

## Adsorptive removal of cationic dye from aqueous solutions using Bardakçı clay

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### Abstract

This study was investigation employed the batch adsorption method using Bardakçı Clay/Van as an adsorbent to remove crystal violet, a cationic dye from an aqueous solution. The effects of pH, adsorbent amount, interaction time and concentration were investigated to determine the optimal adsorption conditions. The optimal adsorption conditions were determined to be pH=6, 0.6 g adsorbent amount, and the adsorption reached equilibrium at the 25th minute. The equilibrium isotherm was determined using the Langmuir, Freundlich and Dubinin–Radushkevich (D–R) adsorption equations. It was discovered to conform to the Langmuir isotherm. In the Dubinin–Radushkevich (D–R) model, the E value was calculated to  $E < 8 \text{ kJmol}^{-1}$ , indicating that the adsorption process occurs physically. Thermodynamic parameters such as enthalpy ( $\Delta H^\circ$ ), Gibbs' free energy ( $\Delta G^\circ$ ) and entropy ( $\Delta S^\circ$ ) were calculated. The adsorption of crystal violet with Bardakçı clay demonstrated that the process was endothermic, occurring both physically and spontaneously.

### Keywords

Bardakçı Clay, Crystal Violet, Adsorption, Adsorption isotherms, Thermodynamics

### Introduction

All living organisms require water to survive (Atasoy, Mercan, Alacabey, & Kul, 2011). Today, water pollution has become a serious concern to humans due to rapid industrialization and population growth (Bhatnagar, Jain, & Mukul, 2005; Senthilkumaar, Kalaamani, & Subburaam, 2006). However, the scarcity of clean water supplies has developed into a significant problem as a result of pollution caused by the discharge of untreated industrial wastewater. Environmental pollution in developing countries has gotten worse due to the uncontrolled population growth, the use of obsolete practices and technologies that consume large amounts of water in agricultural and industrial operations and requires immediate attention (Lee, Low, & Gan, 1999; Saeed, Sharif, & Iqbal, 2010).

Various dyes are used to colour a wide variety of industrial products, including food, textiles, paper,

rubber, plastic, cosmetics, medicine, etc (R. Ahmad, 2009; Banat, Nigam, Singh, & Marchant, 1996; Kumar & Ahmad, 2011). The dye is responsible for many problems and is called stubborn dye due to its non-degradable nature (W. Ahmad et al., 2021). As a result, a significant amount of coloured waste is generated and discharged into water resources (R. Ahmad, 2009; Banat et al., 1996; Kumar & Ahmad, 2011).

Crystal Violet (CV), a purple dye, is a triarylmethane dye that is widely used in the textile industry to dye silk and cotton (Chakraborty, Chowdhury, & Saha, 2011; A. Mittal, Mittal, Malviya, Kaur, & Gupta, 2010; Senthilkumaar et al., 2006), therefore, a minute quantity of CV in water can reduce the access of sunlight and disturb the photosynthesis process (H. Mittal, Al Alili, Morajkar, & Alhassan, 2021). Additionally, it is used to manufacture dye and printing inks (Chakraborty et al., 2011; A. Mittal et al., 2010; Senthilkumaar et al., 2006).

CV is used as a gram stain in medicine, as a bacteriostatic agent in veterinary (A. Mittal et al., 2010) and as an external skin disinfectant in humans (Kumar & Ahmad, 2011). It is also used as an additive to prevent the spread of mould, intestinal parasites, and fungi in poultry feed (Kumar & Ahmad, 2011). CV is carcinogenic, a re-polluting molecule, poorly metabolized by microbes, non biodegradable, and persistent in various environments. CV causes moderate eye irritation and painful light sensitivity. Because it contains cationic dye, it has the potential to cause permanently damage the conjunctiva and cornea. It is highly toxic to mammalian cells and, if absorbed through the skin in harmful amounts, may cause skin and gastrointestinal irritation. In cases of overexposure, it can also lead to respiratory and renal failure (R. Ahmad, 2009; Chakraborty et al., 2011; A. Mittal et al., 2010; Saeed et al., 2010).

Water pollution caused by synthetic dye molecules is detrimental to the environment and has adverse effects on public health (Akar, Özcan, Akar, Özcan, & Kaynak, 2009; Chakraborty et al., 2011; Kiran, İlhan, Caner, Iscen, & Yildiz, 2009). As a result, the majority of these dyes are toxic, carcinogenic or mutagenic. As a result, coloured wastes must be treated appropriately before being discharged into water sources (R. Ahmad, 2009; Choy, McKay, & Porter, 1999; Inthorn, Singtho, Thiravetyan, & Khan, 2004; Kumar & Ahmad, 2011).

Commonly used methods for eliminating inorganic and organic wastes that contribute to environmental pollution and harm human health include chemical precipitation, ion exchange, membrane filtration, coagulation and adsorption (Bhattacharyya & Gupta, 2008; Caliskan, Kul, Alkan, Sogut, & Alacabey, 2011; Lin & Juang, 2002; Riza, Tolga, Ihsan, Salih, & Yunus, 2011).

