Adsorption of the Cationic Dye Ethyl Violet on Acid and Alkali-Treated Wild Carob Powder, A Low-Cost Adsorbent Derived from Forest Waste

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ABSTRACT: *The effect of acid-alkaline treatment of lignocellulosic material (wild carob forest wastes) on Ethyl violet adsorption was investigated. It was found that surface chemistry plays an important role in Ethyl Violet (EV) adsorption. HCl treatment produces more active acidic surface groups such as carboxylic and lactone, resulting in an increase in the adsorption of EV dye. The adsorption efficiency was higher for treated lignocellosic material with HCl (WCHCl) compared to that treated with KOH (WCKOH); maximum biosorption capacities were 170 and 130 mg/g for WCHCl and WCKOH at pH 6, respectively. It was also found that for both treated materials less than 150 min was needed to reach equilibrium. The adsorption of a basic dye (i.e. ethyl violet or basic violet 4) was carried out by varying some process parameters, such as the initial concentration and pH. The adsorption process can be well described by means of a pseudo-second-order reaction model and experimental data were accurately expressed by the Sips and Langmuir models for both WCHCl and WCKOH.*

KEYWORDS: *Adsorption; Wild carob; Isotherm; Kinetics; Modeling.*

INTRODUCTION

Synthetic dyes still pose serious environmental problems when used for dyeing of textile fibers, such as cotton and polyester. Dye effluents, which are often found in aqueous effluents, may include chemicals that have

toxic effects against microbial populations and may be toxic and/or carcinogenic to mammalian animals [1] Many physical, chemical, and biological methods have been developed to remove dyes, such as coagulation/ flocculation, electroflocculation, advanced oxidation, ozonation, membrane filtration, liquid–liquid extraction, electrochemical destruction, ion-exchange, reverse osmosis, irradiation [2-4] and electro-coagulation [5]. Among these methods, adsorption is the most widely used because of its ease of operation and comparably low cost of application [3]. In this regard, activated carbon is the most widely used adsorbent for the removal of dyes from aqueous solutions [1]. However, elimination of organic pollutants by adsorption onto this material is an expensive process because of the high cost of the adsorbent and its regeneration [6-8]. In this context, there are a many research concerning others adsorbents especially those made up of inexpensive material and locally available in abundant quantities [1, 2, 6]. Agricultural and forest waste materials such as baggage pith, saw dust, pine bark, maize cob, rice bran, rice hull, coconut husk fibers, nut shells, and cotton seed hulls have been evaluated as low-cost adsorbents for the removal of dyes and toxic heavy metals [9-11]. However, their adsorption capacities (less than 40 mg/g-adsorbent) are far smaller than that of activated carbon. Thus, great efforts are needed to exploit new promising adsorbents for the removal of dyes from aqueous solutions which therefore constitute important topics in the field of environmental technologies [12, 13]. Various adsorbents, such as yeast cells [14], regenerated spent bleaching earth [1] and acid-actived andesite [6] have been studied for the adsorption of EV from aqueous solutions and some of them showed good adsorption for this dye. For this purpose, modified wild carob by both HCl (WCHCl) and NaOH (WCKOH) was investigated in this study. To our knowledge, except the work of Reffas et al. [15], no other work has been reported regarding its use for dye adsorption.

EXPERIMENTAL SECTION

Preparation of the native biosorbent (native wild carob), dye solution and determination of dye concentrations are reported in our previous work [15]. Acid or basic modified wild carob powder adsorbent was prepared by mixing 10 g of native wild carob powder
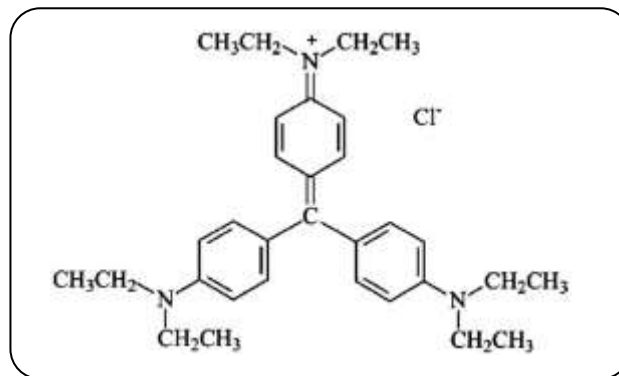

