

Dye adsorption into transition metal-doped zinc oxide nanoparticles supported on natural zeolites to solve wastewater issue

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Abstract. In this work, Fe-doped zinc oxide/natural zeolite (Fe:ZnO/NZ) nanocomposites were prepared using the co-precipitation method with various NZ amounts. The nanocomposites were characterized by X-ray diffraction (XRD), Brunauer-Emmett-Teller (BET) surface area analysis and thermogravimetric analysis (TGA). The nanocomposites were used to remove methylene blue (MB) dye from an aqueous solution. The effect of various NZ amounts and initial MB concentration were tested. The Pseudo-first-order and pseudo-second-order kinetic models were used to explain the adsorption mechanism. The Langmuir and the Freundlich isotherm models were used to fit the adsorption isotherms of the nanocomposites.

1. Introduction

Population growth worldwide has led to an increasing demand for clean water as well as increasing production of wastewater. Wastewater may contain a significant amount of pollutants and microbes that are hazardous for the environment and human health [1-3]. Industrial wastewater is one of the main contributors to water pollution. In particular, dyes used in the textile, paper, and cosmetics industries are a common organic pollutant in wastewater, and they are toxic to aquatic life [1,4,5]. Dye-containing wastewater should be treated before being discharged into the environment. Adsorption is considered an effective treatment for wastewater because of its low cost and simplicity [4].

Natural zeolites (NZ) are good adsorbents and are widely used for environmental remediation owing to their low cost, abundant availability in many parts of the world, good mechanical and thermal properties, presence of individual micropores, and nontoxicity [3,6]. Unfortunately, they show limited capacity for dye adsorption [7]. NZ has been used as a supporter in pure and transition-metal-doped semiconductor nanocatalysts to remove dyes from water [8-11].

Zinc oxide (ZnO) nanoparticles are known for their adsorption capability toward cationic and anionic dyes [8]. In our previous work, we had studied the photocatalytic activity of transition metal iron-doped ZnO (Fe:ZnO) [9] and Fe:ZnO/NZ 10 wt% with various atomic percentage (at%) of metal iron (Fe³⁺) in degrading the cationic dye methylene blue (MB) [12]. In this work, we are going to study the adsorption ability of Fe:ZnO/NZ with constant at% of Fe³⁺ and various amounts of NZ toward MB, in hope that degradation of the dye will increase with increasing amount of NZ.

2. Experimental Details



2.1. Materials

ZnSO₄·7H₂O, FeSO₄·7H₂O, and NaOH were purchased from Merck. NZ were purchased from Sukabumi, Indonesia. All materials were of analytical grade and were used without purification. Distilled water was used to prepare the solutions in the experiment.

2.2. Fe:ZnO/Natural Zeolite Nanocomposite Preparation

The Fe:ZnO/natural zeolite nanocomposites were synthesized by the co-precipitation method. The required molar ratio of ZnSO₄·7H₂O and FeSO₄·7H₂O was mixed in distilled water to form a solution. NZ was then added to the solution with a constant amount (10 wt%, 20 wt%, 30 wt%, and 40 wt%). The mixed solutions were placed in an ultrasonic cleaner operating at 57 kHz for 2 h. After sonication, the mixed solutions were magnetically stirred for 1 h while NaOH solution was added until a pH of 13 was reached. The solutions were then allowed to stand at room temperature for 18 h. Then, the solutions were centrifuged and washed several times with distilled water and ethanol to remove impurities. The final products were dried in a vacuum oven for 4 h at 100 °C.

2.3. Characterization

The structural properties of the samples were characterized using X-ray diffraction (XRD; Rigaku Miniflex 600) operated at 30 kV and 15 mA and monitored in the range $2\theta = 10^\circ$ – 90° . The specific surface area of the samples was investigated by Brunauer-Emmett-Teller (BET; Nova Quantachrome 2000) surface area analysis. The samples' thermal stability was investigated using differential thermal analysis/thermogravimetric analysis (DTA/TGA; Rigaku Thermo Plus EVO2 TG-8121) with alumina as a reference and operated from room temperature to 500 °C.

