

RESEARCH PAPER

Thermodynamics and kinetic studies of methyl orange dye adsorption in magnetic material-silica-zeolite (MM-SiO<sub>2</sub>-NZ) composite

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**Abstract:** Using methyl orange (MO) in dye industries can cause the accumulation of MO waste in aquatic systems, including seawater. A magnetic material-silica-zeolite (MM-SiO<sub>2</sub>-NZ) composite was investigated in vitro to adsorb methyl orange (MO) dye. MM-SiO<sub>2</sub>-NZ composite was characterized using FTIR, XRF, and VSM. Adsorption studies with pH, concentration, contact time, and temperature variations were carried out to determine the adsorption capacity. The MM-SiO<sub>2</sub>-NZ characterization results by FTIR showed the presence of OH groups from Fe-OH, Si-OH, and Al-OH, and there were Fe-O, Si-O, Al-O, Si-O-Si, and Si-O-Fe groups. The results of XRF characterization showed that the metal oxide content of Fe<sub>2</sub>O<sub>3</sub> in magnetic material (MM) was 75.39% and decreased to 52.63% after the MM-SiO<sub>2</sub>-NZ composite was formed. The characterization using VSM indicated the magnetic properties of MM to be 44.083 emu/g, then decreased to 11.407 emu/g after being composited. The adsorption of MM-SiO<sub>2</sub>-NZ tends to follow the Langmuir adsorption isotherm with a Langmuir constant (KL) value of 1.332 L/mg. Furthermore, the adsorption kinetics followed the pseudo-second-order kinetics with a constant value (k<sub>2</sub>) of 3×10<sup>-2</sup> g.mg/min. MO dye adsorption by MM-SiO<sub>2</sub>-NZ took place spontaneously with Gibbs free energy (ΔG), enthalpy (ΔH), and entropy (ΔS) values of -1.109 kJ/mol, -38.687 kJ/mol, and -12.402 kJ/mol, respectively.

Keywords: adsorption, methyl orange, magnetic material, silica, zeolite

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## INTRODUCTION

The textile, printing, and dyeing industries are the largest producers of dye waste, which can damage the environment, including the aquatic system and coastal environment. Dyes can prevent light penetration in water and degrade quite slowly due to the presence of sunlight; thus, the dye's aromatic structure is resistant to environmental influences [1]. Textile dyes are non-biodegradable pollutants, generally made from azo compounds and their derivatives, which are benzene groups [2].

Azo compounds are the most abundant compounds in textile waste. Methyl orange is one of the azo dyes widely used in the dyeing process [2]. In textile dyeing, the dyeing process uses about 24% dye and 67% salt, which will then enter the aquatic

environment as waste. Methyl orange is a synthetic dye that is dominantly used in textile industries in Indonesia and is suspected of producing dye waste in aquatic environments [3]. An earlier study emphasizes that methyl orange compounds are difficult to degrade but are more easily adsorbed [4]. It is necessary to treat waste through chemical, physical and biological processes to deal with the problem of environmental pollution caused by textile dyes [5]. One of the most widely used waste treatment methods is the adsorption method since it is easy to apply, efficient, and environmentally friendly because it does not produce harmful toxic gases [6].

The adsorption process involves an effective interaction between the analyte and the adsorbent surface [7,8]. One of the most frequently

used adsorbents is zeolite. Zeolite is a hydrated silica-alumina crystal containing alkaline or alkaline earth cations in the form of a three-dimensional framework, is acidic, and has pores of molecular size. Using zeolite as a matrix in synthesizing metal oxides is always associated with nanometer-sized zeolite pores. Then it can be used as a barrier to particle accumulation [9]. However, there are several disadvantages to using zeolite as an adsorbent, including the difficulty of separating it from the solution after the adsorption process occurs. Separating zeolite from solution often requires special methods such as filtration and centrifugation [10]. Therefore, supporting material is needed to increase the efficiency of using zeolite as an adsorbent, so it can be easily separated by utilizing a magnetic material. One source of magnetic material that can be used and is abundant in nature is iron sand.

Iron sand is one of the most abundant natural resources in Indonesia. Magnetic material separated from its impurities can be used as an adsorbent. Using magnetic materials as adsorbents are often carried out because separation can be performed only by utilizing an external magnetic field. However, the iron sand magnetic material has several drawbacks, including being very easily oxidized in air and its low stability in a suspension medium which causes the iron sand magnetic material to be unusable for a long time [11]. The magnetic iron sand material coated with silica is a good alternative to prevent oxidation on the surface of the iron sand. Besides that, it also adds active groups to the magnetic material due to the chemical properties of silica. The presence of silanol groups (Si-OH) and siloxane (Si-O-Si) on the surface of silica also makes it possible to form bonds with other compounds [12]. This study proposes the composite production from the mixture of iron sand magnetic material, silica, and zeolite to use as an adsorbent for adsorbing methyl orange dye. The resulting composite is expected to have several advantages, including being easily separated from the matrix using only an external magnetic field and having a high adsorption capacity as an adsorbent.

