption process will remain constant. The methylene blue adsorption process's optimum contact time on natural zeolite/Fe_3O_4 adsorbent is 60 minutes.

3.2.3. Effect of initial adsorbate concentration

The effect of the adsorbate concentration was studied by reacting 25 mg of adsorbent with 40 mL of methylene blue at various concentrations from 5-40 mg/L with a solution pH of 9 and reaction time of 60 minutes. The results are presented in Figure 6.

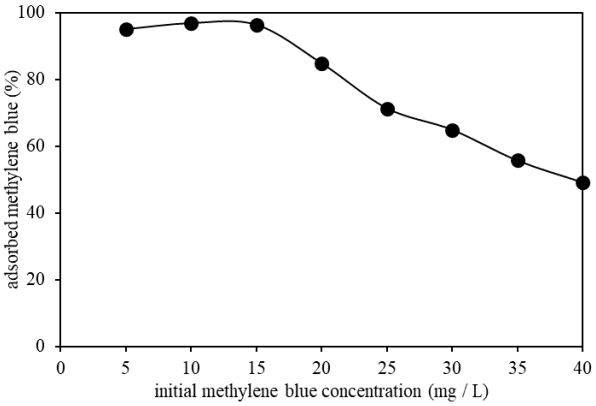

Figure 6. Effect of initial adsorbate concentration

Figure 6 shows an increase in the initial concentration of methylene blue from 5-15 ppm, giving an increase in the percentage of methylene blue adsorbed on natural zeolite/Fe_3O_4 adsorbent. This is because the number of active sites in natural zeolites available is more than the concentration of methylene blue in the solution so that the adsorption process is effective. At the initial concentration of 15-40 ppm of methylene blue, there was a decrease in the adsorbed methylene blue. This is due to the active site's limitation on natural zeolites to adsorb the methylene blue molecular cation. This decrease in methylene blue adsorption indicates that the active site on the natural zeolite is saturated with the methylene blue molecule's cation. Suppose all the active sites on the natural zeolite/Fe_3O_4 adsorbent have been filled with methylene blue molecular cations. In that case, the adsorption process is impeded even though the concentration of methylene blue in the solution is continuously added.

3.2.4. Adsorption Kinetics of Methylene Blue on Natural Zeolite/Fe_3O_4 Adsorbent

The adsorption kinetics of methylene blue in natural zeolite/Fe_3O_4 adsorbent was determined using pseudo-first-order reaction kinetics and pseudo-second-order reaction kinetics models. The pseudo-first-order kinetic equation is presented as follows:

$$\log(q_e - q_t) = \log q_e - \frac{k_1 t}{2{,}303} \qquad (2)$$

Where k_1 is the pseudo-order rate constant (min^{-1}), q_e and q_t are the amount of dye adsorbed (mg g^{-1}) at equilibrium and at time t (min).

The pseudo-second-order kinetics equation is presented as follows:

$$\frac{t}{q_t} = \frac{1}{k_2 . q_e^2} + \frac{t}{q_e} \qquad (3)$$

Where k_2 (g mg^{-1} min^{-1}) is a rate constant of pseudo-second-order

According to the adsorption process of methylene blue on natural zeolite/Fe_3O_4 adsorbent, the kinetic model was determined by comparing the correlation coefficients of the two methods. The kinetics model with a correlation coefficient closer to the value of one is chosen as a suitable kinetics model for the adsorption process of methylene blue on natural zeolite/Fe_3O_4 adsorbent. The pseudo-order reaction kinetics model's linearity is presented in Figure 7, while the pseudo-order reaction kinetics model is shown in Figure 8. The parameters of the calculation of adsorption kinetics are presented in Table 1.

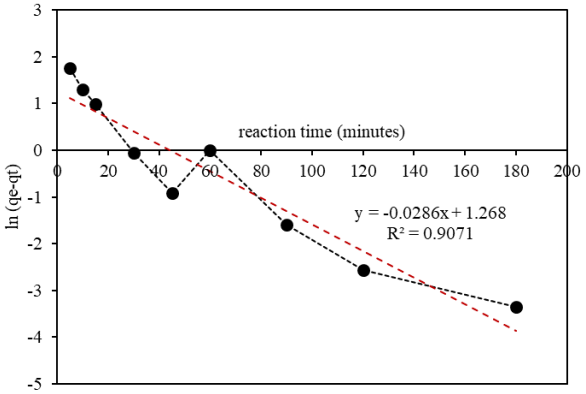

Figure 7. Pseudo-first-order adsorption kinetics model for adsorption of methylene blue on natural zeolite/Fe_3O_4 adsorbent

