



Expressive Removal of Cationic Dyes (Methylene Blue and Crystal Violet) by Carnauba Straw (*Copernicia cerifera*)

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Abstract The current study describes the removal of methylene blue (MB) and crystal violet (CV) dyes from aqueous media using carnauba straw as a bioadsorbent. Batch adsorption experiments were carried out at different conditions of pH (1.0 - 10.0), temperature (25 - 55 °C), time (5 - 360 min) and adsorbate concentration (0.1 - 2.0 mmol L⁻¹). The adsorbent was characterized by thermogravimetry, X-ray diffraction, FTIR, pH_{pzc} and conveniently compared with other lignocellulosic materials. Langmuir, Freundlich and Sips adsorption isotherms were applied and the results showed that the Sips and Langmuir models described better the experimental data regarding both dyes. The maximum adsorbed amounts were 0.294 mmol g⁻¹ for MB (25 °C) and 0.399 mmol g⁻¹ for CV (55 °C). The effect of temperature on the equilibrium adsorption was investigated, indicating different patterns for MB (exothermic) and CV (endothermic).

Keywords lignocellulosic, dye removal, carnauba, bioadsorbent

1. Introduction

The direct discharge of dyes into the environment is a matter of major concern, and their removal from wastewater continues to be a challenge. These colorful substances are used in several industries, such as the textile, pharmaceutical, leather, paper, rubber, cosmetics, plastic and food ones. In terms of pollutants, textile dyes are some of the most harmful environmental contaminants, due to their properties that include toxicity (which can cause allergy, dermatitis and skin irritation) and mutagenicity. Furthermore, most of these products are oxidizing agents, resistant to *photo*- and *bio*- degradation that can also inhibit the photosynthetic activity because of their strong colors, changing the levels of dissolved solids, chemical and biological oxygen demand, and affecting many forms of life. It is currently estimated that there are more than 100 thousand commercially available dyes, with annual



global production over 7×10^5 tons, and that 2 to 15% of them are discharged in effluent from manufacturing operation, while 10% are discharged from textile and associated industries [1-5].

Although many different approaches are available for the remediation of contaminated areas, adsorption remains one of the most used techniques, because of its simplicity, efficiency, convenience, and reasonably low cost. This technical approach is feasible even for substances that are resistant to degradation by biological or physicochemical treatments [6-8]. Moreover, the possibility designing and reusing adsorbents make them not only competitive, but also interesting from the scientific point of view, which generates a diversity of studies and applications.

Currently, most industrial processes use activated carbon as a sorbent due to its adsorption ability and wide commercial availability [9-10]. However, natural materials zeolite, charcoal, such as native agricultural wastes, clays, anion clay can also show excellent adsorptive capabilities, or potential for that, in addition to being cheap and abundant [8-9, 11-12]. Investigation of these adsorbents has caught the attention of many researcher teams that demonstrated their importance as an alternative to the conventional ways [13].

In the present work, the carnauba straw was investigated as an eco-efficient adsorbent with potential to remove cationic dyes from aqueous medium. Carnauba (*Copernicia cerifera*) is popularly referred to as *the tree of life*, or *the tree of a thousand uses* in agreement with all that it provides: the roots are diuretic, used in skin diseases and syphilis; the fruits are utilized for animal feed; the trunks are used in construction, and the straws have greater application as it can be used as raw material for handicrafts and housing covers, moreover the wax powder has wide application in the chemical, pharmaceutical, cosmetic, food and electronics industries [14-15]. Methylene blue (MB) and crystal violet (CV) were chosen as dyes models due their purity, charge, extensive use and present wide literature allowing further comparisons. In addition, both dyes can cause toxic effects on humans and aquatic life. MB is cited as one of the most commonly used water-soluble cationic dyes mainly in textile, paper and printing industries [5, 16-18]. The CV has a major importance in microbiologic methods and is also used in industrial processes [19-20].

2. Experimental

Reagents and solutions

All reagents used were of analytical grade: methylene blue (ISOFAR), crystal violet (ISOFAR), potassium chloride (Merck), hydrochloric acid and sodium hydroxide (Merck).

Freshly distilled water was used to prepare all the solutions.

Preparation and characterization of the sorbent

The carnauba straw was acquired in Barreirinhas, MA-BRA. After the wax removal, the straw was crushed, washed with distilled water, dried at 50 °C for 24 h, and sieved to 0.088 – 0.177mm.

The thermogravimetric (TG) and differential thermogravimetric (DTG) curves were recorded on a TG Instruments Hi-Res TGA 2950 model device, under the following operational conditions: heating rate 10°C/min, temperature range 30 – 790 °C, sample weight 50 mg, under an inert nitrogen atmosphere.

The XRD patterns were obtained with a Shimadzu diffractometer (model XRD7000), operated at 40 kV, 30 mA, using Cu as radiation source (Cu K- α , $\lambda = 154.06$ pm) and scanning from 1.4° to 70°, with a range of 5° min⁻¹. The crystallinity index of the material was calculated according to Balistrieri and Murray [21]. Using the following equation:

$$\%I_C = \left[\frac{I_{200} - I_{am}}{I_{200}} \right] \times 100 \quad \text{Equation 1}$$

where I_{200} corresponds to the intensity in the crystalline peak ($2\theta \approx 22^\circ$), I_{am} represents the intensity of the representative of the amorphous region ($2\theta \approx 18^\circ$), and $\%I_C$ indicates the crystallinity index of the material.

Vibrational absorption spectra in the 4000-400 cm⁻¹ region were obtained using an MB series spectrometer Bomem-Hartmann & Braun. KBr tablets were used, with Fourier transform and resolution of 16 cm⁻¹.