## MATERIALS AND METHODS

### Materials

Iron sand, as a source of magnetic material, was obtained from Bugel Beach, Kulon Progo Regency, Yogyakarta. A Fourier Transform Infrared (FTIR) (Shimadzu FTIR-PRESTIGE 21, Japan), an X-Ray Fluorescence (XRF) (PHILIPS, Netherlands), and a Vibration Sample Magnetometer (VSM) (OXFORD SVM1,2H, United Kingdom) instruments were used to characterize the magnetic material-silica-zeolite (MM-SiO<sub>2</sub>-NZ) composite. An ultraviolet-visible spectrophotometer (UV-Vis) (Agilent 8453, Singapore) was used to quantify the amount of methyl orange

(MO) dye being adsorbed into the MM-SiO<sub>2</sub>-NZ adsorbent.

### Methods

#### Preparation of Iron Sand Magnetic Material

The iron sand was washed and dried at 95°C for 18 hours. The magnetic material from the iron sand was separated using an external magnet. The magnetic material attracted by the magnet was crushed using a mortar and sieved using a 270-mesh sieve, then washed with distilled water and re-dried at 95°C for 18 hours.

#### Preparation and Activation of Natural Zeolite (NZ)

Natural zeolite (NZ) was mashed with a mortar and then sieved using a 270-mesh sieve. Fifty grams of NZ was reacted with 100 ml of 3 M acid chloride at 100°C while stirring at 350 rpm for 3 hours. The zeolite was separated from the solution using filter paper, washed with distilled water until the pH was neutral, and dried at 100°C for 12 hours.

#### Preparation and Characterization of Magnetic Material-Silica-Zeolite (MM-SiO<sub>2</sub>-NZ) Composite

One gram of magnetic material was added to 1 mL of 1 M acid chloride solution for decantation, 3 mL of 13% sodium silicate, and 0.6 grams of zeolite and then stirred until homogeneous. The mixture was added dropwise with 1 M acid chloride while stirring until a gel was formed, then sonicated for 15 minutes and allowed to stand for 18 hours at room temperature before being dried for 5 hours at 70°C. The solid formed was crushed slowly, washed with distilled water, washed with 70% ethanol, and dried in an oven for 5 hours at 70°C. The powder was then crushed and sieved using an 80-mesh sieve to produce MM-SiO<sub>2</sub>-NZ adsorbent, ready to be characterized using FTIR, XRF, and VSM instruments.

#### Thermodynamics and Adsorption Kinetic Studies

Adsorption assessment of MO using an MM-SiO<sub>2</sub>-NZ composite in the present study was carried out under the influence of pH, contact time, concentration, and temperature. Adsorption was performed using the batch method. 10 ml of 25 mg/l MO solution was adjusted to a pH of 3-8 using a buffer solution. The solution was contacted with 0.1 g of MM-SiO<sub>2</sub>-NZ adsorbent, then shaken using a shaker at 100 rpm for 2 hours. The adsorbate was separated from the adsorbent by decantation using an external magnet. Then the absorbance was measured using a UV-Vis spectrophotometer. Adsorption with variations in MO concentrations of 5, 15, 25, 50, and 100 mg/L and variations in temperature of 20, 30, and 40°C was carried out to study the thermodynamics of adsorption. Next, the

adsorption kinetics model was examined by MO adsorption in contact time variations of 0, 5, 10, 30, 60, 120, and 240 minutes.

The number of adsorbed ions per weight of adsorbent at equilibrium was calculated using the equation:

$$q_e = \frac{(C_0 - C_e)V}{M}$$

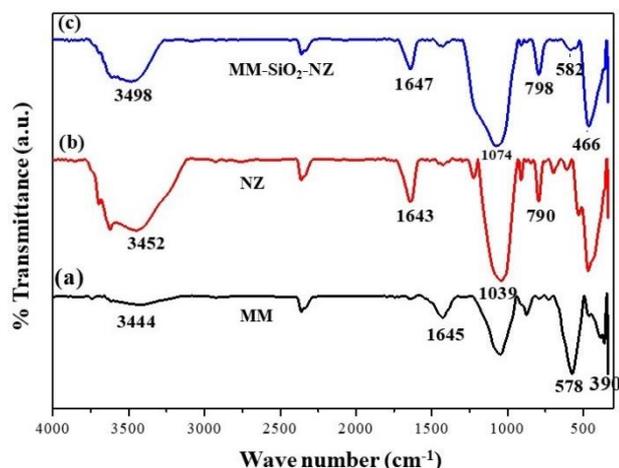
where  $q_e$  (mg/g) is the adsorption capacity at equilibrium,  $C_0$  (mg/l) is the initial concentration of the adsorbate,  $C_e$  (mg/l) is the concentration of the adsorbate at equilibrium,  $V$  is the total liter volume of the solution, and  $M$  (mg) is the mass of the adsorbent.