Fig. 1: Basic violet 4 chemical structure ($C_{31}H_{42}ClN_3$) (EV). MW: 492.14 g/moL.

with 100 ml of 0.1 M HCl or 0.1 M KOH solutions and the mixture was stirred using a magnetic stirrer for 60 min at room temperature. Then, it was thoroughly washed with distilled water to remove adverse residue. The product, hereafter labeled as WCHCl or WCKOH, was again dried at 60°C. The fraction of particle diameter between 250 and 500 μm was selected for characterization of the biosorbents and batch biosorption experiments. An SP-8001 UV/VIS Spectrophotometer of Axiom (Germany, Shimadzu) was used to determine the residual dye concentrations in solution. After withdrawing samples at fixed time intervals and centrifugation, the supernatant was analyzed for residual Ethyl Violet) (EV) (Fig. 1) at λ_{max} corresponding to the maximum absorption for the dye solution (λ_{max}= 596 nm). The calibration curve was plotted between absorbance and concentration of the dye solution to obtain the absorbance - concentration profile.

Batch experiments of a given amount of adsorbent in 50 ml of dye solutions of a known concentration in a series of 250 mL conical flasks were carried out at pH 6 and at room temperature. Experiments were repeated five times. The amount of dye adsorbed onto powder of both WCHCl and WCKOH at time t, Q_t (mg/g) was calculated by means of the following mass balance relationship:

$$Q_t = \frac{(C_0 - C_t)V}{m} \qquad (1)$$

Where C_0 is the initial dye concentration (mg/L), C_t is the concentration of dye at any time t, V is the volume of solution and m is the mass of both WCHCl and WCKOH powders. Origin 8 Software was used to fit models parameters.

Table 1: Surface characteristics of WCHCl and CWKOH.

adsorbent	Acidity (meq g/g)	Basicity (meq g/g)	pHpzc
WCHCl	9.5	2.5	3.73
WCKOH	4	13	6.5

RESULTS AND DISCUSSION

Surface functional groups determination (Acidity and basicity surface)

The number of acid groups was calculated and based on the fact that NaOH neutralizes the carboxyl, lactonic and phenolic groups. The number of basic sites was determined from the amount of HCl that reacts with the functions of surface

The WCHCl was rather acid in agreement with its low content of basicity compared to its acidity. Table 1 shows less alkaline than acid groups confirming its acidic character. Thus, the strongly acid pHpzc of WCHCl can be attributed to the presence of oxygenated surface groups with a little pKa value. In the contrast, the WCKOH was rather basic in agreement with its low content of acidity compared to its basicity. Table 1 shows less acidic than basic groups confirming its basic character.

Influence of the pH

To study the influence of the pH on the adsorption capacity of the biosorbent, WC (treated lignocellulosic material of forest wastes wild carob) for the cationic dye, EV, experiments were performed at an initial concentration of 50 mg/L, 50 mg and pH values ranging from 3 to 10. The basic character of EV is due to the presence of amine groups (Fig. 1), showing a pKa value of 1.3, and hence at pH range 3–10, just alone iminium groups is cationic. Adsorption can also be explained on the basis of an electrostatic interaction between the ionic dye molecule and the charged biosorbent substrate. At the considered pH range, 3–10, the biosorbent was negatively charged for pH values superior to the pHpzc (Fig. 2) and positively charged for pH values below the pHpzc, ~ 3.7 and ~6.5 (Fig. 2) for WCHCl and WCKOH respectively. Since the highest adsorption uptake was measured at slightly acidic pH 6 (42.6 mg/g) and (46,5 mg/g) for WCKOH and WCHCl, respectively (Fig. 3); electrostatic interactions between the biosorbent and the EV cation at pH < 6 ~6,5 and at pH < 4 ~ 3,7 for WCKOH and WCHCl respectively did not favor adsorption. Thus, EV adsorption was most controlled
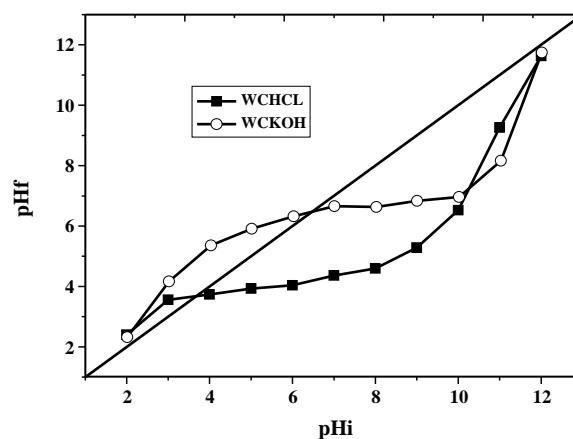

