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Research Article

Investigation of the Adsorption Performance of Aqueous Solution of Malachite Green Dye on Kaolin Clay

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ABSTRACT

In this study, the removal of Malachite green (MG) dye, which has a toxic effect on the aquatic ecosystem, was carried out with kaolin clay, a natural and inexpensive material. In batch adsorption tests, the effects of pH, adsorbent dose, initial dye concentration and contact time were determined. Also, Pseudo first order and Pseudo second order kinetic models and Freundlich, Langmuir and Temkin isotherm models were tested. On the other hand, Scanning Electron Microscope (SEM) and Fourier Transform Infrared spectroscopy (FTIR) analyzes of raw and MG-loaded kaolin clay were performed. According to the results obtained, the removal efficiency was over 99% at 23±2 ^{0}C, pH 7.0 (±0.5), initial MG concentration of 4 mg/L and kaolin dosage of 1.75 g/L. Also, the most suitable kinetic and isotherm models were determined as Pseudo second order (R^2: 0.999) and Freundlich (R^2: 0.960), respectively. Additionally, the amount of MG dye removed per unit kaolin (q_{max}) was calculated as 16.36 mgMG/gkaolin. This study reveals the suitability of using kaolin clay in the adsorption of MG dye.

Introduction

The dyes of different qualities are used in industrial production around the world, including paper, paint, plastic, automotive, cosmetics and textile production. In addition to many organic dyes such as turmeric, onion and henna etc., there are also many synthetic dyes such as acid, direct, reactive, disperse, wat and basic. Almost 10% of these dyes are released into the receiving environment (lake, pond, stream, river and sea) [1].

MG dye is a synthetic organic compound. MG, known as cationic dye, is widely used in many industries such as cotton, wool, fabric, leather, paper, plastic and metal. [2]. In addition, it is also used as a food coloring agent and in medical processes [3]. It is known that this widely used dye causes carcinogenic, mutagenic and teratogenic effects for the ecosystem [4]. It also causes accumulation in the tissues of living creatures in the aquatic ecosystem, especially fish. On the other hand, it has a negative effect on photosynthetic organisms by affecting light transmittance. Thus, it threatens the lives of upper category creatures that feed on photosynthetic creatures [5].

There are many various physicochemical treatment processes such as adsorption, membrane, chemical and electrochemical coagulation/flocculation and ion exchange to minimize the toxic effects of dyes in the environment where they are discharged. There are also chemical purification methods such as advanced oxidation and photocatalytic. In addition, removal is carried out by biological treatment methods including aerobic, anaerobic or hybrid systems [1], [6], [7], [8]. These methods have many advantages and disadvantages, which are closely related to the quantity, quantity and discharge of wastewater. However, treatment technologies that achieve high removal efficiency at low cost are preferred by researchers. In this context, the adsorption process is the frequently preferred process [9], [10].

In the adsorption process, the pollutant is removed by binding to the surface of the adsorbent in various physicochemical aspects. The main reason why this process can be preferred over others is the cost of the adsorbent. In this context, the most commonly used adsorbents are burned by using various chemicals and at high temperatures (500-1000 ^{0}C) [11], [12], [13]. For this purpose, trees such as oak and pine are used as raw materials, and many biomaterials such as walnuts, almonds, hazelnuts, olives and corn are used [14]. Since their production costs are quite high, there is a tendency towards less costly biomaterials (agricultural product wastes such as rice, corn and plant wastes and microalgae, bacterial and fungal cultures) [15], [16], [17] and materials such as zeolite, bentonite and kaolin. Among these, various researches are being carried out on kaolin clay in terms of cost and removal capacity.

Clay minerals are frequently found as precipitates in nature and in the ocean. It is a very porous, earthy and natural material. In general, the majority of kaolin is kaolinite, but it contains various minerals such as quartz and mica [18]. There are ionizable groups within the clay and on its surface. Thus, it has a charge that can easily interact with ions in solution [19]. They are frequently preferred in adsorption processes due to their high absorption capacity, high stability and easy availability [20].

