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Authors: Sevgi GÜNEŞ DURAK

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Removal of Maxilon Golden Yellow GL EC 400% from the Wastewater by Adsorption Method Using Different Clays

Sevgi GÜNEŞ DURAK*¹

Abstract

This study was to evaluate the adsorption capability of clay minerals of halloysite, bentonite, kaolinite, and natural clay (obtained from the Avanos) to remove Maxilon Golden Yellow GL EC 400% (MGY400) from aqueous solution. Different amounts of adsorbents (0.5, 1.0, 1.5 and 2.0 g.) were taken from the samples and obtained the most dye-removal clay material and adsorbent amount were found according to the results. Adsorption was applied on all clays at 25 °C temperature, 200 rpm mixing speed and different contact times (2, 5, 10, 20, 30, 40, 50, 60 min) in the batch reactor. Bentonite provided the highest dyestuff removal. Therefore, the second phase adsorption was continued with bentonite. The adsorption with bentonite were performed at different temperature (13 °C, 25 °C, 50 °C) and pH values (2, 4, 6, 8, 10, 12). When the pH was 12 and the temperature was 25 °C, it was determined that the removal rate of the dyestuff of bentonite reached up to 99.7%. According to the results, adsorption kinetics and isotherms were investigated, and evaluation was made for working conditions.

Keywords: adsorption, bentonite, clay, dyestuff, halloysite

* Corresponding Author: ssevgigunes@gmail.com

¹ Nevşehir Hacı Bektaş Veli University, ORCID: <https://orcid.org/0000-0003-4273-7417>

1. INTRODUCTION

Significant environmental problems occur when the toxic hydrophobic organic components of industrial and agricultural activities increase uncontrollably in the soil and water [1]. The receiving environment in which the wastewater is discharged without treatment can be contaminated with several contaminants including acidic and basic substances, toxic organics, inorganics and heavy metals. Particularly, the solids and dyes resulting from the textile industry are among the important pollutant industries because they disrupt the ecological balance and cause problems in aesthetic terms [2]. In general, wastewater with dyestuff has a strong color, high pH, high chemical oxygen demand and low biodegradability [3]. Therefore, color removal from wastewater must be done before the discharge of wastewater. Many physical, chemical, and biological decolorization methods such as aerobic and anaerobic microbial degradation, coagulation, chemical oxidation, membrane separation processes, adsorption, electrochemical separation, dilution, filtration, flotation and reverse osmosis are applied for color removal. Among these methods, the most economical method is the adsorption method [2].

Adsorption is the collection of the substances dissolved in the solution on a suitable interface. As inorganic and organic substances, silica-based porous inorganic/organic hybrid substances can be used as adsorbents [4]. Adsorption processes are effective and attractive for the removal of dyestuff from the wastewater. The most commonly used of these substances is activated carbon. Activated carbon is expensive as well as it is costly to renew by thermal and chemical procedures when exhausted and leads to sorbent loss [5]. However, the use of low-cost adsorbents makes the treatment more economical. For this, as the adsorbent, the clay material often found in nature is utilized. To achieve a high efficiency of adsorption, the ion exchange capacity of the clay should be high. The substances that are to be removed from the wastewater are called adsorbate. Clay materials are of great interest due to their low costs,

abundant availability, easy accessibility, environmental friendliness and surface reactivity. The structural variability of clays, chemical stability and high specific surfaces were important in clay minerals. Clays are natural and cost-effective adsorbents which are used as catalysts in wastewater treatment [3]. Also, the clays have a high specific surface and are suitable for adsorption and removal of organic contaminants. In the production of nanocomposite polymers, as heavy metal ion adsorbents, in the production of ceramics, paper fillings and coatings, sensors and biosensors are frequently used due to their structural properties such as chemical and mechanical stability and surface diversity [6]. Many color removal studies have been carried out with the adsorption method using clays that are cheap and easy to find in nature [2], [7–11].

Adsorption is divided into three as physical, chemical and ionic. In physical adsorption, Van Der Waals forces are effective and low temperatures are sufficient for adsorption. Here, the adsorption is reversible. Chemical adsorption is irreversible. It usually occurs at high temperatures. In ionic adsorption, it is based on the principle of attracting adsorbents with electrostatic forces on the surface loaded areas. Although there is no distinction for three types, they can occur together and sequentially in an adsorption process.

