

## THERMODYNAMICS OF TEXTILE CATIONIC DYE ADSORPTION ON CLINOPTILOLITE

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**ABSTRACT.** This paper studies the thermodynamics of the adsorption of textile dye on clinoptilolite in order to estimate the potential of this natural material for decolorization. The adsorption of dye in the state of equilibrium in conditions of varying temperature, as well as different models of thermodynamic equilibrium, were analyzed. The most present mineral phase of the adsorbent is the mineral clinoptilolite with a mineral content of about 85% in the tuff. The natural adsorbent, clinoptilolite, originally from Serbia, was characterized by chemical analysis, and dominated by SiO<sub>2</sub> (59.57%). The surface morphology was monitored by electron microscopy. In the research, the concentration of the textile cationic dye (10-110 g·dm<sup>-3</sup>) and the adsorption temperature (293-333 K) were varied, while the amount of clinoptilolite was constant (1 g). To characterize the equilibrium adsorption, the dye removed and the amount of adsorbed dye were calculated. In adsorption thermodynamics, several models have been studied to calculate the most important thermodynamic parameters, free energy change, enthalpy, and entropy change, depending on the choice of thermodynamic equilibrium constant. The activation energy and sticking probability were calculated using a modified *Arrhenius*–type equation.

**Keywords:** *clinoptilolite, adsorption, textile cationic dye, thermodynamics, free energy change, enthalpy change, entropy change, activation energy*

### INTRODUCTION

When dyeing textiles, on average, 50% of the dye is not fixed to the fiber for various reasons. The dye that is not absorbed by the fiber remains as in an aqueous solution and represents waste water, which must be disposed of.

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Wastewater from the textile industry has a high color, salinity due to electrolytes, then there are acids or alkalis, solids, various compounds, etc. The complex chemical structure of synthetic dyes in water makes their removal difficult. Biological, chemical and physical methods are used for the treatment of wastewater from the textile industry [1-3].

There are a variety of techniques for wastewater treatment, adsorption is relatively acceptable for decolorization and removal of other pollutants due to its economical and simple nature. There are various studies investigating the removal of different colors from aqueous solutions treating different adsorbents: coconut fiber, *Persea americana* nuts activated with phosphoric acid, boron-enriched nanoclay, activated carbon from algae, natural zeolites with a three-dimensional structure, polymer composites of zeolite, heulandite, phillipsite and clay mineral kaolin etc. [4, 5].

Clinoptilolites are, by definition, aluminosilicates of alkaline and alkaline earth cations with a three-dimensional crystal structure [6, 7]. Natural zeolite is abundant in the world and is usually considered a cheap material. There are also synthetic zeolites with high ion exchange and adsorption capacity [8].

In this paper, equilibrium adsorption and thermodynamics of textile cationic dye adsorption on natural zeolite-clinoptilolite were investigated. Practically, it is a process of decolorization of model dyed water, modelled on the waste water that is created after dyeing acrylic textiles with a cationic dye. Clinoptilolite was used as an adsorbent, whose porous particles adsorb cationic dye cations from the aqueous solution onto their surface and into the interior in the process of exchange and interactions. The goal was to obtain information about the probability, nature, predict the direction of possible adsorption mechanisms, the spontaneity of the process, as well as the types of interactions that exist between adsorbate and adsorbent.

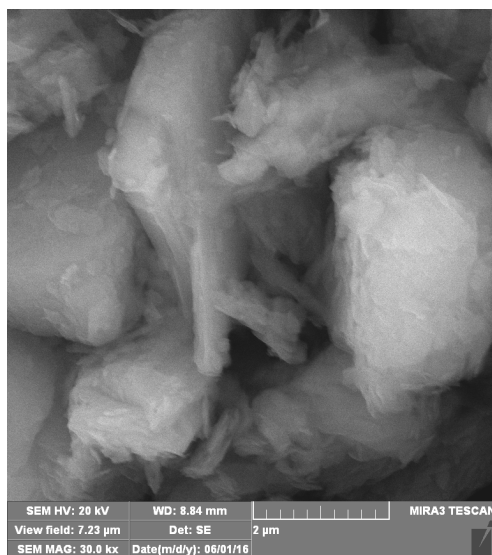
## RESULTS AND DISCUSSION

The adsorption process continues until a thermodynamic equilibrium is established between the remaining amount of adsorbate in the solution and the amount on the adsorbent. In parallel with the adsorption process, the opposite process takes place, the desorption process, which involves the return of primarily adsorbed molecules/adsorbate ions to the solution. A decrease in the rate of sorption and an increase in the rate of desorption lead to their equalization over time, so at a certain moment a thermodynamic equilibrium occurs in the adsorption system [9].

