Adsorption of Bromocresol Purple Dye from Aqueous Solutions onto Attapulgite Surface

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ABSTRACT— The finding of novel pollutants in a multitude of surface water bodies worldwide has recently caused environmentalists to face challenges. Therefore, the development of low-cost, efficient technologies is required to provide a safe, pollution-free water environment. The attapulgite surface was used in this study because it has a good absorbent surface for removing bromocresol purple dye from its aqueous solutions. Because attapulgite has a high absorption capacity, it can be used to remove pollutants in both its normal and modified states. Factors affecting adsorption were studied, such as the weight of the adsorbent surface, the initial concentration of the adsorbent, contact time, and the effect of temperature. Clay was ground, cleaned multiple times with ionic distilled water to remove any potentially dissolving materials, and then dried at 160°C. After that, each vial was filled with attapulgite clay, which was then placed in contact with the adsorbent at varying temperatures in a water bath with a vibrator. Adsorption data were also applied to isothermal models such as the isotherms of the Freundlich, Temkin, and Langmuir. Their constants showed that the Freundlich model is the most appropriate for the system under study. Thermodynamic parameters such as $\Delta G°$, $\Delta S°$ Δ, and $H°$ were also studied, and it was found that the adsorption is of the exothermic type and is non-spontaneous. According to the study, the bromocresol purple dye can be effectively removed using activated attapulgite clay, a cheap and easily accessible adsorbent material that was transported from Iraq.

KEYWORDS: Bromocresol purple dye, Adsorption, Attapulgite clay, Thermodynamic parameter

1. INTRODUCTION

Identifying new pollutants in numerous surface water bodies across the globe has presented environmentalists with problems recently [1], as it appears in yellow-green when the pH is less than 5.2, but when the pH is higher than 6.8, it appears in purple, as the change in acidity constants indicates the disintegration of molecules in aqueous media [2], [3]. Failure to dispose of industrial waste resulting from multiple industries, such as the cosmetics, leather, rubber, and paper industries, in an incorrect manner has led to water contamination with many pollutants, including industrial dyes [4]. This causes harm to the aquatic environment and human health because these dyes cannot be degraded and are also characterized by their high toxicity [5], [6]. Bromocresol purple (BCP) dye ($C_{21}H_{16}Br_2O_5S$) is one of these dyes, which belongs to the family of sulfonphthalein dyes and is an anionic dye [7]. Bromocresol is used in many applications, including its use to determine the quantities of albumin in medical laboratories, as well as in

microbiology to determine lactic acid bacteria through dead cell staining to describe its degree of acidity. It is also used as an indicator of acidity in photographic processing baths. This dye causes many problems for humans as well as for the aquatic environment, especially when it is associated with heavy metals [8], [9]. It turns out that spectrophotometric methods include ion exchange, reverse osmosis, precipitation, and adsorption [10]. Many low-cost adsorbent surfaces that have high removal ability have been used, such as aquatic plants, clay compounds, agricultural products, and microorganisms [11], [12]. Because natural materials such as clay have good qualities, such as a high specific surface area, as well as being available and cheap, and being considered environmentally friendly, they have been used in many types of research to remove dye pollutants from water [13]. Attapulgite is also known as palygorskite [14], which is a mineral clay and is composed of crystalline hydrated magnesium silicates, which are layers of silicates. Attapulgite mainly contains Mg^{2+} ions and abundant amounts of Fe^{3+} and Al^{3+} [15]. Attapulgite has many advantages, including a high surface area, porous structure, moderate exchange of cations, and fibrous morphology. It also has a high absorption capacity, so it can be used in its normal or modified state to remove pollutants [15]. This is because attapulgite mainly contains hydrated magnesium and aluminum silicates, which form thin tetrahedral sheets of SiO_2, octahedral sheets of Al_2O_3, and dihedral and trihedral sheets of MgO. Where a part of each of Si^{4+}, Al^{3+}, or Mg^{2+} is replaced similarly by cations of lower valence which provides a negative charge to the clay sheets which are compensated by inorganic ketones such as (Na^+, K^+, Ca^{2+}) which absorb all the outer surface of the clay and these hydrated ketones make the clay layers with parallel lines which makes the clay structure cohesive and with a distance between the layers estimated at 1-2 nanometers. This distance can expand and accommodate a wide variety of inorganic and organic ketones through exchange processes between simple ketones.

