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# Investigation of a basic dye adsorption from aqueous solution onto raw and pre-treated bentonite surfaces

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## Abstract

The effects of temperature, pH and ionic strength on the adsorption of crystal violet ($CV^+$) by raw, Ni-saturated (Ni-), Co-saturated (Co-) and Zn-saturated (Zn-) bentonite samples were investigated. The amounts of $CV^+$ adsorbed in equilibrium at 298.15 K were 0.27, 0.37, 0.49 and 0.54 mmol $g^{-1}$ bentonite, which correspond to 108%, 148%, 196% and 216% of the cation exchange capacity (CEC) of the raw, Ni-, Zn- and Co-saturated bentonite samples, respectively. The adsorption of the dye on these samples is pH-independent within the range (2.5–8.5), and it increases with ionic strength from 0 to 0.6 mol $l^{-1}$. Thermodynamic and Langmuir parameters showed that cation-saturated bentonite samples have relatively stronger ability than the raw bentonite towards the crystal violet ($CV^+$) cation.

*Keywords:* Metal-saturated bentonite; Adsorption thermodynamics; Charge reversal; Crystal violet; Ionic strength

## 1. Introduction

Cationic dyes, commonly known as basic dyes, are widely used in acrylic, nylon, silk, and wool dyeing. This group of dyes include a broad spectrum of different chemical structures, primarily based on the substituted aromatic groups. Due to the complex chemical structure of these dyes, they are resistant to breakdown by chemical, physical and biological treatments. Furthermore, any degradation by physical, chemical or biological treatments may produce small amount of toxic and carcinogenic products. Adsorption is known to be a promising technique, which has great importance due to the ease of operation and comparable low cost of application in the decoloration process. Although activated carbons have been most widely used for the adsorption of dyes, clay materials have been increasingly gaining attention because they are cheaper than activated carbons and their sheet-like structures also provide highly specific surface area [1–3].

Adsorption of cationic dyes by clay minerals has been widely studied to understand the co-adsorption behavior towards pesticides [4,5], color removal of industrial effluents [6,7], ion type inorganic antibacterial material properties [8,9], ecologically important intermediates [10], and determination of the surface properties of clays [11–15]. Margulies and co-workers [16] showed that when negatively charged clay particles are introduced into an ionic solution, migration of the ions occurs, and either neutral or charged complexes may arise from the binding of monovalent organic cations to monovalent sites through several mechanisms. Furthermore, a second organic cation bound to a neutral complex by hydrophobic interactions leads to a charge reversal of the particle.

In this work, the effects of pH, ionic strength of medium and adsorption temperature on the interaction of crystal violet with the raw, Ni-saturated (Ni-), Co-saturated (Co-) and Zn-saturated (Zn-) bentonite samples were investigated in order to elucidate the role of bentonite surface in the sorption process of basic dye ($CV^+$). Thermodynamic parameters which were obtained from adsorption equilibrium experiments using the van't Hoff equation contribute to the driving force for adsorption reactions.

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## 2. Experimental

### 2.1. Materials

The bentonite sample (from Unye, Turkey) was ground and washed in deionized water several times at a 1:10 clay/water ratio. The mixture was stirred for 3 h and then kept standing overnight. After the clear liquid was decanted off the top, the solid was exposed to slow evaporation to dryness, and then ground and sieved through a 78–120 μm size.

#### 2.1.1. Preparation of cation-saturated bentonites

The sample of raw bentonite was rehydrated with deionized water at a ratio of 10 g raw bentonite:100 ml water and 10 g metal chloride of corresponding salts was added to homoionic form. The resulting mixtures were stirred for 24 h and centrifuged at 3000 rpm until attaining chloride-ion-free form, as shown by the silver nitrate test.

The cation exchange capacities (CEC) of the samples were determined by the adsorption of Cu(II) ethylene diamine complex [17]. The values determined for raw bentonite was 0.25 mmol $g^{-1}$.

### 2.2. Chemical analysis

The chemical compositions of the raw and acid activated bentonites are given in Table 1. The mineralogical composition of the raw bentonite sample was determined from X-ray diffractograms (Fig. 1). X-ray analyses of the samples were made using the three principal lines [18]. The following mineral phases were identified: montmorillonite, quartz (α), calcite, dolomite, magnesite and mica.

