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

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Abstract

The temperature, pH and ionic strength effects on the adsorption of crystal violet (CV) by raw, base activated and Al-saturated sepiolite samples were studied. Al-saturated sepiolite has relatively weak ability for CV adsorption compared to the raw clay, whereas the highest adsorption observed for the base activated sepiolite may be due to the Na^+ ions replaced part of Mg^{2+} located at the edges of the channels. Different thermodynamic parameters for raw and pre-treated sepiolite samples indicate the adsorption of the dye component on a non-uniform surface.

Keywords: Thermodynamics; Cationic dye; Charge reversal; Adsorption isotherm; Crystal violet; Sepiolite

1. Introduction

Cationic dyes, commonly known as basic dyes, are widely used in acrylic, nylon, silk, and wool dyeing. These group dyes include a broad spectrum of different chemical structures, primarily based on substituted aromatic groups. Due to complex chemical structure of these dyes, they are resistant to breakdown by chemical, physical and biological treatment. Furthermore, any degradation by physical, chemical or biological treatments may produce small 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 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 high specific surface area [1–3].

Sepiolite is a clay mineral with a unit cell formula $Si_{12}O_{30}(OH,F)_4(H_2O)_4 \cdot 8H_2O$; a general structure formed by an alternation of blocks and tunnels [4]. In the inner blocks, all corners of silica tetrahedra are connected to adjacent blocks, but in outer blocks some of the corners contain Si atoms bound to hydroxyls (Si–OH). These silanol groups at the external surface of the silicate, are usually accessible to organic species, and act as neutral adsorption sites. In addition to that, some isomorphic substitutions occur in the tetrahedral sheet of the lattice of the mineral form leading to negatively charged adsorption sites which are occupied by exchangeable cations. These characteristics of sepiolite make it a powerful sorbent for organic molecules and organic cations [5]. When a negatively charged particle, such as a sepiolite, is introduced into a solution containing cations, the cations in suspension are driven towards the surface of the particles through several mechanisms. (i) A neutral complex may be formed by binding a monovalent cation to a monovalent negative site on the sorbent surface with electrostatic forces. (ii) Charged complexes arise from the binding of two monovalent organic cations to one monovalent site. (iii) Neutral sites occur at the external surface, a monovalently charged complex may form by the binding of one organic cation and a neutral site [6].

The aim of the present study is to investigate the adsorption behavior of a basic dye onto raw and pre-treated sepiolite samples. Crystal violet (CV) was selected as the modeled basic

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dye for this work as it is used for various purposes: as a biological stain, as a dermatological agent, as a veterinary medicine, as an additive to poultry feed to inhibit propagation of mold, intestinal parasites, and fungus, textile dying, paper printing, etc. For this aim, the nature of adsorption, the adsorption isotherm, pH effect, ionic strength effect, and the enthalpy of adsorption are investigated.

2. Experimental

2.1. Materials

Clay sample was ground and sieved 106 μm size fraction. Then, it was dried at 105 °C for 24 h and used for further experiments. Base activated sepiolite was obtained as follows: 20 g of natural sepiolite was added to a 1 M aqueous solution of NaOH (300 ml) and the suspension was refluxed for 72 h. After this, the suspension was centrifuged and the solid thoroughly washed with distilled water. Homoionic sodium sepiolite was obtained by using a liquid–solid ratio of 10 and 1 M of NaCl at room temperature for 24 h. Al-saturated sepiolite was obtained by using natural sepiolite a liquid–solid ratio of 10 and 1 M of $Al(NO_3)_3$ at room temperature for 24 h. The resulting mixtures were centrifuged at 3000 rpm for 5 min until attaining chloride and nitrate-ion-free form. XRD patterns of the products were taken on an RIGAKU 2000 automated diffractometer using Ni filtered CuK_α radiation. The cation exchange capacities (CEC) of the samples were determined by the adsorption of Cu(II) ethylene diamine complex. The values determined for raw and base activated bentonite were 0.11 mmol g^{-1} and 0.31 mmol g^{-1}, respectively.