The pH_{pzc} value of the adsorbent, pH at the point of zero charge ($\Delta\text{pH} = \text{pH}_i - \text{pH}_f = 0$), was estimated by the addition of solids method [22]. In short, twelve samples of 100.0 mg of the adsorbent were placing in contact with



25.0 mL of KCl solution (0.10 mol L^{-1}), with initial pH (pH_i) ranging from 1.0 to 12, previously adjusted with HCl or NaOH. After 24 h of contact at room temperature and under constant agitation, the adsorbent was removed by filtration and the final pH (pH_f) of the supernatant was measured using a pH meter Digimed, model DM - 31.

Batch sorption studies

All adsorption experiments were conducted in a bath shaker model Luca 222, which provides temperature and stirring speed controls. The values of the investigated parameters and the respective experimental conditions are given in Table 1. The final concentrations of MB and CV in solution were measured using a Varian Spectrophotometer UV-Vis, model Cary 50. Specific analytical curves were prepared for each dye and pH, and the amount of adsorbed dye (Q_{eq} , mg g^{-1}) was calculated according to Eq. (2):

$$Q_{eq} = (C_i - C_f)V/m \quad \text{Equation 2}$$

where C_i , represents the initial and final (or equilibrium, C_{eq}) concentration (mg L^{-1}) concentration of the dye in the solution, respectively; V is the volume of the dye solution (L); and m , is the dry weight of the adsorbent (g).

Table 1: Parameters and their ranges used for the removal of Methylene Blue and Crystal Violet by Carnauba straw

Parameter	Range	Experimental conditions
pH	1.0 - 10 (at intervals of 1.0)	Adsorbent: 100.0 mg Dye: 25 mL (250 mg L^{-1}) Time: 6 h; Temperature: $25 \text{ }^\circ\text{C}$
Time(min)	5, 10, 20, 30, 45, 60, 90, 120, 180, 240, 300, 360	Adsorbent: 100.0 mg Dye: 25 mL (100 and 1000 mg L^{-1}) pH: 6 Temperature: $25 \text{ }^\circ\text{C}$
Temperature($^\circ\text{C}$)	25 - 55 (at intervals of 1.0)	Adsorbent: 100.0 mg Dye: 25 mL (100 mg L^{-1}) pH: 6 Time: 150 min
Dye concentration mmol L^{-1}	0.1 - 2.0 (at intervals of 0.1)	Adsorbent: 100.0 mg Dye: 25 mL (100 mg L^{-1}) pH: 6 Time: 150 min Temperature: 25, 35, 45, 55°C

Kinetics experiments were carried out at the best pH condition and the obtained data were fitted to pseudo-first order [23] (Eq.3) and pseudo-second order (Eq. 4):

$$Q_t = Q_{eq} (1 - e^{-k_1 t}) \quad \text{Equation 3}$$

$$Q_t = \frac{k_2 Q_{eq}^2 t}{1 + Q_{eq} k_2 t} \quad \text{Equation 4}$$

where Q_t (g mol^{-1}) equals the amount adsorbed at time t (min); k_1 (min^{-1}) is the rate constant for pseudo first order equation and k_2 ($\text{g mol}^{-1} \text{ min}^{-1}$) is the rate constant of the pseudo-second order equation.

The effect of the temperature on the adsorptions was used to estimate the thermodynamic parameters ΔH^0 , ΔS^0 , ΔG^0 (Eq. 5) through van't Hoff equation (Eq. 6). The equilibrium constants were evaluated from Eq. 7, according to the literature [24-25]. All the isotherm results were adjusted to the models of Freundlich [26] (Eq. 8), Langmuir [24] (Eq. 9) and Sips [27] (Eq. 10).

$$\Delta G^0 = \Delta H^0 - T\Delta S^0 \quad \text{Equation 5}$$

$$\text{Ln } K_{eq} = \frac{-\Delta H^0}{RT} + \frac{\Delta S^0}{R} \quad \text{Equation 6}$$



$$K_{eq} = \frac{Q_{eq}}{Q_{max} - Q_{eq}} \cdot \frac{1}{C_{eq}} \quad \text{Equation 7}$$

$$Q_{eq} = K_f C_{eq}^{\frac{1}{n}} \quad \text{Equation 8}$$

$$\frac{Q_{eq}}{Q_{max}} = \frac{K_L C_{eq}}{1 + K_L C_{eq}} \quad \text{Equation 9}$$

$$Q_{eq} = \frac{Q_{max} K_s C_{eq}^{\frac{1}{n_s}}}{1 + K_s C_{eq}^{\frac{1}{n_s}}} \quad \text{Equation 10}$$

$$R_L = \frac{1}{1 + K_L C_0} \quad \text{Equation 11}$$

C_{eq} (mol L^{-1}) is the concentration at equilibrium; C_0 (mol L^{-1}) is the initial concentration; Q_{max} is the maximum adsorbed amount mol g^{-1} ; K_L , K_F , K_s and R_L are the constants of Langmuir, Freundlich and Sips, and the dimensionless constant separation factor (Eq. 11), respectively; n is the adsorption parameter for the Freundlich model; n_s is the parameter associated with characteristic of the adsorption sites; K_{eq} indicates the equilibrium constant; R is universal constant of the gases ($8.314 \text{ J mol}^{-1} \text{ K}^{-1}$) and T (K) is the absolute temperature. The changes in enthalpy (ΔH^0), entropy (ΔS^0) and free energy (ΔG^0) are given in kJ mol^{-1} , $\text{J mol}^{-1} \text{ K}^{-1}$ and kJ mol^{-1} , respectively. In order to assure the accuracy of the results, all the experiments in this study were conducted in duplicate.