### 2.3. Thermal analysis

Air dried clay samples were dispersed in 50 ml water. The suspensions were kept in the dark and after 24 h the organoclay was separated by centrifugation. Samples were washed with distilled water to remove excess dye. Thermal studies were carried out on Rigaku TG 8110 analyzer equipped with TAS 100 (range: 20–1000 °C) under flow of air at a heating rate of 10 °C $min^{-1}$. Calcinated α-alumina was taken as the reference.

### 2.4. Adsorption studies

Adsorption of $CV^+$ (analytical grade, chloride salt, obtained from Reidel-de Haen) was carried out in a batch process at various pH, temperature and salt concentration values of the medium. A 50 mg sample was mixed with a 50 ml $CV^+$ solution of known concentration in the polyethylene bottle. The pH values were adjusted by adding a few drops of dilute NaOH or HCl, and were measured by a Jenway 3040 model pH-meter, and were calibrated to pH = 4.0 and 9.0 buffer solutions. The pH increased slightly (0.1–0.3) at the end of the adsorption process. With salt added, the change in pH was between 0.2 and 0.4.

Table 1
Chemical composition of raw bentoite

| Sample | $SiO_2$ (%) | $Al_2O_3$ (%) | $Fe_2O_3$ (%) | CaO (%) | MgO (%) | $Na_2O$ (%) | $K_2O$ (%) |
|---|---|---|---|---|---|---|---|
| Raw bentonite | 62.70 | 20.10 | 2.16 | 2.29 | 3.64 | 0.27 | 2.53 |

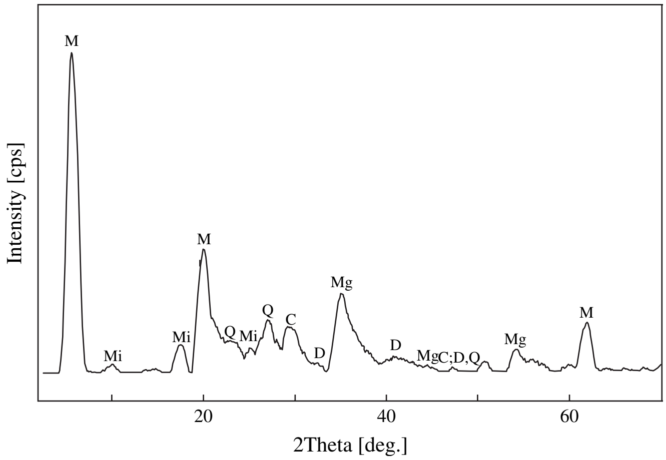
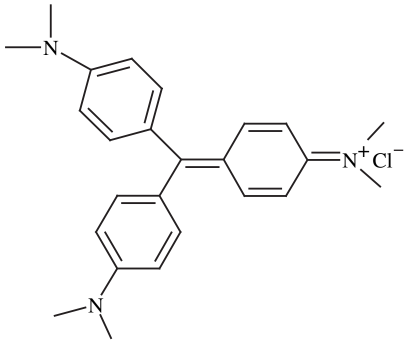


Fig. 1. The XRD patterns of the raw bentonite (M: montmorillonite, Mi: mica, Q: quartz, C: calcite, Mg: magnesite, and D: dolomite).

The adsorption process of $CV^+$ cations on each of the tested samples was completed in 24 h. Rytwo and co-workers [19] reported that the adsorption equilibrium of $CV^+$ on $Na^+$- and $Ca^{2+}$-exchanged montmorillonite was reached within 24 h and 72 h, respectively. Different equilibirium time results were given in the literature; e.g., the adsorption process of methylene blue cations on the montmorillonite samples tested by Ma and co-workers [20] and Rytwo and co-workers [19] reached the equilibrium positions in 4 h and 24 h, respectively. Different equilibirium times arise from different clay content.

The supernatant was centrifuged for 10 min at 5000 rpm at the end of the adsorption period and then it was diluted between the ratios of 1:10 and 1:125 with deionized water for obeying Lambert–Beer's laws and avoiding from dye aggregation. The amount of the dye adsorbed was determined from the difference between initial and equilibrium concentration values by measuring the absorbance at 590 nm by a Unicam UV2-100 spectrophotometer.

