

Adsorptive removal of crystal violet dye from aqueous solutions using natural resource systems

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ABSTRACT

The need for alternative wastewater treatment methods with wide scale applicability led to a new area of interest: the green technology, which dealt with technological interventions for environmental sustainability by focusing on minimizing pollution and use of non-renewable resources. Crystal violet is typical cationic dye which belongs to an important class of commercial dyes and it acts as a mitotic poison, potent carcinogen and a potent clastogene, promoting tumor growth in some species of fish. Therefore, there is an important need to develop eco-friendly and cost-effective treatment methods, which can effectively remove this dye from industrial wastewaters. Modified clinoptilolite was used in this study as a low-cost adsorbent to evaluate its ability to remove crystal violet dye from effluents. The influence of initial dye concentration, sorbent dose, adsorption time and temperature has been analyzed in detail with crystal violet dye. Fit of the sorption experimental data was tested on Langmuir, Freundlich and Temkin isotherm models. It was found that the Langmuir and Temkin models fitted well. The present study demonstrated that modified clinoptilolite has the potential of application as an efficient sorbent for the removal of crystal violet dye from aqueous solutions.

Keywords: Crystal violet; Dye sorption; Zeolites; Isotherm

1. Introduction

Adsorption methods are widely used to remove certain classes of organic and inorganic pollutants from wastewaters, especially those that are not easily biodegradable. Reactive dyes are one of the problematic groups. Many industries such as textile, leather tanning, food, pharmaceutical, plastics and paper production demand a large amount of synthetic dyes and they generate a considerable amount of colored wastewater [1–3].

Due to their chemical structure, many of these dyes are toxic and even carcinogenic and they can also cause environmental pollution problems. The cationic dyes are more toxic than the anionic dyes [1,2]. Among the variety of dyes, crystal violet (hexamethyl pararosaniline chloride)

represents one of the most important cationic ones, which is used in many industrial fields: leather and textile processing industries, paper-making and printing [3]. Crystal violet dye has been also extensively used in human and veterinary medicine as a biological stain and as a mutagenic and bacteriostatic agent in medical solutions. Crystal violet dye doped sol-gel glasses and polymer matrices are being used as working media for solid state dye laser (SSDL) [4–6]. Crystal violet has been reported as a biohazard substance that persists in environment for a long period of time and pose toxic effects. This dye acts as a mitotic poison, potent carcinogen and a potent clastogene, promoting tumor growth in some species of fish [4]. Therefore, there is an important need to develop eco-friendly and cost-effective treatment methods, which can effectively remove this dye from industrial wastewaters [4,5].

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There are several physico-chemical methods reported in literature for the removal of crystal violet: coagulation, flocculation and ion-pair extraction. The use of these methods is limited by some important problems: generation of synthetic dye-bearing sludge, high operation cost and ineffectiveness in treating wastewater with low dye concentration. Biological methods are eco-friendly and cost-effective for the treatment of textile industry wastewaters, but these methods also have certain limitations [2–6].

Adsorption is one of the most researched treatment techniques for the treatment of wastewaters containing dyes and metals. Research studies reported different kinds of adsorbents such as granular activated carbon, agricultural byproducts, graphene oxide, minerals, metal oxides and biopolymers for the removal of these pollutants from aqueous solution [6–11]. Scientific literature has been widely reported that dissolved organic contaminants can be removed efficiently by adsorption method. This unit operation offers also flexibility in design. The suitability of clay as a natural adsorbent has long been recognized [12,13]. The adsorbents obtained from natural sources require chemical and physical modifications to improve their adsorption capacity and performance. Due to their physico-chemical properties (lamellar structure, high surface area, large cation exchange capacity, chemical stability), nanoclay minerals have great potential to remove pollutants, such as heavy metals and organic dyes. They have well-known applications in environmental protection, industry and agriculture [12–16].

This study focuses on natural clay minerals such as clinoptilolite as a potential adsorbent for crystal violet removal. The clay materials were activated by nitric acid solutions at elevated temperature. Modified clinoptilolite was used in this study as a low-cost adsorbent to evaluate its ability to remove crystal violet dye from effluents. The effectiveness of proposed adsorbent is investigated at different conditions to optimize its capacity for crystal violet removal. Adsorption experiments were performed in batch mode and various operational parameters like initial dye concentration, adsorbent dosage, temperature and contact time were studied to optimize the process. Different isotherm models were used for adsorption equilibrium study. Langmuir, Freundlich and Temkin adsorption models were investigated for each reactive dye – adsorbent system, in

order to establish all favourable conditions to uptake of crystal violet dye from aqueous solution.

