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Research Article

Equilibrium Studies for Dye Adsorption onto Red Clay

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ABSTRACT: In this study, it was aimed to remove malachite green, a cationic dye, from aqueous solutions by adsorption method under various experimental conditions by using red clay. Red clay was used because it is abundant in nature and easily accessible in our region. In addition, it has been preferred as an adsorbent because it is used economically without any pre-treatment. The effects of initial malachite green concentration, temperature, adsorbent amount, and contact time on adsorption were evaluated. To examine the percent dye removal effect of the initial malachite green concentration, five different amounts of 25-150 ppm were examined. Five different parts, in the range of 0.5-2 grams, were reviewed to investigate the effect of red clay on the percentage of dye removal. Studies were conducted at four different values, 30-120 minutes, to find the optimum time for the adsorption process. In the adsorption process of red clay and malachite green, experiments were carried out at three different degrees, 298, 313 and 333 K. After reaching equilibrium in the adsorption process, the data obtained were analyzed and studies were carried out by applying them to isotherm models. The results obtained from the adsorption process were compared with Langmuir, Freundlich, Dubinin-Radushkevich and Temkin isotherm models. The experimental studies have been determined to be more compatible with the Dubinin-Radushkevich model. According to the results, it is incompatible with the Langmuir model. Accordingly, it can be said that the adsorption takes place in a multilayer and heterogeneous form.

Keywords: Dye removal, Red clay, Cationic dye, Isotherm.

1. INTRODUCTION

Recently, important events such as low carbon footprint, climate change and water scarcity have been on the agenda more and more. One of the main reasons that cause these negative situations is environmental pollution. Harmful gases and wastewater emitted into the atmosphere during production in industrial facilities are one of the factors that cause environmental pollution. In addition, it is known that water resources have decreased significantly today. In our country and region, where textile production is intense, the need for water is relatively high. Considering all these situations, the purification and reuse of the water used will significantly benefit both nature and the economy.

Industrial wastewater treatment processes to remove water pollutants such as dyes and heavy metals remain challenging for countries today. Paints are used in food, textile paper, cosmetics, etc. It has been used as a colorant in different industries. Even releasing minimal amounts of this paint into the environment poses a serious problem. Dye removal methods from textile

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wastewater; chemical oxidation, foam flotation, adsorption, coagulation, electrodialysis. Among these methods, the adsorption method is known to have a better potential than any other listed process. Among these styles, adsorption seems more advantageous than different styles due to its low cost, easy design and installation, easy availability of the adsorbents used, and the ability to process dyes even at high concentrations. [1-5].

When the studies carried out using activated carbon are examined, it has been proven that it is very effective in removing dyestuffs by the adsorption method. However, since activated carbon is still expensive to produce or procure, there is a trend toward using low-cost adsorbents. Agricultural and industrial by-product wastes can be considered in the class of low-cost adsorbents. In addition, adsorbents such as soil and clay, which are used in their current form without any treatment in nature, are preferred because of their low cost, abundance and ability to remove dyestuffs and metal ions from aqueous solutions. [6, 7].

Clay is a soft and very fine-grained (fine than sand) material. The atoms in the clay material are either in the form of a lattice or a chain arrangement. The main ingredient of clay is aluminum silicate hydrate; depending on its type, compounds of other elements such as sodium, potassium, calcium, magnesium and iron can be found. Depending on the mineral content and chemical composition of the minerals, the color of the clays can be in various shades of white, gray, green, red and brown. Clays can be used as natural adsorbents [8].

This work investigated the adsorption of malachite green dye in an aqueous medium using red clay as an adsorbent in the batch system. Issues such as the adsorption efficiency of parameters such as initial dye concentration, amount of adsorbent, temperature and total contact time were discussed. The results of the studies on the adsorption equilibrium and the obtained findings were compared with the isotherm models.