The structure of the dye studied is shown below:



Crystal Violet

## 3. Results and discussion

### 3.1. Thermal analysis of organo-bentonite complexes

Representative DTA curves of bentonites saturated with $CV^+$ are shown in Fig. 2. According to directions of the various peaks, the DTA curves of the organo-clay can be divided into three regions. In the first region, up to 100 °C, endothermic dehydration of clay is the major thermal reaction (the mass losses for raw and treated bentonite samples are 4.90% and 3.12%, respectively). The second region is between 330 and 600 °C, and the mass losses for $CV^+$ adsorbed raw and Co-saturated bentonite samples in this region are 13.10% and 16.17%, respectively. The exothermic oxidation of adsorbed $CV^+$ is the principial thermal reaction of this region. Exothermic peaks are associated with weight loss which increases with increasing degrees of saturation. The third region occurs at temperatures above 600 °C. The mass loss for raw and Co-saturated samples is 7.13% and 7.80%, respectively, and the exothermic DTA peaks at 622 °C may be related to the dehydroxylation of the simectite mineral and the last stages of the oxidation of the organic matter. From the present results it seems plausible that π-interactions between the aromatic entity and the oxygen plane contribute to the thermal stability of the carbon skeleton of the aromatic matter, and consequently, the exothermic peak appears together the dehydroxylation reaction of the bentonites.

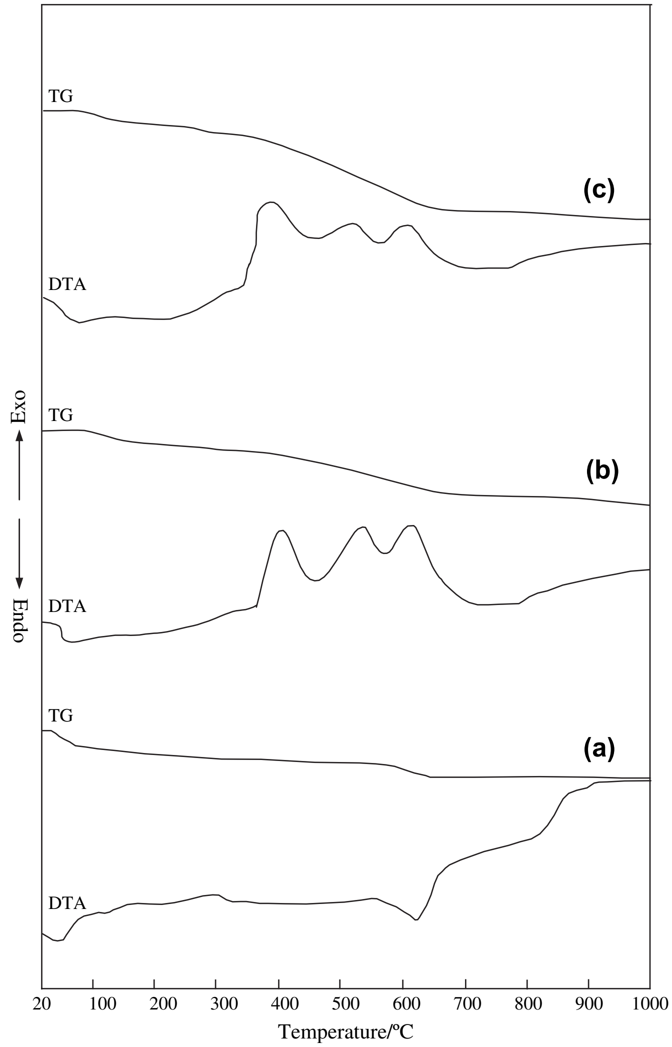


Fig. 2. Thermal analysis of raw- and $CV^+$-treated bentonite samples. (a) Raw bentonite; (b) $CV^+$ adsorbed raw bentonite; (c) $CV^+$ adsorbed Co-saturated bentonite.