Fig. 2: Point of zero charge (pHpzc) for WCHCl and WCKOH.

by electrostatic and dispersive interactions. Two possible mechanisms which may be considered for EV removal were, therefore, electrostatic interactions between the negative adsorption sites of the biosorbent ($-COO-$) and the positively charged dye, as well as the H–π interactions between aromatic rings from EV and –COOH and OH groups [15].

The acid treated biosorbent was strongly acidic Fig. 2. (pH$_{pzc}$ ~ 3.7), and has many carboxyl groups which can increase interactions between the cationic groups of the dye and the carboxylic groups of the adsorbent. However, at the pH of alkaline treated biosorbent, namely at slightly acidic pH, Fig. 2 (pH$_{pzc}$ ~ 6.5), the screening effect of the counter ion, i.e K$^+$ shields the charge of the ionized carboxyl groups on the alkaline treated biosorbent. As a result, the dye molecule is more difficult to transfer and the adsorbed amount of dye decrease.

Additionally at pH < 6 ~ pH$_{pzc}$ ~ 6, 5 and at pH < 4 ~ pH$_{pzc}$ ~ 3, 7 for WCKOH and WCHCl respectively, in this case, the chemical treated sorbent surface has more positive charges than negative ones. Thus, in strong acidic conditions, carboxylic groups are probably protonated and the interaction that could occur between chemically treated sorbent surface and the cationic dye (EV) could be favored by the H–π interactions between the π aromatic rings from EV and —COOH groups [16].

Effect of the contact time

Contact time is among the main parameters for successful deployment of the adsorbent for practical application [11]. Several experiments were conducted in order to determine the time to equilibrium and maximum adsorption of EV onto both adsorbents. In this context, the effect of the contact time under different initial dye concentrations (50 to 200 mg/L) on the adsorption of EV onto both WCKOH and WCHCl is presented in Fig. 4. EV showed for both adsorbents, WCKOH and WCHCl, a fast rate of adsorption during the first 100 min and equilibrium was achieved within 150 min.

Three characteristic zones could be distinguished: maximum rates until twenty minutes, followed by decreasing rates until about 150 min and finally, a plateau was reached corresponding to equilibrium. However, no significant adsorption after 150 minutes for both WCKOH and WCHCl was recorded. Adsorption equilibrium, Qe, increased from 25 to 130 mg/g with increasing initial concentrations from 30 to 200 mg/L, showing that the initial dye concentration plays a major role in the adsorption capacities of EV onto both WCKOH and WCHCl (Fig. 4).

Adsorption kinetics

To describe adsorption kinetics, some kinetic models, pseudo-first-order and pseudo-second-order models, were applied in order to find the adsorption mechanism.

Pseudo-first-order equation

The pseudo-first-order kinetic model is the first order rate equation for the adsorption of a solid/liquid system based on the adsorption capacity [17]. The linear form of the pseudo-first-order equation is given by Eq. (2):

$$\ln\left(Q_e - Q_t\right) = \ln Q_e - k_1 t \tag{2}$$

Where Q_e (mg/g) and Q_t (mg/g) refer to the amount of dye adsorbed at equilibrium and at time t (min), respectively, k_1 (L/min) is the equilibrium rate constant of the pseudo-first-order equation. The rate constants are obtained from the straight line plots of ln (Q_e − Q_t) against t (Fig. 5 a and b).