2.4. Adsorption Test

The organic pollutant model used was MB. The degradation of 100 mL aqueous solution of MB was conducted using Fe:ZnO/NZ nanocomposites under room temperature for 4 h in the dark. Around 10 mL of the solution was removed at given time intervals to observe the degradation of MB using a UV-Vis Hitachi UH5200 spectrophotometer. The degradation percentage and adsorption capacity of the samples were calculated using the following equations:

$$E(\%) = \frac{(C_0 - C_t)}{C_0} \times 100 \quad (1)$$

$$q_e = \frac{(C_0 - C_e)V}{m} \quad (2)$$

where C_0 denotes the initial concentration of MB and C_t is the concentration of MB at time t . q_e represents the equilibrium adsorption capacity of the Fe:ZnO/NZ (mg/g); C_0 and C_e are the initial and equilibrium concentrations of methylene blue (mg/L) in aqueous solutions, respectively; V is the volume of the aqueous MB (mL); and m is the amount of Fe:ZnO/NZ (g).

3. Results and Discussion

XRD measurement is a useful method for studying the structural properties of the samples. Figure 1 shows the XRD patterns of the samples with various NZ amounts. As seen in the figure, the samples show the hexagonal wurtzite structure of ZnO [13]. Increasing the NZ content in the samples does not increase the NZ intensity significantly at around $2\theta=20^\circ$. No undesirable peaks are observed as a secondary phase. This indicates that the nanocomposites were successfully formed. The specific surface area of the samples was determined using BET surface area analysis. The results are shown in Figure 2. They indicate that with increasing NZ content, the specific surface area of the samples also increases.

TGA analysis was used to check the samples' thermal stability and weight loss with temperature. Fig. 3 shows TGA curves of the Fe:ZnO nanoparticle and Fe:ZnO/NZ nanocomposite, respectively. The weight loss of Fe:ZnO after increasing the temperature to 500 °C was ~3.5%, whereas that of Fe:ZnO/40 wt%NZ was ~7.3%. The weight loss of Fe:ZnO was due to boundwater elimination [14,15]. The weight

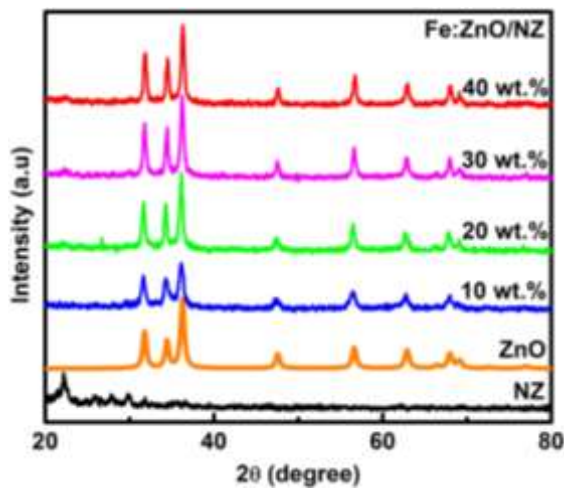


Figure 1. XRD patterns of ZnO nanoparticle and Fe:ZnO/NZ nanocomposites with various amount of NZ.

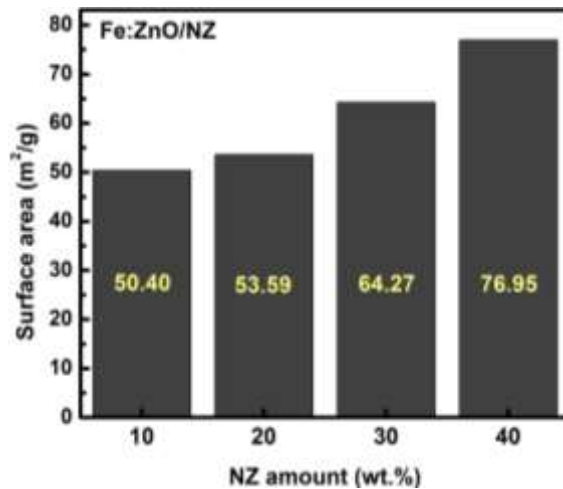


Figure 2. BET Surface area of the samples.

loss of Fe:ZnO/40 wt%NZ was due to the loss of the adsorbed water and iron dopant and water loss associated with silanol nests [15,16].

Figure 4 shows the degradation of MB using the Fe:ZnO catalyst with various NZ amounts (wt%) and initial dye concentration of 20 mg/L. The adsorption of MB in the catalysts reaches equilibrium at 120 min. The degradation of MB also increases as the incorporation of NZ increases. This is attributable to the increasing specific surface area of the samples, indicating that the higher the NZ loading in the samples, the larger is the number of sorption sites on the adsorbent's surface [17]. NZ also has anionic layers, and these interact well with the positively charged MB [1,18].