In this investigation, the BCP dye was extracted from its aqueous solution using attapulgite as an adsorbent surface. The effects of a group of factors affecting adsorption were studied, including the equilibrium time and temperature. Applying the adsorption data to the models, the parameters were found to remove the BCP dye on the attapulgite surface at different temperatures.

2. EXPERIMENTAL

2.1. Materials and methods
Bromocresol purple dye was obtained from the Sigma-Aldrich company. Attapulgite clay was provided by the Geological Survey Department. The chemical structure of BCP is shown in Figure 1.
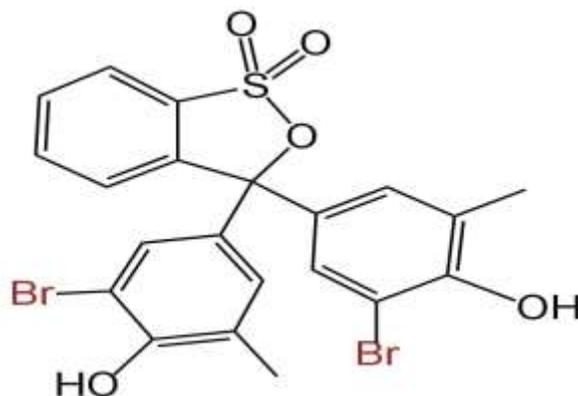

Figure 1- The chemical structure of bromocresol purple dye

2.2. Apparatus
The work used the spectrophotometer Shimadzu S8400, the shaking water bath Korean SW B-25, and

HYSC. The electrical centrifuge 220V (Hettich EBA-20) and a Daihan Labtech oven LDO - 060E.

2.3. Preparation of attapulgite clay

After obtaining the attapulgite clay, it was ground and then washed several times with ionized distilled water to purify it and get rid of materials that can dissolve. After that, it was dried at 160°C, then the material was re-ground again, and then it was sieved using a specific type of sieve to obtain fines of a size of 75 μm.

2.4. Adsorption experiments

Adsorption experiments were conducted by preparing solutions of the dye used BCP in 100 ml volumetric bottles within the range of 15 – 50 mg/L. Where 25 ml of each concentration was taken, 0.8 g of attapulgite clay was added to each vial and placed in contact with the adsorbent in a water bath equipped with a vibrator at different temperatures ranging from (298-313) K for 45 minutes, which is the equilibrium time. It follows from the phrase that the solution is placed in a centrifuge for 15 minutes at a speed of 3000 rpm, and after separation, the absorbance of the clear solutions was measured at the maximum wavelength of BCP dye. The amount of adsorbed material and the removal percentage of BCP dye were found by equations below [14], [16]:

$$q_e = \frac{(C_0 - C_e)v}{m} \dots\dots\dots (1)$$

$$\% \, Remova = \frac{(C_0 - C_e)}{C_0} \times 100 \dots\dots\dots\dots (2)$$

Where m is the mass of attapulgite (g), Co and Ce are the concentration of BCP dye before the adsorption and at equilibrium, respectively.