There are studies on the removal of heavy metals (cadmium, lead, chromium and iron, etc.), various organic/inorganic pollutants and dyes with raw and modified kaolin [14], [21].

This study was carried out to determine the amount of kaolin that effectively removes dye in a short time at low dye concentration. A removal study of MG dye was carried out with kaolin clay, which is a natural and inexpensive product. The effect of environmental parameters (pH, material dose, initial pollutant concentration and contact time) was investigated with batch adsorption tests. The obtained results were tested with 2 different kinetic and 3 different isotherm models, and FTIR and SEM analyzes of raw and MG-loaded kaolin were performed.

Materials and method

Chemicals

All chemicals used in adsorption studies are of analytical purity. Powder malachite green oxalate ($C_{23}H_{25}N_2.C_2HO_4.0.5C_2H_2O_4$, 463.50 g/mol, Sigma-Aldrich), sodium hydroxide in pellet form (NaOH, 40.00 g/mol, ≥99.0%, Sigma-Aldrich) and sulfuric acid in liquid form ($H_2(SO_4)_3$, 1.81 g/cm^3, ≥ 90-91 %, Merck) were used.

Preparation of kaolin clay

Kaolin clay used in experimental studies was sieved in a sieve with a pore size of 75 microns. Then, it was dried in an oven at 50^{0}C for 24 hours and stored in a closed container.

Adsorption studies

Stock solution of MG dye (1000 mg/L) was prepared for adsorption studies. The equation y = 0.1753x + 0.0191 (R^2 = 0.9999) was obtained by creating a calibration curve on a UV-Vis spectrophotometer (Hach DR6000, Germany) at 617 nm wavelength [22], [23], [24] by diluting this stock solution at certain rates.

The absorbance value measured in each experiment was converted to concentration with the help of this equation. Adsorption studies were carried out on an orbital shaker (Heidolp, Unimax1010, Germany) with a mixing speed of 250 rpm. In order to determine the capacity of kaolin to adsorb MG dye, optimum values were determined by studying the variable pH effect, variable adsorbent effect, variable initial MG dye concentration, contact time and variable temperature parameters. Numerical results obtained from each experiment were interpreted with the help of equations 1 and 2.

$$R(\%) = \frac{C_0 - C_e}{C_0}.100 \qquad (1)$$

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

Here, R expresses the removal efficiency of MG dye in %, while C_0 and C_e expressions express the MG concentration in the solution at the beginning and end of the experiment in mg/L. In addition, the expression q_e refers to the amount of MG dye removed per gram of kaolin (mg/g), the expression V refers to the solution volume in L, and the expression m refers to the amount of kaolin in mg.

First of all, time, adsorbent amount, and initial concentration were kept constant to find the optimum pH. In this context, experiments were carried out at varying pHs in a volume of 10 mL, an adsorbent amount of 10 mg, a reaction time of 30 minutes and an initial dye concentration of 4 mg/L. Then, to find the optimum amount of adsorbent, experiments were carried out with varying adsorbent amounts in a volume of 10 mL, pH 7, reaction time of 30 min and initial dye concentration of 4 mg/L, and the amount of adsorbent with the highest removal was selected. Then, a kinetic study was conducted at pH 7, with an initial dye concentration of 4 mg/L and an adsorbent amount of 17.5 mg. However, in order for the experimental study to be carried out easily, 5 times more work was done. That is, the initial dye concentration is 4 mg/L, the solution volume is 50 mL and the amount of kaolin is 87.5 mg. Finally, in order to determine the effect of the initial concentration and make isotherm calculations, other conditions were kept constant but the initial dye concentration was changed.