The factors affecting adsorption are film diffusion, pore diffusion, mixing speed, pH, temperature, type and amount of adsorbent and properties of the solvent. In some studies, it is stated that there is a correlation between the organic matter content of the soil and the adsorption, and in some of them, there is a correlation between the adsorption and the clay content of the soil. However, in other studies, it has been stated that the behavior of the components in the soil is related to the adsorption capacity of different clay minerals and the diversity of the mineralogical structure of the soil [1]. Furthermore, the cationic dye molecules have a very high affinity for clay surfaces and are easily adsorbed when added to the clay suspension [5].

Many isotherms are used to determine the efficiency of adsorption and the factors affecting the adsorption. The most commonly used isotherms are Freundlich and Langmuir Isotherms.

Although the Langmuir equation describes adsorption on very strong homogeneous surfaces, this is not true for natural adsorbents. Because; natural adsorbents show chemical heterogeneity, indicated by different functional groups. The Langmuir equation was developed by the American scientist Irwing Langmuir, known for his work in surface chemistry. The Langmuir isotherm model, which is widely used in the explanation of chemical adsorption processes, can also be used to describe single-layer physical adsorption and adsorption processes from solution. Langmuir has developed an isotherm model for the monomolecular adsorption process by emphasizing that the active centers of the adsorbent micropore size are too small to adsorb in multiple layers [12].

The equation developed by the German physiologist Freundlich describes the physical adsorption phenomena occurring on the surface of the adsorbent in a heterogeneous structure. The surface energy distribution of the adsorbent is heterogeneous in the adsorption systems which are compatible with this equation. In other words, each of the adsorbent surface adsorption sites has different adsorption potential and each area is considered to be homogeneous in itself. Freundlich equation is derived based on the acceptance of adsorption of adsorbed molecules after adsorption on the adsorbent surface.

In this study, halloysite, bentonite, kaolinite and raw clay were used as adsorbents. MGY400 was chosen as a dyestuff. Different amounts of adsorbent (0.5, 1.0, 1.5 and 2.0 g) were taken from the samples and the most color-removing clay material and adsorbent amount was found according to the results. The highest adsorption was obtained from bentonite. Therefore, the experiments in the second stage were continued with bentonite. According to the results, adsorption capacity and isotherms were

examined and the different working conditions (pH, temperature) were evaluated.

2. MATERIALS and METHODS

2.1. Materials

Halloysite, kaolinite and bentonite were obtained from Oltu district of Erzurum. The clay which is defined as raw clay is obtained from Avanos District of Nevşehir. These four clays were first washed with 1 N H₂SO₄ and then with pure water until neutral pH. As the natural clay from the dried clay samples had a larger particle diameter, it was brought to the size range of 150-200 µm with the sieve after being beaten in the muller. Then, four samples were kept in a desiccator for use in batch adsorption test. MGY 400 was used as a dyestuff in the study. The reason for the use of this dyestuff is that it is not widely studied in the literature and is frequently used in the dyeing of fabrics in the textile industry. The chemical structure of MGY 400 is given in Figure 1 [13].

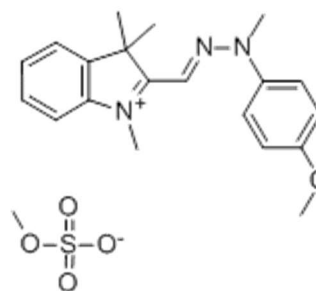


Figure 1 Chemical structure of MGY 400

Halloysite is an alumino-silicate clay mineral and its empirical formula is Al₂Si₂O₅(OH)₄. Halloysite was formed by the hydrothermal change of alumino-silicate minerals [14]. Kaolinite is clay from the industrial mineral group. Its chemical formula is Al₂Si₂O₅(OH)₄. Single-Atom alumina (AlO₆) consists of a layered silicate mineral with tetrahedral silica (SiO₄) layer attached to the octahedral layer by oxygen atoms [15]. The main component of bentonite montmorillonite and it is abundant. It consists of twin layers of tetrahedral silica sandwiching a single octahedral alumina sheet. [3]. The raw clay is brown-red. Red is due to the presence of iron oxide content. The kaolinite

used in the study is white. Research and cation exchange capacity, the pH of the initial solution, and the adsorption curves of the raw clay is a type of kaolinite is possible to say that the red form. The cation exchange capacity of halloysite, kaolinite, bentonite and raw clay was determined as 8, 4, 53 and 6 meq/100 g at pH 7 by applying the ammonium acetate method [16].