2. Material and methods

2.1. Crystal violet stock solution

The cationic dye crystal violet ($C_{25}H_{30}N_3Cl$, $\lambda_{max} = 590$ nm and MW = 407.98 g mol⁻¹) was purchased from Sigma-Aldrich. The structure and the most important characteristics of crystal violet (CV) dye are illustrated in Table 1.

Stock solution of 1,000 mg L⁻¹ crystal violet was prepared by dissolving 1.0 g of the dye in 1 L of distilled water. Different concentrations of crystal violet (CV) dye used in these experiments were prepared by diluting the stock solution with distilled water.

2.2. Sorbent material

Due to the fact that clinoptilolite is found in nature as a major component of volcanic tuffs, the mined rock was subjected to mechanical, thermal and chemical treatments to obtain a purified, clinoptilolite-rich product that can be used in the adsorption processes.

Fine clay fractions (<0.4 mm diameter) separated by sieving from ground Carpathian clinoptilolitic tuff (minerals of heulandite type) were used for this study. Treatment conditions were chosen according to those accepted in chemical industry for obtaining acid modified clays as sorbents. Clay samples were modified by 1 M HNO₃. The original clinoptilolite was pre-treated with 1 M HNO₃ in a reciprocal shaker for 6 h and the solid phase was separated by filtration, washed with distilled water to a neutral pH and dried in an oven at 105°C.

2.3. Sorption procedure for equilibrium and isotherm studies

The influence of initial crystal violet dye concentration (60–150 mg L⁻¹), adsorbent dose (0.3–1 g), contact time (20–100 min) and temperature (25°C–50°C) on the adsorption efficiency have been studied. The mixture dye solution-adsorbent was added to a set of Erlenmeyer flasks. They were agitated at 200 rpm (orbital shaker incubator) until equilibrium was reached. The whole batch studies were carried out at ambient temperature (28°C ± 2°C) for

Table 1
Characteristics of crystal violet dye (CV)

Name	Chemical structure	Molecular formula	MW	Type of dye	λ_{max}
Crystal violet (methyl violet 10B; hexamethyl pararosaniline chloride)		$C_{25}H_{30}ClN_3$	407.98 g mol ⁻¹	Cationic	590 nm

90 min to ensure establishment of equilibrium. The dye concentration solutions were measured after solid–liquid separation. Residual concentration of crystal violet was determined by using a double-beam UV-Vis spectrophotometer (CECIL instrument, Model CE2021-2000) at the maximum wavelength, which is 590 nm.

The amount of crystal violet dye retained by the modified clinoptilolite, q_e (mg g^{-1}) and the percentage dye removal ($R\%$) for all samples was calculated by Eqs. (1) and (2) [10–18]:

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

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

where q_e is the crystal violet uptake (mg dye g^{-1} sorbent); C_0 (mg L^{-1}) is the initial concentration of crystal violet; C_e (mg L^{-1}) is the final dye concentration; V is the volume of the solution (L) and W is the weight of adsorbent (g).

The results from investigating the effect of contact time, initial concentration, adsorbent dose and temperature were used to study the isotherm modeling of the adsorption process.

3. Results and discussion

3.1. Characterization of the sorbent material

Zeolites (aluminosilicates in nature or synthesized) are attractive adsorbents with good ion-exchange capacity, mechanical and chemical stability, high specific surface area, selectivity and also with relatively cheap prices [12–17]. Clinoptilolite, a natural zeolite that is isostructural with heulandite, is a microporous crystalline aluminosilicate with open structure, having the silicic ratio $\text{Si/Al} > 4$. The obtained clinoptilolite was characterized by Fourier-transform infrared spectroscopy (FTIR) and Brunauer–Emmett–Teller (BET) technique.

3.1.1. FTIR analysis

FTIR spectrophotometer (ThermoNicolet IR-100 spectrometer) was used to identify the absorbance bands on the modified clinoptilolite.

Fig. 1 presents the FTIR spectrum of modified clinoptilolite. The absorbance bands at around 790 and 510 cm^{-1} are assigned to the symmetrical T–O (T = Si, Al) stretching and bending, respectively, this indicating the presence of Si–O and Al–O tetrahedrons [19,22]. The absorbance band at around 1,095 cm^{-1} is assigned to the T–O internal asymmetrical stretching vibration [19].

The pore size of a material is an important factor that can reveal the adsorption ability of pollutants onto particles surface. The surface properties of the adsorbent material were studied by means of surface area and total pore volume performed by BET surface area analyser (Autosorb AS-1, Quantachrome). The total volume of the pores has the value 0.210 $\text{cm}^3 \text{g}^{-1}$ and the specific surface area of the material was 30 $\text{m}^2 \text{g}^{-1}$ as determined by the BET method. Clinoptilolite particles are predominantly mesopores and they can assist the diffusion of dye molecules.