### 3.2. $CV^+$ adsorption on cation-saturated bentonite surfaces

The amounts of adsorbed $CV^+$ on bentonite samples are shown in Fig. 3. In the present study, when the amount of $CV^+$ added was between 0.01 and 1.0 mmol dye $g^{-1}$ bentonite, the adsorbed amounts of adsorbed $CV^+$ cations onto raw, Ni-, Co- and Zn-saturated bentonite samples were 0.27, 0.37, 0.49 and 0.54 mmol $g^{-1}$ bentonite, which correspond to 108%, 148%, 196% and 216% of CEC, respectively. This result is different comparing to that of Rytwo and co-workers [21], who showed that the amount of adsorbed $CV^+$ on montmorillonite was 200% of the clay CEC. The difference observed here may arise from the clay crystallinity, morphology and size of the particles and the total surface area of the clays used.

The adsorption behavior of $CV^+$ on bentonite samples may be divided into two parts depending on the concentration ranges: (i) adsorption occurs at the external surfaces of the clay by ion exchange at $CV^+$ concentration below the CEC of the clay; (ii) a second organic cation adsorbs by non-columbic interactions onto clay–organic complex, giving rise to a singly positively charged structure with two organic cations and one negatively charged site in $CV^+$ concentration above the CEC of the clay. In cation-saturated bentonite samples, binding of a $CV^+$ cation to a negative surface site requires saturation of the CEC first. The dye adsorbed well above the CEC value results in charge reversal and increasing

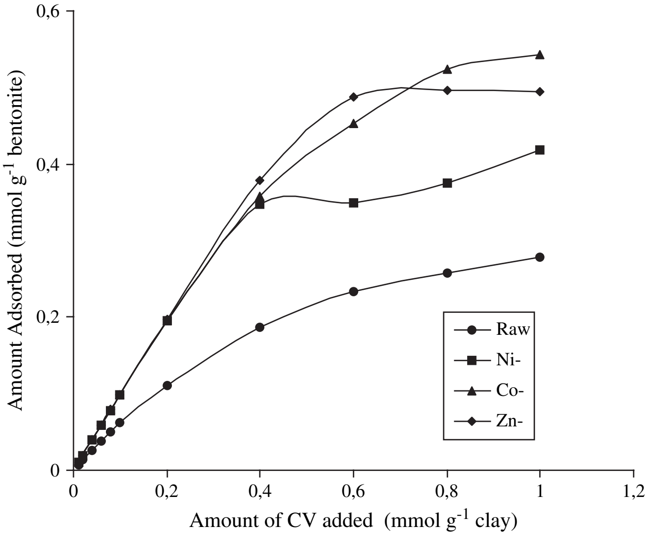


Fig. 3. Adsorption of $CV^+$ on the bentonite samples as a function of the initial $CV^+$ concentration. Contact time, 24 h; temperature, 295.15 K.

the $CV^+$ concentration induces the hydrophobic interactions among large organic molecules.

Sorption of $CV^+$ molecules on cation-saturated bentonite samples showed different sorption behavior from that of the raw bentonite which may be explained by two reasons. (i) It is known that hydrated or partially hydrated metal cations could provide more spaces due to the pore opening effect. The insertion of metal cations into the clay sheets increases the pore size and gives rise to permanent charges at the basal surface [22–25]. The differences in the adsorption capacities of raw and cation-saturated bentonites may be attributed to pore diameters and distortions in the electrical potential influence the adsorption capacity directly. (ii) The increase in the adsorption amounts of $CV^+$ molecules may also arise from enhancing reactivity of XOH (X = Si, Al) groups [26,27], which may be responsible for the particle aggregation, and which is increased by the electrical interaction energy of the clay double layers. Aggregation refers to the collapse of the diffuse double layers and the formation of aggregates of higher spaced parallel platelets.

### 3.3. Adsorption isotherms

The Langmuir model effectively describes the sorption data with all $R^2$ values >0.98.

$$\frac{C_e}{(x/m)}=\frac{1}{kb}+\frac{C_e}{b} \tag{1}$$

where $C_e$ is the equilibrium concentration of $CV^+$ remaining in the solution and $x/m$ is the quantity of $CV^+$ adsorbed per unit weight of adsorbent. The Langmuir constants are called adsorption capacity ($b$) and bonding energy constant ($k$). The Langmuir lines for each adsorbate are shown in Fig. 4, and Langmuir constants and correlation coefficients are given in Table 2.