## RESULTS AND DISCUSSION

### Characterization

#### Fourier Transform Infrared (FTIR)

FTIR instrument with wave numbers of 4000–400  $\text{cm}^{-1}$  was used to determine the functional groups contained in a magnetic material (MM), natural zeolite (NZ), and MM-SiO<sub>2</sub>-NZ composites. The results of the FTIR characterization are presented in Figure 1.



**Figure 1.** FTIR spectra of (a) MM, (b) NZ, and (c) MM-SiO<sub>2</sub>-NZ composite

FTIR analysis results on MM show a stretching vibration of the OH group from Fe-OH at wave number 3444  $\text{cm}^{-1}$ . The bending vibration of the O-H group from Fe-OH was seen at wave number 1645  $\text{cm}^{-1}$ . Furthermore, the stretching and bending vibrations of the Fe-O group were perceived at wave numbers 578  $\text{cm}^{-1}$  and 390  $\text{cm}^{-1}$ , respectively. The results of FTIR analysis on NZ show stretching (at wave number 3452  $\text{cm}^{-1}$ ) and bending (1643  $\text{cm}^{-1}$ ) vibrations of the O-H groups presented in Si-OH. At wave number 1039  $\text{cm}^{-1}$ , there was an asymmetric stretching vibration of the Si-O or Al-O groups from Al<sub>2</sub>SiO<sub>3</sub>. The successful formation of the MM-SiO<sub>2</sub>-NZ composite is shown in

Figure 1 (c), which is characterized by the loss of absorption at wave number 390  $\text{cm}^{-1}$  after coating silica. The appearance of new absorption at wave number 466  $\text{cm}^{-1}$  indicated the presence of Si-O-Fe stretching vibrations [13]. The shift of the wave number to 798  $\text{cm}^{-1}$  indicated the presence of a symmetrical stretching vibration of the Si-O group from Si-O-Si. Furthermore, the shift in numbers from 1039  $\text{cm}^{-1}$  to 1074  $\text{cm}^{-1}$  designated the presence of asymmetric stretching vibrations of the Si-O or Al-O groups of Al<sub>2</sub>SiO<sub>3</sub>. The Si-O or Al-O group is part of the zeolite framework.

### X-Ray Fluorescence

XRF analysis was carried out to determine the oxides levels contained in iron sand (IS), MM, NZ, and MM-SiO<sub>2</sub>-NZ composite samples. The results of the analysis are presented in Table 1. The existence of metal oxides in the samples indicated the successful synthesis of the MM-SiO<sub>2</sub>-NZ composite, which was characterized by the presence of Fe<sub>2</sub>O<sub>3</sub>, SiO<sub>2</sub>, TiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, and CaO oxides and other oxides in minor amounts. The decrease in Fe<sub>2</sub>O<sub>3</sub> oxide content in MM-SiO<sub>2</sub>-NZ to 52.63% and an increase in SiO<sub>2</sub> content to 38.80% designated that the magnetic material had been coated with silica during the formation of the composite. The closing of the Al<sub>2</sub>O<sub>3</sub> group in the NZ possibly caused the invisible Al<sub>2</sub>O<sub>3</sub> content in MM-SiO<sub>2</sub>-NZ.

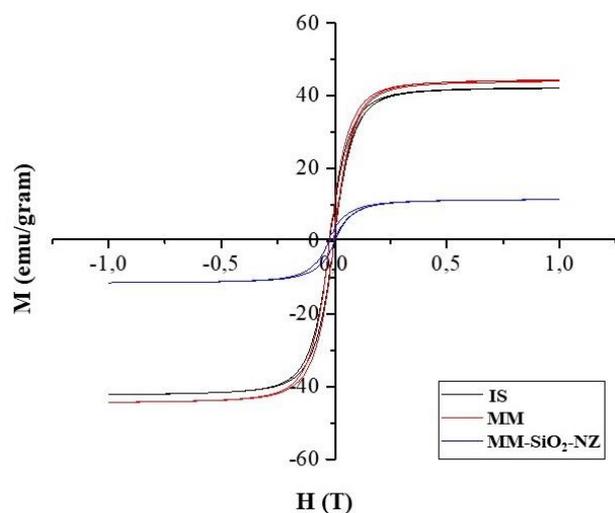
**Table 1.** XRF instrument characterization of IS, MM, NZ, and MM-SiO<sub>2</sub>-NZ composite