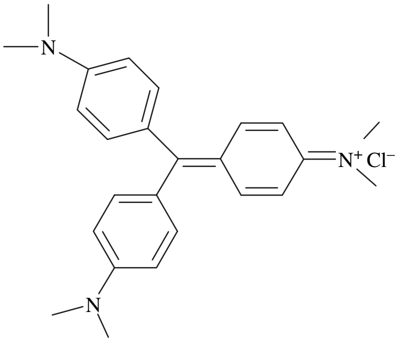
2.2. Adsorption studies

Adsorption of CV (analytical grade, chloride salt, obtained from Reidel-de Haen) was carried out in a batch process by varying CV concentration, pH value, temperature and salt concentration of the medium. Preliminary experiments demonstrated that the equilibrium was established in 24 h. Equilibration for longer times gave the same uptake. Therefore, a contact period of 24 h was finally selected for all equilibrium tests. A 50 mg sample was mixed with a 50 ml CV solution of known concentration in the polyethylene bottle. At the end of the adsorption period, the supernatant was centrifuged for 10 min at 5000 rpm. 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, which was calibrated using pH = 4.0 and pH = 9.0 buffer solutions.

The effect of the 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 0.6 mmol g^{-1} at pH 6.0 for 24 h. To study the influence of pH on the adsorption capacities of the samples for CV sorption, experiments were performed using 0.6 mmol g^{-1} dye solutions with different pH values, changing from 2.5 to 8.5 for 24 h. The pH increased slightly (0.1–0.2) after adsorption. To determine the influence of temperature on the adsorption capacities of the samples for CV sorption, experiments were performed using 0.6 mmol g^{-1} dye solutions at pH 6.0 for 24 h between 295.15 and 309.15 K.

The supernatant was centrifuged for 10 min at 5000 rpm at the end of the adsorption period and was diluted between 1:10 and 1:125 with deionized water for obeying Beer–Lambert's laws and to avoid 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. Mineralogical composition

The mineralogical compositions of the raw and acid treated bentonite samples were determined from X-ray diffractograms (Fig. 1). X-ray analysis of the samples were marked using the

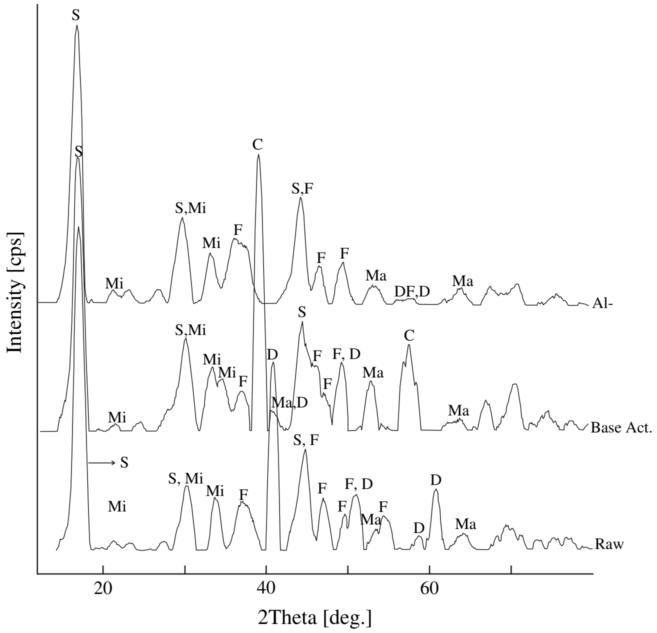


Fig. 1. The XRD patterns of the raw, base activated and Al-saturated sepiolites (S: sepiolite, Mi: mica, F: feldspar, C: calcite, Ma: magnesite, D: dolomite).

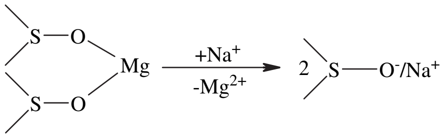
three principal lines [7]. The following mineral phases were identified in the raw sepiolite: sepiolite, feldspar, mica, dolomite and magnesite. In the base activated sepiolite sample, the intensity of sepiolite peak at 6.96, 20.16 and 34.80 (2θ) decreased. At the same time, dolomite peaks at 30.80, 41.04 and 48.64 (2θ) completely disappeared and the main reflections corresponding to calcite were formed. This transformation shows that base activation process replaced the part of Mg^{2+} located at the edges of the channels by Na^{+}, thus dolomite ($CaMgCO_3$) was transformed to calcite ($CaCO_3$). As shown in Fig. 1, Al-saturation process leads to complete disappearance of dolomite at 30.80, 41.04 and 48.64 (2θ).

3.2. CV adsorption on sepiolite samples

In order to elucidate the role of sepiolite surface in the sorption processes of CV, the adsorption on raw, base activated and Al-saturated sepiolite samples was investigated (Fig. 2).