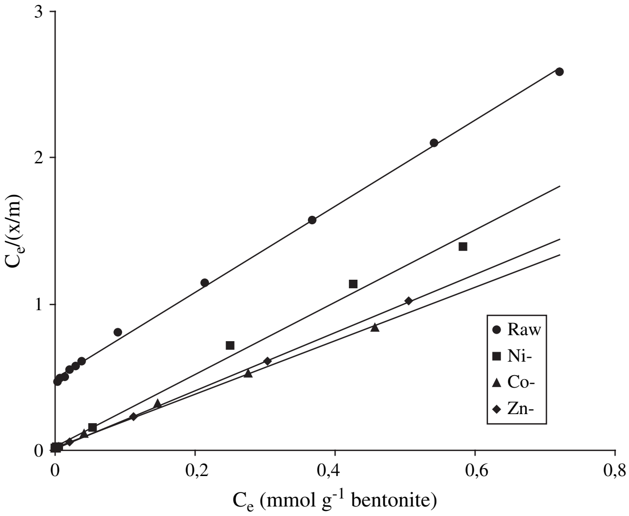


Fig. 4. Langmuir isotherm plots for the adsorption of $CV^+$ on the bentonite samples. Contact time, 24 h; temperature, 298.15 K.

Table 2
Isotherm constants of $CV^+$ adsorption on bentonite samples

| Sample | $b$ (mmol $g^{-1}$) | $k$ (L $g^{-1}$) | $R^2$ |
|---|---|---|---|
| Raw | 0.35 | 0.64 | 0.99 |
| Ni- | 0.41 | 8.96 | 0.99 |
| Co- | 0.56 | 14.86 | 0.99 |
| Zn- | 0.50 | 51.29 | 0.99 |

According to the $b$ parameter (mmol $g^{-1}$), sorption on bentonites occurs following the sequence: Co- (0.56) > Zn- (0.50) > Ni- (0.41) > raw (0.35) bentonite. Adsorption isotherms of $CV^+$ on metal-saturated bentonite are different from that on the raw bentonite, suggesting that metal saturation may influence the adsorptive properties of the bentonites.

### 3.4. Effects of ionic strength and pH

The effect of ionic strength on the adsorption ability of the samples towards $CV^+$ was investigated using NaCl solutions from 0.2 to 0.6 mol $l^{-1}$ in the presence of 1.2 mmol $g^{-1}$ at pH 6.0 for 24 h. The increase in the ionic strength of the medium had different effects on the adsorbed amounts on the bentonite samples (Fig. 5). The increase in the ionic strength also favors the approximation-association process of the clay particles, through which the dye molecules can be entrapped by newly generated centers [12]. It is known that in a clay suspension, the particles are suspended in pure water and do not agglomerate, due to the interaction of the diffuse double layers. In the presence of an electrolyte the particles may approach each other so closely that they aggregate. The addition of the electrolyte led to an increase of the mean aggregate radius. Luckham and Rossi [28] showed that a small addition of Na concentration led to the formation of edge-to-edge type aggregates, whereas a more concentrated solution resulted in the formation of very compact irregular aggregates having a multilayer structure of the face-to-face type.

To study the influence of pH on the adsorption capacities of the samples towards $CV^+$, experiments were performed for

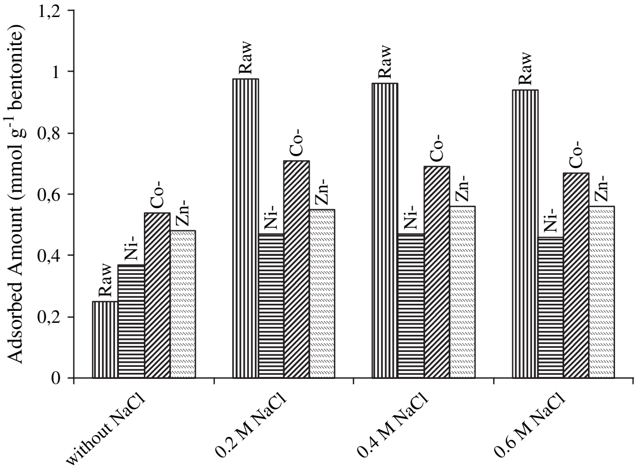


Fig. 5. Adsorption of $CV^+$ on the bentonite samples with NaCl concentration in medium. Contact time, 24 h; temperature, 295.15 K; initial $CV^+$ concentration, 1.2 mmol $g^{-1}$ bentonite.