Oxide	Oxide content (weight %)			
	IS	MM	NZ	MM-SiO <sub>2</sub> -NZ
Fe <sub>2</sub> O <sub>3</sub>	70.18	75.39	4.41	52.63
SiO <sub>2</sub>	11.00	6.6	75.3	38.8
TiO <sub>2</sub>	6.61	7.32	0.52	4.41
Al <sub>2</sub> O <sub>3</sub>	5.00	4	11	-
CaO	4.26	2.82	3.03	1.66
K <sub>2</sub> O	0.38	0.18	5.31	0.76
V <sub>2</sub> O <sub>5</sub>	0.48	0.51	-	0.33
Cr <sub>2</sub> O <sub>3</sub>	0.13	0.11	-	0.082
MnO	0.57	0.53	0.032	0.34
P <sub>2</sub> O <sub>5</sub>	0.78	0.80	-	-
ZnO	0.04	0.05	0.1	0.05
Rb <sub>2</sub> O	0.23	0.22	-	0.19
Eu <sub>2</sub> O <sub>3</sub>	0.59	0.79	-	-
Re <sub>2</sub> O <sub>7</sub>	0.20	0.20	-	-
Bi <sub>2</sub> O <sub>3</sub>	-	0.51	-	-
CuO	-	-	-	0.055

### Vibrating Sample Magnetometer (VSM)

A magnetic properties investigation of the sample was carried out using a VSM instrument that utilizes an external magnetic field at room temperature and an external magnetic field of -1 to 1 T. The obtained information was magnetic properties due to changes in the external magnetic field, which was described by a hysteresis curve. The hysteresis curve can show the relationship between the magnetization (M) and the external magnetic field

(H). Important quantities in determining magnetic properties based on the hysteresis curve are magnetic saturation ( $M_s$ ), field coercivity ( $H_c$ ), and remanent magnetization ( $M_r$ ). The hysteresis curves of the IS, MM, and MM-SiO<sub>2</sub>-NZ composite are shown in Figure 2, and the magnetism parameters are presented in Table 2.



**Figure 2.** VSM hysteresis curves of IS, MM, and MM-SiO<sub>2</sub>-NZ composite

**Table 2.** Magnetism parameters of IS, MM, and MM-SiO<sub>2</sub>-NZ composite

Sample	$M_s$ (emu/gram)	$H_c$ ( $\times 10^{-2}$ Tesla)	$M_r$ (emu/gram)
IS	42.211	0.429	4.094
MM	44.083	1.000	4.693
MM-SiO <sub>2</sub> -NZ	11.407	0.327	1.200

The results of the VSM analysis in Figure 2 and Table 2 show that the entire sample was classified as soft magnetic, which was indicated by the sample's low coercivity values ( $H_c$ ). Sukmadani (2019) emphasizes that samples with low  $H_c$  are categorized as soft magnets, while those with high  $H_c$  refer to strong magnets, i.e., materials that do not easily lose their magnetism. Furthermore, the  $H_c$  value  $\neq 0$  in the IS, MM, and MM-SiO<sub>2</sub>-NZ composite indicated that they have ferromagnetic properties. The formation of the MM-SiO<sub>2</sub>-NZ composite would reduce the magnetic saturation value ( $M_s$ ) to 11.407 emu/gram (Table 2). This was probably governed by the contribution of non-magnetic SiO<sub>2</sub> and NZ, which would reduce the magnetism of MM on MM-SiO<sub>2</sub>-NZ composite.

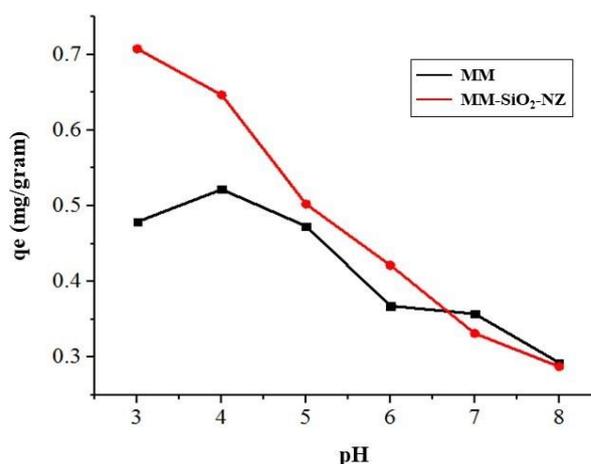
## Adsorption Study

### Effect of pH

Determination of the effect of pH on adsorption capacity is one of the important parameters in adsorption study. Changes in pH can affect the adsorbent's chemical and surface properties, the adsorbate's solubility, and ion competition in the

adsorption process [14]. The relationship between the pH of the solution and the adsorption capacity of MO on MM and MM-SiO<sub>2</sub>-NZ adsorbent is shown in Figure 3.

