

REMOVAL OF CRYSTAL VIOLET BY BIOSORPTION ONTO DATE STONES

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Abstract: The biosorption has the advantage that it can be applied to effluent disposal and thus brings various responses to the regulatory requirements for environmental protection. This study presents the results obtained from the use of date stones (DS) for the elimination of crystal violet (CV) from aqueous medium. Several analysis techniques were used to determine the different characteristics of biosorbent studied (FTIR, TGA-DTA, SEM and pH_{zpc}). The physico-chemical parameters influence of the biosorption such as biosorbent dosage, contact time, temperature, biosorbent particles size and initial dye pH were investigated under static conditions in order to evaluate the process system. The test results show that a gram of date stones may set a maximum amount adsorbed $90.89 \text{ mg}\cdot\text{g}^{-1}$ of CV at 50°C according to the Langmuir isotherm with pseudo-second-order kinetic. Thermodynamic calculations performed shows also that sorption is spontaneous, endothermic and increased randomness in the solid / solution interface.

Keywords: *biosorption, crystal violet, date stones, isotherms kinetic, thermodynamic*

INTRODUCTION

The national and international regulations are becoming more severe, the environmental protection requiring the development and optimization of technologies aimed at reducing the pollution of the water.

So far, despite the efforts of the cleanup of industrial effluents, a significant amount of all kinds of dyes are released into the environment. In developing countries, although the high cost of taking into account the environmental aspect remains a disability, the seriousness of the issue justified the importance attached to the resolution of these problems.

In this context our work is directed towards the treatment of industrial waste water loaded with dyes, which are considered hazardous and toxic micropollutants. World production of dyes is estimated at 700000 tons/year [1], 10 to 15 % of these amounts are lost in the dyeing process [2].

The dyes widely used in many fields (dyeing, textile, printing, leather, paper, plastic, rubber...) [3], have diverse chemical structures with different chromophoric groups (azo, anthraquinone, triarylmethane and phthalocyanine) and a variety of application (reactive dyeing, direct, disperse and vat) [4]. In addition, these dyes are very stable and poorly biodegradable, causing serious problems for living creatures (kidney dysfunction, reproductive system, liver, brain and central nervous system) [5].

In order to valorize lignocellulosic wastes from agriculture, we focused on the use of date stones as cheaper biosorbent, effective and locally available allowing dyes decontamination.

In the present study, we prepared date stones powder to eliminate basic dye, crystal violet from aqueous solution. Date stones are characterized by different analysis such as Fourier transform infrared spectroscopy (FTIR), thermogravimetric and differential thermal analysis (TGA-DTA), scanning electron microscopy (SEM) and the pH at the point of zero charge (pH_{zpc}) was determined.

In this work, we will proceed to a description of the optimum operating conditions of biosorption of crystal violet implemented on date stones prepared by determining experimental parameters influencing biosorption such as: biosorbent dosage, contact time, initial pH of the solution, temperature, and biosorbent particles size. We also evaluate the sorption kinetics study based on two models: pseudo-first-order and pseudo-second-order, then the equilibrium using two models isotherms: Langmuir, Freundlich and Temkin, and thus the calculated thermodynamic parameters.

MATERIALS AND METHODS

Preparation and characterization of DS

Date stones were collected in October 2014 in Tinghir (South-East Morocco). They were thoroughly washed with distilled water to remove the dirt adhering to the surface and then placed in an oven at 110 °C for 24 hours. They were then converted into fine powder by grinding in a grinder Retsch SM 100. The powder of DS is sieved to different sizes and was stored in glass vial bottles for later use. The FTIR spectroscopy was used to identify the chemical groups present in the date stones on a Jasco 4100 spectrometer

using the attenuated total reflectance (ATR) method. The TGA-DTA curves of biosorbent were recorded using a Shimadzu D60 thermobalance with a heating rate of $10\text{ }^{\circ}\text{C}\cdot\text{min}^{-1}$ and temperature range of $25\text{--}600\text{ }^{\circ}\text{C}$. The morphology of DS was examined by SEM and was recorded on Supra 40 VP Colonne Gemini Zeiss instrument at 15 kV tension. The point of zero charge (pH_{zpc}) was determined for the DS using the method reported in the literature [6].

