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Performance of wastewater sludge modified with zinc oxide nanoparticles in the removal of methylene blue from aqueous solutions

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ABSTRACT

The presence of chromogenic substances in water can potentially be carcinogenic and mutagenic, and thus, it may be hazardous to public health. This study was carried out with the objective of investigating the feasibility of using wastewater sludge, modified with zinc oxide nanoparticles, in the removal of the methylene blue (MB) dye from aqueous solution. The stabilization of nanoparticles onto the sludge was performed using the thermal method in order to increase the active adsorption surface. The effects of the operational parameters (including pH, contact time, MB dye concentration, and adsorbent dosage) on the adsorption of MB by the modified sludge were studied in batch mode. The sludge coated with zinc oxide nanoparticles had higher MB dye removal efficiency (%) than that of raw sludge. The MB adsorption amount (Q_e) increases with a reduction in the adsorbent dosage, an increase in pH, and an increase in the initial concentration of the MB dye. At equilibrium, the amount of MB dye adsorbed onto sludge coated with zinc oxide nanoparticles was 6.6 mg/g, while the amount of adsorbed MB dye onto raw sludge was 2.9 mg/g. The adsorption reached equilibrium after 120 min and the adsorption data fitted the Langmuir isotherm model ($R^2 = 0.99$). The modification of sludge with zinc oxide nanoparticles can provide an appropriate substance to function as the adsorbent in the removal of MB dye from aqueous solution.

Keywords: Adsorption; Zinc oxide nanoparticles; MB dye; Wastewater; Biological sludge

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1. Introduction

In recent years, soil and water contamination has been substantially increased due to the disposal of colored wastewaters into such environments [1,2]. In industries, such as dyeing, textile, paper making, printing, leather, tannery, cosmetics, and plastics, chromogenic substances are used to dye the manufactured products. The use of dyes during this process leads to the production of wastewater, containing such materials. The discharge of wastewater containing chromogenic substances can lead to eutrophication and increase in suspended matter, turbidity, and interference in the ecology of the receiving waters. Moreover, it has the potential to become carcinogenic and mutagenic. Due to the disadvantages of the presence of chromogenic substances in aqueous environments, effective treatment of colored wastewater is necessary [3–6]. Different treatment methods, including physical methods (such as adsorption), biological methods, chemical oxidation methods (such as ozonation), advanced oxidation methods (such as photocatalytic analysis), electrocoagulation, etc. are available to remove dye from industrial wastewaters [7]. One of the important dyes used extensively in the dyeing and textile industries is methylene blue (MB). It has a complex aromatic structure which is resistant to chemicals, heat, light, and even biological breakdown [6]. One of the most common methods of removing dye is using surface adsorption processes in which various adsorbents such as activated carbon (powder and granular), coal, peat (decomposed organic substances), wood chips, silica gel, date fibers, sawdust, bentonite, biomass, rice husk, chitosan, etc. may be used. Activated carbon is a suitable dye adsorbent, but due to its high costs, its use is economically not cost-effective [7]. In recent years, many attempts have been made to find cheaper and more easily available adsorbents for the removal of dye. One cheap adsorbent is the sludge produced in wastewater treatment plants, which is considered as a waste product.

Because common adsorbents lack numerous empty spaces (are not porous enough), do not have an adequate active atomic surface, and special surface area, they do not have a high adsorption capacity. But the use of nanomaterials coated on the adsorbent surface can increase the special surface area and as a result improve pollutant removal efficiency [8]. The present research was conducted to study the efficiency of zinc oxide nanoparticles immobilized on sludge as an effective adsorbent used in the adsorption of dye from synthetic wastewater. Additionally, this study investigated the effects of operational parameters such as pH, contact time, dye concentration, and adsorbent dosage on the removal of MB using sludge coated with zinc oxide nanoparticles.

2. Materials and methods

2.1. Materials

The cationic MB dye was purchased from Merck Co, Germany. The zinc oxide nanoparticles used in the present research were obtained from the US Company Nanoamore. The physical properties of the nanoparticles were determined by X-ray diffraction (XRD) spectrometry method (Phillips PNA-analytical diffractometer) and by transmission electron microscopy (FEG Phillips-CM 2000). Fourier transform infrared (FT-IR) analysis was carried out using a spectrophotometer (Tensor 27, Bruker, Germany) to specify the role of surficial functional groups of the sludge coated with zinc oxide nanoparticles in adsorption process. The spectra were recorded in the wave number range between 400 and 4,000 cm^{-1}. Furthermore, the point of zero charge (pH_{pzc}) of the adsorbent was measured using pH drift method [9].