The state of the surface of each adsorbent depends on the method and conditions of production, and it is the availability of the surface that leads

to the rapid adsorption of organic molecules from aqueous solutions. According to the micrograph in Figure 1 (magnification 30.000 $\times$ ), the natural adsorbent used, clinoptilolite, is a powdery material, which has porous particles of various shapes and forms, generally below 10  $\mu\text{m}$  in size. Cubic and spherical morphology is observed for tuff particles. The morphology of clinoptilolite developed through the arrangement of particles in the form of flakes and conglomerates of compact forms.

A similar appearance of the surface morphology of clinoptilolite was also encountered by other authors [10, 11].



**Figure 1.** Micrograph of the surface of the applied adsorbent (clinoptilolite)

Chemical analysis revealed that the raw tuff fraction contains  $\text{SiO}_2$ ,  $\text{Al}_2\text{O}_3$ ,  $\text{CaO}$ ,  $\text{Fe}_2\text{O}_3$ ,  $\text{K}_2\text{O}$  and small amounts of  $\text{MgO}$ ,  $\text{TiO}_2$ ,  $\text{Na}_2\text{O}$ ,  $\text{MnO}$ ,  $\text{P}_2\text{O}_5$ ,  $\text{SO}_3$  and  $\text{Cl}$ . The results are shown in table 1. It is noticeable that silicon cation dominates, which is expected, followed by aluminum, calcium, iron, potassium, etc. cations.

**Table 1.** Chemical analysis (%) of native clinoptilolite sample

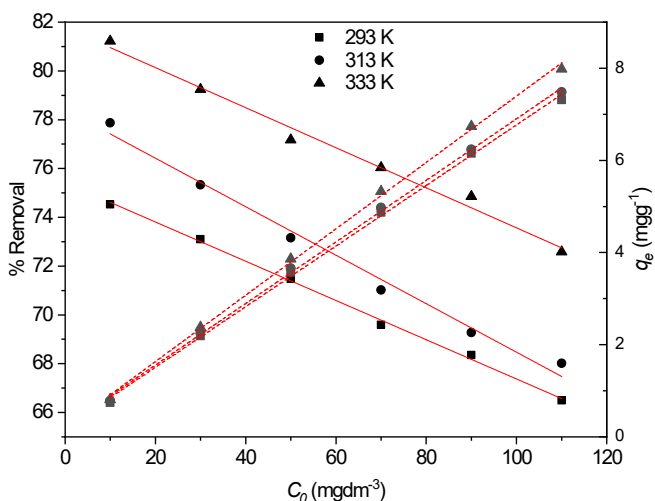
$\text{SiO}_2$	$\text{Al}_2\text{O}_3$	$\text{CaO}$	$\text{Fe}_2\text{O}_3$	$\text{K}_2\text{O}$	$\text{MgO}$	$\text{TiO}_2$	$\text{Na}_2\text{O}$	$\text{MnO}$	$\text{P}_2\text{O}_5$	$\text{SO}_3$	$\text{Cl}$
59.57	11.25	8.41	3.56	2.02	0.91	0.80	0.21	0.15	0.13	0.05	0.009

Similar chemical composition of clinoptilolite was also found by other researchers [12].

Equilibrium adsorption is of essential importance for the research of the process of removing the dye of the aqueous solution with the help of clinoptilolite, whose ability to interact and exchange cations, enables replacement with other organic or inorganic cations.

