

# Kinetic and Thermodynamic of Gentian Violet Removal by 2,3-Dialdehyde Nanocellulose

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## Abstract

In this work, the authors were interested in removal of gentian violet by oxidized nanocellulose, the extracted cellulose from date palm bunches transformed into nanocellulose by acid hydrolysis, and then to 2,3-dialdehyde nanocellulose by selective oxidation. The adsorption removal of gentian violet (GV) onto 2,3-dialdehyde nano-cellulose (DNC) was investigated using batch adsorption technique. The effects of initial solution pH, Time, adsorbent dosage and initial concentration of gentian violet, and temperature were scrutinized. Langmuir, Freundlich, Dubinin-Radushkevich and Temkin adsorption isotherms were applied to analyze the single component equilibrium data. The findings indicated that equilibrium was obtained within 20 min. The highest adsorption capacity was found at pH 8 for the used biosorbent. The experimental isotherm data were analyzed and modeled. The maximum adsorption capacity, Langmuir's  $q_{max}$ , improved from 11.71 to 12.05 mg/g as the temperature increased from 20 to 40°C. The enthalpy  $\Delta H^\circ$  and entropy  $\Delta S^\circ$  values were respectively estimated at 45.4 kJ mol<sup>-1</sup> and -0.206 kJ K<sup>-1</sup> mol<sup>-1</sup>. The adsorption of GV onto (DNC) is a spontaneous process. The findings indicated the pseudo-second order equation could describe the adsorption of gentian violet, indicating that the adsorption process is presumably a chemisorption.

**Keywords:** Date palm bunches, Adsorption, gentian violet, Isotherm, Kinetics.

## Introduction

The amount of synthetic dyes that produced annually around the

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world has been estimated to be around 700.000 tons (Lee J.W. et al., 2006), about 20% of this amount has been unloaded the industrial wastes without previous treatment (Tharcila C.R. et al., 2013). The dye added in water streams would lead in Eco-toxicity and a potential danger of bioaccumulation (Contreras L. et al., 2012). The gentian violet is a synthetic cationic dye that can easily react with negatively charged surfaces of cells membrane, penetrate into cells, and concentrate in cytoplasm (Rajeswari et al., 2017). In many papers, it has been reported that gentian violet could cause carcinogenic effects, is mutagen and toxic to mammalian cells, and it is also a mitotic poison (Jayganesh et al., 2017), it's irritant against skin and digestive tract, and it's harmful for conjunctiva and cornea (Güzel et al., 2015) . The gentian violet use has become a matter of serious concern to researchers because of its characteristics, it is non-biodegradable and persists for longer time in the environment (Benjelloun et al., 2017), therefore, removal of gentian violet from wastewater is of great importance, and several methods have been commonly used for this purpose, including physio-chemical, chemical, biological and integrated treatment process (Miyah et al., 2017). However, most of these technologies have been of high cost, needed long operation time, and have not been eco-friendly (Kumar et al., 2013). While adsorption process is useful and alternative due to its cost, simplicity, performance and possibility of regeneration, the low cost adsorbent can be produced from waste materials like : spent corncob substrate (Xiuwu et al., 2011); pomelo peel (Hameed et al., 2008); Luffa cylindrica fibers (Demir et al., 2008); sunflower seed shells (Osma et al., 2007); olive pomace (Banat et al., 2007); Posidonia oceanica (L.) fibers (Ncibi et al., 2007); wheat shells (Bulut et al., 2006); palm kernel fiber (Ofomaja et al., 2007) and phoenix tree's leaves (Han et al., 2007). Date palm (Phoenix dactylifera L.) is a member of the family Arecaceae (palm family). Date Palm by-product (bunches) is an agricultural waste abundantly available in the south of Algeria, containing considerable amount of cellulose (Gouamid et al., 2013 & 2016), In this work, 2,3-dialdehyde nano-cellulose was used to remove gentian violet from aqueous solution.