3. Results

3.1. The adsorbent weight effect

10 mg/L of the dye was taken at an initial concentration of 25°C. It was found that the weight increases by increasing the percentage of removal of the adsorbed dye until it reaches an ineffective weight, Figure 2.
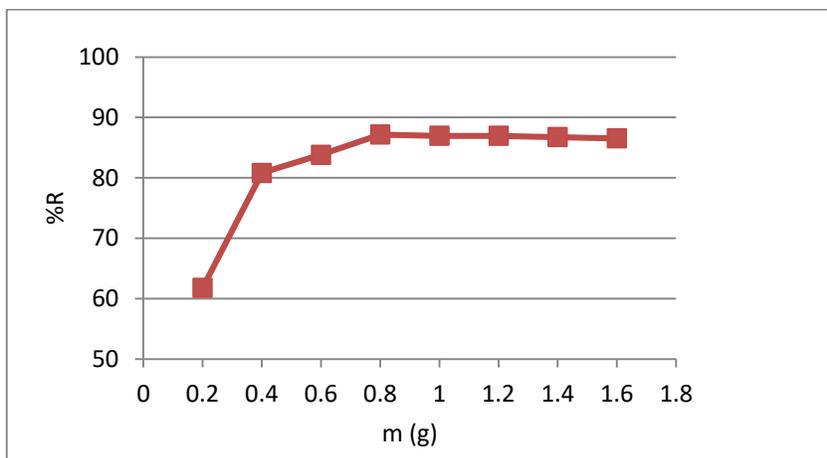

Figure 2- Mass effect on the BCP removal on attapulgite

3.2. The initial concentration effect

To determine the optimal concentration of the adsorbate, several concentrations of BCP dye were taken (10, 15, 20, 25, 30, 35, 40, and 45 mg/L). 0.8 g of the adsorbent surface was used at 25°C, Figure 3.
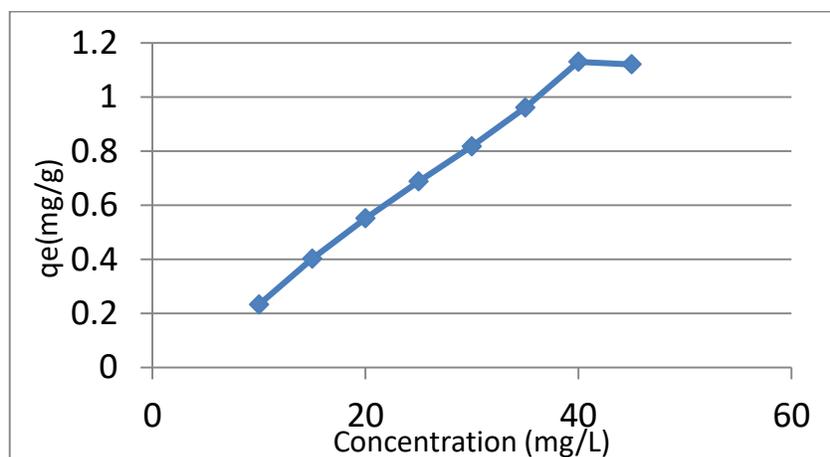
Figure 3- Concentration effect on BCP adsorption

3.3. Effect of equilibrium time

For determining the time required for equilibrium between the adsorbent surface and the adsorbate material, 40 mg/L of BCP dye was taken and placed in contact with 0.8 mg of attapulgite adsorbent surface at 25 ^{0}C. It was found that 45 minutes is the best time to reach the equilibrium, Figure 4.
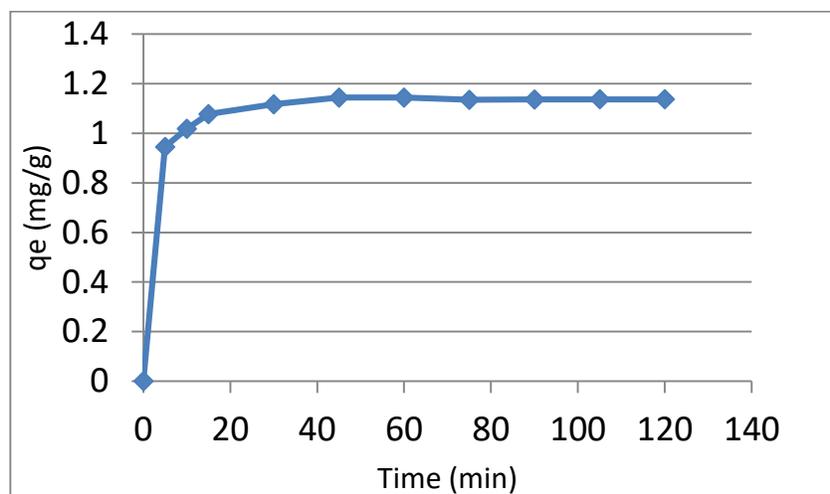