2.2. Adsorption Experiments

Adsorption experiments were performed using a mechanical shaker. Ultrapure water was used for all solutions. In the first stage, the temperature in the agitator was carried out separately for each clay at 25 °C and 200 rpm at the natural pH of each solution and 2, 5, 10, 20, 30, 40, 50 and 60 minutes. To determine the amount of active adsorbent, 0.5 g, 1.0 g, 1.5 g and 2.0 g of each clay were taken and adsorbed with 100 mL solution of dyestuff solution. The initial pH values of the clay-added dyestuff solutions are given in Table 1. There was no significant relationship between natural pH values and different concentrations of four different clays.

Table 1
Initial pHs of clay-added dyestuff solutions (In 100 mL solution)

Clay type/amount	0.5 g	1.0 g	1.5 g	2.0 g
Holloysite	7.56	7.93	8.14	8.22
Bentonite	7.00	7.06	7.01	6.86
Kaolinite	7.16	7.19	7.17	7.15
Raw Clay	7.06	7.18	7.17	7.13

The concentration of dyestuff was prepared as 100 mg/L. Adsorption time ended samples were taken to NÜFE, NF 200 device, and centrifuged for 5 min at a mixing speed of 2400 rpm and then color analyzes of solutions were performed on a spectrophotometer at 438 nm wavelength. By these measurements, the effect of adsorption time, adsorbent material and adsorbent amount on adsorption were investigated. According to the results obtained as the most color removal bentonite provides, so the second stage of the adsorption study was continued with bentonite. For this, using the amount of bentonite (0.5 g) providing the most color removal, at mixing speed of 300 rpm, different contact times (5, 10,

20, 30, 60, 120, 150, 200, 240 and 270 min), different temperatures (13 °C, 25 °C, and 50 °C) and at different pH levels (2, 4, 6, 8, 10 and 12) were studied. The reason for working in wide pH ranges and the wide temperature is that solutions consisting of clay and dyestuff give high pH [17–19] or low pH [20–22] value. The reason for working in wide temperature ranges is the thermal stability in the solution and the changes that may occur in the structural hydroxyl groups [23].

2.3. Data Analysis: Adsorption Capacity

Equation 1 is used to calculate the amount of adsorbed dye at any time in kinetic experiments.

$$q_t(\text{mg/g}) = (C_0 - C_t) \cdot \frac{V}{m} \quad (1)$$

Here C_0 , the initial liquid phase concentration (mg/L); C_t , liquid phase concentration at any one time (mg/L), q_t ; the concentration of dye in any adsorbent (mg/g); V , the volume of dye solution (L); m , mass (g) of clay used.

2.4. Data Analysis: Langmuir and Freundlich Isotherms

The most commonly used isotherms for the determination of adsorption capacity are Freundlich and Langmuir Isotherms. Although the Langmuir equation describes adsorption on very strong homogeneous surfaces, this is not true for natural adsorbents. Because; natural adsorbents, indicated by different functional groups, show chemical heterogeneity [24]. Freundlich equation is an experimentally developed isotherm used for adsorption on heterogeneous surfaces [25]. Freundlich and Langmuir Isotherms are expressed as Equation 2 and Equation 3 [26]:

$$\text{Freundlich isotherm: } \log q_e = \log K_f + (1/n) \log C_e \quad (2)$$

$$\text{Langmuir isotherm: } C_e/q_e = (1/Q_0b) + (C_e/Q_0) \quad (3)$$

Here K_f (mg/g) is the Freundlich constant, n is the Freundlich coefficient. The n parameter

describes the active sites on the adsorbent surface with low energy heterogeneity of these natural adsorbents. This value is also the adsorption density and the value between 1 and 10 is a sign of good adsorption. If n is less than 1, the adsorption is chemical. On the contrary, it can be called physical [24].

Where q_e (mg/g) amount of MGY400 dyestuff adsorbed at equilibrium, C_e (mg/L) unadsorbed MGY400 dyestuff concentration at equilibrium, b is Langmuir constant obtained from plot of $\frac{C_e}{q_e}$ versus C_e . The b value and the initial concentration C_0 used to calculate the separation factor R_L , are expressed as in Equation 4 [27].

$$R_L = 1/(1 + bC_0) \quad (4)$$

It is not desirable to have R_L greater than 1. If R_L is equal to 1, the adsorption is linear, if it is between 0 and 1, the adsorption is suitable, that is, the adsorption can be realized without taking energy from outside [26].