The amounts of adsorbed CV on bentonite samples are shown in Fig. 2. In the present study, when the amounts of CV added were between 0.01 and 1.0 mmol dye g^{-1} sepiolite, the amounts of adsorbed CV cations onto raw, base activated, and Al-saturated sepiolite samples were 0.15, 0.39, and 0.05 mmol g^{-1} sepiolite, which correspond to 136%, 125% and 45% of CEC, respectively (CEC: 0.11 mmol g^{-1} clay and 0.31 mmol g^{-1} clay).

The highest amount of adsorption observed for the base activated sample may be explained in terms of the partial replacement of Mg^{2+} at the edges of the internal surfaces by Na^{+} [8]. Once the Na^{+} form of the sepiolite is obtained, the ion exchange of Na^{+} can be easily achieved than Mg^{2+} by CV cation. Such large adsorbed amounts were explained by the possibility of cationic dye molecules adsorbing on $Si{-}O^{-}$ sites, whereas dye cations can get adsorbed to charged sites (isomorphic exchanges) and neutral sites.



(1)

The differences in the adsorption capacities of samples may be attributed to surface features of sepiolite samples. The lowest adsorption observed for Al-saturated sepiolite may be arised due to two reasons: firstly, Al-saturation process leads to a pore blocking at the basal surface; secondly, Al^{3+} ions likely associate with basal or edge oxygen atoms of the silicate [9–13]. These conclusions may be explained by the fact that the aluminium cation at the edges of the sepiolite may either (i) block some adsorption site near the pore entries, or (ii) neutralize the negative charge; hence the electrostatic attractive interaction between CV molecules and clay particles should be reduced. Thus, Al-saturated sample has relatively weak ability for cation exchange and adsorption as compared to the raw sepiolite sample.

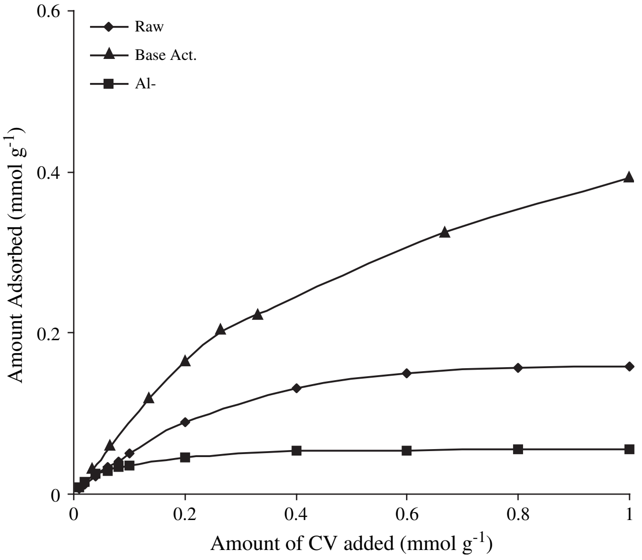


Fig. 2. Adsorption of CV on sepiolite samples as a function of the initial CV concentration. Contact time 24 h; temperature 298.15 K.

3.3. Adsorption isotherms

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

$$\frac{C_e}{(x/m)} = \frac{1}{kb} + \frac{C_e}{b} \qquad (2)$$

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; b and k are Langmuir constants. These constants are called adsorption capacity (b) and bonding energy constant (k). The Langmuir lines for each adsorbate are shown in Fig. 3, and Langmuir constants and correlation coefficients are given in Table 1.

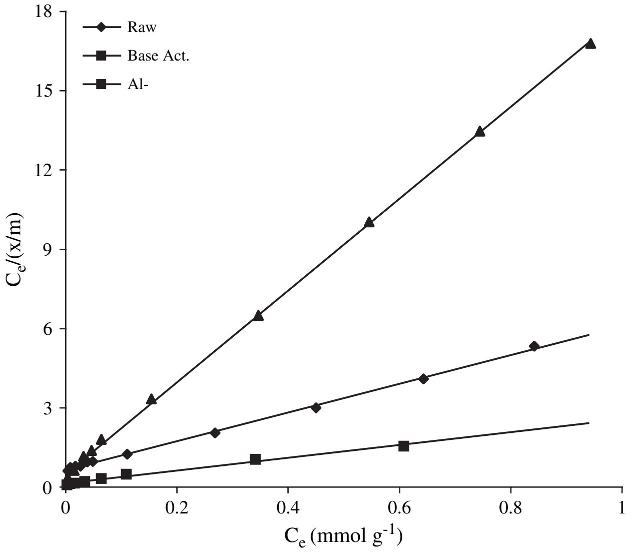


Fig. 3. Langmuir isotherm plots for adsorption of CV on the sepiolite samples. Contact time 24 h; temperature 298.15 K.