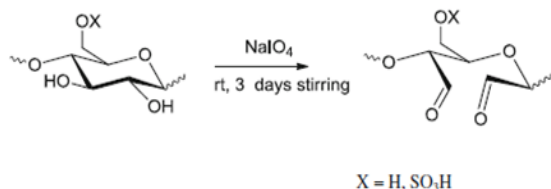
## Materials and Methods

Various pH, contact times, adsorbent doses, temperatures and (GV) concentrations were considered in conducting the adsorption experiments. 250 ml Erlenmeyer flasks were used to

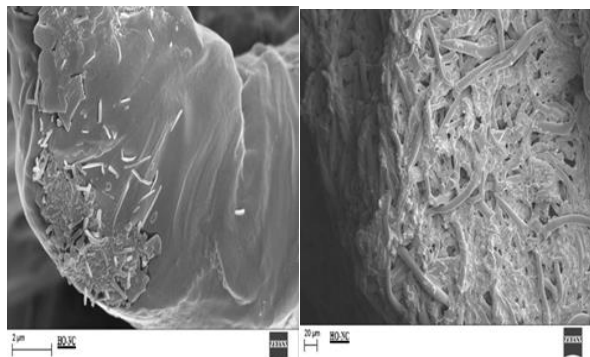
accomplish the experiments, and the total volume of the reaction mixture was maintained at 100 ml. UV-Vis spectrophotometer (Model SHIMADZU 1800) was applied to analyze the equilibrium concentrations of the solution samples, the absorbance values of miscellaneous concentration of gentian violet at maximum absorbance of wavelength (586 nm) were recorded to draw standard calibration curve. For assessing pH, a HANNA instrument pH meter was used; and for stirring the samples, a magnetic stirrer was utilized.

#### Adsorbent

The Date palm by-products were gathered from Ouargla (Algeria) region palm trees, they were picked from twigs and put in clean plastic bags. Then, they were washed with triple distilled water, and placed flat on clean table to dry. After that, the dried fibres were grounded with a grinder. After being grounded, the cellulose was extracted by using (50/50 v/v) of ethanol/acetone to remove the extractive, later treated with (7.5% NaOH) solution, the residue was washed several times by ionized water, the hydrolysis process of extracted cellulose was followed by oxidation in (4% NaIO<sub>4</sub>) solution in the dark at (pH =4) for three days, finally was washed by ionized water, and finally, the product obtained was dialdehyde nano-cellulose.



**Figure 1:** selective oxidation reaction of nano-cellulose



**Figure 2:** SEM Images of dialdehyde nano-cellulose



**Figure 3.** EDS analysis of dialdehyde nano-cellulose

#### Adsorbate

All the chemicals applied were of analytical reagent grade. In all of the experimental studies, distilled water was used. A stock gentian violet solution was dissolved in distilled water to obtain the desired concentration. Working standard was prepared by progressive dilution of stock gentian violet solutions using distilled water. By adding 0.1M NaOH or HCl 0.1M NaOH or HCl to the solution, its pH of solution was kept at a intended value.

#### Biosorption studies

Batch process was applied to conduct the adsorption experiments, 1.00 g of adsorbent was put in Erlenmeyer flasks with 100 mL solution of gentian violet of desired concentration.

The mixture was stirred at 100 rpm at 20, 30 and 40°C. The contact time ranged from 0 to 70 minutes. At the certain time, the flasks were taken out from the agitator, and Whatman filter paper No. 40 was used to filter the reaction mixtures. For thermodynamic study, the experiment was performed using 1g (DNC) added to 100 ml of gentian violet solution in 250 mL flasks. The agitation was at 100 rpm for 20 min at pH=8.0. All the experiments were performed in duplicates. The amount of gentian violet adsorbed at equilibrium per unit mass of biosorbent was determined according to the following equation:

$$q_e = \frac{(C_0 - C_e) * V}{m}$$

Where, m is the mass of adsorbent (g), V is the volume of the solution (L), C<sub>0</sub> is the initial concentration of GV (mg/L), C<sub>e</sub> is the equilibrium concentration of the adsorbate (mg/L) in solution and q<sub>e</sub> is GV quantity adsorbed at equilibrium (mg/g). For the calculation of GV rate adsorption (R %), the following expression was used:

$$R(\%) = \frac{(C_0 - C_e) * 100}{C_0}$$

#### Effect of contact time

Results clearly showed that the adsorption of gentian violet onto (DNC) reached equilibrium in 20 min. At first, the adsorption rose linearly, and there was an instantaneous and extremely fast uptake, and after a while, there was a stationary state. The fast initial uptake was due to the accumulation of GV on surfaces of (DNC) adsorbents which was a quick step. It was found that 20 min was enough for the adsorption to gain equilibrium.

#### Effect of pH

The acidity of solution (pH) is one of the most important parameters controlling the uptake of GV from wastewater and aqueous solutions. The uptake and percentage removal of GV from the aqueous solution were strongly affected by the pH of the

solution .The uptake of GV increased from 4.02 mg/g to 8.52 mg/g when the pH increased from pH 1 to pH 10. GV adsorption was noted to reach high at pH 8. Then, the capacity of adsorption slightly reduced in pH range of 8 to 10.