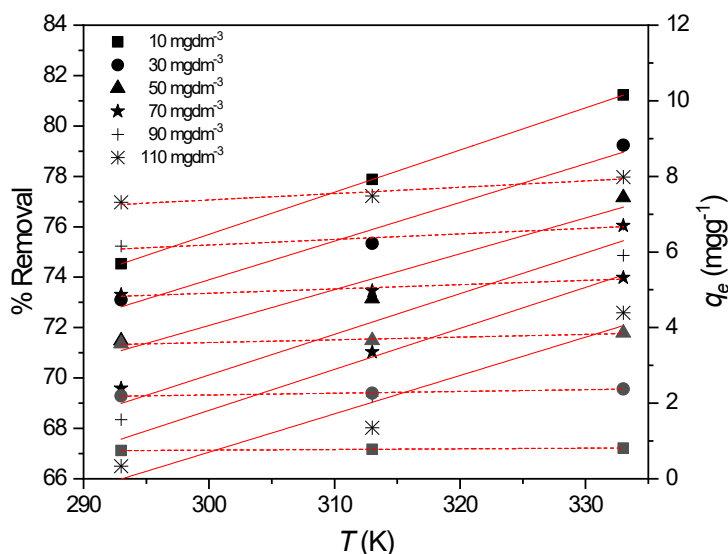
The graph in Figure 2 represents the dependence of the %Removal and the amount of adsorbed dye in relation to the change in the initial concentration of the cationic dye for three adsorption temperatures. Dependencies are represented in the form of fitted curves, in order to demonstrate the functionality of the variables. The % removal has a noticeable decrease with increasing  $C_0$ , while it increases with heating of the solution. On the other hand, the amount of adsorbed dye continuously decreases as the  $C_0$  of the cationic dye increases, with the highest numerical values at the highest temperature. Temperature promotes the adsorption of cationic dye on clinoptilolite, so a temperature of 333 K is the best choice in this case.

Increasing the pH value from 2 to 8.5 led to an increase in the adsorption of cationic blue dye on clinoptilolite. Such changes increase the %Removal of the cationic dye from the aqueous solution due to the electrostatic attraction of the dye molecules and the adsorbent surface. This can be attributed to changes in the charge polarity from positive to negative on the clinoptilolite particles. Above a pH value of 8.5, the negative charge density on the surface of the adsorbent decreases, leading to a gradual decrease in %Removal.



**Figure 2.** The %Removal (full line) and the  $q_e$  (interrupted line) of the cationic dye on clinoptilolite in relation to the initial dye concentration

Figure 3 presents graph of the influence of temperature on the %Removal and  $q_e$ . Dependencies are represented in the form of fitted curves, in order to demonstrate the functionality of the variables. In both cases, there is an increase in these parameters, with the fact that the %Removal changes more noticeably. The  $q_e$  is less sensitive to temperature changes, which is explained by the fact that it depends on several factors, the concentration of dye and adsorbent, as well as the volume of the adsorption solution. The temperature increases the adsorption, which is associated with the higher energy of the dye molecules, which are mostly in a monomolecular state, with the ability to penetrate more intensively and deeply into the porous structure of clinoptilolite.

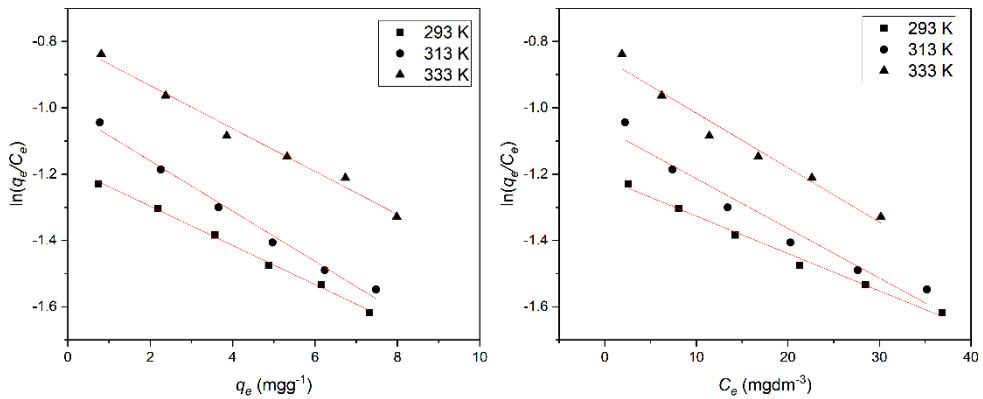


**Figure 3.** The %Removal (full line) and the  $q_e$  (interrupted line) of the cationic dye on clinoptilolite in relation to the change in temperature