Each of them has a number of advantages and disadvantages. Among these approaches, the adsorption technique is the most popular due to its high efficiency, simplicity of design, and ease of use. The main benefits of a potentially successful alternative adsorption for dye removal in wastewater are its adaptability, ease of design, and the fact that it does not lead to the formation of hazardous substances (Derakhshan & Moradi, 2014; Iriarte-Velasco, Chimeno-Alanis, Gonzalez-Marcos, & Álvarez-Uriarte, 2011; Yao, Xu, Chen, Xu, & Zhu, 2010). Various materials are used as adsorbents to purify water. Commonly used adsorbents include; kaolinite (Riza et al., 2011), montmorillonite (Bhattacharyya & Gupta, 2008), pumice (İhsan Alacabey et al., 2021), sediment (İhsan Alacabey, Kul, Şakir, & Alkan, 2020), chitosan (Acet et al., 2018), active carbon (Depci et al., 2011), zeolite (Ji et al., 2021), diatomite (Kul, Alacabey, & Kılıç, 2010).

The primary objective of this study is to remove CV dyestuff from synthetic waters using an adsorption method with clay (BK adsorbent) taken from Bardakçı village in the province of Van. Thermodynamic studies and adsorption isotherm models were examined to evaluate the experimental data. In addition, the BK adsorbent has been characterized.

## Materials and Methods

### Preparation of Adsorbent

BK adsorbent samples were obtained 5cm below the surface after matching in order to prevent contamination.

The BK adsorbent was ground in a mortar and filtered through a 230 mesh sieve for washing. 100 grams of BK adsorbent were washed in 1.7 L of distilled water while, stirring at 150 rpm for 12 hours. After the mixing time was complete, it was left for 12 hours to allow the aqueous phase to separate from the solid phase. The solid phase was filtered and then left to dry for one week at room temperature. The dried BK adsorbent was transferred to a vessel after being sieved through a 230 mesh sieve. Bardakçı clay was stored in a desiccator until used in the experiment. (İ Alacabey, 2006).

### Chemicals

Crystal Violet ( $C_{25}N_3H_3OCl$ ) dyestuff, Hydrochloric Acid (HCl), Sodium Hydroxide (NaOH) used in the study were obtained from Sigma – Aldrich company. These chemicals supplied are of analytical purity.

### Devices

The BK adsorbent's physicochemical properties were determined using standard procedures described by (Riza et al., 2011). The adsorbent was analyzed using a Thermo Scientific ARL Perorm'x Wavelength Distributed X-ray Fluorescence (WD-XRF) Spectrometer to determine the oxides present in the structure. Fourier transform infrared (FTIR, 400 – 4000  $cm^{-1}$  range, Bruker Vertex 70) was used to determine the functional groups present in the BK adsorbent. An X-ray diffraction (XRD, Philips PW 1830-40) device was used to determine the diffraction pattern and interplanetary spacing of the BK adsorbent. The surface morphology of the adsorbent was determined by Scanning Electron Microscopy (SEM, Zeiss). The surface area measurement was performed by Brunauer–Emmett–Teller (BET, Nova 2200e Quantachrome Instruments). The absorption measurements were performed using the UV-Vis spectrophotometer ( $\lambda_{max}=592$  nm for Pg instruments, T80+). Centrifugation (Nüve Nf 200) was used to precipitate the adsorbent.

### Method

Adsorption studies were carried out using the batch system method.

### Adsorption studies

A dyestuff stock solution of 2000  $mgL^{-1}$  diluted to the required starting concentrations was prepared. The following parameters were examined during dye adsorption: pH (2, 4, 6, 8), amount of adsorbent (0.05 g, 0.1 g, 0.2 g, 0.4 g, 0.6 g, 0.8 g, 1.0 g), concentration (10, 30, 50, 70 and 100  $mgL^{-1}$ ), varying interaction times (0, 1, 3, 5, 7, 10, 15, 25, 35, 45, 60, 75, 90 min), and temperature (298 K, 313 K, 323 K). The adsorption capacity ( $mgg^{-1}$ ) and adsorption percentage (%) were obtained from the following equation:

$$q_e = \frac{(C_0 - C_e)V}{m} \quad (1)$$

$$\text{Adsorption (\%)} = \frac{C_0 - C_e}{C_0} \times 100 \quad (2)$$

In Equations 1 and 2,  $C_0$  is the initial concentration of the CV. dyestuff in the solution ( $mgL^{-1}$ );  $C_e$ : final CV dyestuff concentration in solution ( $mgL^{-1}$ ); V: CV is the volume of the dyestuff solution (L), m: is the weight of the BK adsorbent (g), and  $q_e$  ( $mgg^{-1}$ ) is the adsorption

amount at equilibrium (Erol, Yıldız, Alacabey, Karabörk, & Uzun, 2019).

**Results**

**Characterization**

**XRF Analysis**

The quantitative chemical analysis of Bardakçı clay by X-ray fluorescence spectrometry technique is given in table 1.

The findings indicate that the percentage of CaO is quite high. The higher percentage of CaO compared to Na<sub>2</sub>O indicates that the sample is predominantly composed of calcium bentonite (Ca-B). The absence of permanent suspensions in water, that is, the prepared

suspensions collapse rapidly and do not swell significantly in water, demonstrates that the sample is Ca-B (Biçer, 2019; Yalçın, 2010).

As a result of XRF analysis, a Na<sub>2</sub>O + K<sub>2</sub>O/CaO + MgO value ≥ 1 in metal oxides is classified as Sodium Bentonite (Na-B), Intermediate Bentonite when 1/3 < Na<sub>2</sub>O + K<sub>2</sub>O/CaO + MgO value < 1, Na<sub>2</sub>O + K<sub>2</sub>O/CaO + MgO when its value is less than 1/3, it is considered as Calcium Bentonite (Ca-B) (Yalçın, 2010). As shown in Table 1 the Na<sub>2</sub>O + K<sub>2</sub>O/CaO + MgO value is less than < 1/3. This demonstrates that the adsorbent is a Ca-Bentonite type clay. The results obtained are consistent with the literature.