3. Results and Discussion

Characterization of adsorbent

Regarding to biological source, the biomass can be divided into several types or varieties such as herbaceous, aquatic, woody plants, etc. This diversity implies that biomass will exhibit some structural and chemical variations, but the major structural elements will always be cellulose, hemicellulose and lignin. As carnauba straw is a woody biomass, its FTIR spectrum must to show the same or similar functional groups to its correlate species. In fact, as presented in the Fig 1 and clearly specified in the Table 2, this lignocellulosic material showed all the expected peaks for these class of materials [28-31]. The broad band in the range of $3700\text{--}3000 \text{ cm}^{-1}$ was attributed to νOH vibrations of the hydroxyl groups in phenolic and aliphatic structures present in all lignocellulosic materials. The band centered around $3000\text{--}2780 \text{ cm}^{-1}$ is related to νCH groups of the backbone biopolymer, aromatic methoxyl groups and in methyl and methylene groups of side chains. The bands at 1735 cm^{-1} and near to 1626 cm^{-1} were assigned to stretching vibration of the unconjugated carbonyl/carboxyl stretching νCO group and δOH of the absorbed water, respectively.

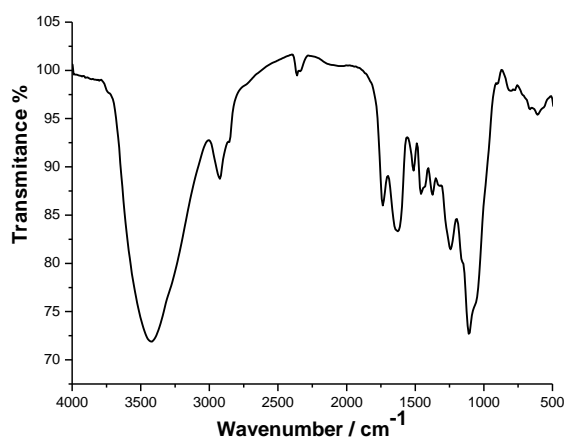


Figure 1: FTIR spectra of untreated carnauba straw



Table 2: FT-IR band assignments for carnauba straw.

Wave number (cm ⁻¹)	Assignment ^a
3700 - 3000	OH stretching
3000 - 2780	C-H symmetrical stretching
1735	C=O stretching vibration
1626	OH bending of absorbed water
1513	C=C aromatic symmetrical stretching
1454	HCH and OCH inplane bending vibration
1371	In-the-plane CH bending
1241	G (guaiacyl) ring stretching
1107	C-C plus C-O plus C=O stretch; G condensed > G etherfied
808	COC,CCO and CCH deformation and stretching
667	C-OH out-of-plane bending

^aPeak assignments were made according to literature [28-30].

The thermogravimetric and derivative curves for carnauba straw under a nitrogen atmosphere are presented in Fig 2. Fernandes et al [31] divided into three stages of weight loss their TGA results for some lignocellulosic wastes (sawdust, marcs, stalks, peach plum and olive pits): up to 200 °C, between 200 and 550 °C, with maximum weight loss at around 330 °C, and the last stage above 950 °C, which is produced at high temperature and the weight loss is very smaller. For the purpose of this study only the first two stages were considered.

The initial decrease can be attributed mainly to water release, and approximately 8.5% of the matrix's mass were lost in this first stage. In the second stage, corresponding to liberation of species from the decomposition of its main components, hemicellulose, cellulose and lignin (CO₂, CO, CH₄ and H₂O), the weight loss was 79%. These values are in line with the reported by literature [32-35]. The first weight loss at the second stage is mainly due to hemicelluloses decomposition, followed by the weight loss of the cellulose and lignin decomposition.

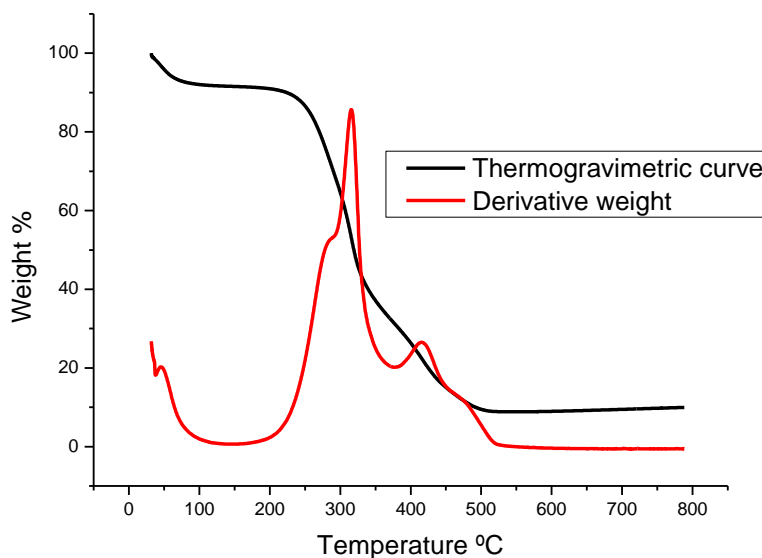


Figure 2: Thermogravimetric curves of in natura carnauba straw

X-ray diffraction (XRD) is an analytical tool used to provide information about structural parameters of the crystalline materials. As hemicellulose and lignin are amorphous, X-ray scattering study of lignocellulosic is possible only due to the highly ordered chain of glucose molecules with (1-4) glycosidic linkage [36]. The amorphous contribution is represented by broader and less clearly refined features in the diffraction pattern.



Fig3 illustrates the X-ray diffraction spectrum of the adsorbent which exhibits one defined peaks at 2θ equals to 22.2° and a shoulder at around 15.8° . According to Tserki *et al*, [37] the first reflection corresponds to the (200) crystallographic plane, while the shoulder is probably due to (110) or ($1\bar{1}0$) planes. As the amorphous materials content is high (lignin, hemicelluloses, and amorphous cellulose), there is the appearance of a shoulder instead the well defined peak. The degree of crystallinity was estimated at 32% in accordance with the peak height method, developed by Segal and co-workers [21, 38]. Trees' cellulose usually have a value around 40% [39-40], suggesting that the obtained value is reasonable.