Preparation of dye solutions

Crystal violet (C.I.42555, MF = $\text{C}_{25}\text{H}_{30}\text{N}_3\text{Cl}$, MW = $407.99\text{ g}\cdot\text{mol}^{-1}$) solutions used in this study were obtained by dilution of a stock solution of the dye concentration by weight of $1\text{ g}\cdot\text{L}^{-1}$. The latter is prepared by dissolving a 1 gram of the dye powder in 1 liter of distilled water using a volumetric flask. The chemical structure of dye is shown in Figure 1.

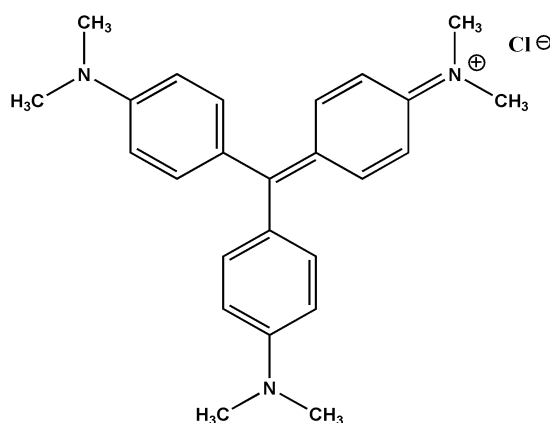


Figure 1. Chemical structure of crystal violet dye

The initial pH of the solution was adjusted using solutions of HCl (0.01 N) or NaOH (0.01 N) using a HANNA pH -meter HI 255 with a combined electrode HI 1332.

Studies of biosorption

Biosorption studies were carried out in 100 mL Erlenmeyer flasks, containing 50 mL of CV solution with initial concentration of $100\text{ mg}\cdot\text{L}^{-1}$, to which is added a definite amount of date stones at constant temperature using thermostatic bath. The effect of experimental factors such as initial solution pH (3 - 10), biosorbent dosage ($1\text{--}8\text{ g}\cdot\text{L}^{-1}$), contact time (5 - 180 min), temperature ($20\text{--}50\text{ }^{\circ}\text{C}$), biosorbent particles size ($50\text{--}1000\text{ }\mu\text{m}$) and concentration initial ($50\text{--}800\text{ mg}\cdot\text{L}^{-1}$) was evaluated in this study. After stirring time, the liquid phase is separated from the residue (crushed) by a centrifuge Sigma 1-6 with the speed 4000 rpm for 15 minutes. After centrifugation, the equilibrium concentrations of the solutions were analyzed using a Techcomp UV2300 UV-Vis spectrophotometer. The standard calibration curve was prepared by recording the absorption of various concentrations values of crystal violet dye at a maximum absorption wavelength $\lambda_{\text{max}} = 590\text{ nm}$ at $pH = 5.46$. The quantity equilibrium adsorbed q_e ($\text{mg}\cdot\text{g}^{-1}$) and the percentage biosorption (%) were calculated using the following eqns. (1) and (2), respectively.

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

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

where: C_0 ($\text{mg}\cdot\text{L}^{-1}$) and C_e ($\text{mg}\cdot\text{L}^{-1}$) are the initial and equilibrium concentrations of solution, respectively, V (L) is the volume of solution and W (g) is the mass of biosorbent used.

RESULTS AND DISCUSSION

FTIR spectroscopy

Figure 2 shows the vibrations of the functional groups present on surface of date stones before and after biosorption of CV, detected by FTIR.