2. MATERIAL AND METHODS

2.1. Materials

In this study, red clay was naturally obtained from the district of Hekimhan in Malatya province. In addition, red clay is abundant in many parts of Turkey and the world. Red clay was used as an adsorbent to separate malachite green from an aqueous solution by adsorption. Before the experimental adsorption process, the red clay was kept in an oven at 100 °C for about one day to reduce the humidity value. The dried red clay was sieved with less than 200 meshes particle size.

In this study, malachite green (MG) was used as the dyestuff separated from the aqueous solution, the adsorbate phase. MG is in the class of cationic dyes. MG, purchased in a dry form ready to be used in studies, has a molecular formula of $C_{23}H_{25}ClN_2$ and a molecular weight of 364.93 (g mol^{-1}). A stock solution was prepared at 1000 ppm to be used in the experiments. New solutions were prepared at the concentrations preferred in the experiments by mixing the stock solution with distilled water at the determined ratios. Filtered samples after adsorption were measured at 601 nm in a UV spectrophotometer. Five-milliliter cuvettes were used for measurements.

2.2. Adsorption Experiments

The sample containers in which the adsorption experiments were carried out, that is, the adsorbent and adsorbate phases came into contact, were made of plastic material with a volume of 50 ml, with a lid. Five different solutions, 25, 50, 100, 125 and 150 ppm, were prepared to examine the effect of initial dyestuff concentration on percent dye removal. Experiments were carried out with five different amounts of red clay 0.5, 1, 1.5 and 2 grams to examine the effect of the adsorbent amount on percent dye removal. Experiments were carried out at four different times, 30, 60, 90 and 120 minutes, to examine the effect of contact time on percent dye removal. Experiments were carried out at three different degrees: 298, 313 and 333 kelvin to investigate the effect of temperature on percent dye removal.
The percentage of dye removal [9] calculated according to the experimental results can be shown with the mathematical expression given below. Eq. (1):

$$\text{Percentage dye removal} = \frac{(C_0 - C_e)}{C_0} \times 100 \qquad (1)$$

The initial dye concentration is represented by Co (mg L^{-1}), Ce indicates the concentration value at equilibrium. The amount of dyestuff adsorbed on the surface per unit weight of the adsorbent is expressed as q_e (mg g-1) and is calculated with (Equation 2) [10]:

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

What is represented by the symbol V (L) in the equation is the volume of the dye solution. The adsorbent mass is shown with m (g). All experiments carried out in adsorption processes were repeated at least twice. The arithmetic mean values obtained from these values were used in the following calculations.

3. RESULTS AND DISCUSSION

3.1. Adsorbent Characterization

Scanning electron microscopy is one of the important analysis methods used to characterize the structure of adsorbents. Here the porosity of the surface and secondary structures can be detected. SEM images of the adsorbent are given in (Figure 1). When the image is examined, it is seen that the red clay has a fibrous structure and various layers.

The surface properties of all adsorbents, whether natural, synthetic, or waste, are significant for the course of the process. Whether the structure is crystalline or amorphous is determined by XRD analysis. The XRD diagram of the red clay is given in (Figure 2). When the peaks appearing in the graph are compared with the literature, it is thought that the adsorbent shows an amorphous structure. There are 2 Theta D 20.72 views.