3.2. Adsorption studies

3.2.1. Effect of initial concentration

Dye adsorption capacity of clinoptilolite, as a function of initial concentration of dye within the aqueous solution is shown in Fig. 2. The initial concentration of dye was changed in the range of 60–150 mg L^{-1} . The adsorbent amount was of 0.5 g and contact time 90 min, using an orbital shaker incubator, at 200 rpm.

The amount of dye adsorbed per unit mass of the adsorbent increased with increase in the initial concentration of crystal violet (Fig. 2a). According to Fig. 2b, crystal violet removal decreased from around 91% at concentration of 60 mg L^{-1} to 83% when the concentration was increased 150 mg L^{-1} . At low concentrations, the dye molecules are adsorbed by specific sites of clinoptilolite; increasing concentrations, the specific sites are saturated and the exchange sites are filled. Higher initial dye concentrations result in an increase in the uptake percentage, but slow the kinetics of the process. The boundary layer resistance to mass transfer increased by increasing the initial dye concentration [18,19].

3.2.2. Effect of adsorbent dosage

The adsorbent dosage is an important factor which influence the adsorption process, since this depends mainly of

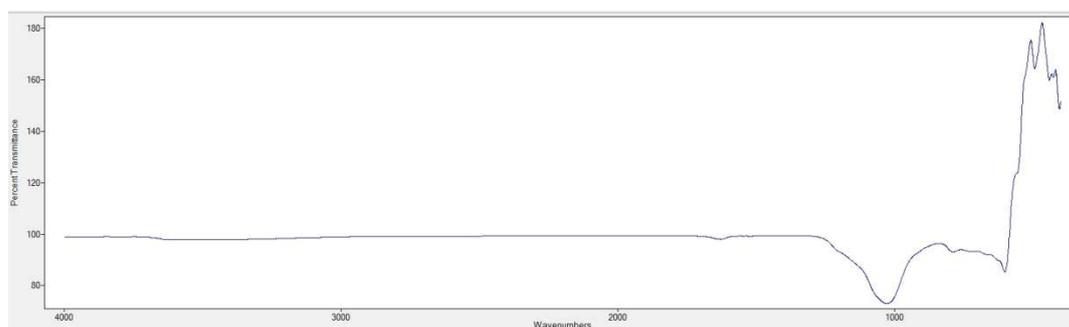


Fig. 1. FTIR vibrational spectra of modified clinoptilolite (CLN-M).

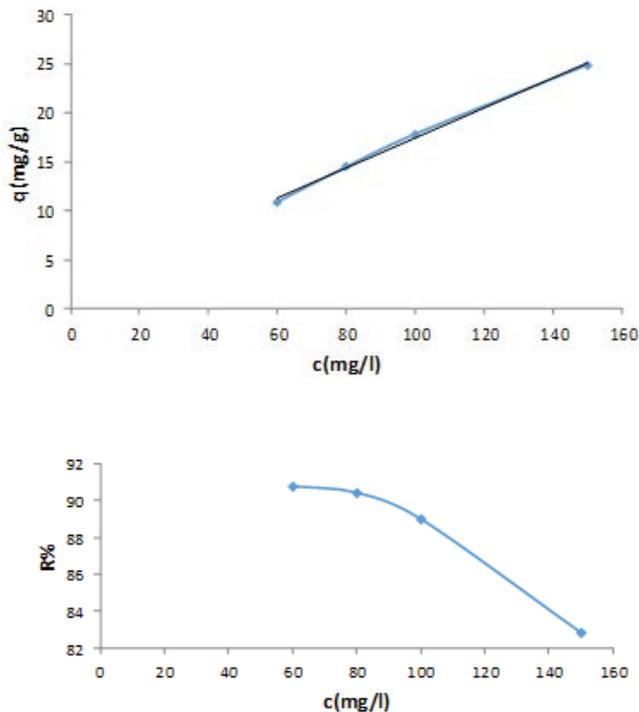


Fig. 2. (a, b) Effect of initial concentration on crystal violet dye adsorption on the modified clinoptilolite.