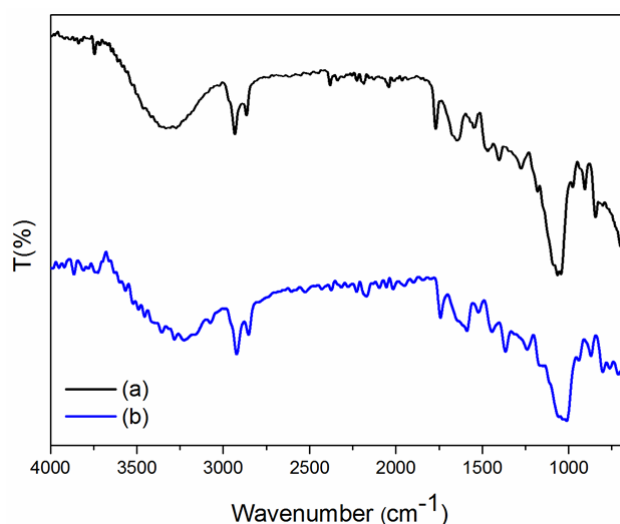


Figure 2. FTIR spectra of DS before (a) and after (b) biosorption of CV

The FTIR spectrum of DS before biosorption of CV (Figure 2a) reveals the presence of a broad band at 3435 cm^{-1} , which corresponds to the O–H bond of elongation vibration. The bands at 2921 cm^{-1} and 2852 cm^{-1} corresponds to the vibration of asymmetric and symmetric stretching, C–H bands of cellulose, respectively [7]. The peak around 1747 cm^{-1} is characteristic of the stretching vibration of C=O carboxylic acids or esters of xylan present in hemicelluloses and lignin [8]. The vibration at 1616 cm^{-1} and 1517 cm^{-1} are attributed to the aromatic C=C deformation of lignin [9]. The bands observed at 1317 cm^{-1} and 1262 cm^{-1} are assigned to the C–O vibration in the methoxy groups of lignin [10]. The peaks between 1147 cm^{-1} and 937 cm^{-1} correspond to stretching vibrations of C–O and C–O–C bonds of cellulose [11]. The band at 869 cm^{-1} is attributed to the C–H deformation in cellulose [10]. After biosorption CV (Figure 2b), we note that the peaks intensity of OH and C=O and C–O decreased, these shifts indicate that an interaction was occurred between CV and these groups [12]. We also

observed the appearance of a new peak at 1581 cm^{-1} which may correspond to the C-N group [13]. These results showed that the date stones contain several functional groups responsible for the crystal violet biosorption such as O-H, C=O and C-O.

TGA-DTA and SEM analysis

The TGA-DTA curves are shown in Figure 3. Analysis of these curves shows that thermal decomposition of DS can be divided into four steps according to the temperature. The first step (7.17 % of mass loss) is endothermic, starts at $25\text{ }^{\circ}\text{C}$ and ends near $105\text{ }^{\circ}\text{C}$. This step corresponds to the dehydration of the surface [14]. The second step (58.31 % of mass loss) is exothermic, between $210\text{ }^{\circ}\text{C}$ and $360\text{ }^{\circ}\text{C}$ which corresponds to degradation of cellulose [15]. The third step (24.74 % of mass loss) is exothermic, from $360\text{ }^{\circ}\text{C}$ to $470\text{ }^{\circ}\text{C}$ which may correspond to the thermal depolymerization of hemicelluloses [16, 17]. The fourth step (7.46 % of mass loss) is exothermic, between $470\text{ }^{\circ}\text{C}$ and $540\text{ }^{\circ}\text{C}$ which may be due to the decomposition of lignin [18].

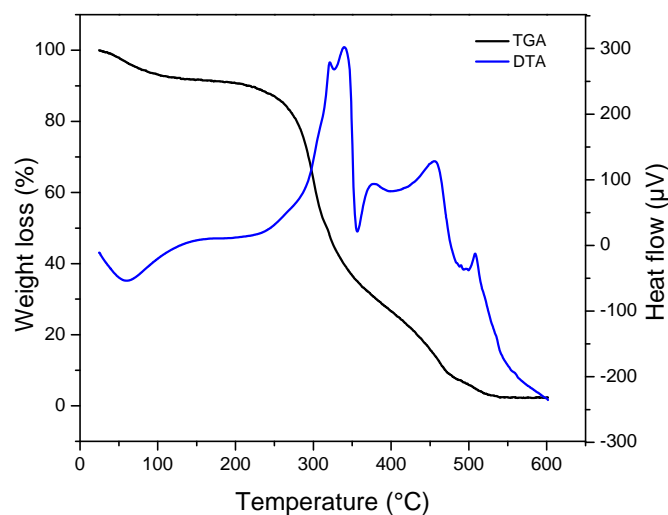


Figure 3. TGA-DTA curves of DS

Figure 4 depicts the SEM micrographs of DS before and after biosorption of CV.