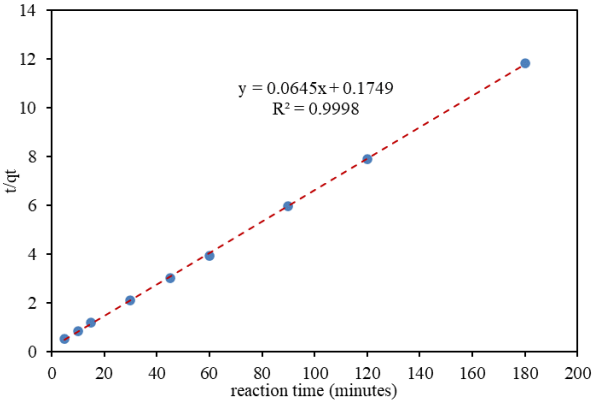

Figure 8. The pseudo-second-order adsorption kinetics model for the adsorption of methylene blue on natural zeolite/Fe_3O_4 adsorbent

Table 1. Kinetics parameters of methylene blue adsorption on natural zeolite/Fe_3O_4 adsorbent

Reaction Kinetics	Parameter	natural zeolite/Fe_3O_4 adsorbent
pseudo-first-order	R^2	0.9071
	q_e (mg g^{-1})	3.5537
	k_1 (minutes^{-1})	0.0286
pseudo-second-order	R^2	0.9998
	q_e (mg g^{-1})	15.5038
	k_2 (g mg^{-1} minutes^{-1})	0.0238

Table 1 shows that the pseudo-second-order kinetics model provides a correlation factor (R^2 = 0.9998), which is closer to one, higher than the pseudo-first-order kinetics correlation factor (R^2 = 0.9071). This shows that methylene blue dye's adsorption process on natural zeolite/Fe_3O_4 adsorbent follows a pseudo-second-order kinetics model. The pseudo-second-order reaction kinetics model assumes an interaction between the adsorbate molecule and the active site on the adsorbent [18, 19]. Therefore, it can be assumed that the adsorption kinetics of methylene blue on natural zeolite/Fe_3O_4 adsorbent is determined by the rate of interaction between methylene blue molecular cations in solution with the active site of natural zeolite. This interaction occurs through the exchange of cations of the methylene blue molecule with monovalent and divalent cations that balance the negative charge $[Al(OH_4]^-$ on the surface of the natural zeolite.

3.2.5. Methylene Blue Adsorption Isotherm on Natural Zeolite/Fe_3O_4 Adsorbent

The adsorption isotherm. It describes how the adsorbate molecules interact with the adsorbent and the equilibrium relationship between the adsorbate concentration adsorbed on the adsorbent and the adsorbate concentration remains in solution. The adsorption isotherm of methylene blue on natural zeolite/Fe_3O_4 adsorbent was determined using the Freundlich isotherm model approach and the Langmuir isotherm model. The linear form of the Freundlich isotherm equation is written as follows:

$$\log q_e = \log K_F + \frac{1}{n}\log C_e \quad (4)$$

Where: q_e is the amount of adsorbate adsorbed at equilibrium by each gram of adsorbent (mg/g), C_e is the adsorbate concentration at equilibrium (mg/L), and 1/n is the adsorption intensity, K_F is the Freundlich constant which is related to the adsorption capacity (L/g).

While the linear form of the Langmuir isotherm equation is written as follows:

$$\frac{C_e}{q_e} = \frac{1}{Q_m}C_e + \frac{1}{K_L.Q_m} \quad (5)$$

K_L is the Langmuir constant (L/mg) related to the adsorption energy, and Q_m is the maximum capacity of the adsorbent (mg/g of adsorbent). The values of adsorption capacity (Q_m) and adsorption constant (K_L) of adsorbate were determined based on the Langmuir equation by making a relationship curve between Ce/qe versus Ce.

The adsorption isotherm of methylene blue on natural zeolite/Fe_3O_4 adsorbent using the Freundlich isotherm model approach is presented in Figure 9, while the Langmuir isotherm model approach is presented in Figure 10.