2.2. Preparation of the adsorbent

The sludge used in the present study was obtained from the return activated sludge of the Shahrak-e-Gharb wastewater treatment plant, Tehran, Iran. In order to prepare the adsorbent, after collecting the sludge from the wastewater treatment plant, it was first dried in an oven at a temperature of 110˚C and then it was ground. The zinc oxide nanoparticles were mixed with the sludge using distilled water (with a zinc oxide to sludge ratio of 0.5:1) and the mixture was put on a shaker for 3 h at 300 rpm. After this stage, the mixture of zinc nanoparticles and sludge was passed through a filter paper and was dried at a temperature of 250˚C for 1 h. Then the mixture was slowly cooled at laboratory temperature [10]. Scanning electron microscopy (SEM, Philips, The Netherlands) was performed on the adsorbent before and after the adsorption of MB dye.

2.3. Experiments

This study was conducted on laboratory scale in batch mode. First, a stock solution of MB dye (1,000 mg/l) was prepared. The assessment of MB dye concentration in the experimental samples was performed using UV–vis spectrophotometry (US Unico 2100-vis) at a maximum wavelength of 663 nm. To adjust the pH of the samples, NaOH and HCl were used. In each adsorption experiment, specific amounts of the adsorbent together with a specific amount of the MB solution were added to the Erlenmeyer flask and were mixed on a shaker. After the necessary

contact time, a sample was taken from the flask and the residual concentration of the MB dye was measured spectrophotometrically after the centrifugation. The MB dye removal efficiency (%) and the amount of adsorbed dye were calculated using Eqs. (1) and (2), respectively:

$$R\,(\%) = \frac{(C_0 - C_t)}{C_0} \times 100 \tag{1}$$

$$q = \frac{V(C_0 - C_e)}{m} \tag{2}$$

In these equations, R is dye removal efficiency (%), q is adsorption capacity (mg/g), C_0 is the initial concentration of the dye (mg/l), C_t is the concentration of dye at time t after adsorption (mg/l), C_e is the dye concentration at equilibrium (mg/l), V is the sample volume (L), and m is the adsorbent mass (g) [11,12]. All the experiments were repeated three times and the averages of the data were used in data analysis. After the experimentation, the behavior of the studied adsorption system was analyzed based on the three models of Langmuir, Freundlich, and Dubinin–Radushkevich (D–R). The Langmuir linear model which is applicable in the study of adsorption phenomena is shown in Eq. (3):

$$\frac{C_e}{Q_e} = \frac{1}{bQ_m} + \frac{C_e}{Q_m} \tag{3}$$

where Q_e is the amount of adsorbed dye per unit weight of the adsorbent (mg/g), C_e is the equilibrium concentration of the adsorbed dye in the solution after the adsorption (mg/l), Q_m is the maximum adsorption capacity (mg/g), and K is the Langmuir constant which can be obtained by plotting C_e/Q_e against C_e [13]. The Freundlich linear model is shown in Eq. (4):

$$\mathrm{Log}\, Q_e = \mathrm{Log}\, K_f + \frac{1}{n}\mathrm{Log}\, C_e \tag{4}$$

where C_e is the equilibrium concentration (mg/l), Q_e is adsorption capacity at equilibrium (mg/g), K and n are Freundlich constants which can be obtained by plotting Log Q_e against Log C_e [14]. The Dubinin–Radushkevich linear model is shown in Eq. (5):

$$\mathrm{Log}\, Q_e = \mathrm{Log}\, Q_m - \beta\epsilon \tag{5}$$

where ϵ (Polanyi potential) = RT ln (1+1/C_e), R is the universal gas constant (kJ/K mol), T is temperature (°K), Q_m is adsorption capacity (mg/g), and β is the adsorption energy (kJ/mol) which is obtained by plotting ln Q_e against ϵ^2 [15].