Pseudo-second-order equation

The pseudo-second-order model is based on the assumption of chemisorption of the adsorbate on the adsorbent [18]. This model is given by Eq. (3):
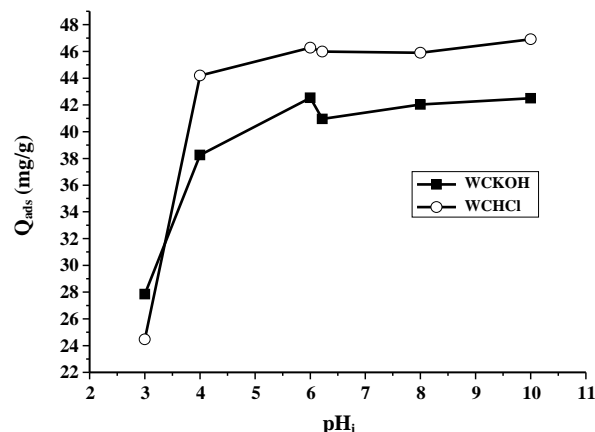
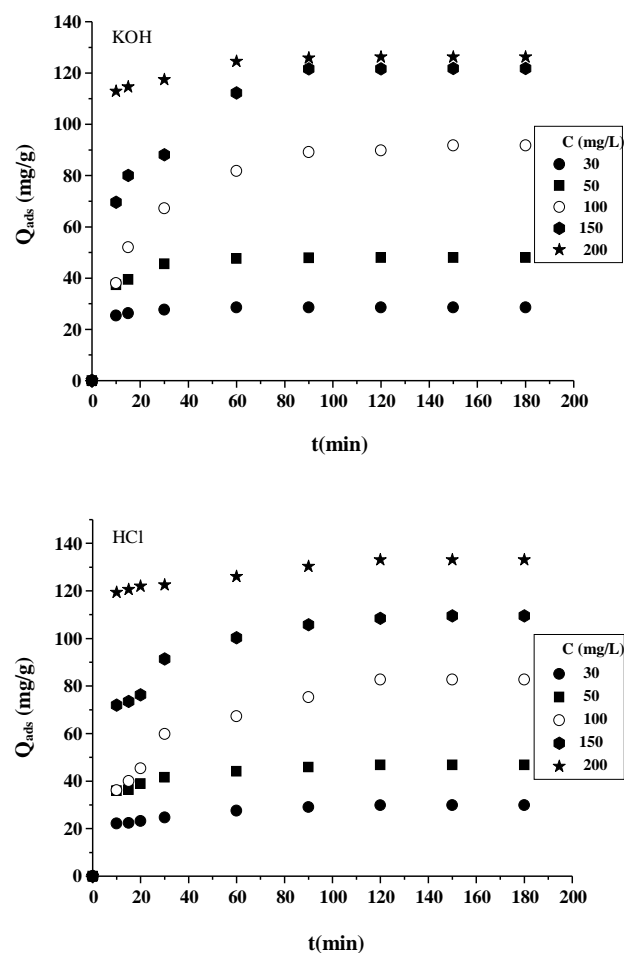

Fig. 3: Effect of pH on EV adsorption by WCHCl and WCKOH.