3. RESULTS and DISCUSSION

3.1. Effect of Initial Adsorbent Amount, Adsorbent Type and Contact Time to Adsorption Rate

One of the two factors that are important for adsorption is film diffusion and the other is pore diffusion. The material to be removed in film diffusion passes through the liquid film surrounding the adsorbent. In pore diffusion, there is a transition to pores in the inner layer of the adsorbent material. Then, the adsorbent bonding process of the desired substance is realized. Adsorption capacity, mixing speed, mixing temperature, starting pH of the mixture solution, the type and amount of adsorbent vary according to the type and amount of the adsorbed material.

The contact time is very important in adsorption applications in wastewater treatment. The fact that the adsorption reaches equilibrium is an indication of the end of the adsorption capacity. Usually, rapid adsorption occurs in the first 5 minutes depending on the surface area of the

adsorbent. By gradually filling up the adsorption areas, the adsorption becomes less efficient. The adsorption at this initial stage reflects the maximum dyestuff adsorption capacity of the adsorbent [2].

When the amount of halloysite, bentonite, kaolinite and raw clay adsorbed at different concentrations were examined, it was determined that the maximum adsorption was obtained in the amount of 0.5 g adsorbent (Fig. 2-5). The adsorption value was decreased for the amounts of 1.0, 1.5 and 2.0 g adsorbents, respectively. One of the reasons is that concentration affects chemical equilibrium. Depending on the maximum amount of adsorbent adsorbed, there is a difference between adsorption capacity and adsorbed adsorbent [28]. Another explanation for this situation is that the unit adsorption q_t decreases as the amount of adsorbent increases. That is, when the adsorption dose increases, the amount of adsorbed increases, but the unit adsorption is less since the adsorbent is calculated per unit [29].