3. Results and discussion

3.1. Characterization of the adsorbent

The morphological properties of dried sludge coated with ZnO nanoparticles are shown in Fig. 1. The results obtained from SEM show that the size of the zinc oxide nanoparticles used in the present study is less than 50 nm. The immobilization on sludge keeps the porous property of these particles at a desirable level and helps provide an appropriate surface for adsorption. The SEM micrographs taken from the modified adsorbent before and after the MB dye adsorption process indicate that the adsorbent possesses proper pores before adsorption to remove the pollutant. After the adsorption process with enough contact time, these pores are filled with the pollutant molecules and this indicates that the MB dye molecules have been transformed from the liquid phase to solid phase during the adsorption process and were separated from the aqueous solution adequately.

To evaluate the effect of functional groups placed on the surface of the adsorbent on the adsorption of MB molecules, FT-IR analysis was performed and the results are shown in Fig. 2. As shown, the peaks located at 3,423, 1,560, 1,419, and 1,036 cm^{-1} are ascribed to the presence of O–H, C=C vibration, C–H bending, and C–O of polysaccharides, respectively [16,17]. The decrease in the intensity of the above-mentioned peaks after the adsorption of MB dye molecules indicated the significant role of these groups in the adsorption process. Moreover, the peak located at 477 cm^{-1}, which is assigned to the Zn–O [18], shifted from the wavenumber of 477 to 489 cm^{-1} during the adsorption process, demonstrating the involvement of this compound in the adsorption of dye molecules. Obviously, immobilization of ZnO in nanosize produces higher surface area containing active functional groups (confirmed by FT-IR analysis at Fig. 2) for an efficient adsorption of MB dye in comparison with pure activated sludge. In addition, the results of SEM analysis (Fig. 1) demonstrated suitable coverage of activated sludge by ZnO. It was shown that the adsorption of MB dye does not influence the structure of ZnO-coated adsorbent. It suggests that this adsorbent can be used as potential adsorbent with high mechanical strength for treating colored solutions.