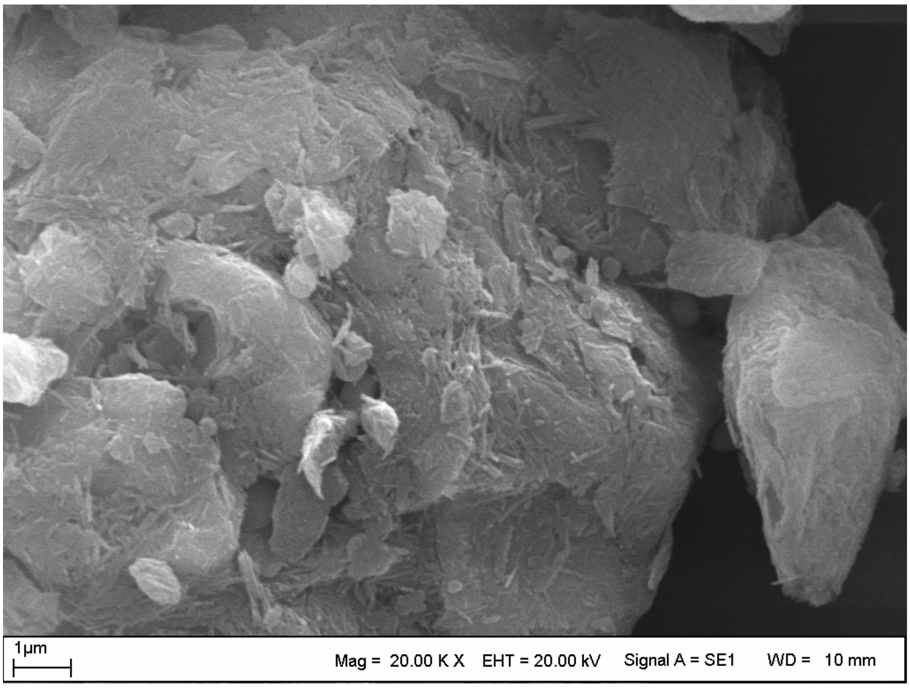

Figure 1. Scanning electron microscope image for red clay.

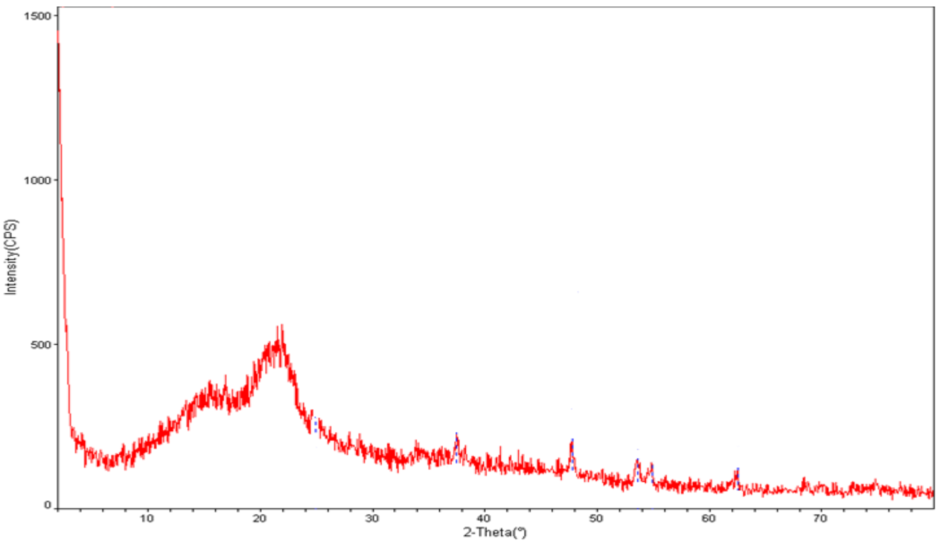

Figure 2. The peaks formed as a result of X-ray diffraction analysis of the adsorbent.

3.2. Effect of Initial Concentration

The effect of the initial concentration for malachite green adsorption is shown in (Figure 3). In this experimental set, where the contact time is one hour and the amount of red clay is 1 gram, it is seen that the dye removal rate increases as the initial concentration increases. However, the yield decreases at values higher than 100 ppm. Experiments were carried out at 298 kelvins and 400 rpm stirring speed.