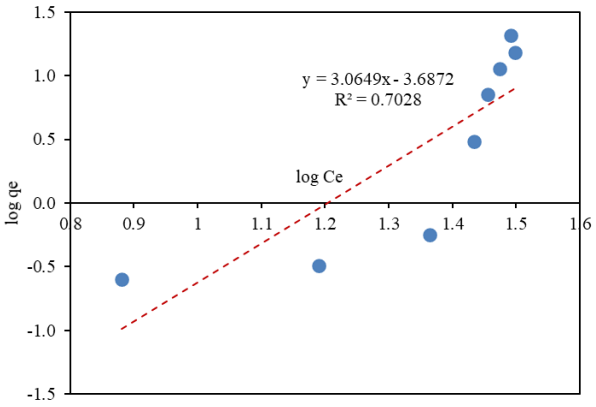

Figure 9. Freundlich isotherm model for adsorption of methylene blue on natural zeolite/Fe_3O_4 adsorbent

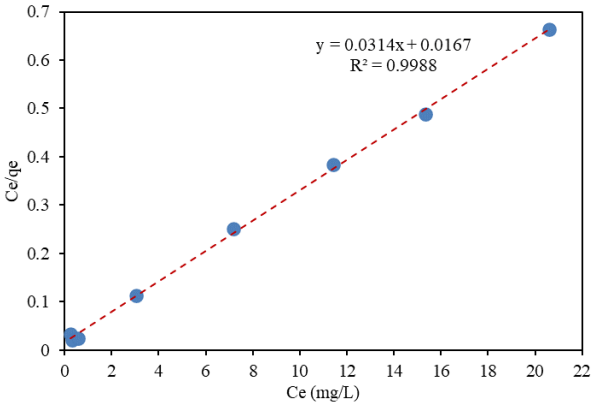

Figure 10. Langmuir isotherm model for adsorption of methylene blue on natural zeolite/Fe_3O_4 adsorbent

The Freundlich isotherm assumes that the active sites on the adsorbent surface are heterogeneous. The adsorbent heterogeneity is caused by differences in functional groups on the adsorbent surface so that the adsorption process produces a multilayer layer on the adsorbent surface [20]. The Langmuir isotherm is based on the assumption that the active site on the adsorbent surface is homogeneous. One active site in the adsorbent only adsorbs one adsorbate molecule, resulting in a monolayer layer on the adsorbent surface. Thus, when the adsorbate has covered the number of active sites on the adsorbent surface, the adsorption process is further inhibited [20]. Methylene blue adsorption isotherm parameters on natural zeolite/Fe_3O_4 adsorbent using the Freundlich isotherm model approach and the Langmuir isotherm model are presented in Table 2.

Table 2. Parameters of Langmuir and Freundlich isotherms

Adsorption isotherm	Parameter	natural zeolite/Fe_3O_4 adsorbent
Freundlich Isotherm	K_F (mg g^{-1})	2.168 x 10^{-4}
	n	0.329
	R^2	0.7108
Langmuir Isotherm	q_m (mg g^{-1})	32.258
	K_L (L mg^{-1})	1.867
	R^2	0.999

Table 2 shows that the Langmuir isotherm model's correlation coefficient is 0.999, higher than the Freundlich isotherm model, which is 0.7108. This shows that the Langmuir isotherm model is more suitable to describe the methylene blue adsorption process on natural zeolite/Fe_3O_4 adsorbent. Thus it can be said that one active site on the natural zeolite/Fe_3O_4 adsorbent is only able to bind one methylene blue molecule cation, so that the methylene blue adsorption process on the natural zeolite/Fe_3O_4 adsorbent forms one layer (monolayer). From the Langmuir isotherm calculation, it is known that the adsorption capacity of methylene blue on natural zeolite/Fe_3O_4 adsorbent is 32.258 mg/g.

4. Conclusion

Based on the results obtained, it can be concluded that Fe_3O_4 was successfully embedded in the natural zeolite surface. Natural zeolite/Fe_3O_4 adsorbent produces magnetic properties so that it is easily separated from the external magnetic field after the adsorption process. The adsorption process of methylene blue dye with natural zeolite/Fe_3O_4 adsorbent followed the pseudo-second-order reaction kinetics and followed the Langmuir isotherm method with an adsorption capacity of 32.258 mg/g.

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