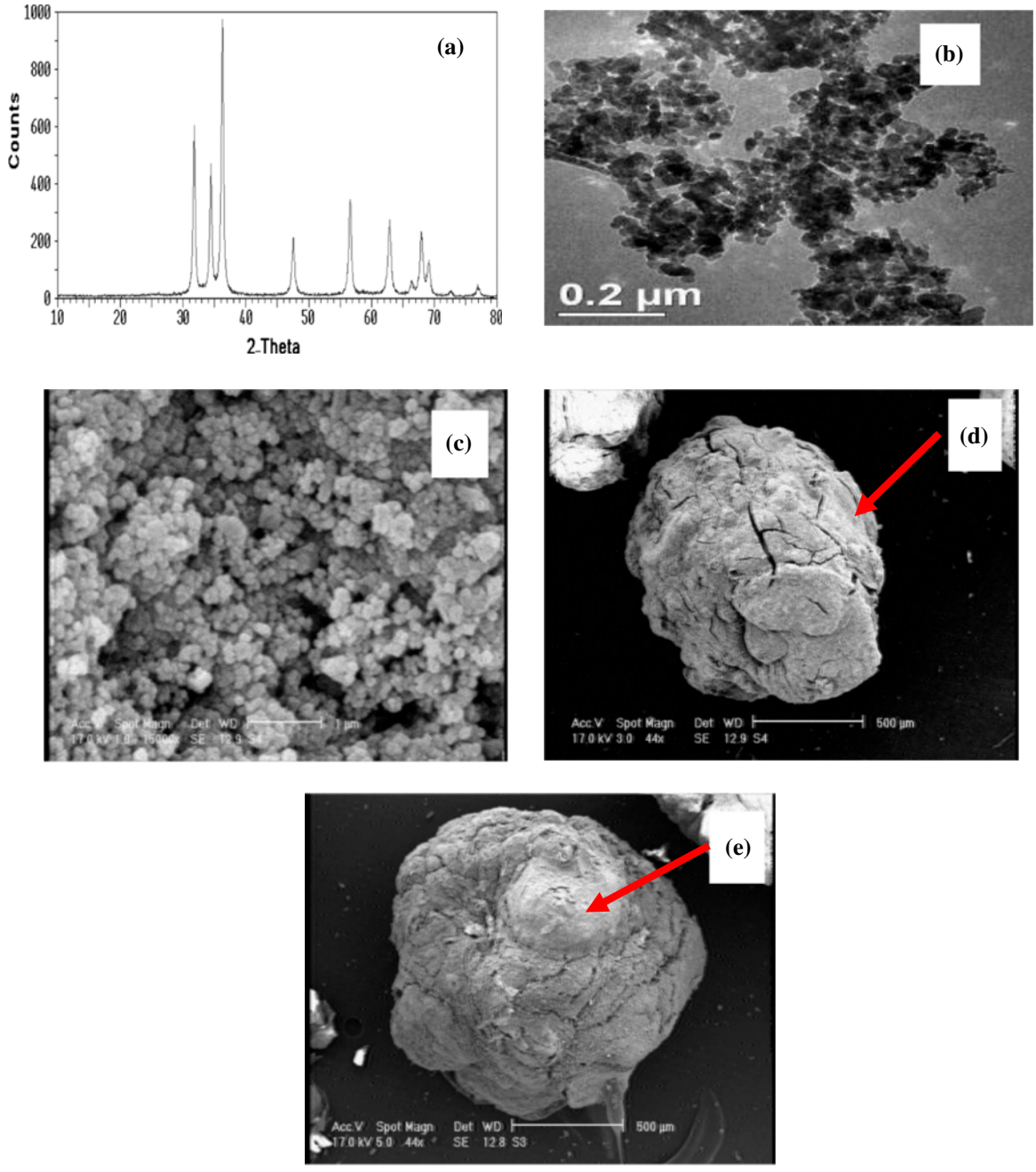

Fig. 1. The morphological properties of dried sludge covered with zinc oxide nanoparticles: (a) XRD spectrometer of the zinc oxide nanoparticles, (b) transmission electron microscopy of zinc oxide nanoparticles, (c) SEM of zinc oxide nanoparticles stabilized on sludge (d) SEM of stabilized adsorbent before dye adsorption, and (e) SEM of stabilized adsorbent after dye adsorption.

3.2. *Effect of pH*

The effect of pH on the adsorption of MB was investigated at five pH levels of 3, 5, 7, 9, and 11 (at a reaction time of 120 min, initial MB concentration of 50 mg/l, adsorbent dosage of 0.5 g/L), the results of which are shown in Fig. 3(a).

As pH increased from 3 to 11, the adsorption of MB by the sludge coated with ZnO nanoparticles increased from 3.13 to 6.9 mg/g, respectively, after a contact time of 120 min (Fig. 3(a)). The amount of adsorbed MB increases as a result of the increase in pH levels. This increase in adsorption together with