Figure 4- Contact time effect on BCP adsorption on attapulgite

3.4. Effect of temperature

The effect of this factor on the attapulgite surface was studied by taking 40 mg/L of the dye and 0.8 mg of the attapulgite surface at different temperatures (298-303-308-312 Kelvin), Figure 5. It was found that the amount of adsorbed dye decreases as the temperature is increased, which means that the adsorption is exothermic for the system studied.
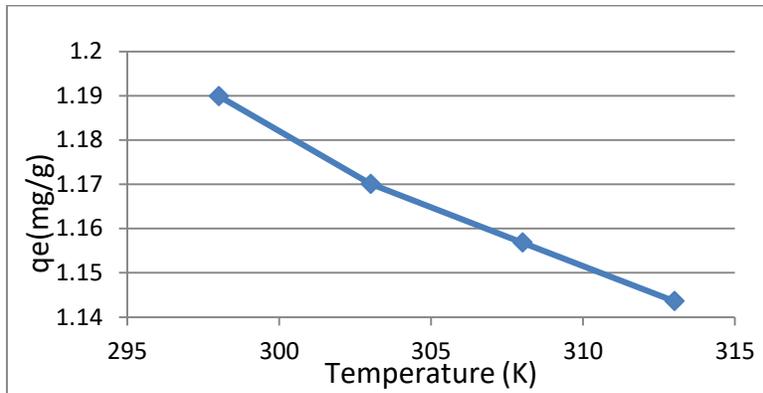
Figure 5- The temperature effect on the BCP onto attapulgite

3.5. Adsorption isotherms

Adsorption isotherms are used to determine the mechanism and type of adsorption by using isotherm models. Three types of isotherms were used in this study: Langmuir, Temkin, and Freundlich. The Langmuir model describes adsorption as forming a single layer of the adsorbed material on the adsorbent surface, where the linear can be found from the following equation [17]:

$$\frac{Ce}{q_e} = \frac{1}{q_{max}K_L} + \frac{Ce}{q_{max}} \qquad \ldots\ldots\ldots\ldots(3)$$

Where q_{max} is the maximum amount of adsorption, qe is the amount of BCP dye adsorbed at equilibrium, C_e is the concentration of BCP dye adsorbed at equilibrium, and k_L is the Langmuir constant. The slope is $1/q_{max}$ while the intercept is $1/q_{max} K_L$, Figure 6.