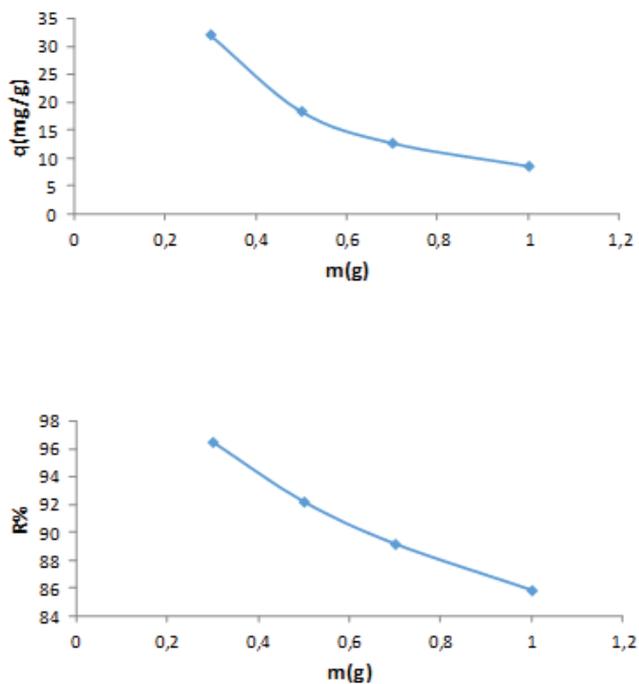


Fig. 3. (a, b) Effect of adsorbent dose on the adsorption of crystal violet dye on the modified clinoptilolite.

the availability of binding sites and the surface area [19]. The adsorbent amount was varied in the range of 0.3–1 g, for 100 mg dye L^{-1} . The adsorption experiments were carried out at the contact time 90 min, using an Orbital Shaker Incubator at 200 rpm.

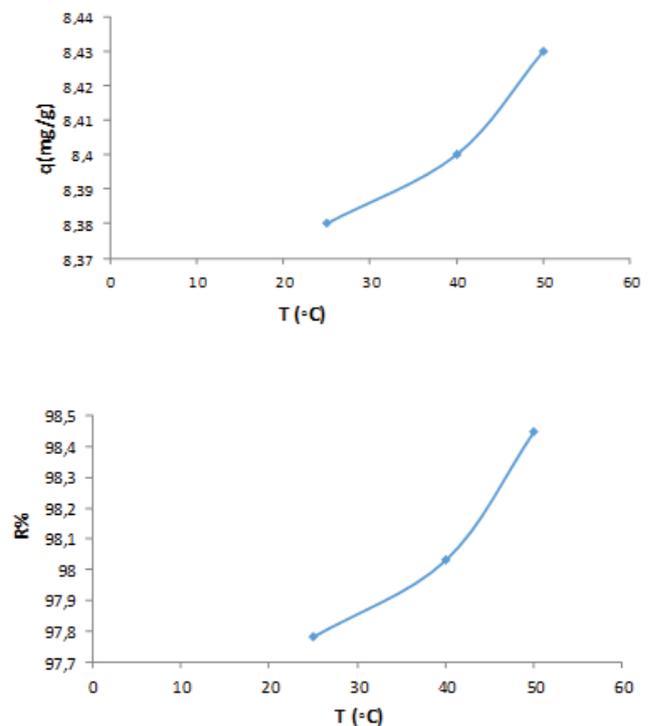


Fig. 4. (a, b) Effect of temperature on the adsorption of crystal violet dye on the modified clinoptilolite.

The modified clinoptilolite exhibited around 97% of dye removal percentage, using adsorbent dosage of 0.3 g. The decrement in adsorption capacity with an increase in adsorbent dosage can be caused by overlapping of active sites at high doses of adsorbent support. At low adsorbent mass, all sites are exposed and the adsorption on the surface is saturated faster [19].

3.2.3. Effect of temperature

Effect of temperature on the adsorption of crystal violet by modified clinoptilolite at equilibrium was investigated at three different temperatures: 25 $^{\circ}C$, 40 $^{\circ}C$ and 60 $^{\circ}C$ at the initial dye concentration of 100 mg L^{-1} , pH 6.0 and the adsorbent dose of 0.7 g, at 200 rpm (Figs. 4a,b).

Temperature is a factor which has significant impact on an adsorption process. The adsorption of crystal violet was noted to enhance with the increase in temperature, indicating that higher temperature favoured the removal of dye by sorption onto modified clinoptilolite (Figs. 4a,b). Temperature influences mobility of dye molecules in aqueous solution and surface properties of adsorbent.

The enhanced adsorption at higher temperatures is due to the greater availability of adsorption sites of adsorbent [19,20].

3.2.4. Effect of contact time

The rate of sorption of crystal violet by modified clinoptilolite was determined by contacting 100 mg L^{-1} of the dye solution (pH 6.0) with 0.7 g modified clinoptilolite, for different intervals of time (20–100 min) at 200 rpm.

Figs. 5a and b present the effect of contact time on the adsorption of crystal violet on modified clinoptilolite powder and it clearly indicate that adsorption increased with increase of the contact time. After 60 min, the adsorption of crystal violet dye nearly reached equilibrium. Once equilibrium has been achieved, the adsorption percentage of crystal violet dye did not change with further increase in contact time because the amount of dye adsorbed reached the steady state with the residual dye in the solution. The contact time between the sorbent and sorbate is an important parameter from an economical point of view, when designing an adsorption system for large scale application in industry [19,20].