To understand the adsorption behavior of the samples, two kinetic adsorption models were used. The first is a pseudo-first-order kinetic model and the second, a pseudo-second-order one. The equations for these models are respectively given as follows [19]:

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303} t \quad (3)$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (4)$$

where q_e and q_t are the sorption capacity at equilibrium and at time t (mg/g), respectively; k_1 and k_2 are the rate constant of the pseudo-first-order kinetic model (1/min) and pseudo-second-order kinetic model (g/(mg min)), respectively; and t is time (min). The fitted data of the pseudo-first-order and pseudo-second-order kinetic reactions are shown in Figure 5 and 6, respectively. The corresponding kinetic parameters from the pseudo-first-order and pseudo-second-order kinetic models are listed in Table 1. As seen from this table, the equilibrium adsorption capacity of the pseudo-second-order-kinetic model was similar to that obtained experimentally, and the R^2 value of the pseudo-second-order kinetic model was higher than that of the pseudo-first-order one. These results indicate that the pseudo-second-order kinetic model had a better fit than the pseudo-first-order one. This means that the adsorption of MB using the Fe:ZnO/NZ followed the pseudo-second-order kinetic model. These results indicate that the adsorption mechanism depends on the amount of solute adsorbed on the surface of the samples and the amount adsorbed at equilibrium [5].

Figure 7 shows the effect of the initial dye concentration in the adsorption process. The figure shows that dye degradation decreases as the initial dye concentration increases. Figure 8 shows that with increasing initial dye concentration, the adsorption capacity of the catalyst improves. This may be due to increasing driving force of the concentration gradient as the initial dye concentration increases [20]. Both Figure 7 and 8 show that the adsorption reached equilibrium at 120 min.

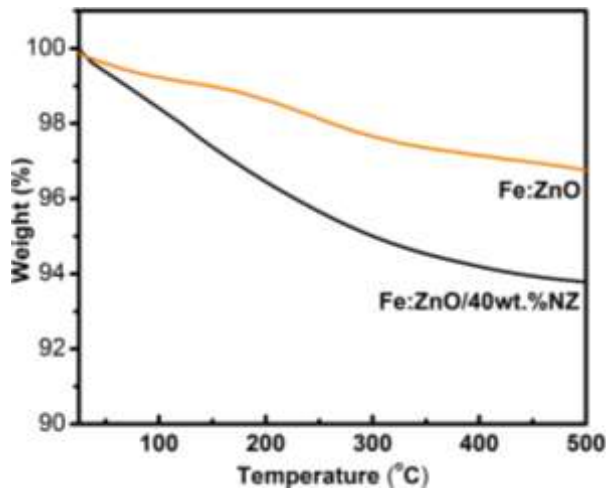


Figure 3. TGA curves of Fe:ZnO and Fe:ZnO/NZ.

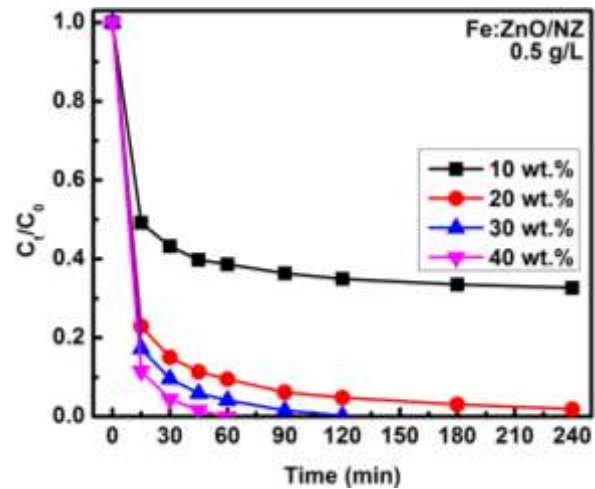


Figure 4. The effect of NZ amount in the MB adsorption process.