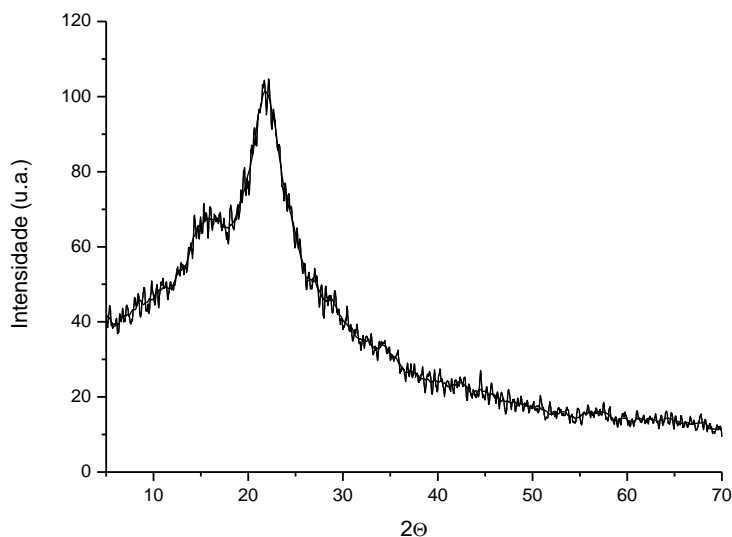


Figure 3: X-ray diffraction spectrum of carnauba straw “in natura”

pH_{pzc}

It is very important to know the nature of the surface charge of the adsorbent in the aqueous media in any adsorption approach. The pH_{pzc} is the parameter that indicates at which particular value of pH the solid will develop positive, negative or zero net electrical density charge on its surface. In case of protonation of the superficial groups, the surface charge of the particles will be positive, $\text{pH}_i < \text{pH}_f$, and when these groups are deprotonated by the solvent, that surface charge will be negative $\text{pH}_i > \text{pH}_f$. Only at pH equal to pH_{pzc} that the net surface charge will be zero.

Fig4 shows the curve of the pH variation as a function of the initial pH for the carnauba straw. Clearly is observed that there are surface groups that alter the hydrogenionic balance of the electrolyte, indicating a pH_{pzc} value around 5.5, very close of the reported values for other lignocellulosic materials [34-35, 41].



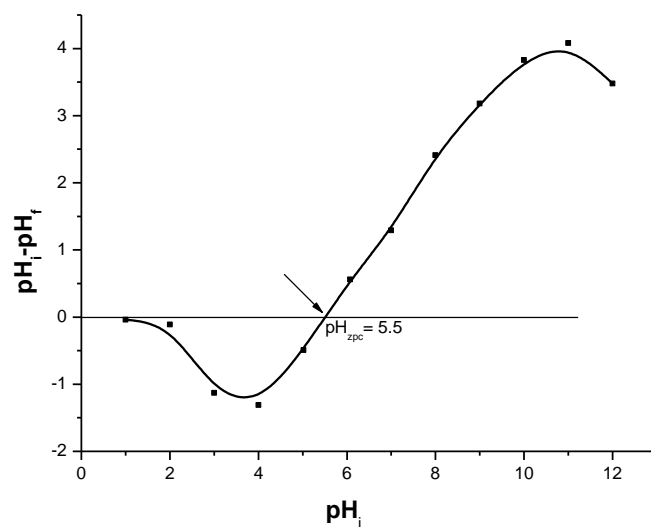


Figure 4: pH_{zpc} curve for carnauba straw ($KCl\ 0.1\ mol\ L^{-1}$; contact time 24 h).

Effect of the pH

Charged species in solution, such as adsorbents and adsorbates, are surrounded by counterions, which can be distributed in a diffuse layer or directly adsorbed at a surface. During the adsorption process, the both electrical layers overlap each other changing the amounts and the distributions of such counterions in solution. These charge balances, as well as the specific interaction adsorbent-adsorbate, reflect in the kinetic and thermodynamic aspects of the adsorption. In view of its importance on the generation of charge and electrostatic interactions, pH plays an important role on the adsorption processes, especially those which are mostly mediated by charge.

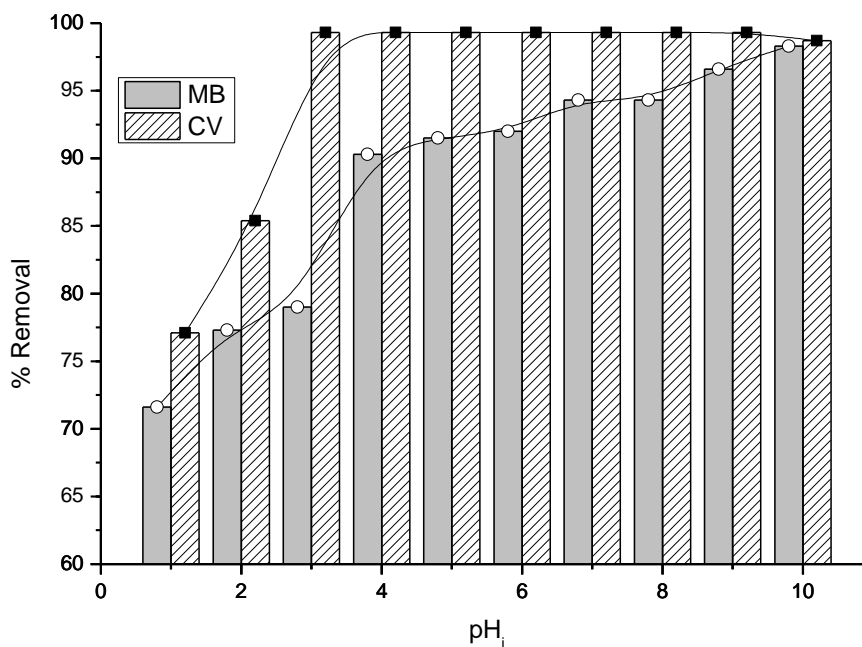


Figure 5: Percentage removal of the dyes methylene blue and crystal violet by carnauba straw, as a function of pH.