3.3. Equilibrium isotherm modeling

The adsorption data were analyzed employing the commonly used Freundlich, Langmuir and Temkin isotherms. The study of the equilibrium isotherms is of fundamental importance for the design and optimization of an adsorption system, for the removal of a pollutant from an aqueous solution. An adsorption isotherm is a plot of the quantity of the sorbate removed per unit sorbent (q_{eq}) as the solid phase concentration of the sorbent against the concentration of the sorbate in the liquid phase (C_{eq}) [19–21].

The equilibrium of adsorption was evaluated by using the following isotherm models:

$$\text{Freundlich isotherm model: } q_e = K_F \cdot C_e^{1/n} \quad (3)$$

where: K_F (mg g^{-1}) and n are Freundlich constants; $1/n$ is the Freundlich exponent related to surface heterogeneity;

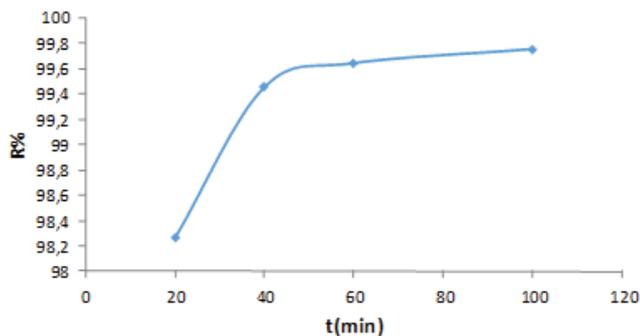
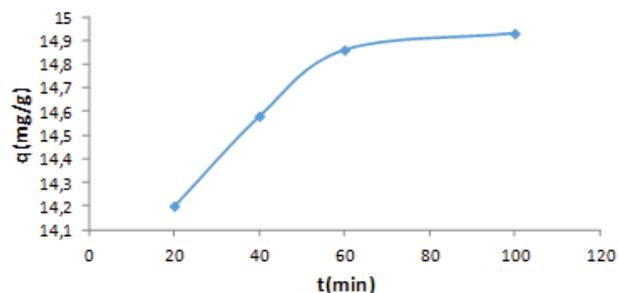


Fig. 5. (a, b) Effect of contact time on the adsorption of crystal violet dye on the modified clinoptilolite.

q_e (mg g^{-1}) the equilibrium sorption concentration of dye per gram of adsorbent; C_e (mg L^{-1}) the concentration of the solute in solution at equilibrium.

Freundlich isotherm model is an empirical expression that encompasses the exponential distribution of sites and their energies and the heterogeneity of the surface [4,5,19–26].

A logarithmic plot linearizing Eq. (3) enables the constant K_F and the exponent $1/n$ to be determined:

$$\ln q_e = \ln K_F + \ln C_e \quad (4)$$

The Langmuir isotherm is based on the assumption of monolayer adsorption on a structurally homogeneous sorbent [4,5,19–26].

$$\text{Langmuir isotherm equation: } q_e = \frac{q_m \cdot K_L \cdot C_e}{1 + K_L \cdot C_e} \quad (5)$$

where C_e (mg L^{-1} or mmol L^{-1}) is the equilibrium concentration; q_e (mg g^{-1}) represents the amount of solute adsorbed per amount of adsorbent; q_m (mg g^{-1}) represents the adsorption capacity; K_L (L mg^{-1}) is the Langmuir constant related to the affinity of the binding sites and energy of adsorption (L mg^{-1} or L mmol^{-1}).

Langmuir linearized form is given as follows:

$$\frac{C_e}{q_e} = \frac{C_e}{q_m} + \frac{1}{q_m \cdot K_L} \quad (6)$$

The Langmuir parameters can also be used to predict affinity between the sorbate and the sorbent using the dimensionless separation factor (R_L), which has been defined as below [3]:

$$R_L = \frac{1}{1 + K_L \cdot C_i} \quad (7)$$

The value of R_L can be used to predict whether an adsorption system is favourable or unfavourable in accordance with the criteria shown in Table 2.

Temkin isotherm model is given as follows:

$$q = \frac{RT}{b} \ln(K_T \cdot C_e) \quad (8)$$

where K_T (L mg^{-1}) and b (kJ mol^{-1}) are Temkin isotherm constants.

Table 2
Characteristics of the Langmuir adsorption isotherms [3]

Separation factor (R_L)	Type of isotherms
$R_L > 1$	Unfavourable
$R_L = 1$	Linear
$0 > R_L < 1$	Favourable
$R_L = 0$	Irreversible

A comparison of the Freundlich (Fig. 6), Langmuir (Fig. 7) and Temkin (Fig. 8) adsorption isotherms shows that the sorption characteristics of crystal violet dye onto modified clinoptilolite followed more closely the Langmuir and Temkin isotherm equations than the Freundlich isotherm equation. This observation is further supported by the closer to unity value of their correlation coefficients (R^2), which is a measure of how well the predicted values from a model match with the experimental data [3]. It may be concluded from these observations that the adsorption of crystal violet by modified clinoptilolite was better defined by the Langmuir and Temkin than by the Freundlich equation, thus indicating that the adsorption of crystal violet by modified clinoptilolite is a chemically equilibrated and saturated mechanism.