24 h using 0.6 mmol $g^{-1}$ dye solutions with pH values changing from 2.5 to 8.5 (Fig. 6). The pH increased slightly (0.1–0.3) following the adsorption.

Fig. 6 points out that adsorption of the $CV^+$ species on bentonite samples is controlled by a pH-independent adsorption mechanism, which occurs partly by ion exchange releasing exchangeable cations in the interlayer and on basal plane surfaces and partly via non-columbic interactions between an adsorbed cation and a neutralized site.

### *3.5. Thermodynamic parameters*

To study the influence of the temperature on the adsorption capacities of the samples towards $CV^+$, experiments were performed using 0.8 mmol $g^{-1}$ dye solutions with pH 6.0 for 24 h at various temperatures.

The thermodynamic parameters of the adsorption process were determined from the experimental data obtained using the following equations:

$$\ln K_d = \frac{\Delta S}{R} - \frac{\Delta H}{RT} \tag{2}$$

$$\Delta G = \Delta H - T\Delta S \tag{3}$$

$$K_d = \frac{C_a}{C_e} \tag{4}$$

where $K_d$ is the distribution coefficient for the adsorption, $\Delta S$, $\Delta H$ and $\Delta G$ are the changes of entropy, enthalpy and the Gibbs energy, $T$ is the absolute temperature, R is the gas constant, $C_e$ (mmol $g^{-1}$) is the equilibrium adsorbate concentration in the aqueous phase and $C_a$ (mmol $g^{-1}$) is the amount of $CV^+$ adsorbed per unit mass of the adsorbent. The values of $\Delta H$ and $\Delta S$ were determined from the slopes and intercepts of the plots of $\ln K_d$ vs. $1/T$. Distribution coefficient ($K_d$) indicate the capability of a clay to retain a solute and also the extent of its movement in a solution phase [30]. According to Gomes and co-workers [31], $K_d$ is a useful parameter for comparing the sorptive capacities of different clays or materials for any particular ion, when measured under the same experimental conditions.

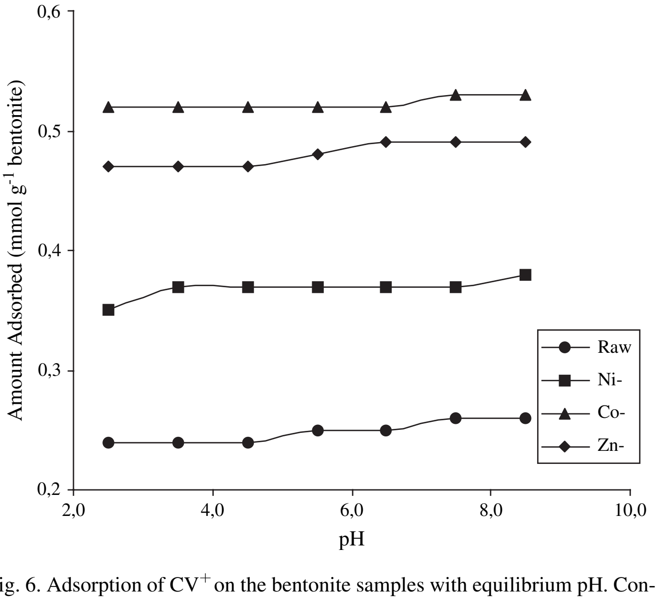


Fig. 6. Adsorption of $CV^+$ on the bentonite samples with equilibrium pH. Contact time, 24 h; temperature, 295.15 K; initial $CV^+$ concentration, 0.8 mmol $g^{-1}$ bentonite.