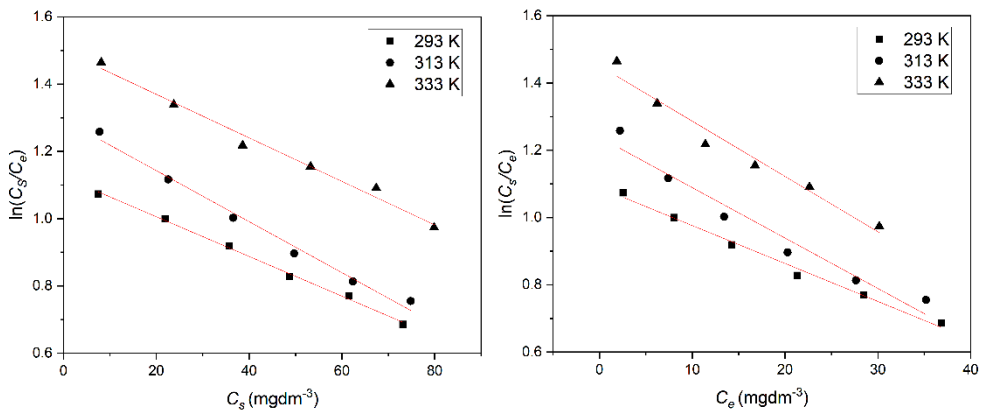
Adsorption is a phenomenon that depends on temperature, and the assessment of thermodynamic parameters reflects the feasibility of the process. Temperature has two main effects on sorption, increasing the temperature increases the rate of diffusion of paint molecules through the external boundary layer as well as through the internal pores of the adsorbent particles. The spontaneity of the system is defined by evaluating the change in free energy, there are also changes in enthalpy and entropy, which also define the conditions for the adsorption process, i.e., binding of cationic textile dye cations to clinoptilolite.

Figures 4 and 5 show the dependence of the variable parameters necessary to calculate the distribution and partition coefficient,  $K_d$  and  $K_p$ , which are used to calculate the thermodynamic equilibrium constant and other thermodynamic parameters. According to the appearance of the straight line after fitting and the distance from the experimental points, high functionality was seen on both graphs, therefore, the results are acceptable and can be used for further calculations and obtaining thermodynamic parameters.

Regarding the way of presenting of distributive and partition coefficient, the graph  $\ln(C_s/C_e):C_s$  ( $R^2=0.9886-0.9971$ ) had somewhat better results, in terms of the  $R^2$  value, compared to the graph  $\ln(q_e/C_e):C_e$  ( $R^2=0.9582-0.9918$ ), as well as the graph  $\ln(q_e/C_e):q_e$  ( $R^2=0.9857-0.9971$ ).

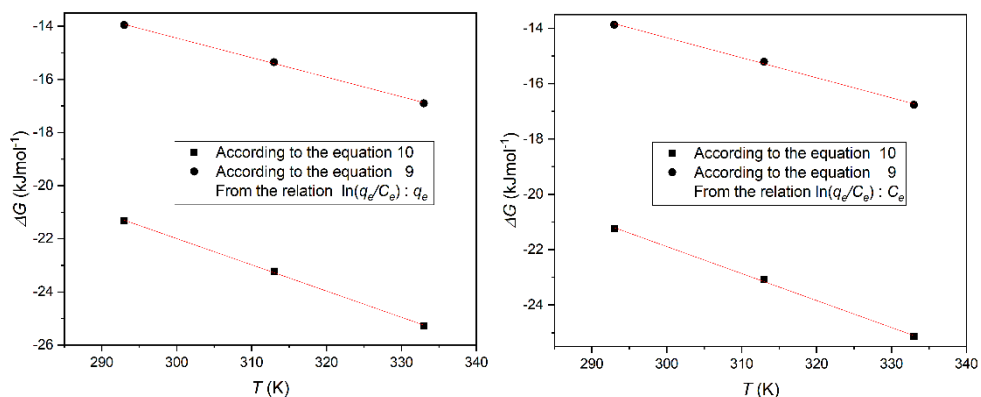


**Figure 4.** Graphs for calculating the distribution coefficient for the process of sorption of the cationic dye on clinoptilolite