Temkin isotherm contains a factor that explicitly taking into the account of adsorbent–adsorbate interactions [23].

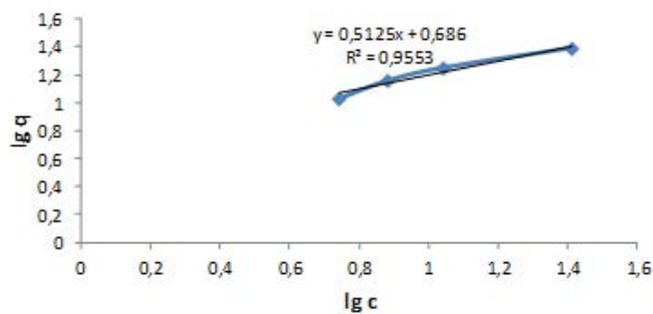


Fig. 6. Linearized Freundlich adsorption isotherm for the sorption of crystal violet on the modified clinoptilolite.

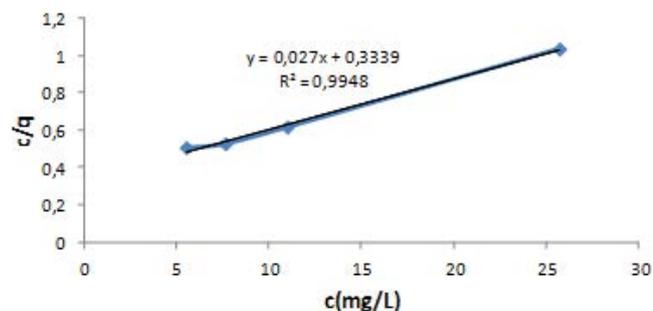


Fig. 7. Linearized Langmuir adsorption isotherm for the sorption of crystal violet on the modified clinoptilolite.

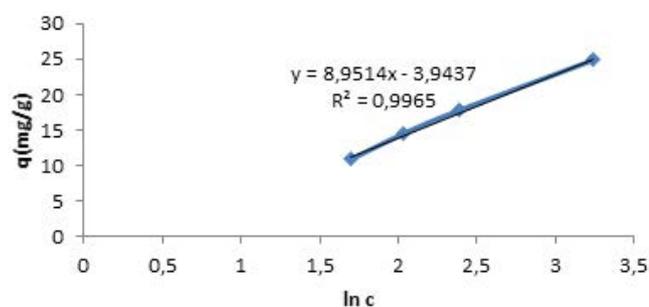


Fig. 8. Temkin adsorption isotherm for the sorption of crystal violet on the modified clinoptilolite.

The value of R_L for the adsorption of crystal violet onto modified clinoptilolite is shown in Fig. 9, which indicates that sorption of dye on modified clinoptilolite was favourable (Table 2). The R_L value is between 0 and 1, which signifies a strong relation for adsorption (Fig. 9).

3.4. Desorption and reusability study of regenerated sorbent material

Crystal violet-loaded clinoptilolite adsorbent, which was initially exposed for 100 mg dye L^{-1} , at pH 6.0 and 30°C, was contacted with 100 mL of 0.5 M NaOH as dye-desorbing agent, for intervals of 20, 40, 60 and 90 min, on a rotary shaker at 200 rpm. The adsorbent was removed by filtration and the quantity of crystal violet dye recovered was determined. After desorption, the adsorbent was washed several times with distilled water and the regenerated material was suitable for new adsorption equilibrium experiments.

The following equation was employed to calculate the desorption efficiency [24]:

$$\eta\% = \frac{C_r \cdot V_t}{(C_o - C_e)V} \times 100 \quad (9)$$

where C_o (mg L^{-1}) is the initial concentration of dye in the feed solution, C_e (mg L^{-1}) is the dye concentration at equilibrium, V (L) is the volume of feed solution, C_r (mg L^{-1}) is the dye concentration in solution after regeneration and V_t (L) is the volume of the regeneration solution.

It was noted that crystal violet dye desorbed rapidly, with the maximum elution achieved in the first 30 min amounting to 82% desorption. Similar observations for the desorption of crystal violet from grapefruit peel waste adsorbent material using NaOH have been reported [3].

The parameters obtained by the fit of the experimental data according to Freundlich, Langmuir and Temkin isotherms are presented in Table 3.

The Freundlich isotherm constants K_F and n_F are constants incorporating all factors affecting the adsorption process, such as intensity of adsorption and adsorption capacity [24–27].