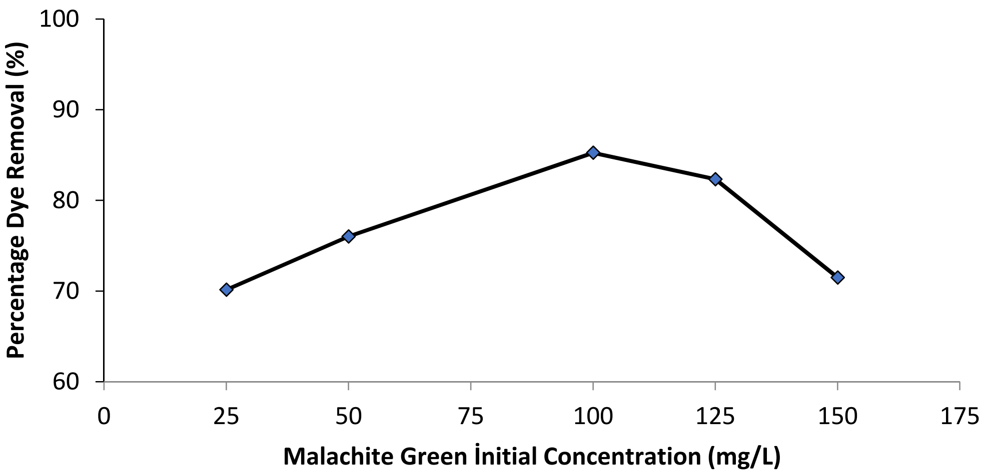

Figure 3. The effect of initial adsorbate concentration (t = 1 h, T= 298 K, 400 rpm, m = 1 g)

3.3. Effect of Adsorbent Dosage

To examine the positive or negative effects of the amount of adsorbent on dye removal, studies were carried out at an initial dye concentration of 100 ppm and a temperature of 298 K at a stirring speed of 400 rpm for 1 hour. Looking at the graph (Figure 4), it can be said that the dye removal efficiency increases as the amount of red clay increases. This is technically expected. However, the removal rates of 1, 1.5 and 2 grams are close. This is an indication that the saturation value has been reached.

3.4. Effect of Contact Time

The results of the adsorption time for malachite green adsorption are described in (Figure 5). When the adsorbing time increases, the removal of dyestuff increases when the adsorbent and adsorbate phases come into contact for a longer time. However, the increase occurs in the first 60 minutes and stabilizes. Times more extended than 60 minutes do not affect dye removal. To see the results of the adsorption time, experiments were carried out at an initial concentration of 100 ppm, using 1 gram of red clay at a stirring speed of 400 rpm and a temperature of 298 K.

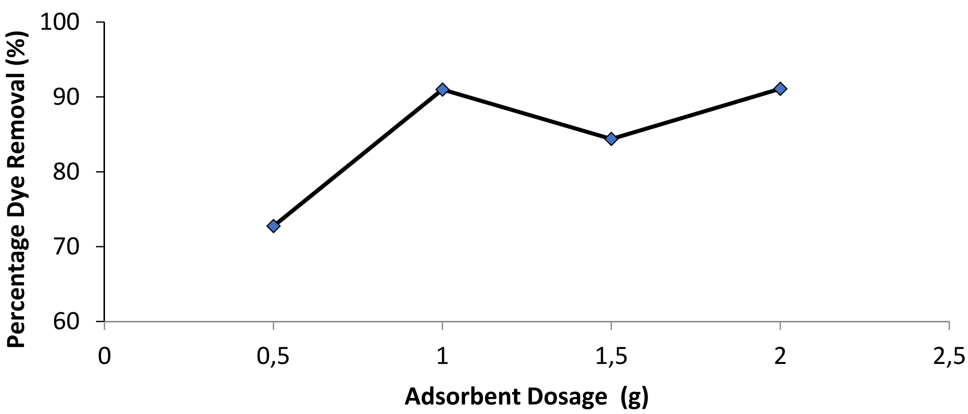

Figure 4. Effect of adsorbent dosage (t = 1 h, T = 298 K, 400 rpm, C_0 = 100 ppm)