Table1. XRF Analysis of BK adsorbent

A. Za	Al <sub>2</sub> O <sub>3</sub>	CaO	Fe <sub>2</sub> O <sub>3</sub>	K <sub>2</sub> O	MgO	MnO	Na <sub>2</sub> O	P <sub>2</sub> O <sub>5</sub>	SiO <sub>2</sub>	TiO <sub>2</sub>
%	%	%	%	%	%	%	%	%	%	%
12.5	10.4	16.1	6.4	1.6	5.8	0.1	1.6	0.2	43.7	1.3

**XRD Analysis**

X-ray powder diffraction analyses of BK adsorbent are shown in Figure 1.

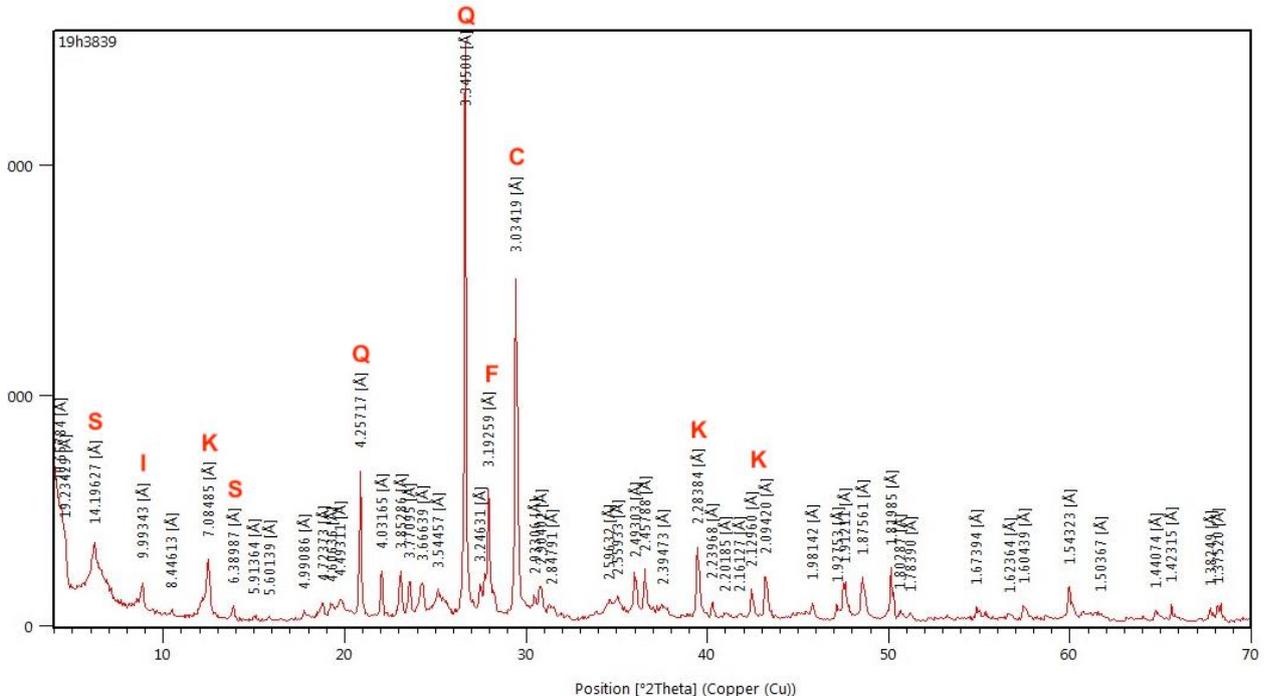


Figure 1. XRD analysis of BK adsorbent (S: Smectite, I: Illite, K: Kaolinite, Q: Quartz, C: Calcite, F: Feldspar)

Qualitative detailed clay analysis, revealed that the BK adsorbent was composed of calcite, quartz, illite, plagioclase, dolomite, chlorite, alkali feldspar and mica minerals.

**FTIR Analysis**

The FTIR spectrum of the BK adsorbent is shown in Figure 2.