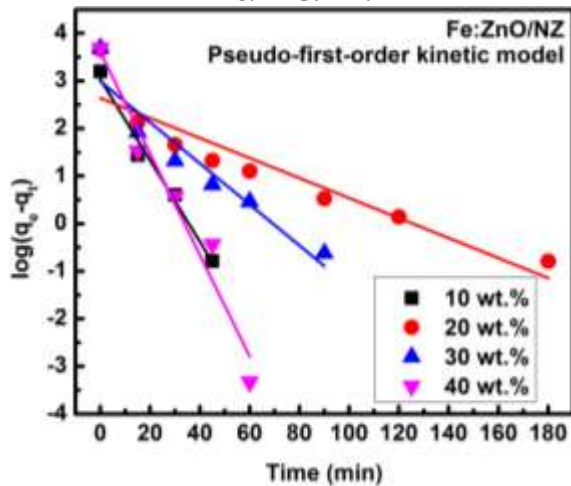


Figure 5. MB adsorption in pseudo-first-order kinetic model.

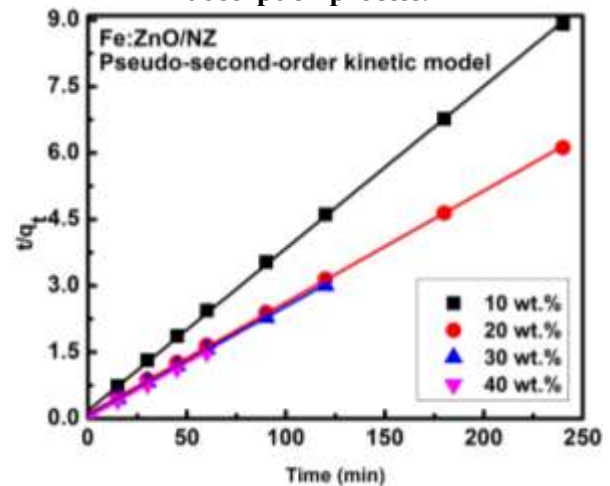


Figure 6. MB adsorption in pseudo-second-order kinetic model.

Table.1 Fitting result from pseudo first and second order kinetic reactions.

Sample	q _e (mg/g) exp	The pseudo-First-order rate			The pseudo-second-order rate		
		q _e (mg/g) cal	K ₁	R ²	q _e (mg/g) cal	K ₂	R ²
10 wt%	24.54	20.76	0.1964	0.97	27.29	0.00748	0.99
20 wt%	39.23	14.00	0.04841	0.85	39.66	0.00611	0.99
30 wt%	39.92	19.91	0.09931	0.89	40.40	0.01009	0.99
40 wt%	40	36.82	0.24548	0.94	40.30	0.02338	0.99

To understand the adsorption mechanism, the experimental data was fitted using the Langmuir and the Freundlich isotherm models [4], as shown in Figure 9 and 10, respectively. The Langmuir model represents chemisorption on a set of distinct localized adsorption sites [4], whereas the Freundlich model describes the relation between the solute concentration on the adsorbent surface and the solute concentration in the liquid. The Langmuir and Freundlich equations are as follows [21]:

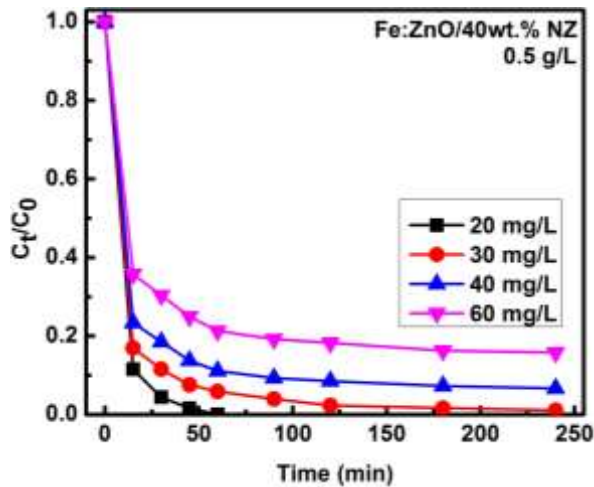


Figure 7. The effect of initial dye concentration in the MB adsorption process.