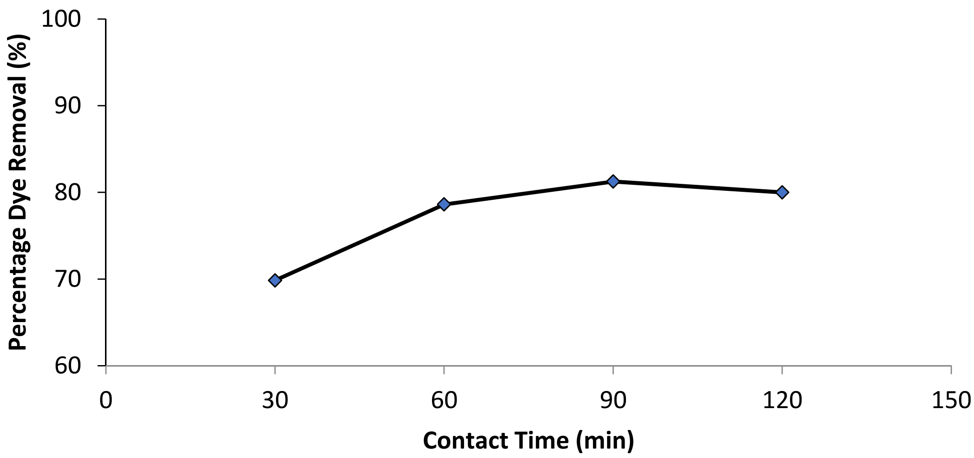

Figure 5. Effect of contact time (m = 1 g, T = 298 K, 400 rpm, C_0 = 100 ppm).

3.5. Effect of Temperature

To determine the relationship between process temperature change and adsorption success rate, it was carried out at three different degrees, 298, 313 and 333 Kelvin, at an initial concentration of 100 ppm, at a mixing speed of 400 rpm for 1 hour and the amount of 1 gram of red clay. When (Figure 6) is examined, as the temperature value is increased, the adsorption efficiency increases. As the temperature increases, it can be thought that the malachite green molecules move more. In this way, it can be believed that an adsorption event is endothermic.

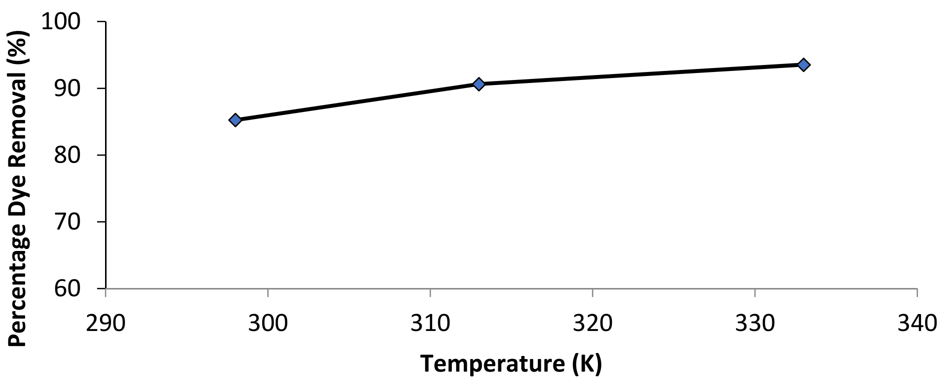

Figure 6. Effect of temperature (m = 1 g, t = 1 h, 400 rpm, C_0 = 100 ppm).

3.6. Adsorption Equilibrium

Isotherms are used to determine the adsorption equilibrium parameters and the physical and/or chemical properties of adsorption. They are used to predict the optimum amount of adsorbent. It is also used to make an assessment about the nature of the interactions that occur between the adsorbent and the adsorbate. The adsorption equilibrium graph is shown in (Figure 7). Four adsorption isotherms commonly used in the literature: Langmuir, Freundlich, Dubinin-Radushkevich, and Temkin are used in the present study.