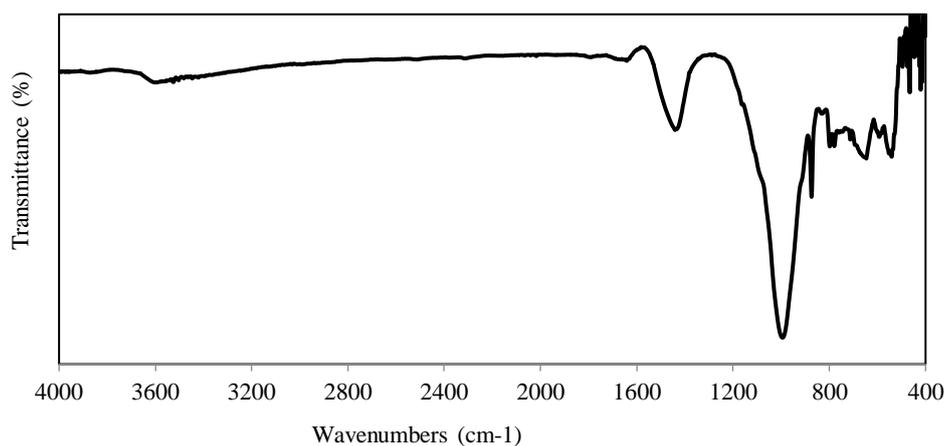


Figure 2. FTIR spectrum of BK adsorbent

The peak in  $3604\text{ cm}^{-1}$  is in the  $-\text{OH}$  groups and is caused by the  $\text{H}-\text{O}-\text{H}$  vibrations of the water adsorbed on the clay surface (Caliskan, Sogut, Savran, Kul, & Kubilay, 2017; Felhi, Tlili, Gaied, & Montacer, 2008; Madejova & Komadel, 2001). The significant sharp peak at  $1435\text{ cm}^{-1}$  indicates Si-O stretching absorption and confirms the presence of a high amount of calcite in the clay. The characteristic bands of the calcite mineral are  $1435$ ,  $873$  and  $713\text{ cm}^{-1}$ . The  $1641\text{ cm}^{-1}$  band corresponds to the vibration of water molecules ( $\text{H}-\text{O}-\text{H}$ ) trapped in the silica matrix. The IR peak at  $1795\text{ cm}^{-1}$  and  $2515\text{ cm}^{-1}$  also indicates the presence of calcite and dolomite. The strong band at  $993\text{ cm}^{-1}$  (due to Si-O stretching) is the main characteristic band of quartz (Biçer, 2019; Caliskan et al., 2017). Other quartz bands at  $798$  and  $779\text{ cm}^{-1}$  are also present (Caliskan et al.,

2017; Gadsden, 1975). The band at  $873\text{ cm}^{-1}$  is bound to Fe-Al-OH of montmorillonite (Caliskan et al., 2017; Felhi et al., 2008; Madejova & Komadel, 2001). The bands at  $495$  and  $476\text{ cm}^{-1}$  are attributed to bending vibrations of Si-O-Al and Si-O-Si, respectively. The stretching vibration of adsorbed water molecules is observed at  $3419\text{ cm}^{-1}$ . Another characteristic band for bending vibrations of adsorbed water appeared as a small band at  $1635.64\text{ cm}^{-1}$ . Stretching vibrations of surface hydroxyl groups (Si-Si-OH or Al-Al-OH) are observed at  $3525\text{ cm}^{-1}$  (Caliskan et al., 2017; Madejová, 2003). The results obtained are consistent with the literature.

#### SEM Analysis

The examination of the BK adsorbent by scanning electron microscopy is presented in Figure 3.

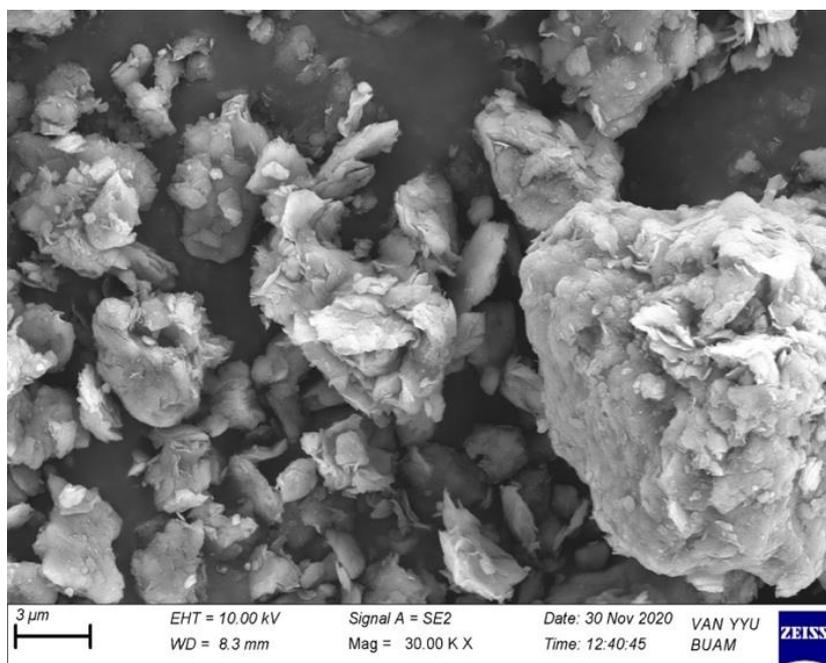


Figure 3. Scanning electron microphotograph of BK adsorbent

The SEM image of the BK adsorbent reveals a variety of sizes and shapes. Quadrangular structures represent calcite, hexagonal structures represent chlorite, hexagonal prism-like shapes represent quartz, shapes like curly lettuce leaf represent smectite (montmorillonite), hexagonal-shaped plates

show kaolinite, shapes like elongated branches represent illite (Caliskan et al., 2017; Karakaya, Karakaya, & Faure, 2007).

#### BET Analysis

The specific surface area of the BK adsorbent was determined as  $57.10\text{ m}^2\text{g}^{-1}$ .

### Adsorption Studies

#### Effect of pH

CV solutions were produced using HCl and NaOH at a concentration of  $10 \text{ mgL}^{-1}$  at 313 K and

pH levels (2, 3, 4, 5, 6, 7, 8). 0.2 g BK adsorbent was used in the batch system to investigate the pH effect. The results obtained are shown in Figure 3.