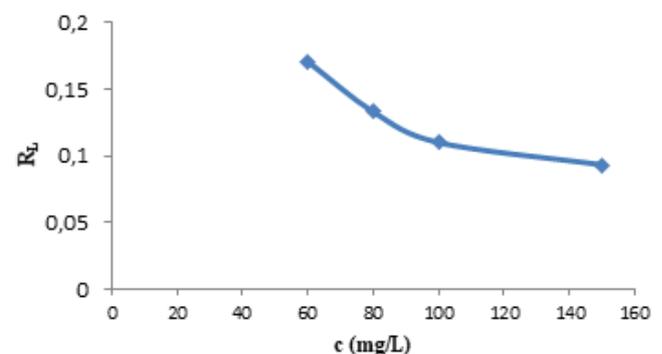


Fig. 9. Value of separation factor R_L for sorption of crystal violet by modified clinoptilolite.

The values of Freundlich parameter n_F reflects the intensity of adsorption. The values of n_F between 1 and 10 represent a favorable adsorption process [26,27].

The data obtained were well fitted to the Langmuir adsorption isotherm applied to equilibrium (the value $R^2 = 0.9948$), this assuming mono-layer adsorption onto a surface with a finite number of identical sites [26].

The Temkin constant b_T related to the heat of adsorption was $0.272 \text{ kJ mol}^{-1}$, at studied temperature ranges. It has been reported that the typical range of bonding energy for ion-exchange mechanism is $8\text{--}16 \text{ kJ mol}^{-1}$ [24]. The low value in this study in case of modified clinoptilolite adsorbent indicates a weak interaction between adsorbate and adsorbent.

3.5. Thermodynamic analysis

The values of the thermodynamic parameters: Gibbs free energy (ΔG), change in enthalpy (ΔH) and change in entropy (ΔS) were evaluated by using Langmuir isotherm constant K_L at different temperatures (Table 4). The free energy of adsorption ΔG can be associated to Langmuir adsorption constant using the following expression [21,28,29]:

$$\Delta G = -RT \ln K_L \quad (10)$$

where T is temperature in Kelvin, R is the gas constant having a value of $8.314 \times 10^{-3} \text{ kJ mol}^{-1} \text{ K}^{-1}$ and K_L is the equilibrium constant obtained from the Langmuir model.

Enthalpy and entropy changes are also related to Langmuir equilibrium constant by the following expression [28]:

$$\ln K_L = \frac{\Delta S}{R} - \frac{\Delta H}{RT} \quad (11)$$

The values of enthalpy change (ΔH) and entropy change (ΔS) were calculated from the slope and intercept of the

Table 3
Parameters of Freundlich, Langmuir and Temkin adsorption isotherm models for crystal violet dye removal

Langmuir model	Freundlich model	Temkin model
$R^2 = 0.9948$	$R^2 = 0.9897$	$R^2 = 0.9965$
$q_m = 37.03 \text{ mg g}^{-1}$	$K_F = 3.25 \text{ mg g}^{-1}$	$b_T = 0.272 \text{ kJ mol}^{-1}$
$K_L = 0.0809 \text{ L mg}^{-1}$	$n_F = 1.45$	$K_T = 1.55 \text{ L mg}^{-1}$
$\Delta G = +6.114 \text{ kJ mol}^{-1}$		

Table 4
Thermodynamic parameters at various temperatures for the adsorption of crystal violet dye onto modified clinoptilolite

T (K)	ΔG (kJ mol ⁻¹)	ΔS (J mol ⁻¹ K ⁻¹)	ΔH (kJ mol ⁻¹)
298	+6.21		
313	+6.50	-10.4	-9.33
333	+6.92		

plot of $\ln K_L$ vs. $1,000/T$ (Fig. 10). Values of ΔG were calculated using Eq. (11).

The values of Gibbs free energy ($\Delta G > 0$) indicate that the adsorption process of crystal violet is non-spontaneous and requires a small amount of energy; the adsorption process occurs naturally. The negative value of the standard enthalpy change ΔH indicates that the dye adsorption process is exothermic. The change in entropy reflects the randomness of the adsorbent interface and the solution during the adsorption of this dye. Negative values of ΔS represent a stable arrangement of the dye molecules on the adsorbent surface [30,31].

The magnitude of enthalpy value is also an indicative of the adsorption mechanism; it suggests adsorption mechanism by physisorption through van der Waals if the value of enthalpy is less 20 kJ mol^{-1} or electrostatic type of forces between dye and adsorbent if it falls between 20 and 80 kJ mol^{-1} [30]. The enthalpy and entropy changes are related to Langmuir equilibrium constant by the Eq. (11). Therefore, the plot of $\ln(K_L)$ vs. $1/T$ was a straight line, the slope and intercept values of which allow the extrapolation of ΔH and ΔS (Fig. 10).