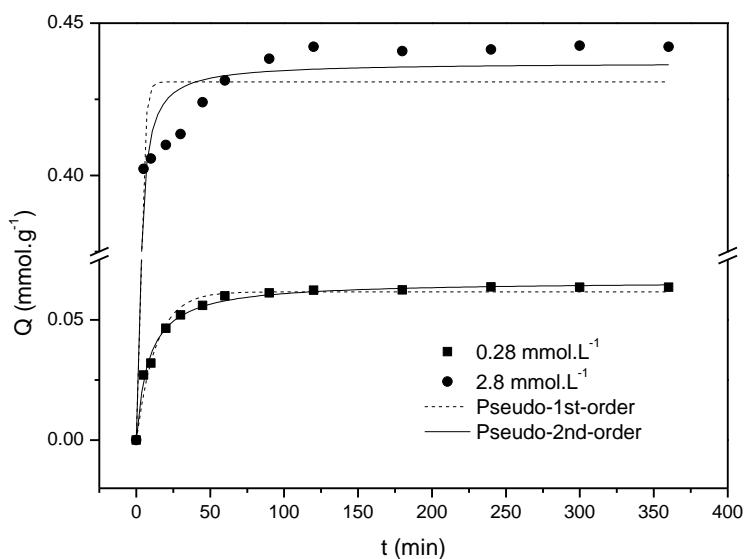
Fig 5 shows the percentages removal of MB and CV dyes by the carnauba straw at different pH values. It is noted the high removal of both dyes in a wide pH range, and a slight improvement in the adsorption with pH increasing.

According to IR results, the mainly functional groups present on the carnauba straw are oxygen-containing species, such as carboxylic, lactonic, phenolic (acids), ketonic, pyronic and p-electron system (basics). Under acid conditions and up to pH_{pzc} , the surface charge of the adsorbent is positive, due the protonation of such acids groups. Since both dyes are positively charged throughout the pH range investigated, the highest dyes removal percentages were achieved at pH tending towards alkaline, due the electrostatic contribution among dyes and surface. At acidic condition, however, it should be borne in mind that the sorption reflects different interactions between adsorbent and adsorbate. Therefore, there are sites that contribute to this process that are charge-independent and, as a consequence, not influenced by pH. The non-protonated sites of the support (for instance carbonyls and aromatic rings) may be responsible for the high adsorption throughout the pH range (> 70%). On the other hand, as the pH shifts to the alkaline region, there is an improvement on removal around 30 %, due to the negative charge on the surface of the adsorbent, representing the electrostatic contribution [42-46].

Usually untreated lignocellulosic materials release extractive (phenolic compounds) into the alkaline medium, what could be a problem. Then, there must be a compromise between the pH of the best removability of the adsorbate and that ensures the structural integrity of the adsorbent. For this reason, the pH established for further studies was 6.0.

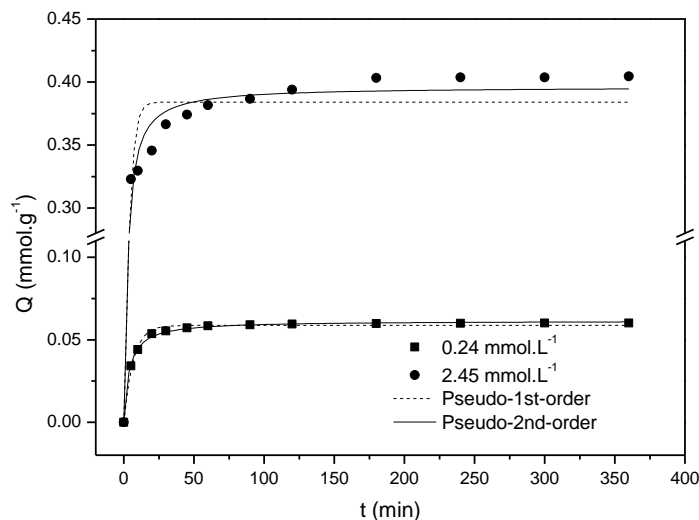
Kinetics of adsorption

Adsorption is often a complex multistep phenomenon, involving mass transfer, diffusion and surface interaction process. Kinetic studies help to describe the solute uptake rate, contact time and also to infer about the efficiency of the sorption [47]. Although kinetic models provide valuable insights of the sorption mechanisms may be not enough to describe the entire process. Lagergren kinetic first-order and the pseudo-second-order equations (Eqs 3 and 4, respectively) have been most widely used models for the adsorption of an adsorbate from aqueous solution. In the present study, the rate constant of the adsorption were determined from these models. Figs 6a and 6b show the kinetic experimental data and the non linear curve-fitting plots of *first-* and *pseudo-second-order*, for two different concentrations of the respective dyes. The obtained parameters for these two models are presented in Table 3.



(a)





(b)

Figure 6: Contact time and kinetics plots of adsorption of the dyes a) methylene blue and b) crystal violet, at solution pH 6.0.

The curves' profile analysis showed that the equilibration time was approximately 120 min for both dyes, and in both concentrations. This was the contact time established for the equilibrium studies. As shown (Table 3), the values of the correlation coefficient and equilibrium capacity (q_{te0}) confirmed the best applicability of the pseudo-second-order equation to the experimental data. Other studies also show a tendency for kinetic models of pseudo-second order for these dyes [3, 4, 47].