Adsorption kinetics

Experiments for kinetic evaluation were carried out at neutral pH at 23±2 ^{0}C. 87.5 mg kaolin was added to a 50 mL volume beaker where the initial MG concentration was 4.0 mg/L. And samples were taken at certain time intervals and these MG concentrations were read on a UV-Vis spectrophotometer. Pseudo first order and Pseudo second order kinetic models were tried to interpret the obtained results. The equation used for the Pseudo first order kinetic model is presented in equation 3 [25] and the equation used for the Pseudo second order kinetic model is presented in equation 4 [26].

$$\text{Pseudo first order: } \ln(\mathrm{q_e} - q_t) = \ln(\mathrm{q_e}) - \mathrm{k_1}t \qquad (3)$$

$$\text{Pseudo second order: } \frac{t}{q_t} = \frac{1}{\mathrm{k_2 q_e^2}} + \frac{t}{q_e} \qquad (4)$$

Here, the expression q_e describes the amount of pollutant removed per unit adsorbent in equilibrium by the reaction on a mg/g basis, while the expression q_t expresses the amount of pollutant removed per unit adsorbent at any time t of the reaction, also on a mg/g basis. The expression k_1 in the equation refers to the first-order adsorption rate constant on the basis of h^{-1}. The expression k_2 refers to the quadratic constant on the basis of g.mg^{-1}.h^{-1}.

Adsorption isotherms

Experiments to determine the most suitable isotherm model were carried out at 23±2 ^{0}C and neutral pH. 1 mg of kaolin was added to 8 different tubes of 10 mL volume, with initial dye concentration ranging from 7.8 to 133.3 mg/L, and at the end of the period, the dye concentrations were read on a UV-Vis spectrophotometer. Freundlich [27], Langmuir [28] and Temkin [29] isotherm models were used to interpret the obtained values. The equations used for these models are presented in equations 5, 6 and 7, respectively.

$$\text{Freundlich: } log(q_e) = log(k_F) + {}^{1}\!/_{n}\, log(C_e) \qquad (5)$$

Here, the q_e expression seen in each model expresses the amount of pollutant removed by the unit adsorbent in equilibrium state on a mg/g basis. k_F is the Freundlich adsorption constant, and *1/n* is a measure of the intensity of adsorption.

$$\text{Langmuir: } \frac{C_e}{q_e} = \frac{1}{q_{max}k_L} + \frac{C_e}{q_{max}} \qquad (6)$$

Here, k_L represents the Langmuir equivalence constant based on L/g. In addition, the dispersion constant (R_L) must be determined. For this, equation no. 7 is used.

$$R_L = \frac{1}{1+a_L.C_0} \qquad (7)$$

Here, R_L expresses whether the isotherm is suitable or not, while a_L expresses the constant related to the adsorption energy on a L/mg basis.

$$\text{Temkin: } q_e = \frac{RT}{b_T}\, ln(k_T) + \frac{RT}{b_T}\, ln(C_e) \qquad (8)$$

Here, *R* refers to the universal gas constant on the basis of 8.314 j/mol.K, *T* refers to the temperature on the basis of *K*, and b_T refers to the Temkin isotherm constant on the basis of kj/mol

Results

Characteristic of kaolin clay

Fourier transform infrared spectroscopy (FTIR)

In order to understand the adsorption of MG dye on kaolin clay, FTIR spectra of raw and MG-loaded kaolin were determined. FTIR spectrum results of raw and MG loaded kaolin clay are presented in Figure 1. There are various differences in functional groups before and after adsorption. Si-O-Mg, Si-O-Si and Si-O-Al stretching vibrations were observed in the 467-789 cm^{-1} bands in both raw and MG charged particles [30]. Additionally, hydroxyl groups were detected in the 900 bands and the 3618 and 3691 cm-1 bands [31]. Si-O and Si-O-Si stretching vibrations are observed in the 1032 cm^{-1} bands [31] and -CH groups are observed in the 2800-3000 cm^{-1} bands [32].