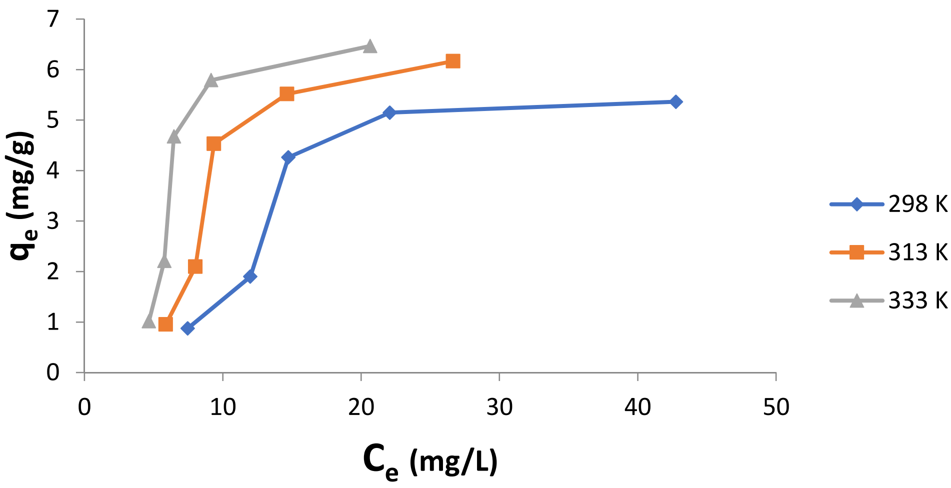

Figure 7. Adsorption equilibrium graph

3.6.1. The Langmuir İsotherm Model

With the Langmuir isotherm [11], an idea can be obtained about the number and structure of active sites on the adsorbent surface. When all active sites are filled, when maximum adsorption is achieved, it provides information about the saturation of these sites. It is possible to write the linear equation derived from the Langmuir model according to (Equation 3):

$$\frac{C_e}{q_e} = \frac{1}{Q_0\ b} + \frac{C_e}{Q_0} \tag{3}$$

Equilibrium concentration Ce (mg/L), q_e is the amount retained on the adsorbent surface in equilibrium (mg/g), Q_0 is the Langmuir constant (mg.g-1) that represents the system thermodynamically, and b shows the direct adsorption energy (L/mg).
In addition, the following results are the separation factor R_L obtained by the Langmuir isotherm can give an idea about the properties of adsorption [11]. R_L values are calculated from the following Eq. (4):

$$R_L = \frac{1}{1+bC_0} \tag{4}$$

As it is known, C_0 is the initial malachite green concentration (mg L^{-1}).

3.6.2. The Freundlich İsotherm Model

The assumptions of the Freundlich isotherm model [12] are as follows; After the active centers of the adsorbent are filled, an exponential decrease in adsorption energy occurs. The mathematically linear form of the Freundlich model is expressed by Equation (5):

$$\ln q_e = \ln K_f + \frac{1}{n} \ln C_e \tag{5}$$

Kf is a fixed number for the adsorption system associated with the bond energy. The value of 1/n gives information about the distribution of high-energy regions on the adsorbent surface compared to the other areas. It depends on whether the adsorption process is physical or chemical and, therefore, thermodynamically energized [12].

3.6.3. The Dubinin-Radushkevich (DR) İsotherm Model

The D-R model, based on the type, number, etc. of interactions between adsorbate particles in the aqueous solution, gives information about its features. It also allows calculating the kind of adsorption reaction and the reaction activation energy. The mathematical expression of my model is shown in the following equation Eq. (6).