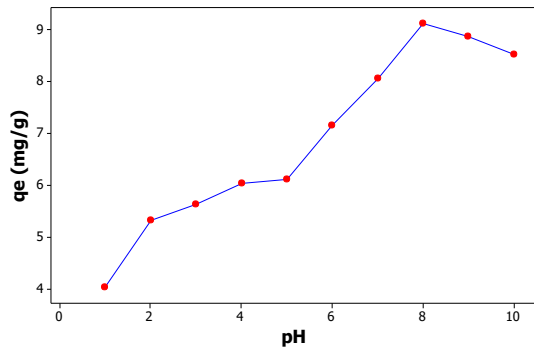


Figure 4: pH effect on quantity adsorbed

Adsorption Isotherm

The four most common adsorption isotherm models including Langmuir, Freundlich, Temkin and Dubinin-Radushkevich (D-R), were used to gain information about the adsorbate–adsorbent interaction. The Langmuir equation could be obtained by the linearized form (Gouamid et al., 2013):

$$\frac{C_e}{q_e} = \frac{1}{K_L * q_{max}} + \frac{C_e}{q_{max}}$$

where qe is the adsorption capacity at equilibrium (mg/g), qmax is the maximum adsorption capacity (mg/g), KL is the Langmuir equilibrium constant related to the affinity of binding sites and energy of adsorption, and Ce is the equilibrium solution concentration (mg/l). According to (Vasanth Kumar et al., 2005), the most important properties of the Langmuir isotherm can be expressed in terms of separation factor or equilibrium parameter RL that can be assessed using the relationship :

$$R_L = \frac{1}{1 + K_L C_0}$$

Where C0 is the highest initial concentration (mg/l). The value of RL shows whether the type of isotherm is irreversible adsorption (RL=0), favorable adsorption 0< RL < 1 unfavorable adsorption (RL>1), or linear adsorption (RL=1). In the present investigation, RL for (DNC) had values less than 1, showing favorable adsorption. The Freundlich equation was given by (Gouamid et al., 2013):

$$\text{Log}(q_e) = \text{Log}(K_F) + \frac{1}{n} \text{Log}(C_e)$$

Where KF is the Freundlich constant (mg/g) and 1/n is the adsorption intensity. Log

(qe) was plotted against log(Ce) and a straight line was fitted in the data. The D-R equation has been given by (Gouamid et al., 2013):

$$\text{Ln}(q_e) = \text{Ln}(q_m) - \beta \varepsilon^2$$

where qe is the amount of GV adsorbed onto (DNC) at equilibrium (mg/g), qm is the D-R monolayer capacity (mg/g), β is a constant related to sorption energy (mol<sup>2</sup>kJ<sup>-2</sup>), and ε is the Polanyi potential which is related to the equilibrium concentration as follows:

$$\varepsilon = RT \text{Ln} \left[ 1 + \frac{1}{C_e} \right]$$

where R is the gas constant (8.3145 J K<sup>-1</sup>mol<sup>-1</sup>), T is the temperature in K. The mean energy of adsorption (E) was estimated by using the following formula:

$$E = (2\beta)^{-0.5}$$

The Temkin isotherm was also applied in the current examination to fit with the experimental data, and it can be shown as:

$$q_e = K_1 \text{Ln}(C_e) + K_2$$

Where K1 and K2 are Temkin isotherm constants. Temkin isotherm includes a factor that clearly adsorbs the species-adsorbent interactions. This isotherm considers that (i) the heat of adsorption of all the molecules in the layer reduces linearly with coverage due to adsorbent-adsorbate interactions, and that (ii) the adsorption includes a uniform distribution of binding energies, up to some maximum binding energy.

Resultats and Discussion

All of the constants have been presented in Table 1.

Table 1- The Value of Parameters for Each Isotherm Model Used in The Studies.