Table 3: Results from fitting pseudo-first and pseudo-second-order models for the adsorptions of methylene blue (MB) and crystal violet (CV) by carnauba straw

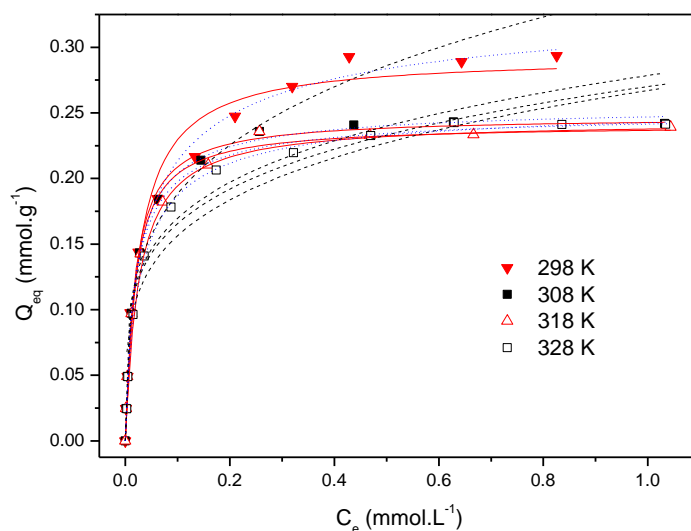
Dye	Concentration (mmol L ⁻¹)	1 st Order			2 nd Order			
		q_{exp} (mmol g ⁻¹)	k_1 (min ⁻¹)	q_{te0} (mmol g ⁻¹)	r^2	k_2 (mmol-1g min-1)	q_{te0} (mmol g ⁻¹)	r^2
MB	0.28	0.064	0.075	0.062	0.977	1.795	0.066	0.994
	2.80	0.443	0.520	0.431	0.988	3.879	0.437	0.995
CV	0.24	0.060	0.152	0.059	0.991	4.334	0.062	0.998
	2.45	0.405	0.318	0.384	0.962	1.629	0.396	0.988

Adsorption isotherms and temperature effect

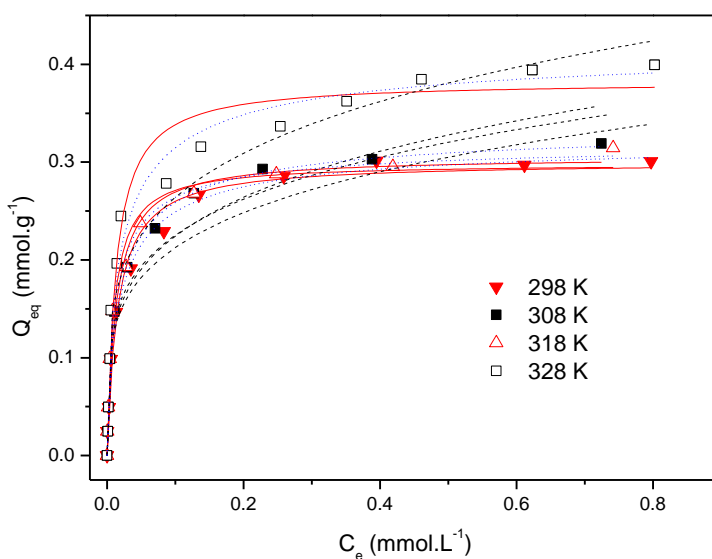
Once the pH and the equilibration time were defined, adsorption isotherms were performed at different temperatures (298, 308, 318 and 328 K). The experimental data are presented in Figs 7a and 7b along with the Freundlich, Langmuir and Sips nonlinear curves given by Eqs. 8 - 10, respectively.

The analysis of the isotherms showed that all were type I, which is characterized by an increase in the adsorbed amount, followed by a formation of a plateau at higher concentrations. Usually in this kind of isotherm the formation of a monolayer of adsorbed molecules occurs. Comparing isotherms, it is clear that the temperature produces some changes in the amount of MB and CV adsorbed, and that the equilibrium data were best represented by Sips and Langmuir isotherm equations. Table 4 summarizes the calculated adsorption parameters.





(a)



(b)

Figure 7: Adsorption isotherms for a) methylene blue and b) crystal violet on carnauba straw. The tendency plots are related to the models of: (—) Langmuir; (---) Freundlich, and (····) Sips. pH 6.0; 120 min

However, although the Sips model provided the highest adjusted R-square values, the Langmuir equation predicted better the maximum amount adsorbed. As R^2 values for both models, Langmuir and Sips, were quite similar, the former was used subsequently to estimate the thermodynamic parameters [43, 48-50].

Table 4 summarizes the experimental values for the maximum adsorbed quantities at each studied temperature and only to CV adsorption it was initially observed an positive effect of temperature, indicating an endothermic process. This may possibly due to the increase in the number of active sites and the mobility of the dye molecules at higher temperature [38]. In contrast, the adsorption to MB appeared to have an exothermic effect, in which the adsorption capacity decrease when the temperature rises [39].



Rytwo and Ruiz-Hitzky [51] studied the enthalpies of adsorption of methylene blue and crystal violet onto montmorillonite by direct calorimetric measurements. Their results also indicated different adsorption patterns for MB and CV, and that the enthalpy of adsorption can be a function of the adsorbed amount. MB, for example, showed endothermic at low loads, but became exothermic at higher adsorption ratios. This behavior indicates changes in the equilibrium coefficient according to Van't Hoff's equation.

Hameed and Ahmad [52] investigated the adsorption of Methylene blue (MB) by garlic peel. They found that the adsorption capacity increased from 82.64 to 142.86 mg/g when the temperature increased from 30 °C to 50 °C indicating that the adsorption is endothermic in nature. The adsorption of Crystal violet (CV) on phosphoric and sulphuric acid activated carbons (PAAC and SAAC) prepared from male flowers coconut tree. The effect of temperature on the adsorption rate was studied by carrying out a series of experiments at 28, 33, 38, 43 and 48 °C for both the carbons. The adsorption of crystal violet on PAAC and SAAC increased from 19.8% to 96.80% and 7.02% to 48.83%, respectively. This suggests that the adsorption process is endothermic in nature when temperature was increased from 28 to 48 °C at pH 6 and initial dye concentration of 40 mg/L. They concluded that increasing temperature may produce a swelling effect within the internal structure of the carbons enabling more dye molecules diffusion into carbon. Further, they also believed that the possibility of increase of the number of active sites for the adsorption with the increase of temperature. This may also be a result of an increase in the mobility of the dye molecule with the rise of temperature.