$$q_e = q_m \exp\ (K\ \varepsilon^2\ ) \tag{6}$$

ε equals the empirical value RT ln(1 + 1/Ce). q_e can be considered the amount of dye adsorbed to the red clay surface per unit (mol/L). qm is the numerical amount of saturation capacity of the layer (mol/g), as this model is assumed to be a single layer. Ce is the value of the density of the solution at equilibrium. (mol/L). K' (mol^2/kJ^2) is an indicator of the thermodynamic energy of adsorption and is a constant value. R is the ideal gas constant (kJ/mol^*K) and T is the temperature (K). The linear form of the Dubinin-Radushkevich isotherm model [13] is given in (Equation 7);

$$\ln q_e = \ln q_m -\ K\ \varepsilon^2 \tag{7}$$

The K value is represented by the average adsorption energy (E, kJ.mol-1) arising from the adsorption process and Eq. (8):

$$\mathrm{E} = \frac{1}{\sqrt{2K}} \tag{8}$$

3.6.4. The Temkin İsoterm Model

According to the Temkin model assumption, all molecules in the layers are considered to occupy the active centers without interacting due to the reduction of the reactive effect between the adsorbent and the adsorbent. Therefore, it is assumed that the heat of adsorption decreases in parallel with the coating of the surface. The linear mathematical expression of the Temkin isotherm [14] can be defined by the following Equation (9):

$$q_e = \frac{R_T}{b_T} \ln A_T + \frac{R_T}{b_T} \ln C_e \tag{9}$$

AT is a constant number expressed by the binding energy and represents the maximum value.
The constant coefficients of the equations representing the adsorption isotherm models were calculated through error analysis using linearized versions of the isotherm mono equations. Obtained constant values and coupling coefficients R^2 are shown in (Table 1). When the table is examined, it can be said that it does not fit the Langmuir model since the R^2 value is very low. This is due to the layered structure of red clay. Since the R^2 value is higher in the D-R isotherm than the others, it can be considered to fit this isotherm. According to this model, it can be accepted that the clay has a porous structure and a heterogeneous structure. In the

Freundlich isotherm, on the other hand, it is seen that the K_f value increases as the temperature increases. This is because the adsorption capacity changes in heterogeneous multilayer adsorption with temperature change.

Table 1. Isotherm constants

Isotherm	298 K	313 K	333 K
Langmuir			
Q_0 (mg /g)	36.9	52.356	84.561
b (L/mg)	0.048	0.046	0.025
R^2	0.629	0.596	0.606
Freundlich			
K_f (L/g)	1.582	2.030	3.863
n	0.968	0.879	0.969
R^2	0.751	0.719	0.597
D-R			
q_m (mol. g^{-1}).10^3	1.59	1.78	1.93
K ($mol^2.kJ^{-2}$)	0.003	0.003	0.003
E ($kJ.mol^{-1}$)	12.91	12.91	12.91
R^2	0.931	0.942	0.883
Temkin			
A_T	1.589	1.817	1.452
b_T	90.37	75.19	81.42
R^2	0.805	0.825	0.722

4. CONCLUSIONS

Below are the results of malachite green adsorption on red clay:

- The red clay obtained from the Hekimhan region can be used as an adsorbent for the transport of malachite green, a cationic dye, from its aqueous solution by adsorption method.
- The effects of many parameters, such as initial dyestuff concentration, amount of adsorbent, adsorption time and temperature on the percentage of dye removal, were analyzed. The adsorbent amount and contact time determined optimum levels. It was determined that the yield increased as the temperature increased.
- The test results were evaluated regarding four different isotherm models. It was determined that the model with the lowest correlation coefficient values was the Langmuir isotherm model, while the highest values were observed in the Dubinin-Radushkevich isotherm model. It can be thought that the correlation coefficient is in the range of 0-1 and the results closer to 1 are more compatible with the applied model.
- The fact that the experimental data do not fit the Langmuir isotherm can indicate that the red clay has a multilayered structure. Compliance with the Dubinin-Radushkevich isotherm shows that the adsorbent has a heterogeneous and porous structure.

Acknowledgments

The datasets generated during and/or analyzed during the current study are available from the corresponding author upon reasonable request.

Declaration of Competing Interest
There is no conflict of interest.

Author Contribution
All authors contributed equally to every step of the article.

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