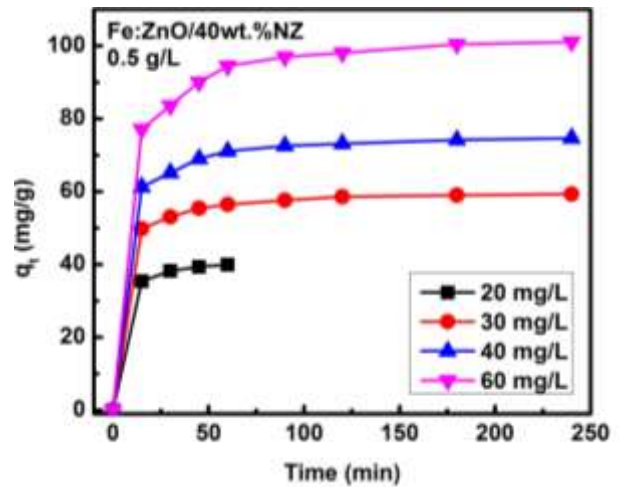


Figure 8. Amount of MB adsorbed on Fe:ZnO/NZ nanocomposites with different initial dye concentration.

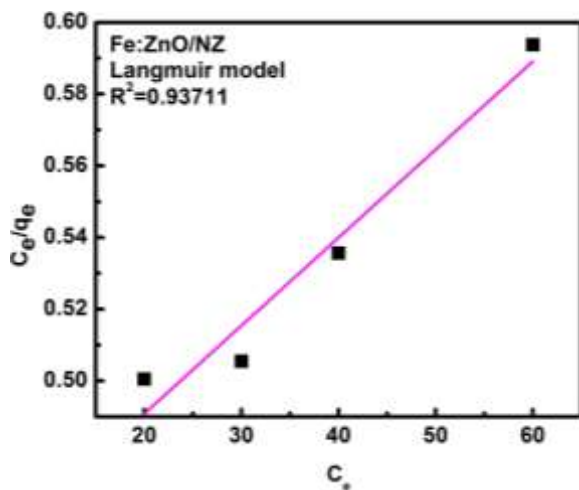


Figure 9. Langmuir isotherm model.

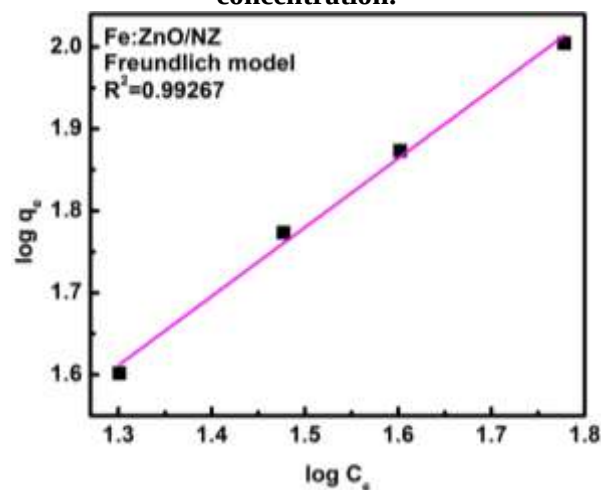


Figure 10. Freundlich isotherm model.

Table 2. Adsorption isotherm parameter.

Sample	Langmuir adsorption-isotherm model			Freundlich adsorption-isotherm model		
	q_m (mg/g)	K_L	R^2	n	K_f	R^2
Fe:ZnO:NZ	406.5	0.006	0.94	1.19	1.68	0.99

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

$$\log q_e = \log K_f + \frac{1}{n} \log C_e \quad (6)$$

The isotherm parameters obtained from the Langmuir and Freundlich adsorption isotherm models are listed in Table 2. As seen from this table, the maximum adsorption capacity of Fe:ZnO/NZ is 32 mg/g, and R^2 of the Freundlich isotherm model is higher than that of the Langmuir isotherm model. These results indicate that the equilibrium data would be better described by the Freundlich model.

4. Conclusion

Fe:ZnO/NZ nanocomposites were successfully synthesized by the co-precipitation method with no undesirable peaks are observed as a secondary phase. With increasing amount of NZ, the specific surface area of the samples also increased. TGA measurement showed that Fe:ZnO/NZ lost more weight (~3.8%) than Fe:ZnO. MB adsorption into the nanocomposites increased as the amount of NZ increased. The kinetic data of the samples fitted the pseudo-second-order kinetic model where the equilibrium adsorption capacity was similar to that obtained experimentally, and the R^2 value of the pseudo-second-order kinetic model was higher than that of the pseudo-first-order one. The adsorption equilibrium data fitted the Freundlich isotherm model better than Langmuir isotherm model because the R^2 value of the Freundlich isotherm model is higher than that of the Langmuir isotherm model. In the future, we intend to couple other materials with Fe:ZnO to degrade organic dyes in aqueous solution.

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