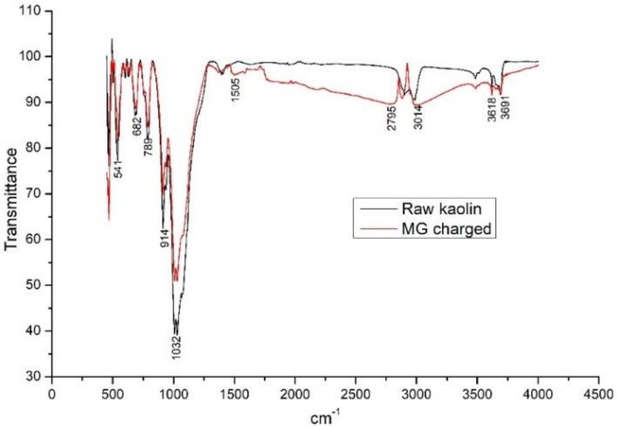


Figure 1. FTIR diagram before and after reaction

Scanning electron microscopy (SEM)

Before the reaction, the morphological structures of raw and MG-loaded kaolin clay were tried to be determined by SEM analysis. Figure 2 (a) shows the general appearance of raw kaolin clay. Here, the image appears clear, clear and bright in terms of surface features. In addition, the surface structure of clay is quite irregular and has a partially indented porous structure. On the other hand, the image of MG-loaded kaolin clay is presented in Figure 2(b). It can be said that in the image loaded with MG, the roughness of the clay surfaces is partially reduced and the overall image becomes blurred. Thus, it is very important for the MG dye to adhere to the irregular and porous surface [33].

Influence of experimental parameters

Effect of pH

pH is a very effective parameter in adsorption. Various experiments were carried out to determine the effect of pH on the adsorption of MG dye by kaolin clay. Experiments were carried out at room temperature and 250 rpm. 10 mg kaolin was added to 10 mL tubes with an initial MG dye concentration of 4 mg/L and the initial pH values were adjusted to 3, 5, 7 and 9. After 30 minutes, centrifugation was performed and dye measurements were performed in the upper phase water.

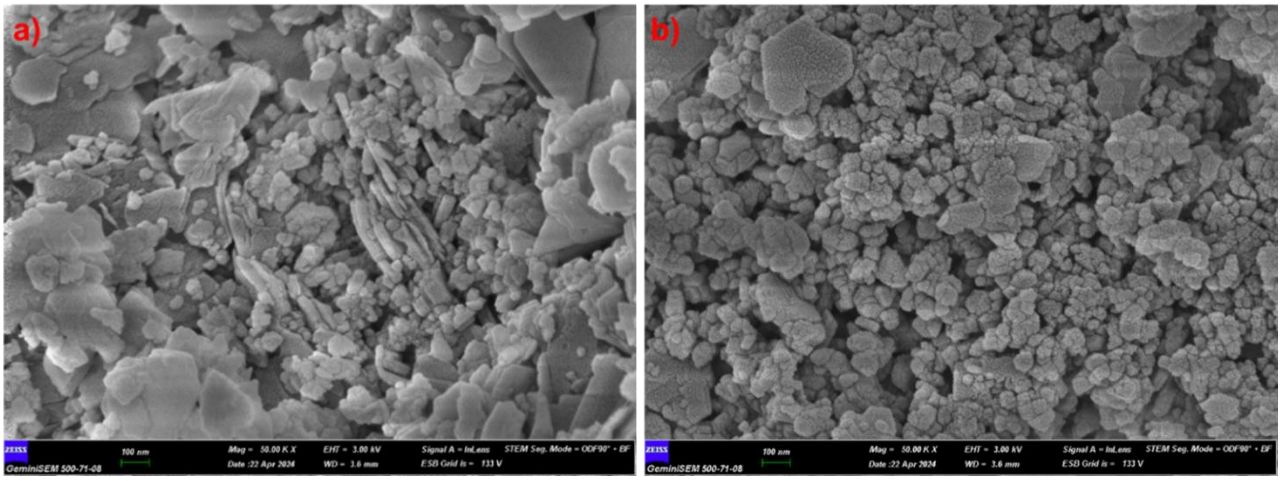


Figure 2. SEM images of kaolin clay before and after reaction; a) Raw kaolin clay, b) MG charged.