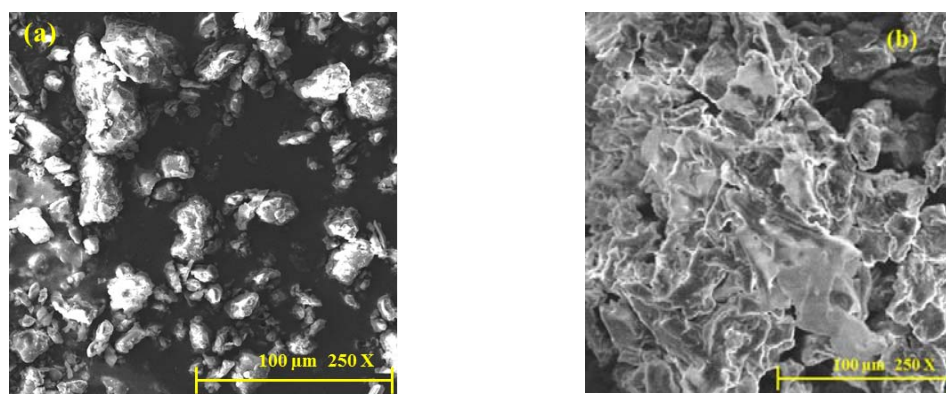


Figure 4. SEM micrographs of DS (a) and CV-loaded DS (b)

Before dye uptake (Figure 4a), it reveals the surface texture and porosity of biosorbent. It can be observed that the rough surface is filled with cavities and irregular holes. After CV biosorption (Figure 4b), the pores are absent on the surface of CV-loaded DS, suggesting the biosorption of CV onto DS.

Effect of contact time

The time effect it allows to determine the time required to reach biosorption equilibrium. We followed the time contact crystal violet on our biosorbent. The results obtained are presented in Figure 5.

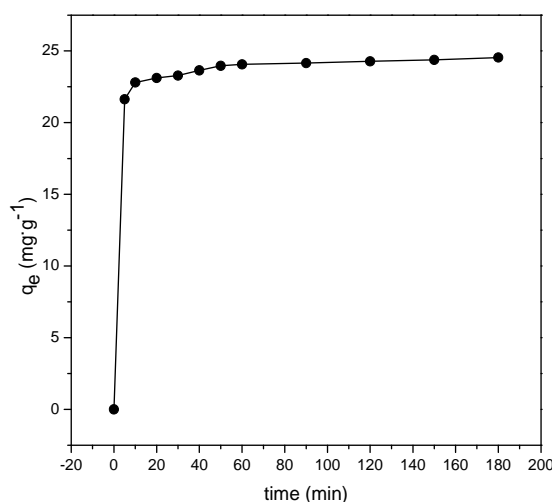


Figure 5. Effect of contact time on the biosorption of CV onto DS: $C_0 = 100 \text{ mg}\cdot\text{L}^{-1}$, $T = 20 \text{ }^\circ\text{C}$, $d = 4 \text{ g}\cdot\text{L}^{-1}$, $\text{pH} = 5.46$, $s = 50 - 100 \text{ }\mu\text{m}$

The shape of this figure shows an increase of the amount adsorbed to 60 min, which reflects the biosorption equilibrium and indicating a saturation of biosorption of crystal violet. The first phase of biosorption takes place in a few tens of minutes. Then we observe a second, slower phase that can last up to 60 minutes to 180 minutes. After 60 minutes, the effect of contact time has no effect on the adsorption capacity of the crystal violet, so the adsorption equilibrium is reached at 60 minutes [19].

Effect of biosorbent dosage

The objective of this study is to determine the optimal dose of biosorbent that we can use in the next step. Figure 6 presents the obtained results.

The percentage removal of CV on DS increased from 86.93 % to 96.36 % when the biosorbent dosage was increased from $1 \text{ g}\cdot\text{L}^{-1}$ to $4 \text{ g}\cdot\text{L}^{-1}$. This may be attributed to the increase biosorbent surface area and availability of more biosorption sites [20]. After $4 \text{ g}\cdot\text{L}^{-1}$, the removal efficiency of CV is almost steady. Consequently, $4 \text{ g}\cdot\text{L}^{-1}$ was used as optimal biosorbent dosage for further experiments.