From the obtained results in Table 1, the K_L and q_{max} have fluctuated with an increase in temperature.
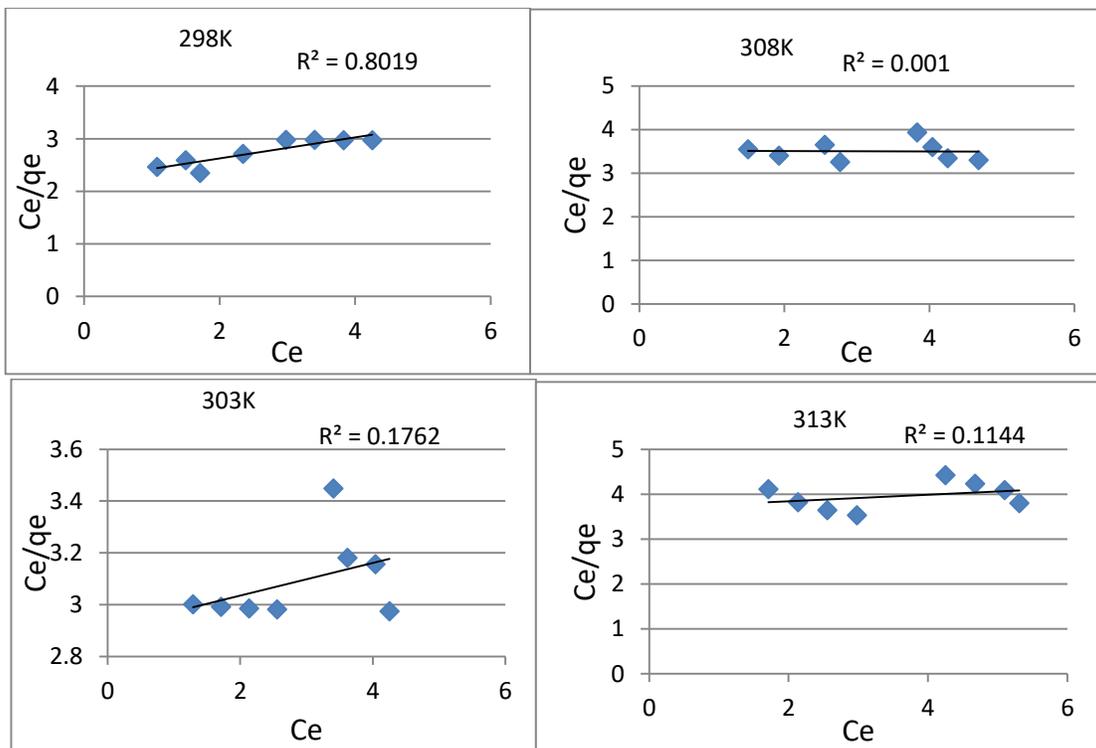

Figure 6- Langmuir adsorption isotherm of BCP dye on the attapulgite surface at different temperatures

Table 1. Langmuir constants of the BCP on the attapulgite surface

Thermal degree	R^2	q_{max} (mg/g)	k_L(L\mg)
298	0.8019	4.99002	0.090067
303	0.1762	15.84786	0.021695
308	0.001	161.2903	0.00176
313	0.1144	13.58696	0.019923

The Temkin model shows that the result of the interaction between the adsorbent and the adsorbent surface leads to a decrease in the temperature of adsorption due to covering the adsorbent surface, and it can be expressed by the following equation [18].

$$q_e = B \ln A_T + B \ln C_e \ldots\ldots\ldots\ldots(4)$$

Where qe is the amount of dye adsorbed at equilibrium, B is a Constant related to the heat of sorption, A_T is the Temkin isotherm equilibrium binding constant, and C_e is the amount of dye adsorbed at equilibrium. By plotting ln Ce versus qe, A_T and B can be found from the intercept and slope [19], Figure 7.