The optimum adsorption of MO on the MM adsorbent occurs at pH 4, while that on the MM-SiO<sub>2</sub>-NZ adsorbent occurs at pH 3 (Figure 3). The MO adsorption capacities of MM and MM-SiO<sub>2</sub>-NZ adsorbents were 0.521 mg/g and 0.707 mg/g, respectively. The increase in the adsorption capacity of the MM-SiO<sub>2</sub>-NZ composite showed that adding silica and zeolite could increase the absorption ability of the dye from the adsorbent. It is important to note that the optimum adsorption of MO on MM and MM-SiO<sub>2</sub>-NZ composite occurs at acidic pH. In acidic solutions, electrostatic repulsion occurs between protonated MO dyes from the surface of the adsorbent. Hence the interaction between H<sup>+</sup> ions and MO dye molecules increases. At a higher pH (alkaline), the adsorption capacity value decreases. Such a decrease was caused by an increase in the concentration of OH<sup>-</sup> ions which would reduce the cationic properties of the MO dye.

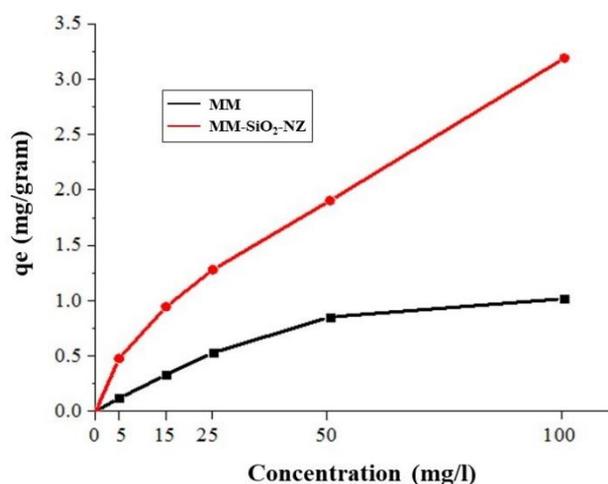


**Figure 3.** Relationship between pH of the solution and the adsorption capacity of MO on MM and MM-SiO<sub>2</sub>-NZ composite

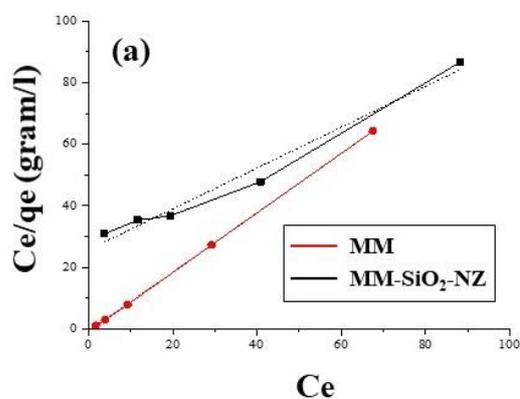
### Adsorption Isotherm

A study of the effect of variations in concentration (5 - 100 mg/L) of MO dye on the adsorption capacity of MM and MM-SiO<sub>2</sub>-NZ composite was carried out to determine the maximum adsorption capacity and the adsorption isotherm. Figure 4 shows a curve for the effect of MO concentration on the adsorption capacity of MM and MM-SiO<sub>2</sub>-NZ. It shows that the adsorption capacity continues to increase with increasing MO concentration. The adsorption capacity of MM-SiO<sub>2</sub>-NZ at an MO concentration of 5 mg/L was 0.119 mg/g, then increasing to 1.017 mg/g and 3.189 mg/g at MO concentrations of 100 mg/L and 200 mg/L, respectively. The increase in

adsorption capacity proves that the MM-SiO<sub>2</sub>-NZ composite made from zeolite and silica can maximize the adsorption ability of MO dyes. The activated zeolite will have more pore cavities since it has been cleaned from metal oxides which are considered impurities, so the surface area is also larger [7].



**Figure 4.** Effect of MO concentration on the adsorption capacity of MM and MM-SiO<sub>2</sub>-NZ



The isotherm of MO adsorption was determined using two models, i.e., Langmuir and Freundlich isotherms. The Langmuir isotherm is based on monolayer adsorption on a homogeneous adsorbent active site, while the Freundlich isotherm describes adsorption on a heterogeneous surface. Langmuir isotherm follows an equation:

$$\frac{C_e}{q_e} = \frac{C_e}{q_m} + \frac{1}{K_L q_m}$$

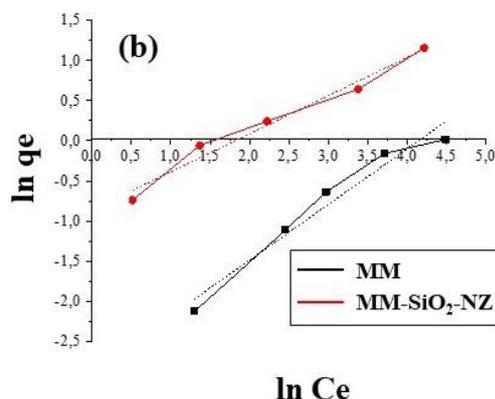
where  $q_m$  (mg/g) is the maximum adsorption capacity and  $K_L$  (l/mg) is the Langmuir constant. Adsorption using Freundlich isotherm follows an equation:

$$\log q_e = \log K_F + \frac{1}{n} \log C_e$$

$K_F$  (l/mg) is the Freundlich constant, and  $n$  is the heterogeneity factor.