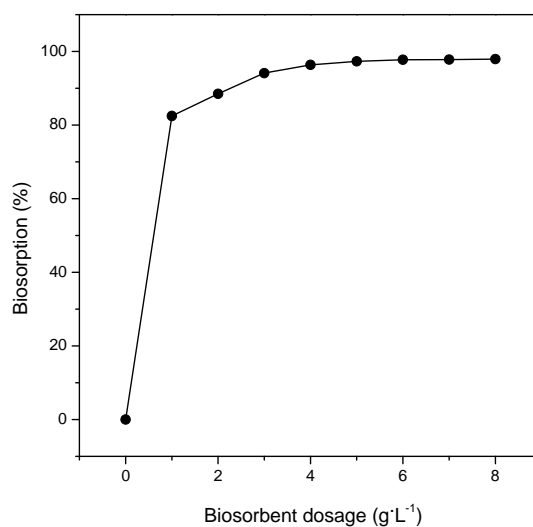


Figure 6. Effect of biosorbent dosage on biosorption of CV onto DS: $C_0 = 100 \text{ mg}\cdot\text{L}^{-1}$, $T = 20^\circ\text{C}$, $t = 60 \text{ min}$, $\text{pH} = 5.46$, $s = 50 - 100 \mu\text{m}$

Effect of temperature

Figure 7 shows the effect of temperature of biosorption of crystal violet on date stones.

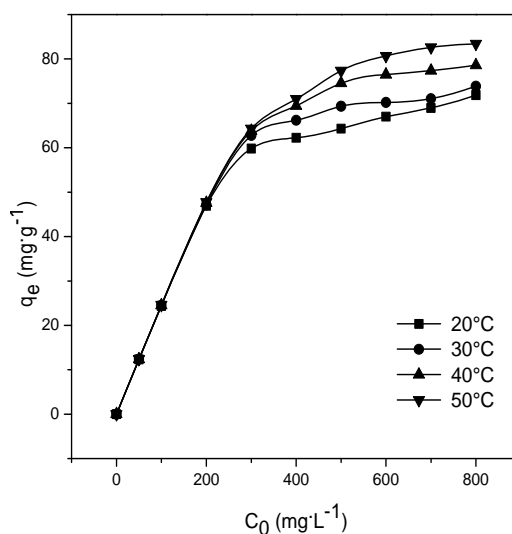


Figure 7. Effect of temperature on biosorption of CV onto DS: $t = 60 \text{ min}$, $d = 4 \text{ g}\cdot\text{L}^{-1}$, $C_0 = 50 - 800 \text{ mg}\cdot\text{L}^{-1}$, $\text{pH} = 5.46$, $s = 50 - 100 \mu\text{m}$

The analysis of the results shows that the increase in temperature promotes the retention of crystal violet onto date stones. An increase in temperature also results in mobility of dye molecules [21]. Furthermore, when the temperature increases, it may produce swelling effect within the internal structure of DS allowing to the dye molecule to penetrate more [22]. Therefore, the amount adsorbed of dye increases.

Effect of initial pH of the solution and pH_{zpc}

The pH of dye solution is an important parameter in adsorption process. The results of this study are presented graphically in Figure 8. It shows that the biosorption of the dye on date stones increases regularly with the pH. Indeed the biosorption of CV on the surface of the biosorbent is affected by the surface charge of the biosorbent and the initial pH of the solution [23]. When the pH of the solution increases, the number of sites of negative charges, in surface of the biosorbent, increases, favoring the attraction of positive molecules of CV [24].

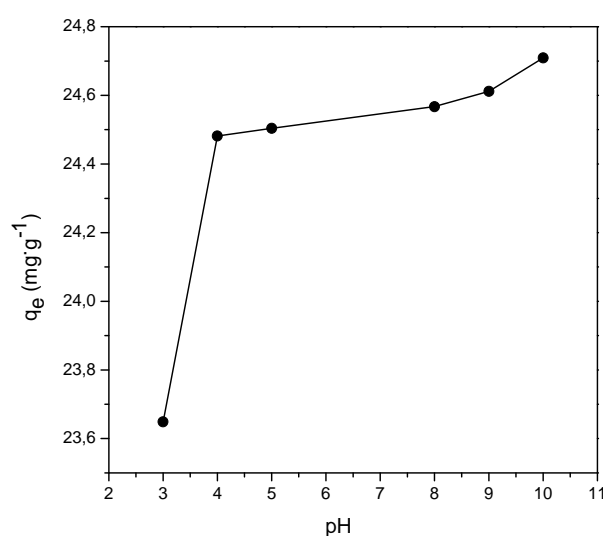


Figure 8. Effect of pH on biosorption of CV onto DS:
 $C_0 = 100 \text{ mg}\cdot\text{L}^{-1}$, $T = 20 \text{ }^\circ\text{C}$, $d = 4 \text{ g}\cdot\text{L}^{-1}$, $t = 60 \text{ min}$, $s = 50 - 100 \text{ }\mu\text{m}$

The pH_{zpc} of DS is 5.6 (Figure 9). The biosorbent surface has a net negative charge at pH greater than pH_{zpc} , inversely at pH lower than pH_{zpc} . Consequently, the $pH > pH_{zpc}$ helps to increase the biosorption of cations, which confirms the preceding results [25].