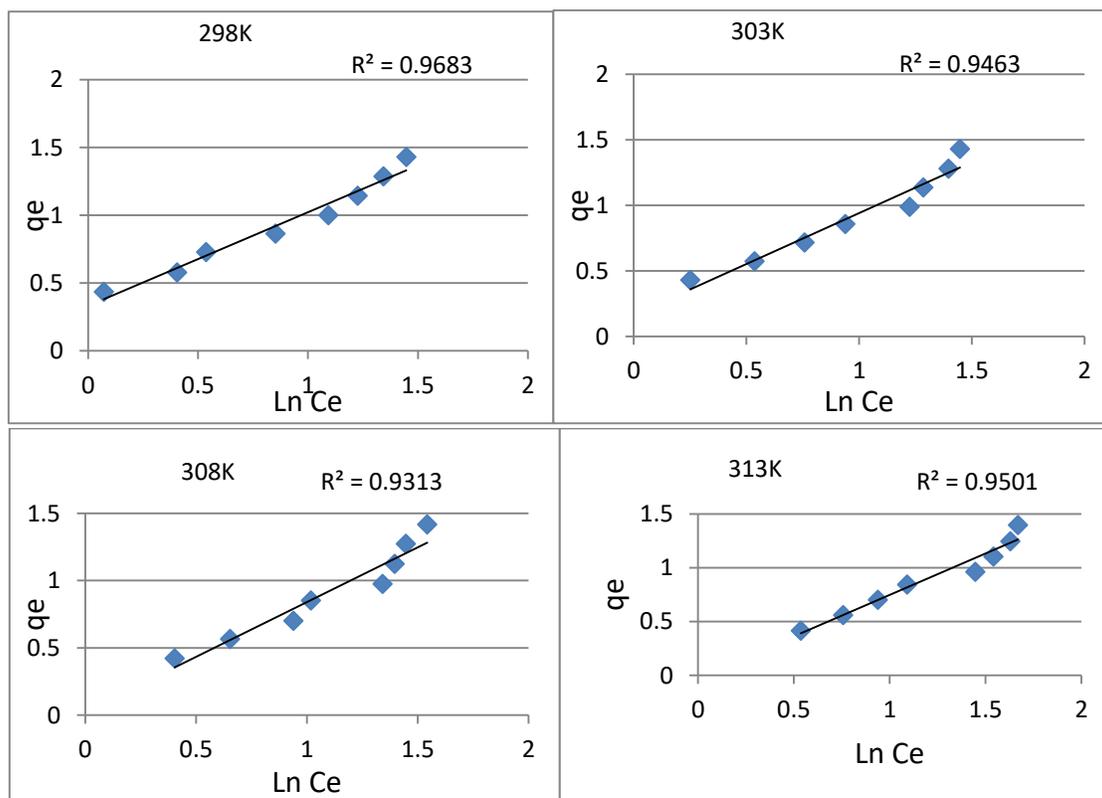As shown in Table 2, the values of A_T and R^2 decreased with increasing temperature.

Figure 7- The Temkin adsorption isotherm of BCP dye adsorption on the attapulgite surface at different temperatures

Table 2. Temkin constants of the BCP on the attapulgite

Temperature (K)	R^2	A_T(L\g)	B(J\mol)
298	0.9683	1.610018	0.6925
303	0.9463	1.231222	0.7793
308	0.9313	1.030445	0.8156
313	0.9501	1.025586	0.7679

Freundlich states that the adsorption process is unpredictable and may form multiple layers of the adsorbed material [20], and its linear shape is:

$\ln q_e = \ln K_f + \frac{1}{n} \ln C_e$ ………(5)

Where each of q_e represents the BCP amount adsorbed, both n and K_F are Freundlich constants, which can be found by plotting $\ln q_e$ versus $\ln C_e$ [21], Figure 8.