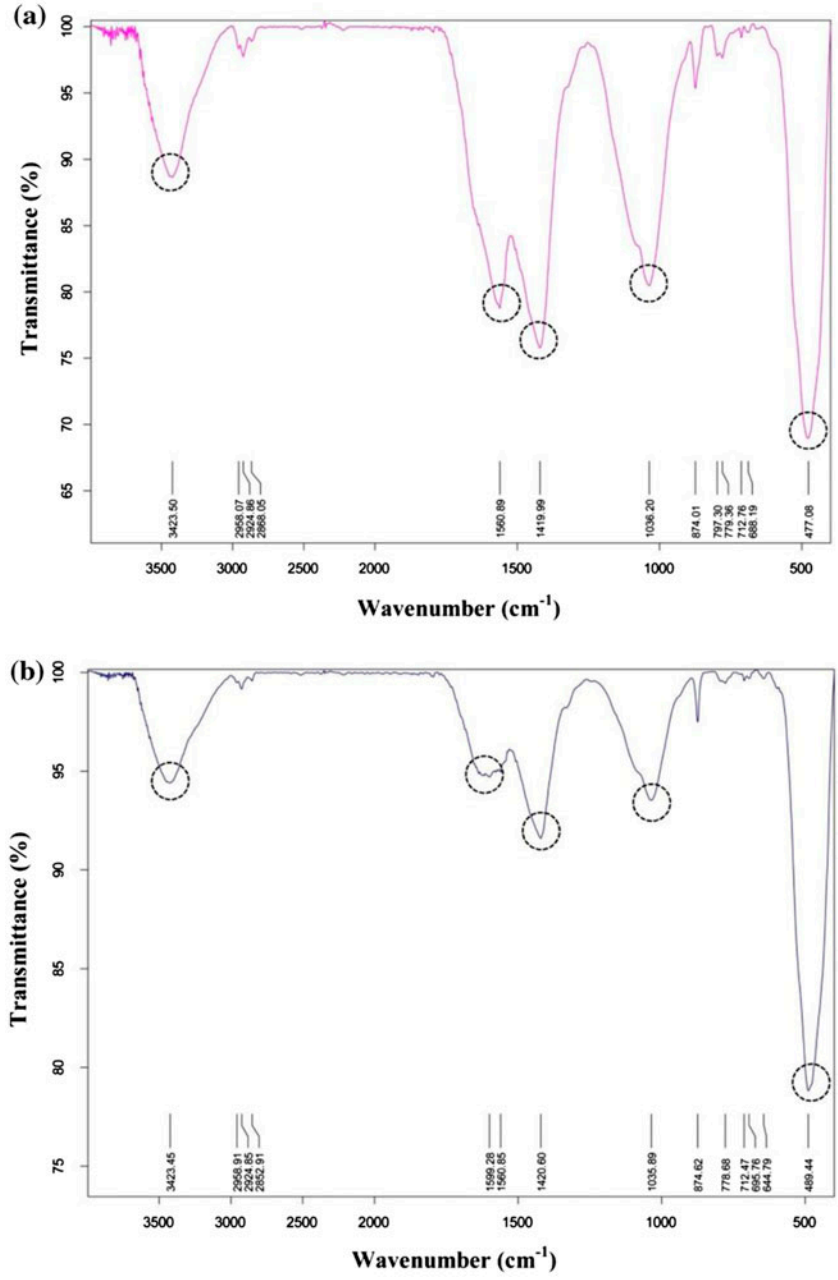

Fig. 2. FT-IR spectra of the adsorbent before (a) and after (b) the adsorption of dye.

the increase in the amount of the hydroxide ion in the environment (basic pH) is a result of adsorbent surface charge change and the level of ionization of the MB present in the solution. On the other hand, the cationic MB molecule has functional groups S and H which are ionized in water and cause its molecule to become cationic (cationization of the MB molecule is mainly attributed to the N atoms). As a result, the increase in the pH level leads to an increase in the anionic charge of the adsorbent surface. Consequently, the adsorbent surface acquires hydroxyl active groups. Under these conditions, a strong attraction force is generated between the adsorbent surface (negative charge) and the MB molecules (positive charge). This optimum electrostatic attraction leads to better adsorption of the pollutant onto the adsorbent particles in comparison with the acidic conditions (in which the repellent force is stronger) [5]. Fig. 3(c) also shows the pH_{pzc} of the sludge modified with zinc oxide nanoparticles which is an appropriate approach to describe