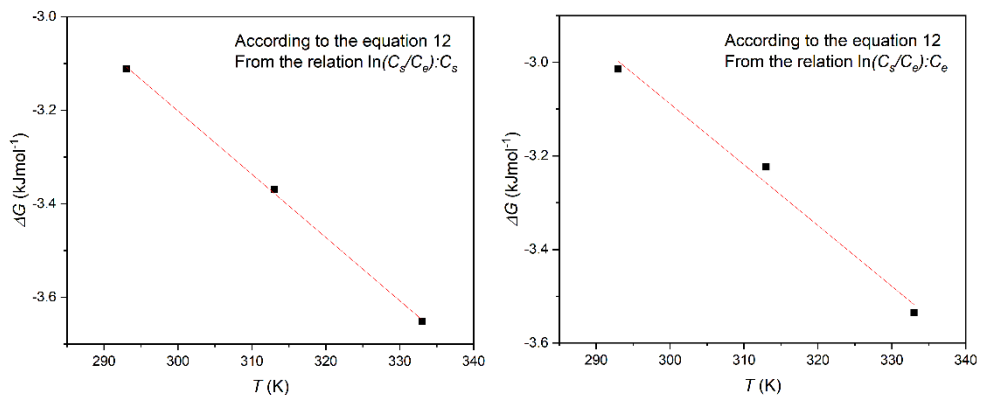


**Figure 5.** Graphs for calculating the partition coefficient for the process of sorption of the cationic dye on clinoptilolite

Figures 6 and 7 show two graphs that describe  $\Delta G : T$  dependencies, through the distribution or partition coefficient. A strong functionality of the fitted lines following the experimental points was observed. Based on these graphs, thermodynamic parameters, enthalpy and entropy of the adsorption process were determined by calculation. In general, the values of  $\Delta G$  can determine the character of the interactions between the dye molecules and the clinoptilolite, i.e., whether it is physisorption or chemisorption.



**Figure 6.** Free energy as a function of temperature ( $\Delta G$  was calculated by equilibrium constant from the distribution coefficient)



**Figure 7.** Change in free energy as a function of temperature ( $\Delta G$  was calculated by equilibrium constant from the partition coefficient)

Table 2 gives numerical data for the basic thermodynamic parameters obtained on the basis of the equilibrium constant,  $K_{eq}$ , calculated from the distribution coefficient and the partition coefficient.

**Table 2.** Thermodynamic parameters for the adsorption of cationic dye on clinoptilolite

Method of calculation	Temp. (K)	$\Delta G$ (J·mol <sup>-1</sup> )	$\Delta H$ (J·mol <sup>-1</sup> )	$\Delta S$ (J·mol <sup>-1</sup> ·K <sup>-1</sup> )	$R^2$
According to the relation $\ln(C_s/C_e)$ : $C_s$ and Equation 12	293	-3.11	0.85	0.013	0.9992
	313	-3.37			
	333	-3.65			
According to the relation $\ln(C_s/C_e)$ : $C_e$ and Equation 12	293	-3.01	0.81	0.013	0.9875
	313	-3.22			
	333	-3.53			
According to the relation $\ln(q_e/C_e)$ : $C_e$ and Equation 9	293	-13.87	7.38	0.072	0.9980
	313	-15.21			
	333	-16.77			
According to the relation $\ln(q_e/C_e)$ : $C_e$ and Equation 10	293	-21.24	7.38	0.098	0.9989
	313	-23.08			
	333	-25.14			
According to the relation $\ln(q_e/C_e)$ : $q_e$ and Equation 9	293	-13.95	7.64	0.074	0.9991
	313	-15.35			
	333	-16.9			
According to the relation $\ln(q_e/C_e)$ : $q_e$ and Equation 10	293	-21.33	7.64	0.099	<b>0.9995</b>
	313	-23.23			
	333	-25.28			

According to the numerous values for the coefficient of determination,  $R^2$ , in this table, a high dependence of the variables is observed, practically, in all cases, this error parameter is in between 0.9875 and 0.9995. The validity of the results is hereby absolutely accepted.

A slight advantage is given to the distribution coefficient, i.e. the relation  $\ln(q_e/C_e)$ :  $q_e$ , considering  $R^2=0.9995$  (according to the equation 10).