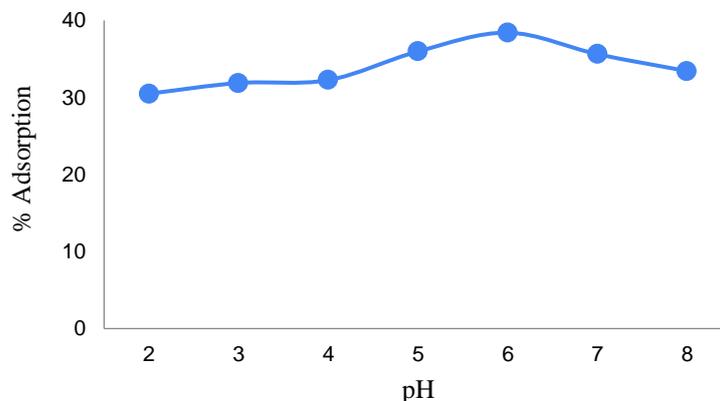


Figure 4. The effect of pH on BK adsorbent of CV dyestuff (adsorbent amount = 0.2 g, concentration =  $10 \text{ mgL}^{-1}$ , temperature = 313 K)

The percentage of CV dyestuff adsorption (%) versus the pH values of the BK adsorbent is given in Figure 4. It is understood that the CV dyestuff selectivity of the BK adsorbent increases at pH=6. The optimum adsorption percentage was obtained at pH = 6. The effect of pH on adsorption is related to its ability to ionize adsorbing molecules. The number of positively charged ions on the surface of the BK adsorbent reaches a maximum at pH=6. Due to the cationic nature of CV, the adsorption percentage increases with increasing pH, as the adsorption capacity and the number of OH<sup>-</sup> ions accumulated on the adsorbent surface increase. The low CV dye removal performance of BK adsorbent in pH >6 and pH <6 solutions is due to the fact that dye cations do not prefer adsorption due to the existing electrostatic

repulsion. In addition, the presence of H<sup>+</sup> ions competing for adsorption sites on the BK adsorbent with dye cations reduces CV adsorption. The reduced percentage of dye removal in an alkaline medium may be due to adsorbent surface hydrolysis, which creates positively charged areas (Collins & Elijah, 2019; Tural, Ece, & Tural, 2018). Similar results have been reported for adsorption on CV dyestuff using acid-activated clay (Collins & Elijah, 2019) and potato skin (Lairini et al., 2017).

#### Effect of Adsorbent Amount

CV dye solutions were prepared at pH: 6 and  $10 \text{ mgL}^{-1}$  concentration. At 313 K, the quantity of adsorbent was studied with 0.05 g, 0.1 g, 0.2 g, 0.4 g, 0.6 g, 0.8 g, 1 g BK adsorbent. The results are shown in Figure 5.

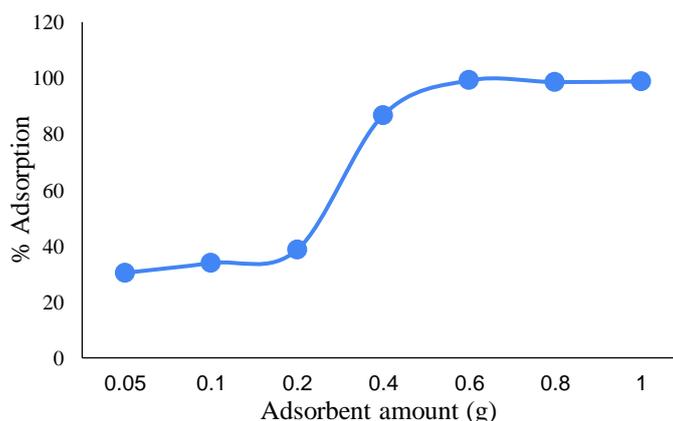


Figure 5. The effect of the amount of adsorbent on the BK adsorbent of the CV dyestuff (pH:6.0, concentration =  $10 \text{ mgL}^{-1}$ , temperature = 313 K)

The adsorption capacity is affected by the amount of adsorbent, which is an important parameter in determining the amount of adsorption (Kumari, Krishnamoorthy, Arumugam, Radhakrishnan, &

Vasudevan, 2017). As the amount of adsorbent increases, so does the surface area of the adsorbent for CV dye molecules and the active sites for adsorption increase. This is because the CV dyestuff does not

saturate the active sites on the adsorbent surface. As the amount of adsorbent increases, so does the adsorption percentage. As a result, specific surface areas are associated with adsorption. It is understood that a specific amount of BK adsorbent can only adsorb a specific amount of dyestuff (Tural et al., 2018). Thus, the adsorption capacity of the dye rose as the amount of adsorbent increased and reached an equilibrium value of 0.6 g of adsorbent (Figure 5) (Bayramoglu, Altintas, & Arica, 2009; Kumari et al., 2017). The adsorbent comes into contact with less CV dyestuff after equilibrium, which means that the active sites in the adsorbent remain

unsaturated. Therefore, the adsorption value decreased (Tural et al., 2018). The remaining studies were carried out 0.6 g of adsorbent.

#### Effect of Interaction Time

The batch system was used to investigate the interaction time of CV dyestuff solution ( $70 \text{ mgL}^{-1}$ , pH: 6.0) at 313 K temperature with BK adsorbent (0.6 g). The effect of interaction time (0, 1, 3, 5, 7, 10, 15, 25, 35, 45, 60, 75, 90 min) on BK adsorption on CV dyestuff is shown in Figure 6.