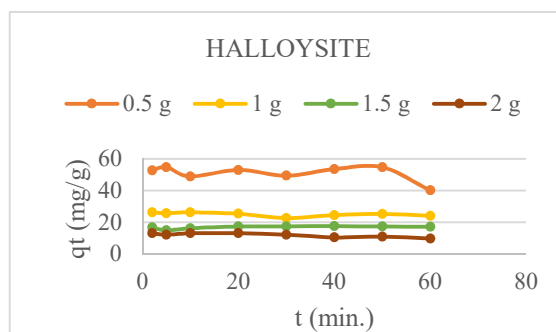


Figure 2 Changes according to the time of the amount of adsorption halloysite

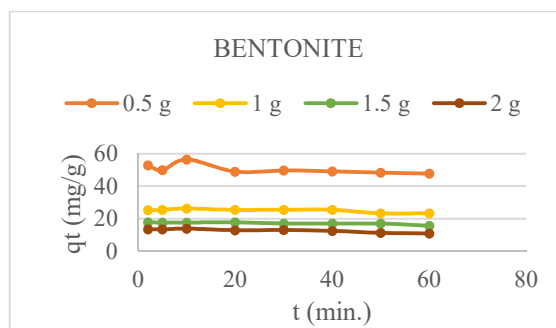


Figure 3 Changes according to the time of the amount of adsorption bentonite

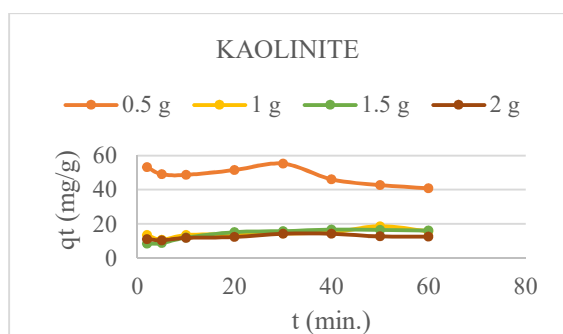


Figure 4 Changes according to the time of the amount of adsorption kaolinite

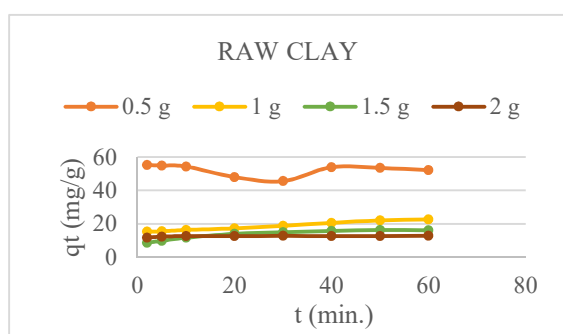


Figure 5 Changes according to the time of the amount of adsorption raw clay

When halloysite was used as the adsorbent, to reach maximum adsorption, the optimum contact times were determined as 5 minutes (54.65 mg/g) for 0.5 g adsorbent, 2 minutes (26.19 mg/g) for 1 g adsorbent, 20 minutes (17.3 mg/g) for 1.5 g adsorbent and 20 minutes (13.04 mg/g) for 2 g adsorbent (Fig. 2).

When bentonite was used as the adsorbent, to reach maximum adsorption, the optimum contact times were determined as 10 minutes (56.53 mg/g) for 0.5 g adsorbent, 10 minutes (26.27 mg/g) for 1 g adsorbent, 20 minutes (17.76 mg/g) for 1.5 g adsorbent and 10 minutes (13.86 mg/g) for 2 g adsorbent (Fig. 3).

When kaolinite was used as the adsorbent, to reach maximum adsorption, the optimum contact times were determined as 30 minutes (55.24 mg/g) for 0.5 g adsorbent, 50 minutes (18.63 mg/g) for 1 g adsorbent, 40 minutes (16.65 mg/g) for 1.5 g adsorbent and 30 minutes (14.21 mg/g) for 2 g adsorbent (Fig. 4).

When raw clay was used as the adsorbent, to reach maximum adsorption, the optimum contact

times were determined as 10 minutes (54.37 mg/g) for 0.5 g adsorbent, 60 minutes (22.69 mg/g) for 1 g adsorbent, 50 minutes (16.20 mg/g) for 1.5 g adsorbent and 60 minutes (12.80 mg/g) for 2 g adsorbent (Fig. 5).

When all results were examined, it was found that there were similar properties between halloysite and bentonite, and between kaolinite and raw clay.

The fact that halloysite has similar properties with bentonite can be explained by the fact that it has the same unstable structure with bentonite in terms of zeta potential. Therefore, it is possible to say that the zeta potential of halloysite is around -30 mV [30]. It is possible to say that the zeta potential value of bentonite, which gives similar values with halloysite in terms of contact time and amount of adsorption required for maximum adsorption, is around -30 mV. When the zeta potential value is below and above -30 mV and +30 mV, the material structure is stable. Therefore, the unstable structure of bentonite can be easily connected with MGY400, resulting in shorter and greater amounts of adsorption. Kaolinite can change from unstable to stable as the pH increases. In some studies, as the pH decreases, the zeta potential value of kaolinite approaches about -30 mV, so its stability decreases, and its binding capacity increases [31]. However, the ratio of adsorbent in the starting solution also affects zeta potential [32]. The time required for the raw clay to reach maximum adsorption is similar to that of kaolinite. Moreover, the increase of the adsorbent rate in the solution negatively affected both the adsorption time and the amount of adsorption.

However, as all of the clay types were examined, it was determined that bentonite provided the maximum dyestuff sorption (56.53 mg/g) and as soon as possible (5 min). According to this, the next step of experimental studies was continued with 0.5 g of bentonite, which provides the most effluent yield.

3.2. Effect of Initial pH, Adsorption Temperature and Contact Time to Adsorption Rate

In the second stage where the only bentonite was used, the temperature and pH were studied at six different pH values of 2, 4, 6, 8, 10 and 12 with three different temperatures as 13, 25 and 50 °C to determine the effect of the adsorption. The highest sorption in all temperature values was obtained at pH 12 (Fig. 6, Fig. 7 and Fig. 8). After pH 12 value, the optimum pH was determined as 10. The sorption amounts obtained at pH 2, 4, 6 and 8 values were similar. The optimum temperature for pH 2 was 25 °C (Fig. 7), the optimum temperature value for pH 4 was similar to 13 and 25 °C (Fig 6 and Fig. 7). The optimum temperature value for pH 6, pH 8 and pH 10 was 25 °C (Fig. 7) and for pH 12 the optimum temperature value was 50 °C. (Fig. 7 and Fig. 8). The reaction rate increases as the temperature increases. The adsorbent surface becomes active and adsorption capacity increases. That is the strength of the intermolecular forces between the adsorbent and the adsorbate increases [33]. When all the results are evaluated, it is possible to say that the most effective removal efficiency for adsorption is obtained at 25 °C and this is an advantage. Because there will be no energy requirement for heating or cooling to provide color removal in the regions with a temperate climate where the temperature is between 20-30 °C throughout the year. This will provide an economic advantage.