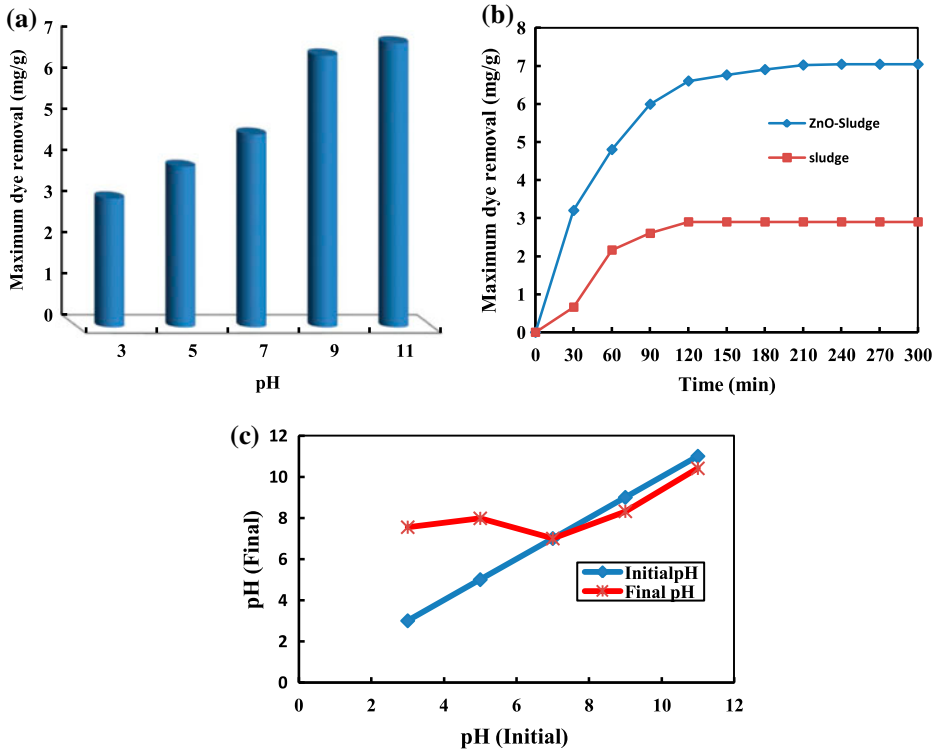

Fig. 3. (a) The effect of pH on the removal capacity (initial dye concentration 50 mg/l; initial adsorbent amount 0.5 g /100 cc; contact time 120 min), (b) The effect of contact time on the removal capacity (pH 9; initial dye concentration 50 mg/l; initial adsorbent amount 0.5 g/100 cc), and (c) pH_{pzc} plot.

the mechanism of the adsorption process under different initially adjusted pHs. As it is evident from Fig. 3(c), the pH_{pzc} of the sludge coated with ZnO nanoparticles was estimated to be 7. Regarding pH_{pzc}, it can be stated that the surface of sludge modified with zinc oxide nanoparticles will be de-protonated at pH values higher than 7 [19]. Li et al. [20] studied the adsorption of the MB dye by three different carbonated adsorbents (activated carbon, graphite oxide, and carbon nanotubes) and reported that the MB removal efficiency increases as the pH levels go up from 5 to 9.

3.3. Effect of contact time

Fig. 3(b) shows the effect of reaction time at 10 different intervals (30, 60, 90, 120, 150, 180, 210, 240, 270, and 300 min).

The amount of adsorbed MB by the raw and modified sludge at the optimum time of 120 min is 2.9 and 6.6 mg/g, respectively (Fig. 3(b)). These results indicate that stabilizing the raw sludge with nanoparticles causes more MB dye to be adsorbed on the surface of the adsorbent. Considering Fig. 3(b), the maximum amount of adsorption takes place during the early hours of adsorption, and after that the adsorption diagram almost plateaus. The adsorption of chromogenic substance happens at high speed during the first few minutes and the speed is reduced as the amount of adsorption increases. This issue can be explained by the fact that the amounts of the chromogenic substance in the environment and the number of the active points present on the surface of the adsorbent are reduced. It can be seen that after 120 min, the amount of adsorption does not increase significantly. Under this condition, the amount of adsorption is controlled by the transfer of the adsorbed chromogenic substance from the surface of the adsorbent particles to the inside of the adsorbent particles. Therefore, a time interval of 120 min was selected as the necessary time to achieve equilibrium. Ozer et al. [21] reported an equilibrium time of 2 h for the removal of the MB dye using activated carbon produced from hazelnut husks.

3.4. Effect of the adsorbent dosage

To study the effect of the adsorbent dosage on the adsorption of MB dye, the experiments were performed