**Table 3.** Adsorption isotherm parameters of MM and MM-SiO<sub>2</sub>-NZ

Adsorbent	Langmuir Isotherm Model			Freundlich Isotherm Model		
	R <sup>2</sup>	K <sub>L</sub> (L/mg)	q <sub>m</sub> (mg/g)	R <sup>2</sup>	K <sub>F</sub> (L/mg)	n
MM	0.978	0.025	1.507	0.957	0.056	1.438
MM-SiO <sub>2</sub> -NZ	0.999	1.332	1.039	0.975	0.422	2.103



**Figure 5.** Adsorption isotherm models of MM and MM-SiO<sub>2</sub>-NZ for (a) Langmuir and (b) Freundlich

Based on the Langmuir and Freundlich adsorption isotherm equations, the values for the isotherm parameters of  $R^2$ ,  $K_L$ ,  $q_m$ ,  $K_F$ , and  $n$  can be determined from the slope and intercept of the curve. Figure 5 shows a curve of the Langmuir and Freundlich adsorption isotherm models, and the adsorption isotherm parameters are presented in Table 3.

The adsorption curve of MO dye on MM and MM-SiO<sub>2</sub>-NZ adsorbents shows a correlation value ( $R^2$ ) of the Langmuir isotherm, which was greater than the Freundlich isotherm (Table 3). The Langmuir isotherm model assumes that adsorption occurs in monolayers with homogeneous energy levels. The type of adsorption is chemisorption, meaning that the

adsorption occurs chemically, indicating the formation of a stronger bond between the adsorbate and adsorbent in covalent and hydrogen bonds. Table 3 shows that the value of the equilibrium constant on the Langmuir isotherm ( $K_L$ ) is different from that of the Freundlich isotherm ( $K_F$ ), which results from the differences in the assumptions put forward by Langmuir and Freundlich. Langmuir asserted that all sites on the surface are homogeneous, while Freundlich stated that the active sites on the surface of the adsorbent are heterogeneous. It is one of the factors that cause the difference in the values of these constants. Accordingly, the adsorption energy for the two isotherms is also different [15].

### Adsorption thermodynamics

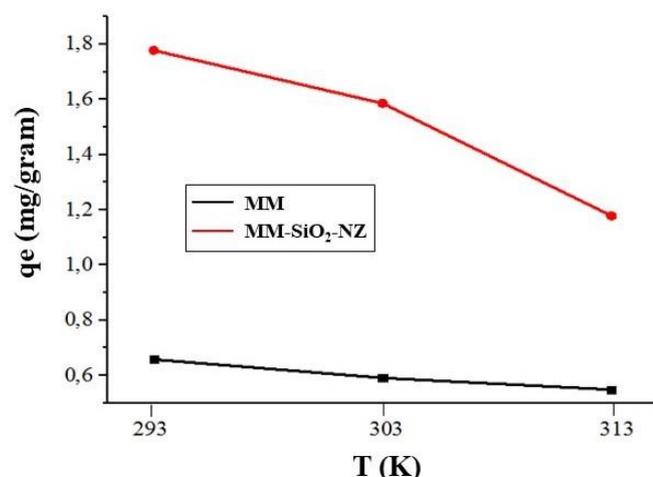
The effect of temperature is one factor affecting the adsorption process. Temperature can affect adsorption capacity and efficiency by increasing the adsorption ability of MM and MM-SiO<sub>2</sub>-NZ adsorbents to MO dye. The thermodynamic parameters of adsorption are determined through the values of enthalpy ( $\Delta H$ ), entropy ( $\Delta S$ ), and Gibbs free energy ( $\Delta G$ ) [16,17]. Adsorption thermodynamic studies are studied using thermodynamic equations. The thermodynamic parameters are calculated using the following equation [18]:

$$\ln K_C = -\frac{\Delta H}{RT} + \frac{\Delta S}{R}$$

$$\Delta G = \Delta H - T\Delta S$$

$$\Delta G = -RT \ln K_C$$

where  $\Delta H$ ,  $\Delta S$ ,  $\Delta G$ , and  $T$  are enthalpy, entropy, Gibbs free energy, and temperature (in Kelvin), respectively.  $K_C$  is the adsorption equilibrium constant. In this case,  $K_C = C_o - C_e/C_e$ .  $R$  equals 8.314 J/molK, which is the gas constant. The relationship between  $\ln K_C$  and  $1/T$  produces a straight line curve with slope and intercept values equal to  $\Delta H/R$  and  $\Delta S/R$ , respectively.