In the experiments performed for bentonite at 13 °C and different pHs, the amount of dyestuff initially adsorbed at all pHs was low while the adsorption at all pHs increased to 60 minutes. After 60 minutes, it continued in a balanced manner (Fig. 6). At a temperature of 25 °C, the sorption at all pH values increased to 60 minutes, which continued up to 240 minutes and the concentration of the dyestuff adsorbed to 270 minutes started to decrease (Fig. 7). At a temperature of 50 °C, the amount of adsorbed dyestuff at pH 10 and 12 reached the maximum level at 60 minutes. Until 270 minutes, it continued in a balanced manner. Similar values were obtained at pH 2, 4, 6 and 8, while the

amount of dyestuff initially induced showed a fluctuating increase, reaching the highest level at 240 minutes for each of the four pHs and decreased slightly at 270 minutes (Fig. 8).

Depending on the zeta potential, when the pH decreases, the negatively charged sites on the sorbent surface increase whereas the positively charged sites and the adsorption decreases [29], [34]. The number of hydroxyl groups increases with increasing pH, so the attraction area on the surface of MGY400 and adsorbent expands, increasing the number of negatively charged sites [35].

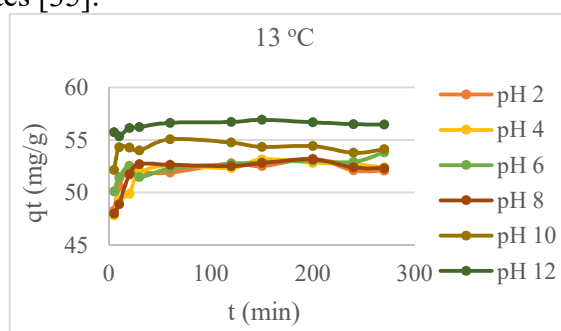


Figure 6 Amount of adsorbed substance at different pH values for 13 °C temperature

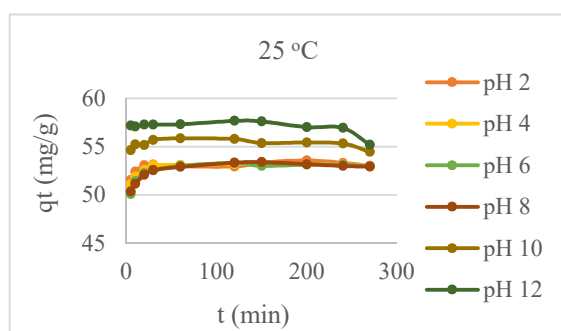


Figure 7 Amount of adsorbed substance at different pH values for 25 °C temperature

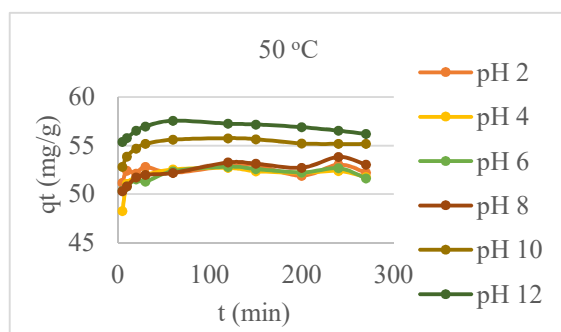


Figure 8 Amount of adsorbed substance at different pH values for 50 °C temperature

The pK_a value is a measure of the acid power in the dyestuff solution. According to all results, it is possible to say that the pK_a value of the adsorbate is less than 6.5 [36]. In the 7-12 pH range, the surface of bentonite is positively charged and dyestuff is negatively charged (PK_a of dyestuff <6.5) [37]. Because, when we examine the adsorption capacity of bentonite according to the pH values of the initial solution, there was a significant increase in capacity after pH 6.5, while the adsorption capacity at the values before pH 6.5 gave similar results. However, the fact that MGY400 is included in the cationic dyes class is also a reason why adsorption is more efficient at high pH [38].