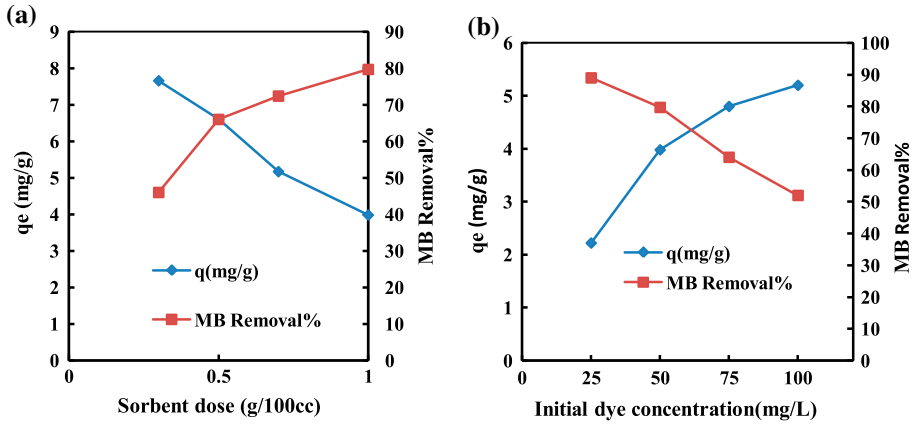

Fig. 4. (a) The effect of initial adsorbent amount on the removal efficiency (initial dye concentration 50 mg/l; pH 9; contact time 120 min) and (b) The impact of initial dye concentration on the removal efficiency (pH 9; contact time 120 min; initial adsorbent amount 1 g/100 cc).

with four different adsorbent dosages (0.3, 0.5, 0.7, and 1 g/l), at a reaction time of 120 min, an initial pH of 9, and an initial MB concentration of 50 mg/l. The results of these analyses are shown in Fig. 4(a).

An experiment of the effect of the amount of the adsorbent on pollutant adsorption showed that an increase in the adsorbent mass from 0.3 to 1 g lead to an increase in the MB removal efficiency (%) from 46 to 79.7% (Fig. 4(a)). The increase in the MB removal efficiency (%) as the adsorbent dosage increases is the result of an increase in the area of the active surface effective in the adsorption process. Based on Fig. 4(a), the results of the present research show that although an increase in the adsorbent dosage present in the MB solution leads to an increase in the removal efficiency and the amount of the remaining dye in the wastewater is reduced, the adsorption amounts based on Fig. 4(b) shows that as the amount of the adsorbent increases from 0.3 to 1 g, and the amount of chromogenic molecules adsorbed per unit of the adsorbent mass decreases from 7.66 to 3.98 mg/g. The results show that even though the amount of the remaining dye decreases as the adsorbent dosage increases, the amount of the adsorbed dye per unit of the adsorbent mass decreases as the adsorbent dosage increases. As the adsorbent dosage increases, the amount of pollutant adsorbed is reduced per unit of the adsorbent mass, because some of the active target adsorbent sites remain unsaturated. This issue leads to a decrease in interparticle distribution. These conclusions have been confirmed by Barka et al. [22] and Kumar and Porkodi [23]. Based on the performed calculations, the optimum amount for the adsorbent was determined to be 1 g/100 cc and this amount was used for consequent experiments.

3.5. Effect of MB concentration and isotherm study

To determine the effect of initial MB concentration on the efficiency of the process, various MB concentrations (25, 50, 75, 100 mg/l) at a reaction time of 120 and an initial pH of 9 were examined. The results of these analyses are shown in Fig. 4(b).

Initial pollutant concentration is another factor which affected adsorption efficiency. The data related to the effect of dye concentration on its adsorption capacity are presented in Fig. 4(b). It can be seen that as the dye concentration increases from 25 to 100, the amount of dye adsorbed per adsorbent mass unit increases from 2.22 to 5.2 mg/g. An increase in the concentration of the MB chromogenic molecules leads to the creation of an important driving force due to the increase in the number of impacts between dye molecules and adsorbent molecules and this overcomes the resistance against mass transfer (mass transfer acceleration). These conditions cause more MB molecules to be adsorbed by the adsorbent particles and consequently the adsorption capacity increases. The conclusions drawn from Ghaedi et al. [24] study confirm the same issue. One of the most important features of adsorption with different adsorbents is the study of adsorption isotherms. In the present study, the isotherm diagrams are shown based on the three models mentioned above (Fig. 5). The adsorption isotherms provide equations to explain the equilibrium status of the adsorbed particles between the liquid and solid phases and simplify the assessment of feasibility of the application of this process. In this study, a model for the MB dye adsorption onto dried sludge covered with zinc oxide nanoparticles has been presented using different isotherms at a fixed