**Figure 6.** Effect of temperature on adsorption capacity of MM and MM-SiO<sub>2</sub>-NZ to MO dye

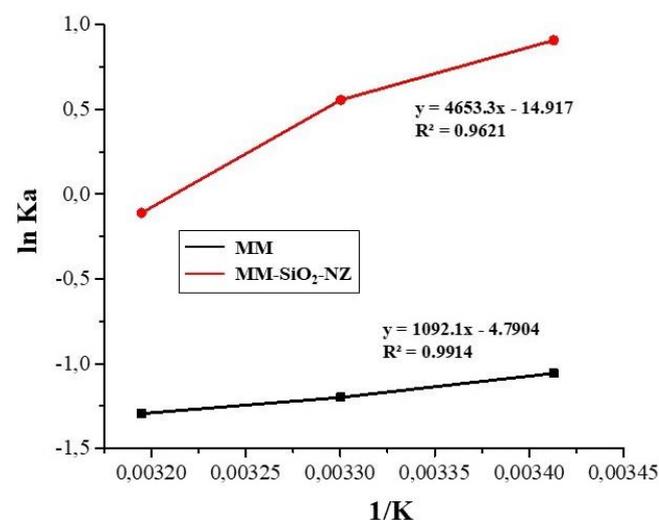
**Table 4.** Thermodynamic parameters of MO adsorption by MM and MM-SiO<sub>2</sub>-NZ

T (K)	MM			MM-SiO <sub>2</sub> -NZ		
	$\Delta H$ (kJ/mol)	$\Delta S$ (kJ/mol)	$\Delta G$ (kJ/mol)	$\Delta H$ (kJ/mol)	$\Delta S$ (kJ/mol)	$\Delta G$ (kJ/mol)
293			2.589			-2.349
303	-9.079	-398.273	2.987	-38.687	-12.401	-1.109
313			3.386			0.130

Figure 6 shows that the adsorption capacity of MM and MM-SiO<sub>2</sub>-NZ adsorbents decreased with increasing temperature. The adsorption capacity of MM was 0.658 mg/g, and MM-SiO<sub>2</sub>-NZ was 1.777 mg/g at 20°C

(293K). The curve of the relationship between  $\ln K$  and  $1/T$  is presented in Figure 7, and the values of the adsorption thermodynamic parameters are tabulated in Table 4.

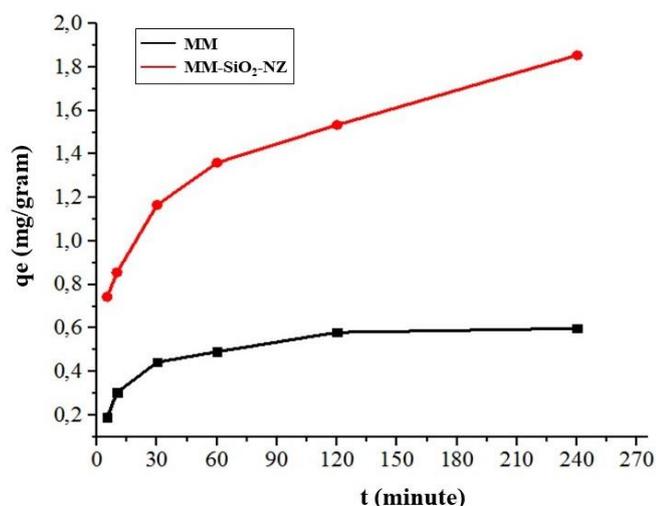
The adsorption enthalpy values of MO on MM and MM-SiO<sub>2</sub>-NZ obtained in this study were -9.079 and -38.687 kJ/mol, respectively. The negative enthalpy value ( $\Delta H$ ) indicated that the adsorption process was exothermic. The entropy change ( $\Delta S$ ) value for MM adsorbents was -398.273 kJ/mol, and that for MM-SiO<sub>2</sub>-NZ was -12.401 kJ/mol (Table 4). The negative entropy indicated a decrease in disorder during the adsorption process of MO dye by MM and MM-SiO<sub>2</sub>-NZ. The value of the Gibbs free energy change ( $\Delta G$ ) of the MM adsorbent was positive, indicating that the adsorption process was not spontaneous. Thus the MO dye adsorption process was not easy take place at low temperatures. For the MM-SiO<sub>2</sub>-NZ adsorbent,  $\Delta G$  was negative, which means that the adsorption took place spontaneously.