Fig. 4: Effect of the contact time and the initial EV concentration on the adsorption capacity of both WCHCl and WCKOH adsorbents. (T=25°C, agitation speed = 200 rpm, pH= 6).
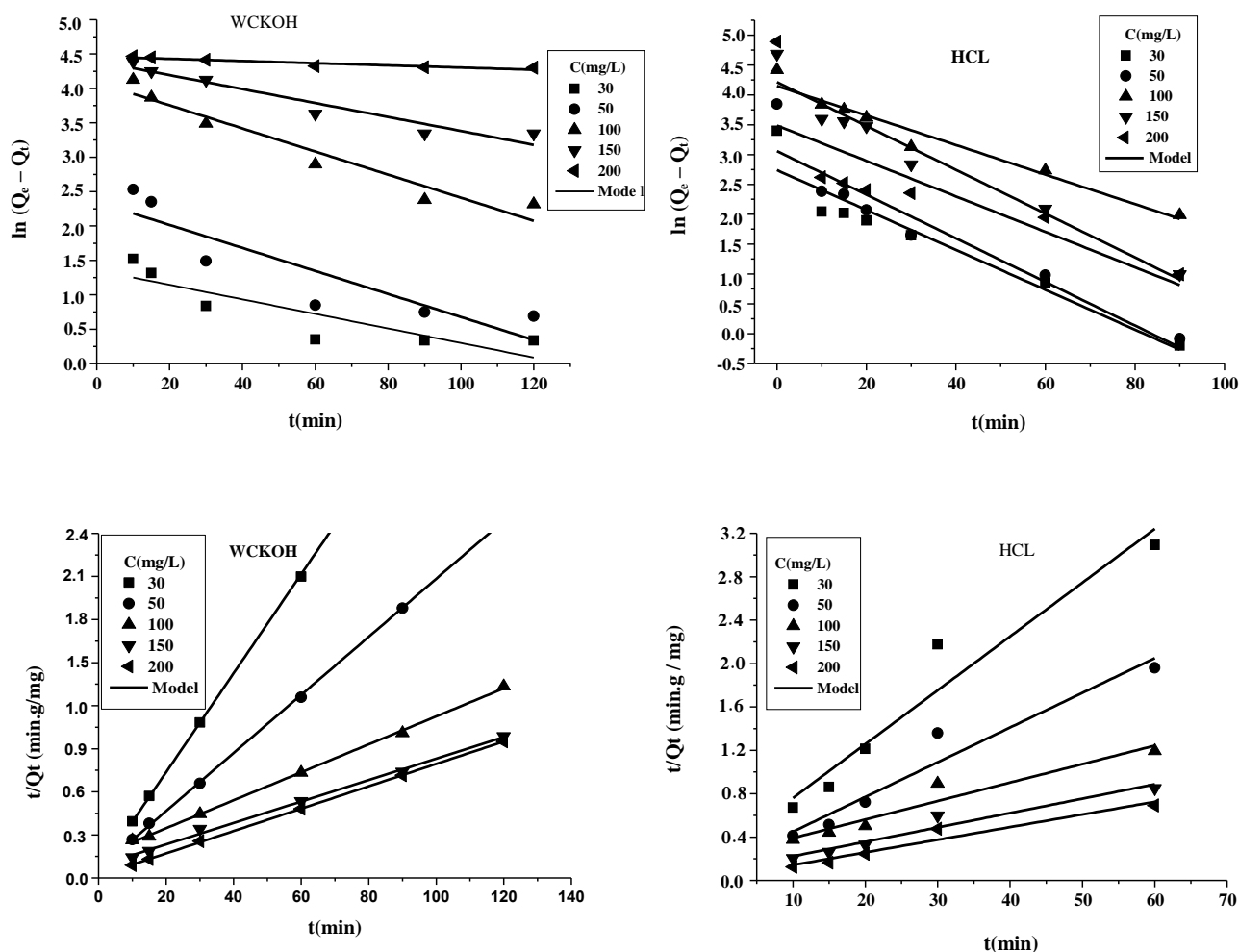
Fig. 5: Experimental (symbols) and calculated data (continuous lines) by means of pseudo-first order (a, b) and pseudo-second-order kinetic model (c, d) for EV adsorption onto both WCKOH and WCHCl adsorbents at various concentrations. (T=25°C, agitation speed = 200 rpm, pH=6).

$$\frac{t}{Q_t} = \frac{1}{k_2 Q_e^2} + \frac{1}{Q_e} t \tag{3}$$

where k_2 (g/(mg min)) is the equilibrium rate constant of the pseudo second-order equation. The straight line plots of t/Q_t against t are tested to obtain the rate parameters.