While the removal efficiency was 87.75% at pH 3, the efficiency increased to 95.75% as the pH increased. But the efficiency increase is around 8.3%. Experimental studies can continue at the highest efficiency, but the studies were carried out at neutral pH (7±0.5) since the efficiency is not significantly high and additional chemical consumption will be required to increase the pH. In literature, the removal efficiency of MB dye at high pH was high, but it was reported that the increase in efficiency was not relatively high [34].

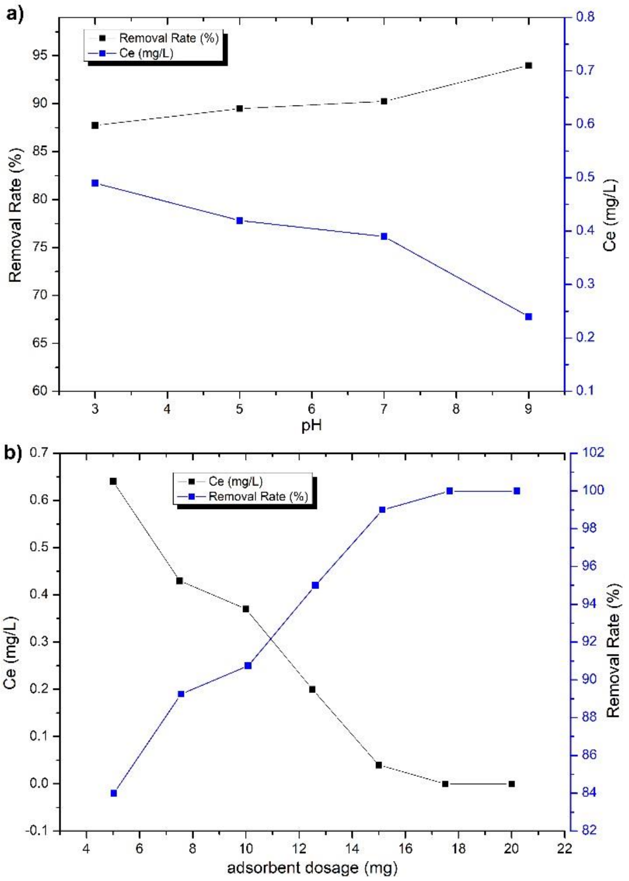


Figure 3. a) Effect of the initial pH (V: 10 mL, C_0: 4 mg/L, T: 298 K, adsorbent dosage: 1,0 g/L, reaction time: 30 min.), b) Effect adsorbent dosage (V: 10 mL, C_0: 4 mg/L; T: 298 K, pH: 7.0 (±0,5), reaction time: 30 min.)

Effect of adsorbent dosage

The effect of the change in the amount of adsorbent on the pollutant removal efficiency was tried to be determined. For this purpose, experiments were carried out under similar environmental conditions. Kaolin was added in the range of 5-20 mg (increase amount of 2.5 mg) to 7 different test tubes with a volume of 10 mL at an initial dye concentration of 4 mg/L and neutral pH. MG analysis was performed at the end of the 30-minute experimental period. Accordingly, while the removal efficiency was around 84% in the experiment with 5 mg kaolin, the removal efficiency also increased as the amount increased. Ultimately, while the removal efficiency reached 99% in the presence of 15 mg kaolin, no dye concentration in the solution was observed when the presence of kaolin increased to 17.5 mg. When the literature is examined, when the amount of adsorbent is purified in the adsorption of MG dye onto kaolin clay, the removal efficiency increases proportionally. This can be explained by the fact that less pollutant falls on more surface area of the adsorbent [5].

Effect of initial dye concentration

Experiments were carried out under the same environmental conditions to determine the effect of the change in initial pollutant concentration on the removal efficiency. MG dyes were added to 8 different test tubes with a volume of 10 mL, each containing 10 mg of kaolin clay, with the initial dye concentration varying between 7.8-133 mg/L, and dye analyzes were performed at the end of the period. Accordingly, while the removal efficiency was 70.53% in the presence of 7.8 mg/L MG, the q_e value was calculated as 5.5 mg/g. At the initial MG concentration of 133 mg/L, the removal efficiency was calculated as 12.25% and q_e was calculated as 16.33. Accordingly, as the MG concentration increased, a decrease in the removal efficiency was observed, but an increase was observed in the amount of dye removed per unit adsorbent. The reason for this is that as the pollutant concentration increases, the transfer of the pollutant onto the adsorbent becomes easier due to the increase in the repulsive force between the molecules. When the literature was examined, it was reported that the q_e value increased with increasing dye concentration in studies conducted with similar dyes [35].