3.3. Langmuir and Freundlich Isotherms

Table 2 and Table 3 show the Langmuir and Freundlich Isotherms for halloysite clay. According to the results, the adsorption was physical and the surface energy distribution of the adsorbent was heterogeneous and becomes more heterogeneous when the value approaches zero [29] as bentonite containing 0.5 g of adsorbent. Also, n values greater than 1 indicate that the adsorption was physical. It is also possible to say that maximum adsorption was obtained at a concentration of 0.5 g clay when K_f values were examined.

For bentonite clay, the Freundlich Isotherm was more suitable than the R^2 values. This indicates that the adsorption was physical. When n values were examined, 0.5 g. n value for bentonite was determined as 12.73. This is undesirable. When the K_f values are examined, it is possible to say that the maximum adsorption was obtained at a concentration of 0.5 g clay.

Kaolinite clay also conforms to the Freundlich Isotherm. This indicates that the adsorption was physical. When n values were examined, it is possible to say 11.01 for 2 g kaolinite and physical adsorption for other amounts. When all amounts and K_f values are examined, it is possible to say that 1.0 g of kaolinite was suitable for adsorption.

Table 2
Langmuir Isotherms and Isotherms Constants for Halloysite, Bentonite, Kaolinite, and Raw Clay

	Langmuir Isotherm	Langmuir Isotherms Constants		
	R^2	b (L/mg)	Q_{max} (mg/g)	R_L
Halloysite				
0.5 g	0.68	0.00022	103.09	0.97
1.0 g	0.90	0.0012	38.61	0.95
1.5 g	0.92	0.0030	23.47	0.93
2.0 g	0.87	0.0095	11.198	0.90
Bentonite				
0.5 g	0.80	0.000043	476.19	0.98
1.0 g	0.93	0.0012	37.31	0.95
1.5 g	0.89	0.0018	37.31	0.93
2.0 g	0.67	0.0021	40.65	0.92
Kaolinite				
0.5 g	0.65	0.00019	121.95	0.977
1.0 g	0.83	0.107	1.20	0.88
1.5 g	0.84	0.035	3.47	0.89
2.0 g	0.64	0.00074	116.28	0.92
Raw Clay				
0.5 g	0.81	0.00012	175.43	0.98
1.0 g	0.91	0.0195	4.127	0.92
1.5 g	0.82	0.036	3.303	0.89
2.0 g	0.97	0.0058	16.313	0.91

When the adsorption values for Raw Clay were examined, it was seen that the determination of ion exchange capacity and initial pH value at the beginning of the study were similar with the evidence of kaolinite (Table 1, Table 2 and Table 3).

Table 3
Freundlich Isotherms and Isotherms Constants for Halloysite, Bentonite, Kaolinite and Raw Clay

	Freundlich Isotherm	Freundlich Isotherms Constants	
	R^2	K_f (mg/g)	n
Halloysite			
0.5 g	0.91	60.64	5.98
1.0 g	0.97	31.21	5.94
1.5 g	0.98	20.96	5.66
2.0 g	0.96	16.75	4.38
Bentonite			
0.5 g	0.93	55.19	12.73
1.0 g	0.98	31.32	5.88
1.5 g	0.97	20.04	7.09
2.0 g	0.91	14.71	7.35

Kaolinite			
0.5 g	0.90	60.09	6.32
1.0 g	0.95	170.46	1.07
1.5 g	0.96	33.02	2.10
2.0 g	0.84	13.57	11.01
Raw Clay			
0.5 g	0.95	57.95	8.25
1.0 g	0.98	58.85	1.97
1.5 g	0.95	35.44	2.07
2.0 g	0.99	15.87	5.63

According to the adsorption isotherms, it was determined that color removal from bentonite clay was higher. Accordingly, different temperature ranges and different starting pH values were continued with bentonite clay. Tables 4 and 5 show the Langmuir and Freundlich Isotherm values at pH values of 2, 4, 6, 8, 10 and 12 for 13 °C, 25 °C and 50 °C. It is possible to say that adsorption for 13 °C is suitable for Langmuir Isotherm as a single layer of physical adsorption. The maximum adsorption was obtained at pH 12. When the b values were examined, the maximum adsorption energy was obtained at pH 8 and the best value was obtained at pH 12 according to R_L value and all of the adsorptions were carried out without the need for external energy. It was similar for the adsorption capacity of 25 °C and 50 °C. Although the R^2 values for pH 12 were low, it can be said that the Langmuir isotherm complied with the other parameters.