Pseudo-first and pseudo-second kinetic models were applied (Fig.5 c and d) and characteristic parameters were calculated (Table 2). The highest correlation coefficients were found for the pseudo –second order model onto both adsorbent of EV ($R^2 > 0.99$). It is evident from these results that experimental data followed a pseudo-second-order kinetic model for both WCKOH and WCHCl
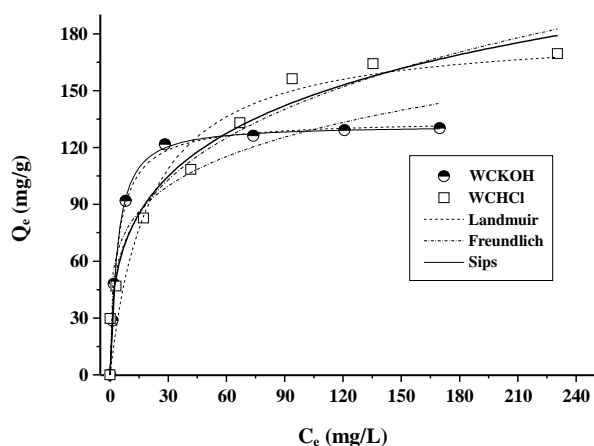
adsorbents at all investigated initial dye concentrations (Fig.5 c and d). Contrarily, the pseudo-first-order model showed less accurate fitting of experimental data. Similar trends were found by *Tsai et al.* [1].

Adsorption isotherm analysis

Adsorption isotherms of EV onto MWC are displayed in Fig.6, showing that the chemical treatments affected significantly the adsorbed amounts, which were higher in the case of acid treatment (WCHCl) if compared to alkaline treatment (WCKOH); adsorption uptake were ~ 170 mg/g and ~ 130 mg/g for WCHCl and WCKOH, respectively. Adsorption can be explained on the basis of an electrostatic interaction between the ionic dye

Table 2: Kinetics parameters for EV biosorption onto both WCHCl and WCKOH at different concentrations. (T=25 ± 2°C; pH= 6).

Sample	C_0	Q_{exp}	Pseudo first order			Pseudo-second order		
	(mg/l)	(mg/g)	Q_e (mg/g)	K_1 (min^{-1})	R^2	Q_e (mg/g)	K_2 (g/mg min)	R^2
WCHCL	30	29.91	15.49	0.0334	0.893	31.03	0.00520	0.9995
	50	46.84	21.31	0.0365	0.875	48.15	0.00460	0.9998
	75	82.73	63.39	0.0247	0.949	92.25	0.00058	0.9977
	100	109.54	67.54	0.0367	0.945	114.94	0.00108	0.9996
	200	133.08	32.68	0.0296	0.573	134.77	0.00310	0.9997
WCKOH	30	28.60	3.88	0.0105	0.707	28.99	0.025	0.9999
	50	48.03	10.49	0.0167	0.746	49.43	0.006	0.9997
	75	91.75	59.75	0.0168	0.921	102.67	0.0007	0.9987
	100	121.75	81.15	0.0101	0.906	133.87	0.0006	0.996
	200	126.21	86.74	0.0016	0.847	128.21	0.0041	0.9998

Fig. 6: Equilibrium isotherms for EV onto WCHCl and WCKOH adsorbents. Comparison between experimental data (symbols) and predictions of the Langmuir, Freundlich, and Sips models (lines) (T=25°C, agitation speed = 200 rpm pH=6).

molecule and the charged biosorbent. Indeed, according to the pH_{pzc} values, 6.5 and 3.7, the alkaline treated biosorbent and the acid treated biosorbent were positively and negatively charged at pH 6, respectively. Adsorbent treatment led to a strong increase of its adsorption capacity of the dye (EV) if compared to the untreated wild carob powder [15]. The adsorption of cationic dyes is favored on acidic materials by mechanisms involving to some extent electrostatic forces, but the main role is played by the dispersive forces. These results can be therefore justified by a mechanism involving the

predominance of the dispersion forces compared to the electrostatic interactions.

Equilibrium data, commonly known as adsorption isotherms, describe how adsorbates interact with adsorbents and hence are critical in optimizing the use of adsorbents and provide information on the type and the capacity of the adsorbent. Experimental data points were fitted to the *Langmuir* [19], *Freundlich* [20] and *Sips* [21] empirical models, which are the most frequently used two- and three-parameter equations in the literature; they describe the non-linear equilibrium between adsorbed pollutant on the adsorbent (Q_e) and pollutant in solution (C_e) at a constant temperature.