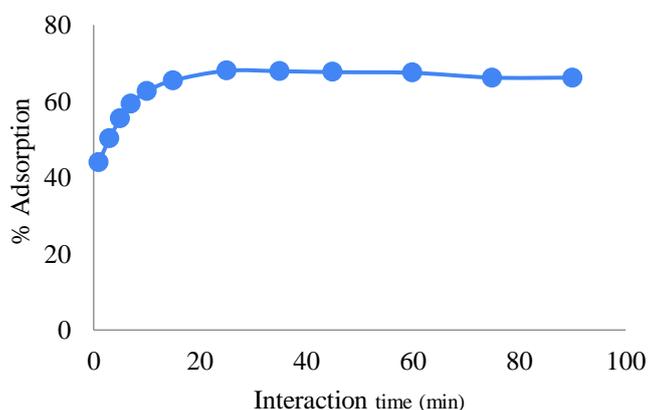


Figure 6. The effect of interaction time on the amount of adsorption (pH:6.0, adsorbent amount = 0.6 g, concentration =  $70 \text{ mgL}^{-1}$ , temperature = 313 K)

As shown in Figure 6, the CV dye adsorption ability of BK adsorbent is rapid at the beginning, then slow adsorption occurs, and the adsorption reaches equilibrium at 25 min. The fact that the equilibrium is reached quickly shows that the BK adsorbent is very efficient for CV dye adsorption. The adsorption tendency of the CV dyestuff as a function of the interaction time revealed that the adsorption occurred in two different stages. The first fast phase occurs in a very short amount of time, followed by the slow adsorption phase which takes a relatively longer amount of time. Slow adsorption is observed after reaching equilibrium, due to the reduction of vacancies when the binding sites reach saturation. As a result, the adsorption capacity did not change significantly. Furthermore, slow adsorption

may be due to the intraparticle diffusion process dominating adsorption (Manzoor, Nadeem, Iqbal, Saeed, & Ansari, 2013; Shoukat, Bhatti, Iqbal, & Noreen, 2017; Ullah, Nadeem, Iqbal, & Manzoor, 2013). These results are in line with previous studies for different adsorbents as a function of contact time (El Haddad, Slimani, Mamouni, ElAntri, & Lazar, 2013; Mahamad, Zaini, & Zakaria, 2015; Ogata, Imai, & Kawasaki, 2015; Shoukat et al., 2017).

#### Effect of Concentration

With a 25 minute interaction time, the adsorption of CV dyestuff on the BK adsorbent (0.6 g) at 313 K was investigated with solutions of various concentrations (10, 30, 50, 70 and  $100 \text{ mgL}^{-1}$ ) (Figure 7).

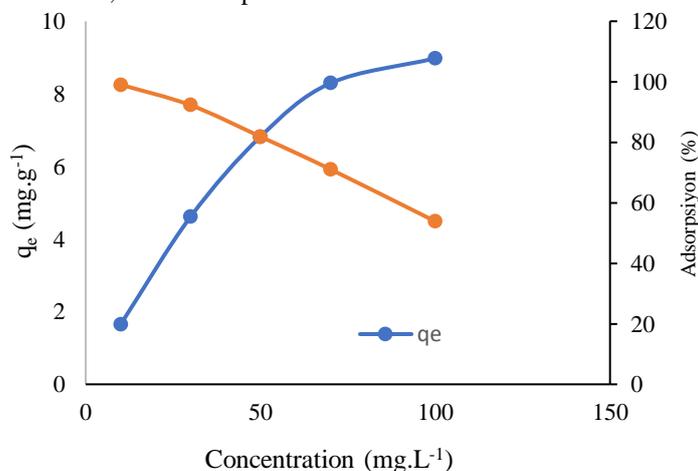


Figure 7. Effect of dye concentration on adsorption capacity (pH = 6.0, temperature = 313 K, amount of adsorbent = 0.6 g, interaction time: 25 min)

The adsorption capacity increases as the CV dyestuff concentration increases, whereas the adsorption percentage decreases. Adsorption of CV dyes is highly

concentration-dependent. The amount of dye surrounding the active sites on the adsorbent surface is mostly responsible for the increase in  $q_e$  values as CV

concentrations increase.. As the concentrations of CV dyestuff increases, more dyestuff surrounds the adsorption areas on the adsorbent surface, and therefore the CV is adsorbed more by the adsorbent. The percentage of adsorption decreases as the concentration increases, while the amount of adsorbent remains constant (Tural et al., 2018). The adsorbed percentage of dyestuff fell from 99 percent to 54 percent while the adsorption capacity of BK adsorbent increased from 1.65 mgg<sup>-1</sup> to 8.98 mgg<sup>-1</sup>, (although the concentration increased from 10 mgL<sup>-1</sup> to 100 mgL<sup>-1</sup>). Similar results have been previously reported by other researchers for different adsorbents before (R. Ahmad, 2009; Aksakal & Ucun, 2010; Idrissi, Miyah, Benjelloun, & Chaouch, 2016; Lairini et al., 2017; Shoukat et al., 2017). The maximum amount of CV dye adsorbed by the BK adsorbent is 8.98 mg.g-1 (Figure 7).

### Adsorption Isotherms

The balance between the CV dyestuff concentration remaining in the aqueous solution and the adsorbed CV dyestuff concentration was determined using Langmuir, Freundlich and Dubinin Radushkevich (D R) isotherm models.