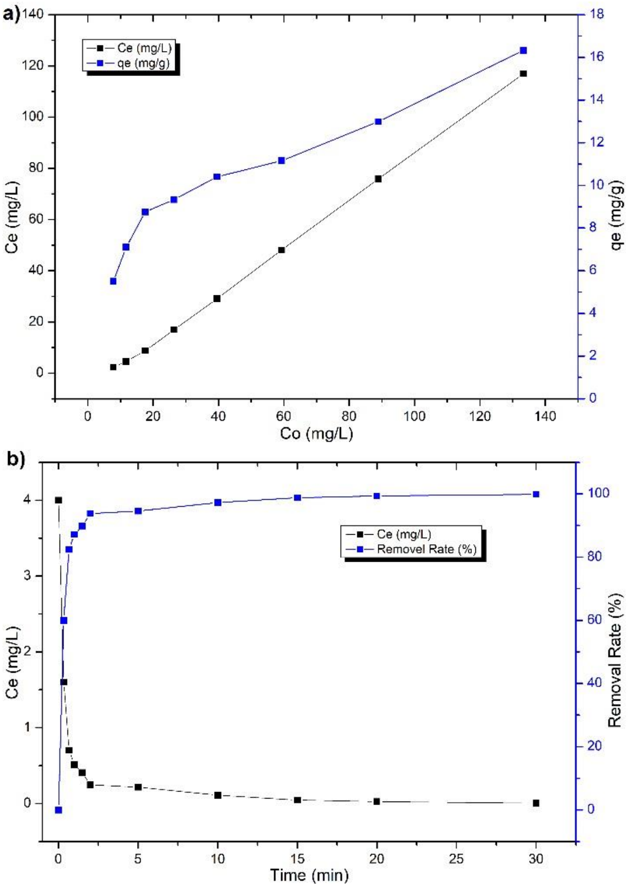


Figure 4. a) Effect of initial dye concentration (V: 10 mL, m: 1 g/L, T: 298 K, adsorbent dosage: 1,0 g/L, reaction time: 30 min.), b) Effect contact time (V: 50 mL, C_0: 4 mg/L, adsorbent dosage: 1,75 g/L) T: 298 K, pH: 7.0 (±0,5))

Effect of contact time

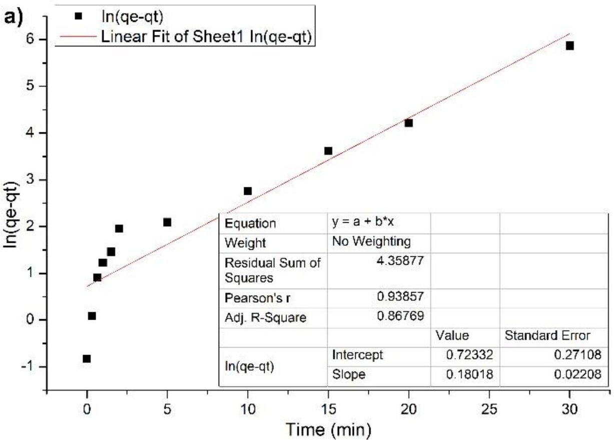
The contact time of the adsorbent and the pollutant is very important in terms of removal efficiency. To determine this effect, under similar environmental conditions, 1.75 mg of kaolin clay was added to MG dye with a concentration of 4 mg/L in a volume of 50 mL and samples were taken at certain time intervals. Accordingly, while the efficiency was 59.96% in the first 20 seconds of the experiment, the efficiency increased to 87.19% in the 1st minute. It has been reported that as time progresses, although the efficiency increases, the rate of increase decreases and when the 20th minute is reached, the efficiency exceeds 99%. Finally, at the 30th minute and later, the dye concentration in the solution fell below the measurement limits. Similarly, in the literature, it has been reported that while high removal efficiency was achieved in a short contact time, the increase in efficiency continued but the rate of increase decreased as the time increased [36].