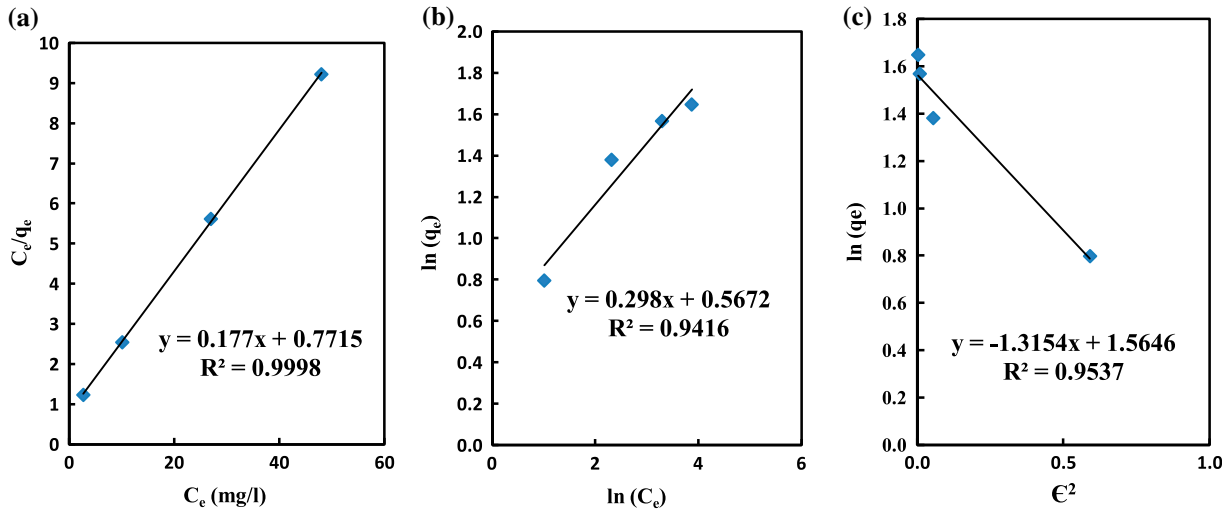

Fig. 5. (a) Langmuir adsorption diagram, (b) Freundlich adsorption diagram, and (c) D–R adsorption diagram.

Table 1
The parameters and correlation coefficients of MB dye adsorption based on Langmuir, Freundlich, and D–R models

	Langmuir isotherm			Freundlich isotherm			D–R isotherm		
Adsorbate	Q_m (mg/g)	b (l/mg)	R^2	K_f (l/mg)	n	R^2	Q_m (mg/g)	E (kJ/mol)	R^2
MB	5.65	0.23	0.999	1.760	3.356	0.941	4.755	0.617	0.953

temperature (25 ± 1˚C) and varying dye concentration levels a diagram of which can be seen in Fig. 5. The adherence of each system has been determined by plotting each isotherm's diagram and calculating the correlation coefficient of the model (R^2) based on the experimental results. Bases on the obtained results, the Langmuir model R^2 value (0.999) is higher than the same value for the other two models, which shows that dye adsorption by the sludge adsorbent follows the Langmuir model. Using the Langmuir model, the maximum adsorption amount was calculated to be 5.65 mg/g. In the Langmuir model, it is assumed that the adsorbed substances (dye molecules) attach to certain points on the adsorbent surface and a single-layered adsorption process takes place and no reactions occur between the adsorbed molecules. In Table 1, the MB dye adsorption data modeling is presented based on the Langmuir, Freundlich, and D–R models. Ghaedi et al. [8] reported that in dye removal using zinc oxide nanoparticles, silver, and palladium stabilized on activated carbon, the adsorption by activated carbon adheres to the Langmuir model with a higher correlation coefficient. In another study, Zhou et al. [25] reported that the results of the adsorption study closely matches the Langmuir model and has the highest correlation coefficient with it. These results correspond with the results of the present study.

4. Conclusions

The present study demonstrated that sludge modified with zinc oxide nanoparticles is an effective adsorbent in the removal of the MB cationic dye from textile and dyeing wastewaters. The MB adsorption process using this adsorbent was greatly affected by the solution pH, such that in basic pH_s, the adsorption amount increases. The adsorption process achieves equilibrium after about 120 min. At equilibrium, the amount of dye adsorbed onto sludge covered with zinc oxide nanoparticles was 6.6 mg/g, while the dye adsorption amount onto raw sludge alone was 2.9 mg/g. The maximum single-layered adsorption capacity obtained under the experimental conditions of the present study was 5.65 mg/g.

Acknowledgments

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