The Langmuir isotherm model assumes uniform energies of adsorption onto the adsorbent surfaces. Furthermore, the Langmuir equation is based on the assumption of the existence of monolayer coverage of the adsorbate at the outer surface of the adsorbent where all adsorption sites are identical. The Langmuir equation is given as follows [19]:

$$\frac{Q_e}{Q_m} = \frac{K_L C_e}{1 + K_L C_e} \tag{4}$$

Where Q_e is the equilibrium dye concentration on the adsorbent (mg/g); C_e, the equilibrium dye concentration in solution (mg/L); Q_m, the monolayer capacity of the adsorbent (mg/g); and K_L is the Langmuir constant.

The Freundlich isotherm model assumes neither homogeneous site energies nor limited levels of adsorption.

Table 3: Langmuir, Freundlich and Sips constants for the adsorption of Ethyl Violet onto WCKOH and WCHCl.

Model	Parameters	WCKOH	WCHCl
Langmuir	Q_{exp} (mg/g)	130	170
	Q_m (mg/g)	134.4	182.2
	K_L (L/mg)	0.25	0.036
	R^2	0.995	0.941
Freundlich	$1/n_F$	0.21	0.28
	K_F (mg/g)(L/mg)$^{1/n}$	48.87	36.59
	R^2	0.897	0.974
Sips	Q_{ms} (mg/g)	131.58	462.46
	K_S (L/mg)	0.269	0.0012
	m	1.14	0.377
	R^2	0.996	0.978

The Freundlich model is the earliest known empirical equation and is shown to be consistent with the exponential distribution of active centers, characteristic of heterogeneous surfaces [20]:

$$Q_e = K_F C_e^{1/n} \qquad (5)$$

Where Q_e is the equilibrium dye concentration on the adsorbent (mg/g); C_e, the equilibrium dye concentration in solution (mg/L); K_F and $1/n$ are empirical constants indicative of adsorption capacity and adsorption intensity, respectively.

The Sips isotherm is a combination of the Langmuir and Freundlich isotherms [21]:

$$\frac{Q_e}{Q_{ms}} = \frac{(K_S C_e)^m}{1 + (K_S C_e)^m} \qquad (6)$$

Where Q_{ms} is the maximum monolayer adsorption (mg/g), K_s is the Sips constant (L/mg) and m the exponent of the Sips model.

Experimental data of EV adsorption on both WCKOH and WCHCl were fitted to the isotherm models; the graphical representations of these models are presented in Fig. 6 and all constants are collected in Table 3. It can be seen that Sips and Langmuir models led to the most accurate estimations with correlation coefficients R^2 close to 1 (Table 3). However, for the WCHCl adsorbent, the Langmuir model compared to the Sips model appeared to be the most appropriate leading to a maximum adsorption

capacity of $Q_{m,cal} = 182.45$ mg/g, namely close to the experimental value (170 mg/g). The Freundlich model underestimated experimental data for WCKOH compared to the WCHCl. The high value of "m" from the Sips model (Table 3) confirmed that EV sorption onto WCKOH occurred by the formation of a multilayer.

In summary, experimental data for adsorption equilibrium of the considered cationic dye was accurately fitted by the Sips, Langmuir and Freundlich models in the case of WCHCl; while for WCKOH, Sips and Langmuir models described better experimental result if compared to the Freundlich model. Maximum sorption capacities (Q_{ms}) obtained from the Sips and Langmuir models were 131.58 and 134.4 mg/g for WCKOH and 462.46 and 182.2 mg/g for WCHCl at pH 6 and 298 K, respectively.
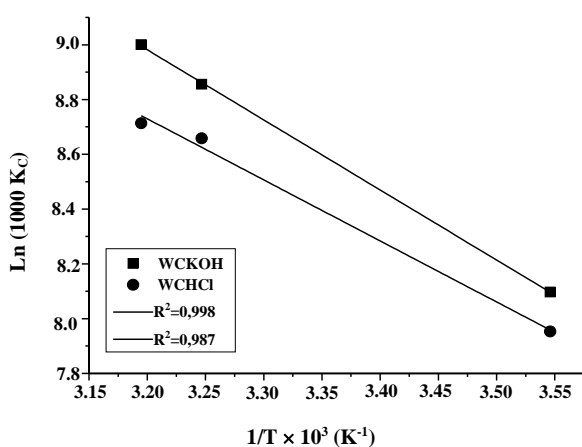
Thermodynamic analysis