Adsorption kinetics

In order to determine the mechanism of removing MG dye from kaolin clay, the numerical data obtained from the analyzes performed in the laboratory were tested in kinetic models. In this context, the results of the linear forms of the Pseudo first order and Pseudo second order kinetic models are presented in Table 1. In addition, the graph created from the data obtained with the equation is presented in Figure 5.

Table 1. Results of the calculated kinetic models for the adsorption of MG dye onto kaolin clay.

Kinetic models	Pseudo first order	Pseudo second order
Parameter	$k_1 = 0.051$	$k_2 = 0.217$ $q_e = 2.294$
R^2	0.868	0.999



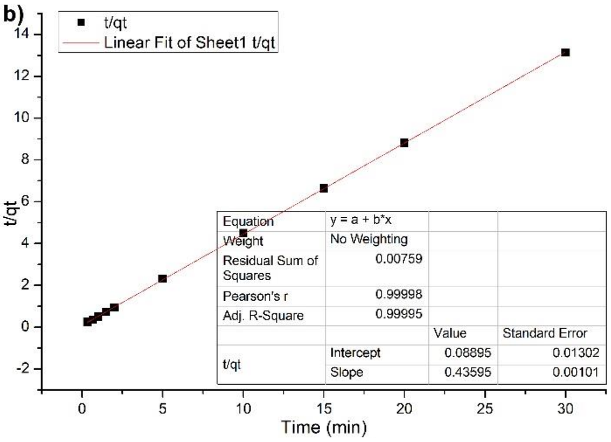


Figure 5. Regression curves of kinetic models a) Pseudo first order, b) Pseudo second order.

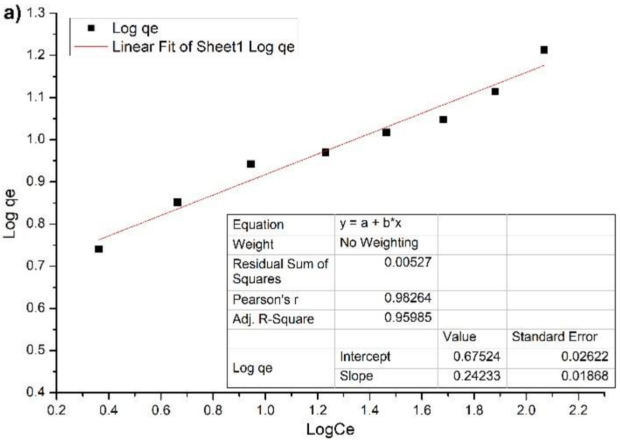
Accordingly, the R^2 value of the Pseudo first-order model was calculated as 0.868, and the R^2 value of the Pseudo second-order kinetic model was calculated as 0.999. According to R^2 values, the most suitable kinetic model for the adsorption of MG dye on kaolin clay is the Pseudo second order model. When the literature was examined, in a study in which MG dye was removed with activated carbon, it was reported that the most appropriate model was Pseudo second order with an R^2 value of 0.999 [37]. Additionally, in a study in which MG dye was removed by using waste ginger materials as biosorbents, it was reported that there was a Pseudo second order kinetic model with an R^2 value of 0.996 [38].

Adsorption isotherm

The results obtained to determine which of the Freundlich, Langmuir and Temkin isotherm models is the most suitable are presented in Table 2. On the other hand, the obtained graphics are displayed in Figure 6.

Table 2. Results of isotherm models calculated for the adsorption of MG dye on kaolin clay.