The weakest result (according to  $R^2$ , according to the equation 12) was shown by the application of the  $K_p$  for calculating the  $K_{eq}$  according to the relation  $\ln(C_s/C_e)$ :  $C_e$ , on the basis of which the thermodynamic parameters were obtained.

In best case,  $\Delta G$  has negative numerous values (-21.33 to -25.28 kJ·mol<sup>-1</sup>), which indicates the spontaneity of the dye adsorption process at 293, 313 and 333 K. Thus, this confirms the practicality of adsorption, there is a good affinity of dye molecules for the adsorbent, the interaction takes place through physisorption.



It is known that  $\Delta G$  for physisorption ranges between -20 and 0  $\text{kJ}\cdot\text{mol}^{-1}$ , physisorption and chemisorption are in the range of -20 and -80  $\text{kJ}\cdot\text{mol}^{-1}$ , while pure chemisorption is in the range from -80 to -400  $\text{kJ}\cdot\text{mol}^{-1}$  [13].

Negative value of  $\Delta G$  decreases with increasing temperature, which indicates that the sorption process in this case is favorable, spontaneous in nature and more efficient at higher temperatures. The decrease in the value of  $\Delta G$  with increasing temperature favors the process of exhausting the textile cationic dye to clinoptilolite from an aqueous solution at high temperature.

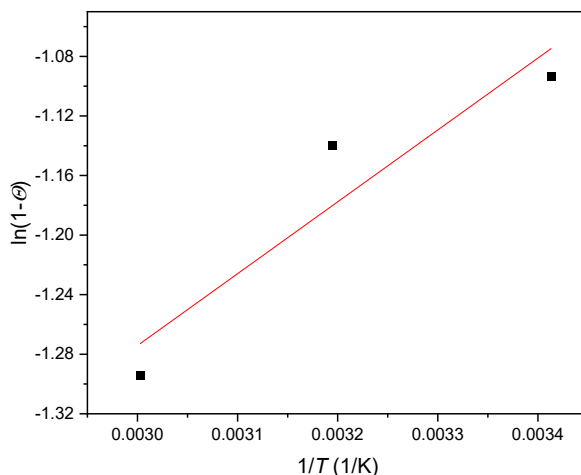
In best case, the values for the enthalpy change,  $\Delta H$ , are positive ( $7.64 \text{ kJ}\cdot\text{mol}^{-1}$ ) and reflect the endothermic nature of the sorption process, while the lower value of the required amount of heat characterizes the phenomenon of physisorption. This result can also be an indicator of the occurrence of single-layer adsorption, moreover, physisorption can be explained by the presence of groups on the adsorbate and adsorbent capable of forming electrostatic or ion-exchange compounds [6].

In the most favorable case, positive value of the entropy changes  $\Delta S$ , ( $0.099 \text{ kJ}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$ ), corresponds to an increased degree of freedom at the solid/liquid interface, as a result of the adsorption of dye molecules. In this particular case, values for  $\Delta S$  are approaching zero, i.e., negative values, which confirms the physical adsorption [6].

The graph in Figure 8 serves to determine the sticking probabilities and activation energies. The dependence of the variables on the graph is relatively high,  $R^2=0.8906$ .

The result obtained for the activation energy in this research ( $4.01 \text{ kJ}\cdot\text{mol}^{-1}$ ) indicates that the adsorption of dye on clinoptilolite takes place through a physical mechanism, which is in accordance with previous results for other thermodynamic parameters. A smaller amount for  $E_a$ , assumes that the reactions are relatively fast, the process of adsorption of cationic blue dye on clinoptilolite is endothermic, i.e., the value of  $E_a$  suggests that the increase in temperature favored the adsorption of the dye.

From the graph section in Figure 8, the value for the parameter  $S^*$  was also obtained. This parameter is defined as a function of the adsorption system that shows the potential of the adsorbate to remain on the adsorbent. A value of  $S^*$  between 0 and 1 favors adsorption. In this case, the sticking probability has a value less than unity and slightly greater than zero ( $S^*=0.066$ ), which means that it is a matter of favorable binding of the dye to clinoptilolite.



**Figure 8.** Variation of surface coverage with temperature during the adsorption of cationic dye on clinoptilolite

## CONCLUSIONS

The process of textile cationic dye adsorption on clinoptilolite was analyzed by evaluating the thermodynamic parameters that reflect the feasibility of the process. The change of free energy, enthalpy and entropy were calculated based on the equilibrium constant obtained in different ways: from distribution and partition coefficients.