#### Langmuir Isotherm

It is calculated using the linear equation of the Langmuir isotherm in Equation 3.

$$\frac{C_e}{q_e} = \frac{1}{q_m K_L} + \frac{C_e}{q_m} \quad (3)$$

$C_e$  (mgL<sup>-1</sup>) is the equilibrium concentration,  $q_e$  (mgg<sup>-1</sup>) is the adsorption capacity at equilibrium,  $q_m$  (mgg<sup>-1</sup>) is the maximum adsorption capacity,  $K_L$  (Lmg<sup>-1</sup>) is the Langmuir adsorption constant. According to Langmuir isotherm theory, the adsorbate material assumes a single layer on a homogeneous adsorbent surface (Kireç, Alacabey, Erol, & Alkan, 2021). Correlation coefficients ( $R^2$ ) of 0.9935, 0.9968 and 0.9972, respectively, were calculated for the CV dyestuff (Table 2).

In equation 4, starting concentration is  $C_0$  (mgL<sup>-1</sup>). In addition, the separation factor ( $R_L$ ) is a unitless constant that is used to predict whether or not an

adsorption process is favourable.  $R_L$  values indicate that adsorption is unfavorable when ( $R_L > 1$ ), linear when ( $R_L = 1$ ), when favorable ( $0 < R_L < 1$ ), and irreversible when ( $R_L = 0$ ) (Caliskan et al., 2011).

$$R_L = \frac{1}{1 + K_L C_0} \quad (4)$$

#### Freundlich Isotherm

The linear equation of the Freundlich isotherm is given in equation 5 (Erol, 2016).

$$\ln q_e = \ln K_F + \frac{1}{n} \ln C_e \quad (5)$$

The adsorption capacity is denoted by  $K_F$  (Freundlich constant), and  $n$  is the adsorption intensity. According to Freundlich, the adsorption sites on the surface of an adsorbent are heterogeneous, which means that they consist of different types of adsorption sites (Kireç et al., 2021).

#### Dubinin-Radushkevich (D-R) Isotherm

The Dubinin-Radushkevich (D-R) isotherm was calculated using equations 6, 7, 8.

$$\ln q_e = \ln q_m - k \varepsilon^2 \quad (6)$$

$$\varepsilon = RT \ln \left( 1 + \frac{1}{C_e} \right) \quad (7)$$

$$E = (2k)^{-1/2} \quad (8)$$

$q_e$  is the quantity of CV dye adsorbed per unit BK adsorbent (mgg<sup>-1</sup>),  $k$  is the the adsorption energy (mol<sup>2</sup>/kJ<sup>2</sup>) constant,  $q_m$  is the DR adsorption capacity (mgg<sup>-1</sup>),  $\varepsilon$  is the Polanyi potential (kJmol<sup>-1</sup>),  $T$  is the temperature (K), and  $R$  is the gas constant (kJ/Kmol).

Equation 8's adsorption energy  $E$  (kJmol<sup>-1</sup>) gives information about the adsorption mechanism. The adsorption process is classified as chemical, ion exchange or physical adsorption based on the determined  $E$  value. In the case of  $E < 8$  kJmol<sup>-1</sup>, the adsorption mechanism is realized by physical interactions. Regarding  $8 < E < 16$  kJmol<sup>-1</sup>, the adsorption process is proceeded by ion exchange.  $E > 16$  kJmol<sup>-1</sup> values indicate that chemical interactions are used to realize the adsorption mechanism (İhsan Alacabey, 2014).

Table 2. Langmuir, Freundlich and D-R isotherm constants

T(K)	Langmuir			Freundlich				D-R		
	$K_L$ (Lmg <sup>-1</sup> )	$q_m$ (mgg <sup>-1</sup> )	$R^2$	$n$	$1/n$	$K_F$ (mgg <sup>-1</sup> )	$R^2$	$q_m$ (molg <sup>-1</sup> )	$E$ (kJmol <sup>-1</sup> )	$R^2$
298	0.2957	8.8797	0.9935	3.1870	0.3138	2.7117	0.9853	6.5180	2.6024	0.8523
313	0.4969	9.2842	0.9968	3.5165	0.2844	3.3974	0.9856	7.0329	3.7111	0.8750
323	0.6084	10.2475	0.9972	3.5731	0.2829	3.9085	0.9765	7.5570	4.3640	0.8609

Table 3.  $R_L$  values for adsorption of CV onto BK adsorbent

$C_0$	298 K	313 K	323 K
10	0.2527	0.1675	0.1412
30	0.1013	0.0629	0.0519
50	0.0634	0.0387	0.0318
70	0.0461	0.0279	0.0229
100	0.0327	0.0197	0.0162

The adsorption was found to be suitable for the Langmuir model, as shown in Table 2. In other words, it demonstrates that the adsorption is monolayer and homogeneous (İhsan Alacabey et al., 2020; Erol, Tatar, Veyisoğlu, & Tokathı, 2021). It was determined that the RL separation factors of  $0.0162 \leq R_L \leq 0.2527$  for the CV dyestuff on the BK adsorbent were between 0 and 1, which indicated favourable adsorption (Table 3).

The Freundlich constant ( $K_F$ ) varies between 2.7117 mg/g and 3.9085 mg/g, depending on the adsorption capacity and the temperature range examined. Since the  $K_F$  value increases with increasing temperature, the adsorption interaction is endothermic. The constant  $n$  determines the type of process: if  $n=1$ , the adsorption is linear; if  $n<1$ , adsorption is a chemical process; if  $n > 1$ , the adsorption takes place in a physical process (İhsan Alacabey, 2022). Thus, from Table 2, the  $n$  values for all the temperatures examined in this study was determined as 3.1870, 3.5165, and 3.5731. The most common condition is  $n>1$ . Any factor that causes dispersion of surface areas or a decrease in adsorbent-adsorbate interaction due to increased surface density can cause it. Values in the range of 1-10 show that CV dyestuff on BK adsorbent is adequate for adsorption and represents physical adsorption on the adsorbent (Shin & Kim, 2016).