Isotherm models	Parameters		R^2
Freundlich	$k_F = 4.74$	$1/n = 0.242$	0.960
Langmuir	$k_L = 0.089$	$R_L = 0.407$ $q_{max} = 16.36$	0.958
Temkin	$B_T = 1.032$	$k_T = 3.881$	0.907



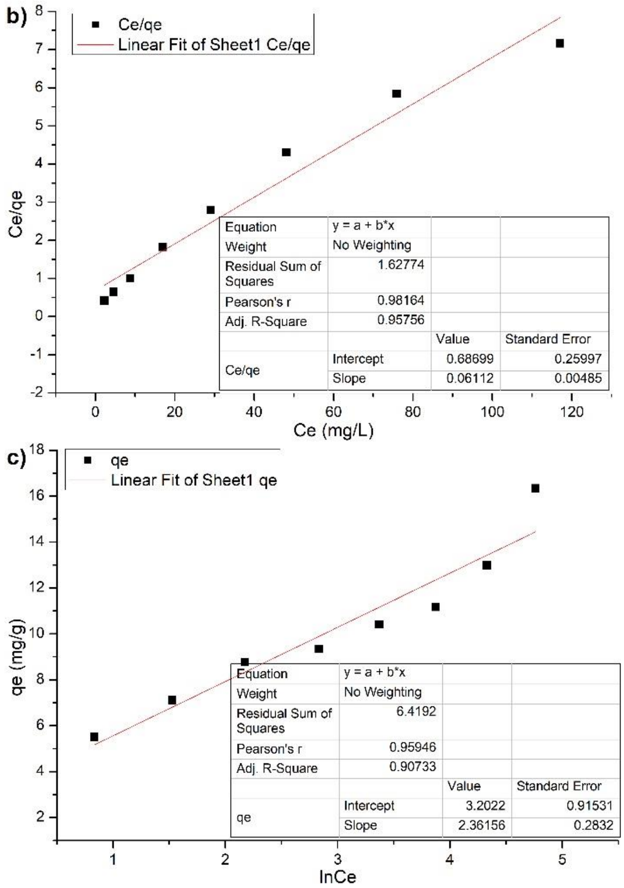


Figure 6. Regression curves of isotherm models (a) Freundlich, b) Langmuir, c) Temkin.

When Table 2 and Figure 6 are examined, the R^2 values of the Langmuir and Temkin models are calculated as 0.958 and 0.907, respectively. On the other hand, the R^2 value of Freundlich isotherm model result is calculated as 0.960. Accordingly, it was determined that the most appropriate isotherm model for the adsorption of MG dye on kaolin clay was Freundlich. Additionally, when looking at the amount of MG dye removed per unit kaolin, this value was calculated as 16.36 mg/g. When the literature was examined, in a study on the removal of MG dye with a composite material, it was reported that the most appropriate model was the Freundlich (R^2:0,99) isotherm. On the other hand, the pollutant removal capacity of the composite material was reported to be 44.85 mg/g [39]. Differently, the adsorption of MG dye with rice bran, a natural material, was investigated. In the study, it was reported that the most appropriate model was Freundlich and its q_m value was 68.972 [40].

Conclusions

In this study, the adsorption of MG dye, which causes toxic effects in water, was carried out with kaolin, a cheap, naturally obtained material. The effects of varying pH, adsorbent amount, dye concentration and contact time were investigated, which are effective parameters on adsorption, were examined. According to the results obtained from batch adsorption tests, it was determined that the most suitable kinetic model for the removal of MG dye was Pseudo second order (R^2: 0.999), and the most suitable isotherm model was Freundlich (R^2: 0.960). Also, it was determined that the removal efficiency of MG dye was over 99% at room temperature and neutral pH under conditions where the initial bye concentration was 4 mg/L and the amount of kaolin was 1.75 g/L. In addition, FTIR and SEM analyzes were performed on both untreated clay and MG-loaded kaolin clay to obtain information about the characterization of the material. This study found that kaolin clay, a natural and inexpensive material, is effective in removing MG dye.

Ethics committee approval and conflict of interest statement

Ethics committee approval is not required for this study.

There is no conflict of interest for this study.

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