T°C	Langmuir isotherm constants				Freundlich isotherm constants		
	qmax (mg/g)	KL	RL	R <sup>2</sup> (%)	KF	n	R <sup>2</sup> (%)
20	11,71	1.072	8,15	97,99	6,82	2,04	85,71
30	12.03	1,277	6,86	97,96	7,12	2.33	87.02
40	12.05	1,332	6,38	97,97	7.23	2,74	83,21
T°C	Temkin isotherm constants			D-R isotherm constants			
	K1	K2	R <sup>2</sup> (%)	qm,D-R	E (KJ/mol)	R <sup>2</sup> (%)	
20	1.02	5,84	88.01	9,32	6,75	92,5	
30	0,911	6,21	85,82	9,41	6,27	93,7	
40	0,899	6,44	85,34	9,39	6,29	94.0	

Thermodynamic Parameters

Thermodynamic quantities such as change in Gibbs free energy (ΔG°), change in enthalpy of adsorption (ΔH°), and change in

entropy ( $\Delta S^\circ$ ) have been considered to identify the mechanism of adsorption. The thermodynamic equilibrium constant  $K_d$  for adsorption was determined by (Gunay et al. 2007) by plotting  $\ln(q_e/C_e)$  versus  $q_e$ , and extrapolating to zero  $q_e$ . The increase in  $K_d$  with increase in temperature indicated the endothermic nature of the process. The  $\Delta G^\circ$ ,  $\Delta H^\circ$ , and  $\Delta S^\circ$  were calculated using the equations:

$$\Delta G^\circ = -RT \ln(K_d)$$

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$$

A plot of  $\ln(K_d)$  versus  $1/T$  was found to be linear,  $\Delta H^\circ$  and  $\Delta S^\circ$  were determined from the slope and intercept of the plot; respectively.

#### Kinetic studies

A quantitative understanding of the adsorption was possible with the help of kinetic models. The pseudo-first-order kinetic model, as expressed by (Gouamid et al., 2013), can be written as:

$$\text{Log}(q_e - q_t) = \text{Log}(q_e) - K_1 \cdot t / 2.303$$

Pseudo-second-order sorption rate equation (Gouamid et al., 2013) may be expressed as follows :

$$\frac{t}{q_t} = \frac{1}{K_2 q_e^2} + \frac{1}{q_e} \cdot t$$

The initial rate of the intraparticle diffusion was given by the following equation:

$$q_t = K_p t^{1/2}$$

Where  $K_p$  is the intraparticle diffusion rate constant, ( $\text{mg/g} \cdot \text{min}^{1/2}$ ). Such plots may present a multilinearity (Annadurai et al. 2002 ; Wu et al. 2001) , indicating that two or more steps take place.

Table 2- Thermodynamic parameters calculated for the adsorption of GV on DNC

T°C	Ln( $K_d$ )	$\Delta G^\circ$ (Kj/mol)	R <sup>2</sup>
20	6,15	-14,981	94.31
30	6,77	-17,054	93,9
40	7,34	-19,100	94.26
$\Delta H^\circ$ (Kj/mol)		45.4	
$\Delta S^\circ$ (Kj/K.mol)		-0.206	

Table 3- Kinetic Parameters Estimated and Correlation Coefficients Associated

Pseudo-order-order constants			
$K_1$ (min <sup>-1</sup> )	$q_e$ (mg/g)	R <sup>2</sup> (%)	
0,055	2,33	95.31	
Second-order-order constants			
$K_2$	$q_e$	$h$ (mg/g.min)	R <sup>2</sup> (%)

0,042	11,514	4,660	99,99
Intraparticle diffusion constant			
$K_p$ (g/mg.min <sup>1/2</sup> )		R <sup>2</sup> (%)	
0,247		99,70	

#### Conclusion

Kinetic and thermodynamic studies were made for gentian violet adsorption from aqueous solution onto (DNC) at pH 8. Langmuir, Freundlich, Temkin and Dubinin-Radushkevich isotherms were used to analyze the equilibrium data. The parameters of each isotherm and related correlation coefficients were assessed. The Langmuir isotherm gave the best correlation for the sorption of gentian violet onto (DNC). The suitability of the pseudo first- and second-order equations and intraparticle diffusion kinetic model for the adsorption of GV onto (DNC) was also discussed. The adsorption of GV could be described by the intraparticle diffusion model up to 17 min. The intraparticle diffusion model indicated that the external surface was totally covered before 08 min, and the final equilibrium adsorption (stage 3) was started after 17 min. The GV was slowly transported via intraparticle diffusion into the pores and was finally retained in micro-pores. The pseudo second-order kinetic model agreed very well with the dynamical behaviour for the adsorption of GV onto (DNC) for different initial concentrations of GV over the whole range studied. It might be concluded that (DNC) might be used as adsorbent for the removal of GV from the wastewater.

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