The $\Delta H$, $\Delta S$ and $\Delta G$ values are negative for adsorption of $CV^+$ on raw bentonite (Table 3) in agreement with the results of Rytwo and Ruiz-Hitzky [32], who used a concentration value well above 0.6 mmol dye $g^{-1}$ clay for adsorption on Wyoming montmorillonite. But Ma and co-workers [20] reached positive $\Delta H$ and $\Delta S$ values using 2.5 mmol dye $g^{-1}$ clay for adsorption on Na-, Ca- and Cu-montmorillonite samples. Generally, the change in adsorption enthalpy for physisorption is between $-20$ and 40 kJ $mol^{-1}$, but chemisorption is in the range of $-80$ to $-400$ kJ $mol^{-1}$. The negative value of the change in enthalpy ($-83.81$ kJ $mol^{-1}$) indicate that the adsorption is chemical in nature involving strong forces of attraction, and is also exothermic, thereby demonstrating that the process is stable energetically. The negative $\Delta G$ values found here indicate that the adsorption process is thermodynamically feasible at room temperature. In this study, the positive $\Delta H$ and $\Delta S$ values were obtained for pre-treated bentonite samples. The positive value of $\Delta H$ reflects that the adsorption process is endothermic in nature, but the activation energy necessary for it is not very large. The negative value of $\Delta H$ for $CV^+$ adsorption on raw bentonite indicates that the adsorption of $CV^+$ cations on this surface occurs mainly through an ion-exchange mechanism, whereas the positive values of the adsorption heats observed on the metal-saturated samples show that the adsorption on these samples are accompanied not only by the ion exchange but also by the release of water molecules hydrated around the exchangeable cations. The positive values of $\Delta S$ suggest the increased randomness at the solid–solution interface during the adsorption of $CV^+$ on pre-treated bentonites, since adsorbed $CV^+$ led to decreasing number of water molecules surrounding $CV^+$ cations and thus the degree of freedom of the water molecules increases. Because the reorientation or restructuring of water around $CV^+$–bentonite complex is very unfavorable in terms of entropy, since it disturbs the existing water structure and imposes a new and more disordered structure on the surrounding water molecules. The large differences in the values of the thermodynamic parameters between raw and pre-treated bentonite samples suggest that a non-uniform thermodynamic process participate in the bentonite–$CV^+$ interaction. Furthermore, slightly positive entropy values of $CV^+$ adsorption process on treated bentonite samples indicate an irregular increase of the randomness at the bentonite–solution interface during adsorption.

## 4. Conclusions

This study investigated the adsorption of a basic dye, namely crystal violet, onto raw and cation-saturated bentonite samples. Increasing the ionic strength increased the adsorption of $CV^+$ onto bentonite samples. Adsorption equilibrium was correlated

Table 3
Calculated thermodynamic parameters for adsorption of CV$^+$ on bentonite samples

| Sample | $\Delta H$ (kJ/mol) | $\Delta S$ (kJ/mol K) | $\Delta G$ (kJ/mol) | | | | $R^2$ |
|---|---|---|---|---|---|---|---|
| | | | 295.15 K | 300.15 K | 305.15 K | 309.15 K | |
| Raw | −83.81 | −0.26 | −4.41 | −3.06 | −1.72 | −0.64 | 0.97 |
| Ni- | 54.58 | 0.18 | −0.39 | −1.32 | −2.25 | −3.00 | 0.98 |
| Co- | 41.94 | 0.14 | −0.99 | −1.71 | −2.44 | −3.02 | 0.98 |
| Zn- | 39.03 | 0.13 | −0.66 | −1.33 | −2.00 | −2.54 | 0.99 |

Contact time, 24 h; temperature, 295.15 K; initial CV$^+$ concentration, 0.8 mmol g$^{-1}$ bentonite.

reasonably well by Langmuir isotherm. The adsorption of CV$^+$ on bentonite suspensions is highly affected by the bentonite surface features. Metal cation exchange process leads to pore widening and increase in the reactivities of basal and edge surface groups. Thus, the adsorption capacities of the cation-saturated bentonites were higher than that of the raw and acid activated bentonite. Thermodynamic results indicate that CV$^+$ adsorption onto bentonite samples is spontaneous. The adsorption enthalpies and entropies prove that the clay surfaces do not exhibit a uniform behavior towards the CV$^+$ moieties.

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