Table 1
Langmuir isotherm constants of CV adsorption on sepiolite samples

Sample	b (mmol g^{-1})	k (l mmol^{-1})	R^2
Raw	0.18	0.28	0.99
An.	0.41	3.07	0.98
Al-	0.05	0.12	0.99

According to the b parameter (mmol g^{-1}), sorption on sepiolites occurs following the sequence: base activated > raw > Al-saturated > acid act. Bentonite adsorption isotherms of CV on metal-saturated bentonite are different from the raw bentonite, suggesting that metal saturation may influence the adsorptive properties of bentonites.

3.4. Effect of pH and ionic strength

Fig. 4 indicates that adsorption on raw and base activated sepiolites show the pH-dependent dye sorption mechanism. Amphoteric sites silanol groups of sepiolite, are conditionally charged, and so pH-dependent charges can accumulate at the edges by direct H^+ or OH^- transfer from aqueous phase. Observed pH-independent plot in Fig. 4 for Al-saturated sepiolite points out that surface feature of Al-saturated sepiolite is different from that of raw sepiolite.

The influence of ionic strength on the adsorption ability of the sepiolite samples for CV was investigated using NaCl solutions of concentrations ranging from 0.2 to 0.6 mol l^{-1}. As shown in Fig. 5, increasing the ionic strength of the medium exhibited a different effect on the adsorbed amounts of CV on the base activated sepiolite from the others. Fig. 5 suggests that increased ionic strength favors the approximation–association process of the raw and Al-saturated particles, giving rise to new sites where dye molecules can be trapped [14]. Decreasing adsorbed amount of CV on raw and Al-saturated sepiolite samples after 0.2 mol l^{-1} NaCl concentration value shows that enhancing the positive surface charge by increasing the ionic strength of medium [15]. But in the base activated sepiolite sample, increase in Na ions in solution may increase the magnitude of positive surface potential by binding to the edge sites, which reduces the adsorbed amount of CV cations on the sample.

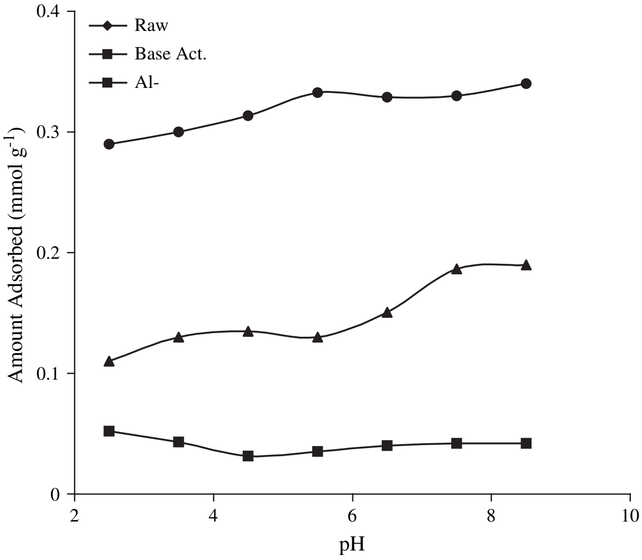


Fig. 4. Adsorption of CV on sepiolite samples with pH. Contact time 24 h; initial CV concentration 0.8 mmol g^{-1} clay; temperature 298.15 K.

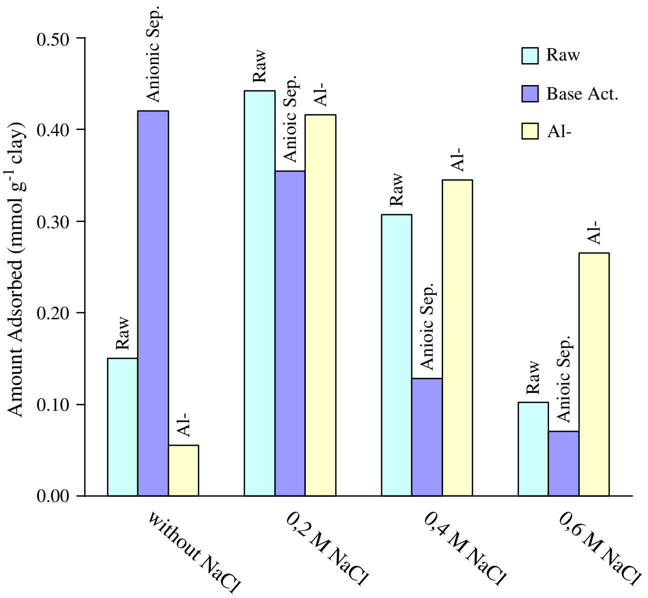


Fig. 5. Adsorption of CV on sepiolite samples with NaCl concentration in medium. Contact time 24 h; initial CV concentration 0.8 mmol g^{-1} clay; temperature 298.15 K.