The equilibrium parameter R_L , or constant separation factor (Eq. 11), obtained from Langmuir isotherm and which can be used to predict whether the adsorption system is favorable or not, was calculated in function of the temperature and its values are also presented in Table 4. As all R_L values varied between 0 and 1 ($0 < R_L < 1$), the sorptions were favorable [53-54].

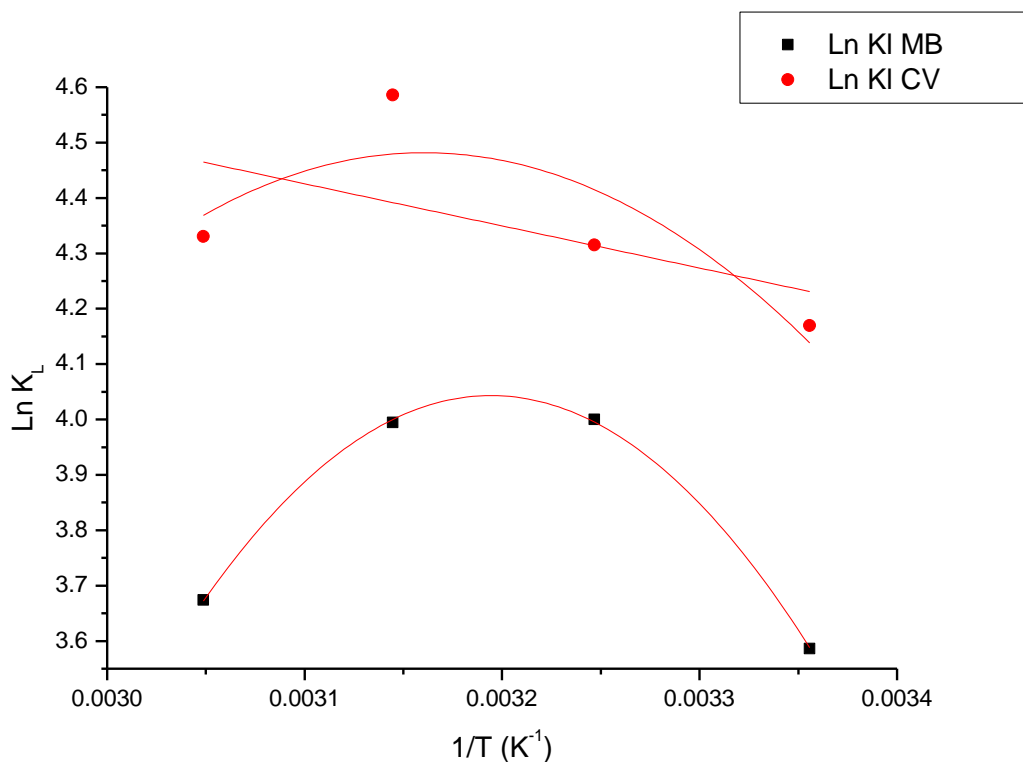
Table 4: The effect of the temperature on adsorptions of methylene blue (MB) and crystal violet (CV) by carnauba straw and results from fitting isotherm models (Eqs. 8 to 11)

Model	T(K)	MB				CV			
		q_{exp} (mmol g ⁻¹)	q_{teo} (mmol g ⁻¹)	K_L/R_L (L mmol ⁻¹)	R^2	q_{exp} (mmol g ⁻¹)	q_{teo} (mmol g ⁻¹)	K_L/R_L (L mmol ⁻¹)	R^2
Langmuir	298	0.294	0.293	36.1/0.22	0.980	0.301	0.299	64.7/0.13	0.987
	308	0.243	0.247	54.6/0.15	0.996	0.319	0.305	74.8/0.12	0.984
	318	0.239	0.241	54.3/0.16	0.994	0.315	0.299	98.1/0.09	0.986
	328	0.243	0.244	39.4/0.20	0.992	0.399	0.383	76.0/0.12	0.973
Freundlich	298	0.294	3.8	0.342	0.956	0.301	4.4	0.356	0.927
	308	0.243	4.6	0.278	0.906	0.319	4.2	0.386	0.932
	318	0.239	4.7	0.270	0.909	0.315	4.6	0.373	0.915
	328	0.243	4.3	0.267	0.902	0.399	4.4	0.446	0.942
Sips	298	0.294	0.343	7.54	0.995	0.301	0.324	1.3 / 18.3	0.995
	308	0.243	0.255	27.8	0.999	0.319	0.340	1.4 / 16.1	0.995
	318	0.239	0.251	24.3	0.997	0.315	0.320	1.3 / 26.9	0.994
	328	0.243	0.256	17.5	0.997	0.399	0.424	1.5 / 13.7	0.981

Thermodynamic Study

The temperature directly influences the adsorbed amount increasing the kinetic energy and mobility of the dye molecules, changing diffusion patterns and solubility equilibria [2, 55]. In some cases the temperature dependence of ΔH° can not be ignored, and a non-linear variation between $\ln K_{eq}$ and $1/T$ is observed. The Fig 8 corresponds to van't Hoff's graphics regarding the studied adsorption processes, which allowed the determination of the thermodynamic parameters.