There is a very high functionality of linear regression curves when determining thermodynamic parameters. Accordingly, the results are valid, i.e., adequate and applicable.

The free energy change during adsorption was negative, which corresponds to the spontaneous and dominant physical process of dye sorption onto clinoptilolite. This confirms the feasibility and spontaneous nature of sorption at the applied temperatures, with a good degree of affinity of the dye molecules for the surface of the adsorbent through physisorption.

A positive value for the enthalpy change during dyeing reflects the endothermic nature of the interactions, while a smaller numerical value characterizes the phenomenon of physisorption.

A positive value for the entropy change confirms that it is physical sorption with possible partial participation of chemisorption.

The lower value of the activation energy emphasizes the physical sorption, the reactions are relatively fast, and the increase in temperature promotes the adsorption of the dye.

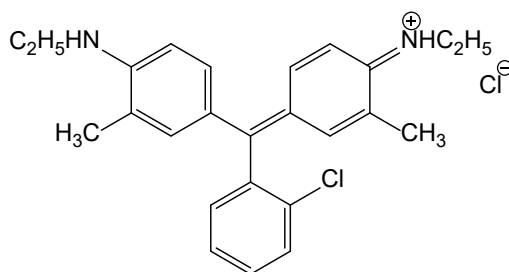
A numerical value for the sticking probability of less than one suggests favorable binding of the cationic dye to the fibers.

## EXPERIMENTAL SECTION

As an adsorbent, natural zeolite, clinoptilolite, from Serbia, was used. The most present mineral phase is clinoptilolite, with a mineral content of about 85% in the tuff.

Before the adsorption experiment itself, clinoptilolite was prepared, which involved repeated washing with distilled water and drying in air.

The research used a triarylmethane class textile blue cationic dye C.I. Basic Blue 5 (Fig. 9), whose molecular formula is  $C_{25}H_{28}Cl_2N_2$ , the molar mass is  $427.41 \text{ g}\cdot\text{mol}^{-1}$ . It is mainly used for dyeing and printing textiles. The initial concentrations of this dye in the experiment were defined in relation to the amount of dye of the same type remaining in the water after commercial textile dyeing.



**Figure 9.** The structure of the applied textile blue cationic dye

Adsorption of a basic (cationic) dye from an aqueous solution was carried out at pH 8.5, in laboratory conditions, in closed reactors, placed on a device with a base rotation of 120 rpm, at 293, 313 and 333 K.

The amount of clinoptilolite in all cases was 1 g, while the solution of constant volume ( $0.1 \text{ dm}^3$ ), contained dye with an initial concentration of 10 to  $110 \text{ mg}\cdot\text{dm}^{-3}$ . The adsorption time, with continuous mixing, was 5–60 min.

X-ray fluorescence spectrometry (XRF) on an ED2000 energy dispersive spectrometer (Oxford Instruments, Great Britain) was used for the chemical composition of the adsorbent.

A scanning electron microscope TESCAN MIRA 3 XMU was used to analyze the surface of the samples.

The apparatus Cary 100 Conc UV-VIS, Varian was used to determine the concentration of the dye in the solution during adsorption ( $\lambda_{max}$  605 nm).

The %Removal of cationic dye [14] is calculated using the equation:

$$\% \text{Removal} = \frac{C_0 - C_t}{C_0} \cdot 100 \quad (1)$$

where:  $C_0$  ( $\text{mg}\cdot\text{dm}^{-3}$ ) initial concentration of dye (adsorbate);  $C_t$  ( $\text{mg}\cdot\text{dm}^{-3}$ ) dye concentration in time  $t$ .

The amount of dye adsorbed on the adsorbent [14] was calculated according to the following formula:

$$q_{t,e} = \frac{C_0 - C_{t,e}}{w} \cdot V \quad (2)$$

where:  $q_{t,e}$  ( $\text{mg}\cdot\text{g}^{-1}$ ) amount of adsorbed dye in adsorption time ( $t$ ) and equilibrium time ( $e$ );  $C_0$  ( $\text{mg}\cdot\text{dm}^{-3}$ ) initial dye concentration;  $C_{t,e}$  ( $\text{mg}\cdot\text{dm}^{-3}$ ) the concentration of the dye in the solution during the adsorption time ( $t$ ) and equality with time ( $e$ );  $w$  (g) adsorbent mass;  $V$  ( $\text{dm}^3$ ) total volume of solution for adsorption.