3.5. Thermodynamic parameters

The thermodynamic parameters of the adsorption process were determined from the experimental data obtained at various temperatures using the equations

$$\ln K_d = \frac{\Delta S}{R} - \frac{\Delta H}{RT} \quad (3)$$

$$\Delta G = \Delta H - T\Delta S \quad (4)$$

$$K_d = \frac{C_a}{C_e} \quad (5)$$

where K_d is the distribution coefficient for the adsorption, ΔS, ΔH and ΔG are the changes of entropy, enthalpy and the Gibbs energy, T is the absolute temperature, R is gas constant, C_e (mmol g^{-1}) is 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 ΔH and ΔS were determined from the slopes and intercepts of the plots of $\ln K_d$ vs. $1/T$. Distribution coefficient (K_d) indicates the capability of clay to retain a solute and also the

Table 2
Thermodynamic parameters for adsorption of CV on sepiolite samples

Sample	ΔH (kJ/mol)	ΔS (kJ/mol K)	ΔG (kJ/mol)				R^2
			295.15 K	300.15 K	305.15 K	309.15 K	
Raw sep.	−18.79	−0.06	−1.29	−1.00	−0.70	−0.46	0.96
Base act.	34.83	0.12	−0.59	−1.19	−1.79	−2.27	0.98
Al-ES	62.27	0.21	−0.19	−1.25	−2.31	−3.15	0.99

extent of its movement in a solution phase [16]. According to Gomes and co-workers [17], K_d is a useful parameter for comparing the sorptive capacities of different clays or materials for any particular ion, when measured under same experimental conditions.

The values of ΔH, ΔS and ΔG are negative for adsorption of CV on surface of base activated sepiolite (Table 2) which is in agreement with the results of Rytwo and Ruiz-Hitzky [18], who used 0.6 mmol g^{-1} for adsorption of CV and methylene blue (MB) on Wyoming montmorillonite. But Ma and co-workers [19], who used 2.5 mmol g^{-1} for adsorption of MB on Na-, Ca- and Cu-mont. samples obtained positive ΔH and ΔS values. In our study, the absolute values of ΔH and ΔS are positive for raw and Al-saturated and negative ΔG values of CV adsorption on all sepiolite samples show that the adsorption process is thermodynamically spontaneous around room temperature. Negative ΔG values of CV adsorption on raw and Al-saturated samples show that this adsorption processes is controlled by entropy, since adsorption to these samples is often accompanied by the ion exchange, and in these cases hydrated water molecules are also released during adsorption, heats of adsorption are endothermic. The difference in values of the thermodynamic parameters between raw and pre-treated sepiolite samples suggests a non-uniform thermodynamic process participating in the clay−CV interaction. It is also seen that the positive entropy value of CV adsorption on raw and Al-saturated sepiolite samples which is indicative of the slow adsorption of dye cations. Furthermore, positive entropy value of CV adsorption on treated bentonite samples indicates the increased randomness at the sepiolite−solution interface during adsorption, and small entropies show that bentonite structure did not change significantly as a result of adsorption.

4. Conclusions

The adsorption of dye in sepiolite suspensions is highly affected by the sepiolite surface features. The observed experimental results may be concluded as follows:

- The amount of adsorbed CV cations on the base activated sepiolite is 2.6 fold higher than raw sepiolite.
- So the basic activation leads to the replacement of part of Mg^{2+} located at the edges of the channels by Na^+, the reactivity of basal and edge surface groups is enhanced and consequently the adsorption capacity of base activated is increased.
- Observed lowest adsorption capacity on the Al-saturated samples arising from the aluminium cation exchange process leads to pore blocking and the reactivity of basal or edge oxygen atoms of the silicate.
- Adsorption of the CV molecule on these surfaces is controlled by several mechanisms. (i) pH-independent adsorption, part of the adsorption is by an exchange mechanism releasing exchangeable cations in the interlayer and on basal plane surfaces and part of the adsorption is via non-coulombic interactions to one adsorbed cation and neutralized site. (ii) Amphoteric sites Si−OH groups of sepiolite are responsible for a pH-dependent adsorption on the clay edges.
- The calculated adsorption enthalpy and entropies showed that clay surfaces are not uniform in nature towards the adsorption of CV.
- Adsorption of cationic dyes on sepiolite can be considered as a simple, fast and economic method for their removal from water and wastewater.

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