As seen in Table 2, since the  $E$  value is less than  $< 8$  kJmol<sup>-1</sup>, the adsorption process is physical.

#### Adsorption Thermodynamics

Table 4. Thermodynamic parameter values for adsorption of CV dyestuff on BK adsorbent

$C_0$	$\Delta H^\circ$ , kJ/mol	$\Delta S^\circ$ , J/mol	$\Delta G^\circ$ , kJ/mol		
			298 K	313 K	323 K
10	39.68	165.16	-9.52	-12.07	-13.63
30	33.87	127.98	-4.17	-6.45	-7.30
50	27.24	101.23	-3.11	-3.92	-5.78
70	16.19	59.56	-1.60	-2.34	-3.12
100	11.60	38.85	-0.04	-0.40	-1.05

$\Delta H^\circ$ ,  $\Delta G^\circ$  and  $\Delta S^\circ$  values are given in table 4.  $\Delta H^\circ$  values were determined to be in the range of 39.68 to 11.60 kJ mol<sup>-1</sup>. Positive  $\Delta H^\circ$  values indicate that the adsorption is endothermic. Also, the adsorption enthalpy is less than 40 kJ mol<sup>-1</sup>, which indicates that the physical mechanism is controlling the adsorption processes (Caliskan et al., 2011; Sogut & Caliskan, 2017). In addition,  $\Delta S^\circ$  values were found to range from 165.16 to 38.8 JK<sup>-1</sup>mol<sup>-1</sup>. Positive values of  $\Delta S^\circ$  indicate an increase in randomness at the solid-liquid interface during CV adsorption onto the adsorbent (İ Alacabey, 2006). Negative  $\Delta G^\circ$  values show that adsorption occurs spontaneously (Alkan, Kul, Alacabey, & Erol, 2014). These values decrease as the temperature increases. Also, adsorption is better obtained at higher temperatures (Caliskan et al., 2011).

#### Conclusion

The removal of CV dyestuff in the aqueous solution on the BK adsorbent was examined using the batch adsorption method.

Gibbs free enthalpy ( $\Delta G^\circ$ ), adsorption entropy ( $\Delta S^\circ$ ) and adsorption enthalpy ( $\Delta H^\circ$ ) all play an important role in determining the adsorption type in thermodynamics. It is calculated by using equations 9, 10, 11, 12.

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \quad (9)$$

$\Delta G^\circ$  is free energy change (kJmol<sup>-1</sup>),  $\Delta S^\circ$  is Entropy change (kJmol<sup>-1</sup>K<sup>-1</sup>),  $\Delta H^\circ$  is enthalpy change (kJmol<sup>-1</sup>T<sup>-1</sup>),  $T$  is the temperature (K).

$K_c$  is calculated using equation 10 in the calculation of Gibbs free energy in the adsorption process.

$$K_c = C_a/C_e \quad (10)$$

$C_a$  is the concentration of the substance adsorbed by the BK adsorbent (mgL<sup>-1</sup>),  $C_e$  is the concentration of the substance remaining in the solution (mgL<sup>-1</sup>), and  $K_c$  is the equilibrium constant,

The cut-off point of the graph of  $K_c$  drawn against the initial CV dyestuff concentrations ( $C_0$ ) yields the  $K_c$  value. Afterwards, if the  $K_c^0$  value is written in equation 11, the Gibbs free energy of adsorption is found. The Gibbs free energy determines the degree of the adsorption process' spontaneity.

$$\Delta G^\circ = -RT \ln K_c^0 \quad (11)$$

$$\ln K_c^0 = \frac{\Delta S^\circ - \Delta H^\circ}{R} \times \frac{1}{T} \quad (12)$$

$R$  is the gas constant (8.314 J mol<sup>-1</sup> K<sup>-1</sup>).

Using equation 12,  $\Delta H^\circ$  and  $\Delta S^\circ$  are calculated from respectively the slope and the cut-off point of the graph of  $\ln K_c^0$  drawn against the  $1/T$  value.

1. The Langmuir model provides the optimal adsorption, which is monolayer and homogeneous, based on the equilibrium adsorption data for CV aqueous solution.

2. The  $K_F$  value increases with increasing temperature in the Freundlich model, which indicates that the adsorption interaction is endothermic. The  $n$  value in the range of 1-10 indicates that it is suitable for CV dyestuff adsorption on the BK adsorbent and represents the physical adsorption on the adsorbent.

3. The fact that the  $E$  value is less than 8 kJmol<sup>-1</sup> in the Dubinin-Radushkevich (D-R) model indicates that the adsorption process is physical.

4. The adsorption enthalpy values are less than 40 kJ mol<sup>-1</sup> in all cases studied, confirming that the adsorption process is regulated by a physical rather than a chemical mechanism (Sogut & Caliskan, 2017).

This study showed that the adsorption process for Crystal Violette removal with Bardakçı Clay, endothermic, both physically and spontaneously. As a

result, it shows that Bardakçı Clay can be used as a low-cost, effective adsorbent for CV removal.

### Compliance with Ethical Standards

#### Conflict of interest

The authors declared that for this research article, they have no actual, potential or perceived conflict of interest.

#### Author contribution

The contribution of the authors to the present study is equal. All the authors read and approved the final manuscript. All the authors verify that the Text, Figures,

and Tables are original and that they have not been published before.

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Ethics committee approval is not required.

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