**Figure 7.** Relationship between  $\ln K$  and  $1/T$  during MO adsorption

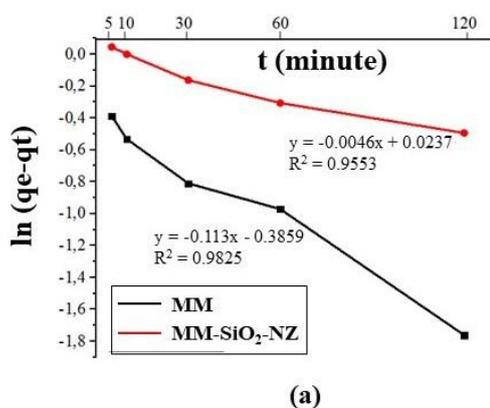
### Adsorption Kinetics

The contact time effect of MO on MM and MM-SiO<sub>2</sub>-NZ was treated to study the adsorption kinetics. Figure 8 shows that the adsorption capacity increased sharply at the beginning of the adsorption process because there were many active sites on the surface of the MM and MM-SiO<sub>2</sub>-NZ composite that had not yet bonded to the active sites on MO. As contact time progresses, the empty surfaces of the MM and MM-SiO<sub>2</sub>-NZ composite would decrease, triggering the adsorbent's ability to decrease. The optimum contact time for MO dye adsorption on MM adsorbent occurred at a 120-minute with an adsorption capacity of 0.580 mg/g. In comparison, that for MM-SiO<sub>2</sub>-NZ adsorbent occurred at a 240-minute with an adsorption capacity of 1.854 mg/g.



**Figure 8.** Effect of contact time on adsorption capacity of MM and MM-SiO<sub>2</sub>-NZ to MO dye

Adsorption kinetics studies were carried out to predict the adsorption rate of MO dye on MM and MM-SiO<sub>2</sub>-NZ adsorbents [19]. The adsorption kinetics study was examined using pseudo-first and -second orders equations. Curves of pseudo-first order and pseudo-



second order kinetics of MM and MM-SiO<sub>2</sub>-NZ are shown in Figure 9 and tabulated in Table 5.

**Table 5.** Reaction kinetic parameters of pseudo-first order and pseudo-second order of MM and MM-SiO<sub>2</sub>-NZ

Adsorbent	Pseudo-first order			Pseudo-second order		
	R <sup>2</sup>	q <sub>e</sub> (mg/g)	k <sub>1</sub> (g/mg.min)	R <sup>2</sup>	q <sub>e</sub> (mg/g)	k <sub>2</sub> (g/mg.min)
MM	0.982	0.411	2.6 × 10 <sup>-2</sup>	0.999	0.629	1.29 × 10 <sup>-2</sup>
MM-SiO <sub>2</sub> -NZ	0.955	1.056	1.1 × 10 <sup>-2</sup>	0.989	1.925	3 × 10 <sup>-2</sup>

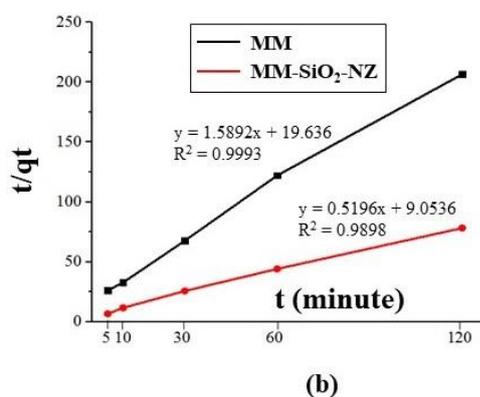
The pseudo-first-order linear equation follows:

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303} t$$

where q<sub>e</sub> and q<sub>t</sub> are the number of ions adsorbed on the adsorbent at an equilibrium (mg/gram) and at a t-time, respectively, k<sub>1</sub> is the first-order adsorption rate constant (minute<sup>-1</sup>). Pseudo-second order follows an equation:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t$$

where k<sub>2</sub> is the second order adsorption rate constant (gram/mg.minute)



**Figure 9.** Adsorption kinetics curves of (a) Pseudo-first order and (b) Pseudo-second order

The adsorption rate constant value indicates the adsorption rate of MO dye on MM and MM-SiO<sub>2</sub>-NZ adsorbents to achieve equilibrium and optimum adsorption time. The adsorption kinetics study of MO dye showed that the adsorption tended to follow a pseudo-second-order reaction kinetics with rate constants (k<sub>2</sub>) values of 1.29×10<sup>-2</sup> gram/mg.minute and 3×10<sup>-2</sup> gram/mg.minute, as well as the adsorption capacities (q<sub>e</sub>) of 0.629 mg/gram and 1.925 mg/gram, for MM and MM-SiO<sub>2</sub>-NZ composite, respectively.

## CONCLUSIONS

This study summarizes that based on the characterization results from FTIR, XRF, and VSM, the iron sand magnetic material-silica-zeolite (MM-SiO<sub>2</sub>-

NZ) composite was successfully synthesized. Using MM-SiO<sub>2</sub>-NZ composite as MO dye adsorbent on a laboratory scale is optimum at acidic pH. Adsorption proceeds rapidly and follows pseudo-second-order kinetics. The adsorption equilibrium follows the Langmuir adsorption isotherm and proceeds spontaneously. The application of the present study results on an industrial scale in the future is wide open to reduce the pollution load caused by dye waste in aquatic environments in general.

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