The thermodynamic parameters reflect the feasibility and the spontaneous nature of a biosorption process. Parameters such as the free energy change (ΔG), the enthalpy change (ΔH) and the entropy change (ΔS) can be estimated using equilibrium constants varying with temperature. The free energy change of the adsorption reaction is given using Equation (7) as reported by *Milonjic* [22] and *Reffas et al.* [15]:

$$\Delta G^\circ = -RT\ln(\rho K c) \qquad (7)$$

Where ΔG° is the free energy change (kJ mol^{-1}), R the universal gas constant (8.314 J mol^{-1}K^{-1}), T the absolute

Table 4: Thermodynamic parameters for the adsorption of EV on WCHCl and WCKOH.

Adsorbent	Temperature (K)	ΔG° (kJ/mol)	ΔH° (k J/ mol)	ΔS° (J/ mol. K)
WCHCl	282	-18.99	21.29	142.87
	298	-21.28		
	308	-22.71		
	313	-23.42		
WCKOH	282	-18.67	18.55	131.98
	298	-20.78		
	308	-21.10		
	313	-22.76		

Fig. 7: Van't Hoff equation for EV adsorption onto both WCKOH and WCHCl adsorbents.

temperature (K), K_C the thermodynamic equilibrium constant (L/g) (Eq. 7) and ρ the water density (g/L). ΔH° and ΔS° values of the biosorption process were calculated from the Van't Hoff equation Eq. (8):

$$\ln(\rho K_C) = -\frac{\Delta H^o}{RT} + \frac{\Delta S^o}{R} \tag{8}$$

$$K_C = \frac{Q_e}{C_e} \tag{9}$$

ΔH and *ΔS* can be then deduced from the slope (ΔH/R) and the intercept (ΔS/R) of the plot of Ln (ρK_C) versus *1/T*. (Fig.7)

The calculated thermodynamic parameters are given in Table 4. In general, the change in free energy for physisorption is between – 20 and 0 kJ/mol. and in a range of −80 to – 400 kJ/mol for chemisorption [23].

The obtained values, about -20 kJ/mol, for all tested temperatures, were characteristics of a spontaneous physisorption process; it was in agreement with the low impact of the temperature on the EV adsorption (Fig.7). The positive value of enthalpy showing that the adsorption of ethyl violet onto both adsorbents is endothermic. These results are consistent with those found by *Tsai et al.* [1] for the same dye onto spent bleaching earth. The positive value of entropy change suggested an increasing randomness at the solid-solution interface during the adsorption of EV onto both adsorbents.

CONCLUSIONS

Acid and basic treated wild carob were investigated for the removal of cationic dye (EV) and the main results are as follows:

● Chemical treatments affect significantly the adsorbed amounts, which were higher in the case of acid treatment (WCHCl) if compared to an alkaline treatment (WCKOH).

● The adsorption capacity was found to be 170 and 130 mg/g for WCHCl and WCKOH, respectively.

● Experimental data for adsorption equilibrium of considered cationic dye was accurately fitted by the Sips, Langmuir and Freundlich models in the case of WCHCl; while for WCKOH, the Sips and Langmuir models described better the experimental results if compared to the Freundlich model.

● Kinetic data were closely fitted by the pseudo-second-order kinetic model for both adsorbents.

● The thermodynamics of the adsorption process revealed that it was an endothermic, spontaneous and physisorption process.

This study showed that both WCHCl and WCKOH are efficient biosorbents for the removal of Ethyl violet from wastewater.

For practical application, contaminated materials can be incinerated at a temperature greater than 500 °C (calcination) in order to reuse them as new adsorbents (activated carbon). The corresponding work is in progress in the laboratory.

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