Table 4
Langmuir Isotherms and Isotherms Constants for Bentonite at 13 °C, 25 °C and 50 °C

	Langmuir Isotherm	Langmuir Isotherms Constants		
	R^2	b (L/mg)	Q_{max} (mg/g)	R_L
13 °C				
pH 2	0.73	0.00014	147.05	0.979
pH 4	0.96	0.00019	113.63	0.978
pH 6	0.94	0.00012	178.57	0.979
pH 8	0.50	0.0002	112.36	0.978
pH 10	0.67	0.000037	526.32	0.980
pH 12	0.90	0.0000054	3333.3	0.982
25 °C				
	R^2	b (L/mg)	Q_{max} (mg/g)	R_L
pH 2	0.98	0.0001	208.33	0.979
pH 4	0.99	0.00011	181.81	0.98
pH 6	0.94	0.00013	158.73	0.979

pH 8	0.97	0.00012	166.66	0.98
pH 10	0.96	0.00002	909.09	0.98
pH 12	0.37	7.08×10^{-8}	25000	0.98
50 °C	R^2	b (L/mg)	Q_{max} (mg/g)	R_L
pH 2	0.98	0.00011	178.57	0.98
pH 4	0.95	0.00021	105.26	0.978
pH 6	0.98	0.00014	147.05	0.975
pH 8	0.95	0.00011	181.81	0.98
pH 10	0.92	0.00003	625	0.98
pH 12	0.59	0.0000014	12500	0.98

Table 5
Freundlich Isotherms and Isotherms Constants for Bentonite at 13 °C, 25 °C and 50 °C

	Freundlich Isotherm	Freundlich Isotherms Constants	
	R^2	K_f (mg/g)	n
13 °C			
pH 2	0.80	58.75	8.88
pH 4	0.29	52.66	39.37
pH 6	0.98	58.32	9.15
pH 8	0.49	59.56	7.26
pH 10	0.68	55.91	19.45
pH 12	0.97	55.80	36.10
25 °C			
	R^2	K_f (mg/g)	n
pH 2	0.99	57.81	10.06
pH 4	0.99	58.13	9.48
pH 6	0.99	58.60	8.75
pH 8	0.99	58.40	9.02
pH 10	0.99	55.86	21.36
pH 12	0.77	56.07	71.94
50 °C			
	R^2	K_f (mg/g)	n
pH 2	0.99	58.24	9.37
pH 4	0.99	60.38	7.08
pH 6	0.99	58.90	8.49
pH 8	0.99	58.20	9.30
pH 10	0.99	56.02	16.66
pH 12	0.89	55.95	58.47

4. CONCLUSIONS

The adsorption isotherms were obtained under different adsorption conditions (temperature, pH, contact time) for MGY400 adsorption of halloysite, bentonite, kaolinite and raw clay.

MGY400 is a less commonly used dyestuff in the literature. Also, the clay materials used in the study are completely natural and it was tried to be shown that adsorbents with the potential to be used in color removal from wastewater can be obtained economically and can be effective in color removal. Therefore, it has been determined that a rare type of adsorbate is used in the current study, and an effective color removal can be achieved with easily available adsorbents that have no financial value. In addition, the adsorption study was carried out in wide pH and temperature ranges.

The obtained values are expressed by the adsorption isotherms, Freundlich ($r \geq 0.84$) and Langmuir ($r \geq 0.64$) adsorption equations. Q_{\max} values ranged from 1.20 to 476 mg/g. The b values expressing the adsorbent-adsorbate interaction energy ranged between 0.000043 and 0.107 L/mg.

It can be seen that the adsorption of dyestuff by clay minerals depends on the structure of raw clay minerals. When all adsorption data were examined, it was found that the maximum color removal efficiency was obtained from 0.5 g bentonite clay. It was determined that as the starting pH of the solution increased, the efficiency of adsorption increased, besides, adsorption occurred as physical adsorption and monolayer physical adsorption.

The results show that it is necessary to know in advance the fractions of clay minerals to be used in water and soil treatment technologies. The type of clay minerals will determine the effectiveness of this technology and contribute to the selection of the type of substance to be adsorbed.

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The author of the paper declares that she complies with the scientific, ethical and quotation rules of SAUJS in all processes of the paper and that she does not make any falsification on the data collected. In addition, she declares that Sakarya University Journal of Science and its editorial board have no responsibility for any ethical violations that may be encountered, and that this study has not been evaluated in any academic publication environment other than Sakarya University Journal of Science.

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