The change in free energy,  $\Delta G$  [4], under equilibrium conditions is defined as follows:

$$\Delta G = -R \cdot T \cdot \ln(K_{eq}) \quad (3)$$

where:  $K_{eq}$  - the thermodynamic equilibrium constant (dimensionless quantity);  $R$  ( $8.314 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ ) gas constant;  $T$  (K) temperature.

The relationship between [4] the standard Gibbs free surface energy change, the standard enthalpy change ( $\Delta H$ ) and the standard entropy change ( $\Delta S$ ) is as follows:

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

From equations (3) and (4) the following equation is obtained:

$$\ln(K_{eq}) = -\frac{\Delta H}{R \cdot T} + \frac{\Delta S}{R} \quad (5)$$

By reviewing the relevant literature, it was found that several different approaches are used to determine  $K_{eq}$ . The equilibrium constant can be derived from the distribution coefficient ( $K_d$ ) and the partition coefficient ( $K_p$ ). The key fact is that the thermodynamic equilibrium constant should be dimensionless.

$K_d$  and  $K_p$  are expressed as follows:

$$K_d = \frac{q_e}{C_e}; \quad K_p = \frac{C_s}{C_e} \quad (6)$$

where:  $C_s$  ( $\text{mg}\cdot\text{dm}^{-3}$ ) the equilibrium concentration of the dissolved substance on the adsorbent;  $C_e$  ( $\text{mg}\cdot\text{dm}^{-3}$ ) equilibrium concentration of adsorbate in solution.

$K_d$  is obtained by plotting  $\ln(q_e/C_e)$  against  $C_e$  or  $q_e$  [13].

According to this, the coefficient  $K_d$  has a dimension, so its translation into a dimensionless quantity is done by multiplying with the density of water (1000) or by multiplying with the number 55.5 and the molar mass of the dye [15, 16], in the second case:

$$K_{eq} \text{ (dimensionless)} = 1000 \text{ (g}\cdot\text{dm}^{-3})\cdot K_d \text{ (dm}^3\cdot\text{g}^{-1}) \quad (7)$$

$$K_{eq} \text{ (dimensionless)} = 55.5 \text{ (mol}\cdot\text{dm}^{-3})\cdot M_w \text{ (g}\cdot\text{mol}^{-1})\cdot K_d \text{ (dm}^3\cdot\text{g}^{-1}) \quad (8)$$

$$\Delta G = -R\cdot T\cdot\ln(1000\cdot K_d) \quad (9)$$

$$\Delta G = -R\cdot T\cdot\ln(55.5\cdot M_w\cdot K_d) \quad (10)$$

where: number 55.5 - the number of moles of water per liter;  $M_w$  - molar mass of the dye ( $\text{g}\cdot\text{mol}^{-1}$ ).

The  $K_p$  value is obtained by plotting the graph  $\ln(C_s/C_e)$  against  $C_e$  or  $C_s$  and extrapolating to zero [17, 18].

In this case, the partition coefficient agrees with the equilibrium constant, so there was no need to convert it into a dimensionless quantity.

$$K_{eq} \text{ (dimensionless quantity)} = K_p \quad (11)$$

$$\Delta G = -R\cdot T\cdot\ln(K_p) \quad (12)$$

The effect of temperature on adsorbate adsorption can be explained by analyzing the activation energy [19] from the modified *Arrhenius*-type equation:

$$S^* = (1-\theta) \cdot \exp\left(\frac{-E_a}{R\cdot T}\right) \quad (13)$$

where:  $S^*$  - the sticking probability and depends on the temperature of the system,  $E_a$  ( $\text{kJ}\cdot\text{mol}^{-1}$ ) the activation energy.

Surface coverage ( $\theta$ ) is estimated [19] by the following equation:

$$\theta = \frac{1-C_e}{C_0} \quad (14)$$

where:  $C_0$  ( $\text{mg}\cdot\text{dm}^{-3}$ ) the initial dye concentration.

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