3.6. Comparison of the maximum adsorption capacity of various adsorbents towards crystal violet dye

A large variety of low-cost adsorbents with good adsorption capacity have been examined for their ability to remove various types of pollutants from water and wastewater. Due to this reason, in the present study, the adsorption capacity of modified clinoptilolite was compared with other natural and synthetic adsorbents used in the crystal violet dye adsorption process and the results are reported in Table 5.

4. Conclusions

Modified clinoptilolite was used in this study as a low-cost adsorbent to evaluate its ability to remove crystal violet dye from effluents. Experiments were made as a

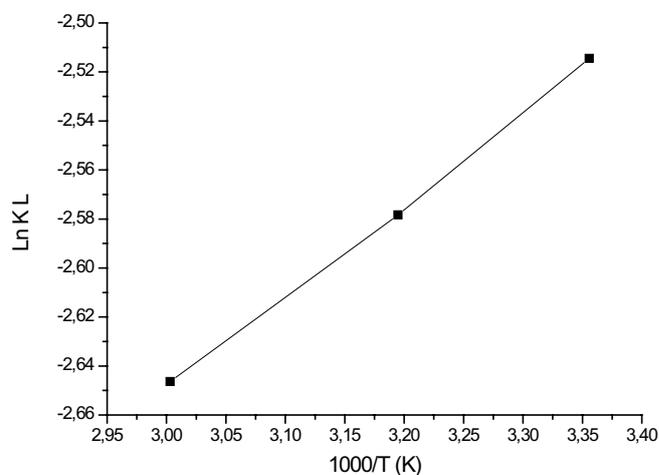


Fig. 10. Van't Hoff plot for estimation of thermodynamic parameters for the adsorption of crystal violet dye onto modified clinoptilolite.

Table 5
Comparison of the maximum adsorption capacity of various adsorbents towards crystal violet dye

Adsorbent	q_e (mg g ⁻¹) crystal violet dye	Reference
Activated carbon	35.64	[31]
Leaf biomass of <i>Calotropis procera</i>	4.14	[32]
Polyvinyl alcohol/agar/maltodextrin	19.17	[33]
Azolla and fig leaves modified with magnetite iron oxide nanoparticles	25	[34]
Soil-silver nanocomposite	1.91	[35]

function of some important operational parameters including initial dye concentration, sorbent dose, adsorption time and temperature. The experimental adsorption data were evaluated with the isotherm equations of Langmuir, Freundlich and Temkin models. The experimental equilibrium sorption data obtained from batch studies fit well to Langmuir adsorption isotherm equation, indicating monolayer adsorption. The dimensionless parameter R_L has also been calculated using the Langmuir constant. The values of R_L have been found to be between 0 and 1, which again suggest favourable adsorption. The adsorption of crystal violet by modified clinoptilolite was better defined by the Langmuir and Temkin than by the Freundlich equation, thus indicating that the adsorption of crystal violet by modified clinoptilolite is an equilibrated and saturated mechanism. It is important to point out that the experimental data fitted well both Langmuir and the Temkin adsorption isotherms models, indicating that both models are suitable for describing the adsorption equilibrium of crystal violet dye in the studied concentration ranges.

The calculation of the adsorption energies shows that it is a spontaneous and exothermic physical adsorption. The results indicate that modified clinoptilolite has a good adsorption capacity for crystal violet dye. This study concludes that the modified clinoptilolite could be employed as inexpensive adsorbent as an alternative to commercial activated carbon for the removal of cationic dyes from water and wastewater, in general and for the removal of crystal violet in particular. In addition, natural clinoptilolite is cheaper than commercially available activated carbon, although their performance was comparable.

Symbols

C_o	—	Initial concentration in aqueous solution, mg L ⁻¹
C_{eq}	—	Concentration of dye at equilibrium, mg L ⁻¹
K_L	—	Langmuir constant, L mg ⁻¹
K_F	—	Freundlich constant, L mg ⁻¹
m	—	Mass of dry adsorbent, g
$1/n$	—	Freundlich parameter
q_{eq}	—	Equilibrium concentration in solid phase, mg g ⁻¹
q_m	—	Maximum adsorbed per unit mass of adsorbent, mg g ⁻¹
R_L	—	Equilibrium parameter of isotherm
K_T	—	Temkin isotherm constant, L mg ⁻¹
T	—	Temperature, K

t	—	Time, min
ΔG	—	Free energy of adsorption, kJ mol ⁻¹
ΔH	—	Change in enthalpy, kJ mol ⁻¹
ΔS	—	Change in entropy, J mol ⁻¹ K ⁻¹
R	—	Universal gas constant, 8.314 J mol ⁻¹ K ⁻¹

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