Figure

8: van't Hoff graphics for adsorption of the dyes methylene blue ($y = 2.28x - 14.8$) and crystal violet ($y = 1.18 - 2.7x$) in carnauba straw in natura, pH 6 and contact time 180 minutes

Table 5: Calculated thermodynamic parameters for the adsorptions of methylene blue (MB) and crystal violet (CV) by carnauba straw

Dye	T (K)	K _{eq.} (L mol ⁻¹).10 ⁴	-ΔG° (kJ mol ⁻¹)	ΔH° (kJ mol ⁻¹)	ΔS° (J mol ⁻¹)	R ²
MB	298					
	308					
	318					
	328					
CV	298					
	308					
	318					
	328					

The absence of a more precise explanation on dye's adsorption can be attributed to the fact that the surface of the material is highly heterogeneous, and also due to its large number of functional groups. The pHzpc of the material was estimated to be 5.5. Thus, when the medium is highly acid (pH 1), the surface will be positively charged, whereas at pH 6 it can be considered a deprotonated surface. The studied adsorbates have a cationic nature and, at pHs near neutrality, both methylene blue (pKa = 5.6) [25] and crystal violet will be deprotonated (pKa's = 1.15 and 1.8) (Costa et al 2013). Thus, Figs 9 and 10 shows a simplified scheme of the adsorption of methylene blue and crystal violet dyes regarding the carnauba straw "in natura" and are in accordance with the discussions in the study of the pH. In these Figures, I represent hydrogen bonds, II simulates π-π interactions and III indicates electrostatic attractions.



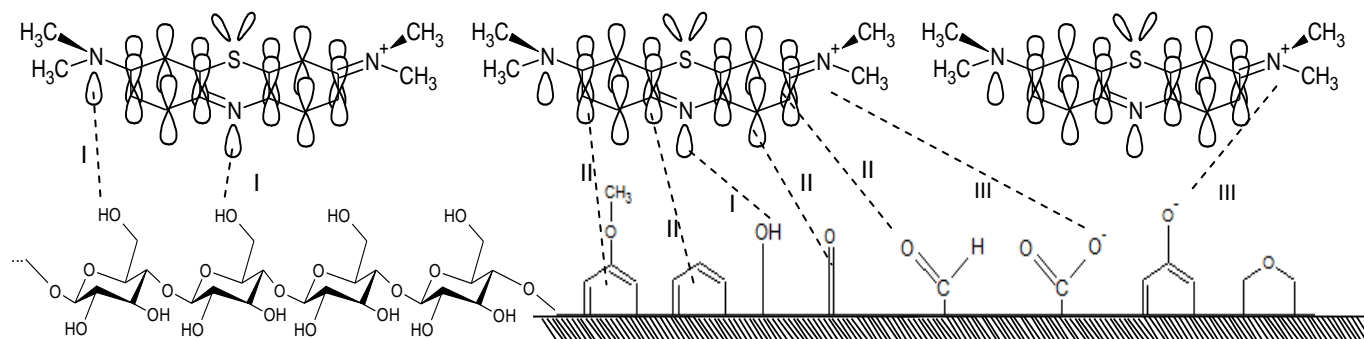


Figure 9: Possible interactions between the methylene blue and carnauba straw in natura at pH 6.

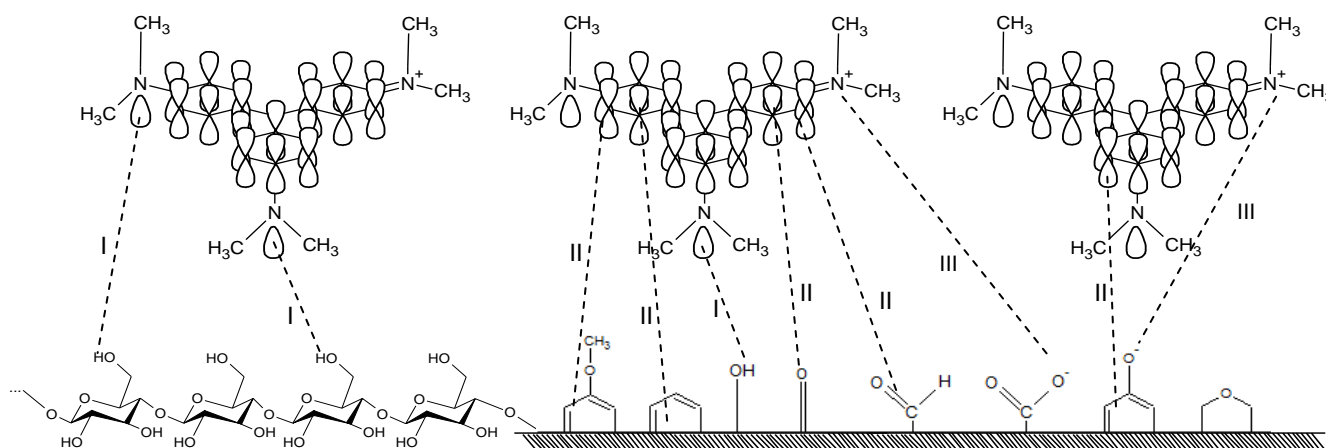


Figure 10: Possible interactions between the crystal violet dye and carnauba straw "in natura" at pH 6

4. Conclusion

In addition, it is clear the technical viability of this lignocellulosic material as biosource for the removal of dyes in aqueous medium.

Both blue methylene and crystal violet dyes are highly adsorbed by carnauba straw "in natura". Moreover, more than 70% of the adsorption seems to be independent from the medium's pH. The adsorption mechanisms correspond to a second order kinetics, with an equilibration time next to 120 min for both dyes. The adsorption results were shaped to Sips equation so that the theoretical and experimental values of the maximum quantities of dyes adsorbed by the carnauba straw "in natura" are cohesive. The carnauba straw appears as an economically viable alternative before the commercial adsorbents, since these materials have high cost regarding the production, especially activated carbon. Another pertinent point is such biomass' availability, being a renewable source. Thereby, it is of great environmental interest the use of the carnauba straw "in natura" for removing dyes.

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