Both the n and K_f values in Table 3 decrease with increasing temperature, suggesting that the intensity and capacity are decreased by increasing the temperature.
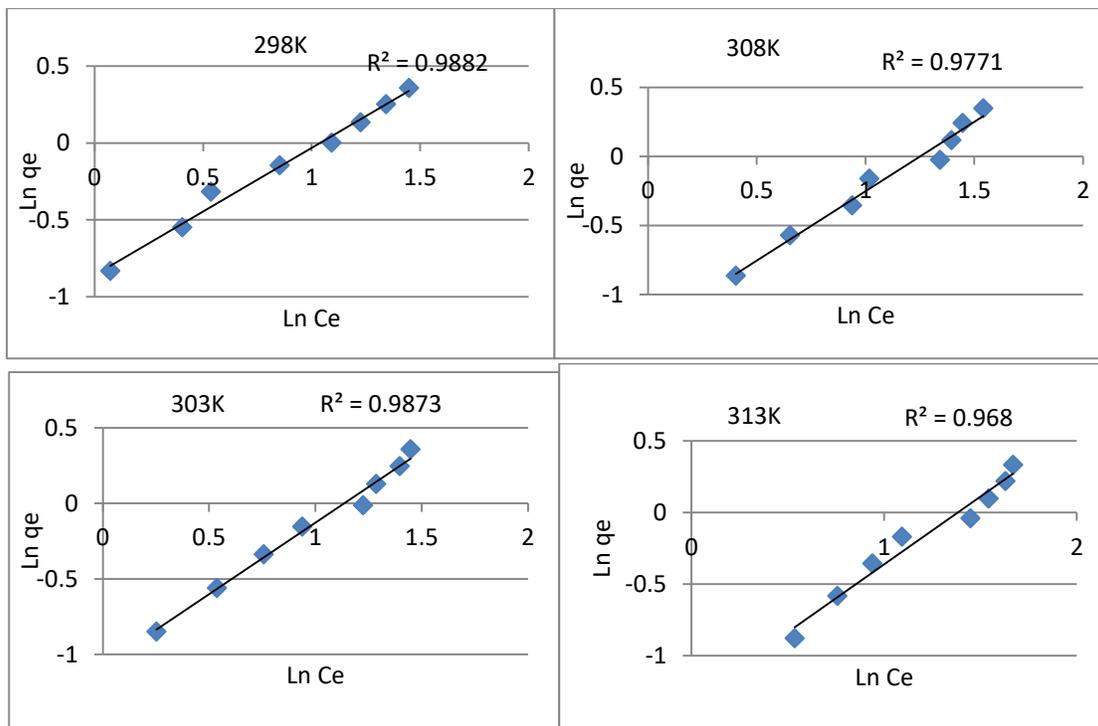

Figure 8- Freundlich adsorption isotherm of BCP dye adsorption on the attapulgite surface at different temperatures

Table 3. Freundlich constants of the BCP adsorption on the attapulgite

Temperature (K)	R^2	n	k_f (mg\g)
298	0.9882	1.211	0.424
303	0.9873	1.057	0.342
308	0.9771	0.997	0.285
313	0.968	1.056	0.270

3.6. Thermodynamic parameters

The changes in entropy (ΔS°), enthalpy (ΔH°), and Gibbs free energy (ΔG°) were calculated for the BCP dye adsorption on the attapulgite surface using the following equation:

$In\ k = \dfrac{-\Delta H^{\circ}}{RT} + Constant \ldots \ldots \ldots \ldots (6)$.

Where R is the general constant for gases, and T is the absolute temperature.

Where ΔH° was calculated from the graph between Ln k versus 1/T (Van't Hoff equation), Figure 9.

The value of ΔG° was also calculated from the equation below:

$$\Delta G° = -R T \ln K \ldots\ldots\ldots(7)$$

The change in entropy ΔS° was calculated from the equation below:

$$\Delta G° = \Delta H° - T \Delta S° \ldots\ldots\ldots(8)$$

As shown in Table 4, the ΔH° value indicates that the process of BCP dye on the attapulgite is exothermic.
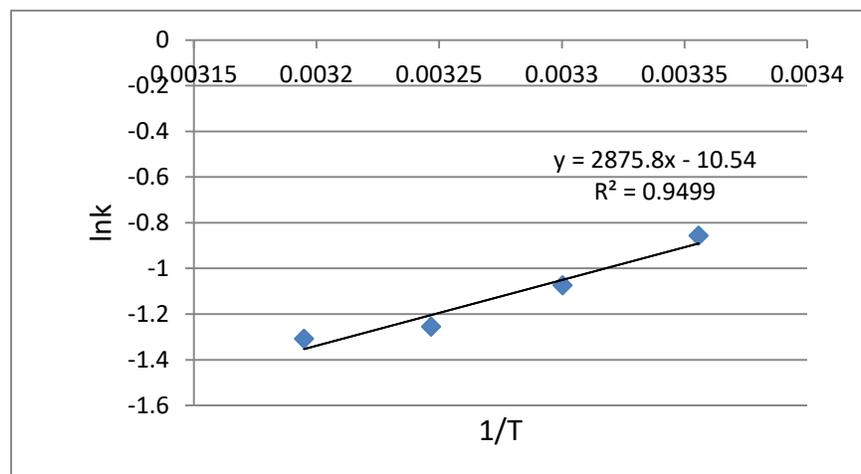

Figure 9- Van't Hoff equation diagram for the adsorption of BCP dye on the attapulgite surface

Table 4. Coefficients of the BCP adsorption on the attapulgite

Temperature (K)	ΔG° (J/mol)	ΔH° (J/mol)	ΔS° (J/mol)
298	3937.4		-241.375
303	2650.641	-67992.7	-233.146
308	1777.646		-226.527
313	645.1057		-214.29

4. Discussion

This study found that the weight increases as the percentage of removal of the adsorbed dye. It can be attributed to the increased absorption sites available on the surface resulting from the increased surface area of the attapulgite until it reaches an effective weight because it has reached a state of saturation [22]. Another finding is that the adsorbate material increases with increasing dye concentration. This is because the mass is transferred to the adsorbent surface [23] that is, the mass is transferred between the solution and the solute, where the dye molecules move to the surface of the solid and stick to it, then spread within the solid structure of the attapulgite, which leads to the best adsorption rate occurring at a concentration of 40 mg/L. This is because when the concentration of the BCP dye increases, the number of its molecules increases, and since the amount of the absorbent material contains a limited number of active sites that have the ability to absorb the dye, therefore, when the concentration increases more, its molecules will remain in the solution, where after that, increasing the concentration becomes ineffective in the adsorption rate [24]. The results of this study also concluded that 45 minutes is the best time to reach equilibrium. This indicates that the absorption capacity increases rapidly first during the first 20 minutes due to the presence of unoccupied adsorption sites available for adsorption of BCP dye and that the number of these sites is large on the surface of the attapulgite, which allows the dye ions to bind to these sites and that they finally reach equilibrium at minute 45 when these sites are filled on the surface of the absorbent material [24].

The current investigation found that the amount of adsorbed dye decreases when the temperature is increased, which means that the adsorption is exothermic for the system studied [25]. This is because rising temperatures cause the dye molecules' kinetic energy to rise as well, causing them to separate the surface. From the results obtained, we note that the values of KL and qmax at the temperatures under study fluctuate, as do the values of R^2, which means that the Langmuir model is not suitable for the surface studied. The values of A and R^2 decreased with increasing temperature, which confirms that the system needs low temperatures for the adsorption process to occur. However, the values of B are increased by increasing the temperature, and this means that the Temkin is unsuitable for the system.

Both the n and K_f values in Table 3 decreased by increasing the temperature, suggesting that the intensity and capacity are decreased by increasing the temperature, and this confirms that the nature of the studied surface is exothermic. The values of R^2 also indicate the suitability of the Freundlich adsorption model for the system under study [26], [27]. As shown in Table 4, the $\Delta H°$ value indicates that the process of BCP dye on the attapulgite is exothermic. These may be explained by increasing the temperature and increasing the kinetic energy of the BCP dye. A positive $\Delta G°$ was also found, and this indicates that the adsorption process is non-spontaneous. There was a negative value of entropy ($\Delta S°$), thus indicating that the randomness between liquid and solid in the adsorption processes was decreased [28], [29].

5. Conclusion

The study demonstrates that activated attapulgite clay, a readily available and inexpensive adsorbent material extracted from Iraq, can be used as an effective adsorbent for the removal of the bromocresol purple dye. The factors affecting the adsorption and its ability were also studied, and the time of equilibrium establishment was found to be 45 minutes. On the contrary, Langmuir, Temkin, and Freundlich isotherms were used to describe the results obtained. The Freundlich isotherm is more appropriate for our system, as demonstrated by the application of the Langmuir and Temkin isotherms to the experimental results of the study system. Thermodynamic functions were also found, and the process was exothermic at all temperatures studied.

6. Conflict of interest

No

7. References

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