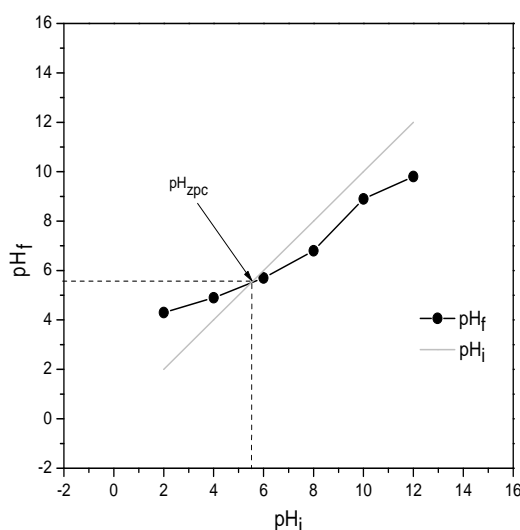


Figure 9. The pH_{zpc} of DS

Effect of biosorbent particles size

The effect of biosorbent particles size on removal of crystal violet was studied. The results obtained are shown in Figure 10.

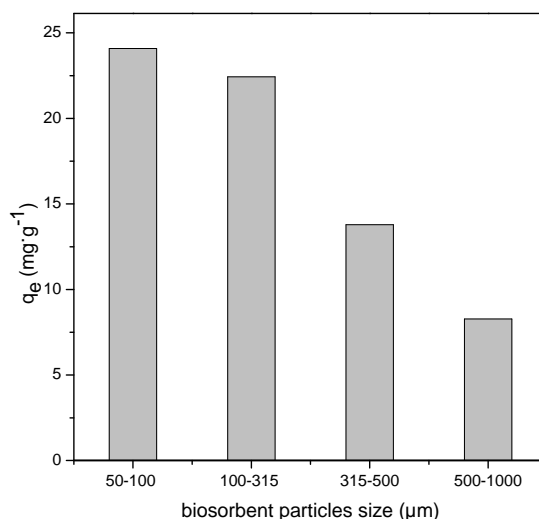


Figure 10. Effect of particles size on biosorption of CV onto DS: $C_0 = 100 \text{ mg}\cdot\text{L}^{-1}$, $T = 20 \text{ }^\circ\text{C}$, $d = 4 \text{ g}\cdot\text{L}^{-1}$, $t = 60 \text{ min}$, $\text{pH} = 5.46$

The analysis of these results shows that removal efficiency of crystal violet by DS increases from 8.27 to 24.09 $\text{mg}\cdot\text{g}^{-1}$ when the particle size decreases from 1000 to 50 μm . Indeed, the adsorption phenomenon increases with increasing surface area. Thus the surface area available for adsorption will be greater for smaller particles, and thus efficiency biosorption of crystal violet increases with decreasing particle size [26].

Kinetic biosorption

In order to investigate the biosorption kinetics of CV on DS, two kinetics models, namely pseudo-first-order and pseudo-second-order, were used in this study.

The pseudo-first-order equation is given by eqn. 3 [27]:

$$\log (q_e - q_t) = \log (q_e) - \frac{K_1}{2.303} t \quad (3)$$

where: q_t ($\text{mg}\cdot\text{g}^{-1}$) and q_e ($\text{mg}\cdot\text{g}^{-1}$) are the amounts adsorbed at time t and equilibrium, respectively and K_1 (min^{-1}) is the pseudo-first-order rate constant for the biosorption process.

The pseudo-second-order equation can be expressed following eqn. (4) [28]:

$$\frac{t}{q_t} = \frac{1}{K_2 q_e^2} + \frac{1}{q_e} t \quad (4)$$

where: K_2 ($\text{g}\cdot\text{mg}^{-1}\cdot\text{min}^{-1}$) is the constant of the pseudo-second-order rate.

The results are shown in Figure 11 (a, b).

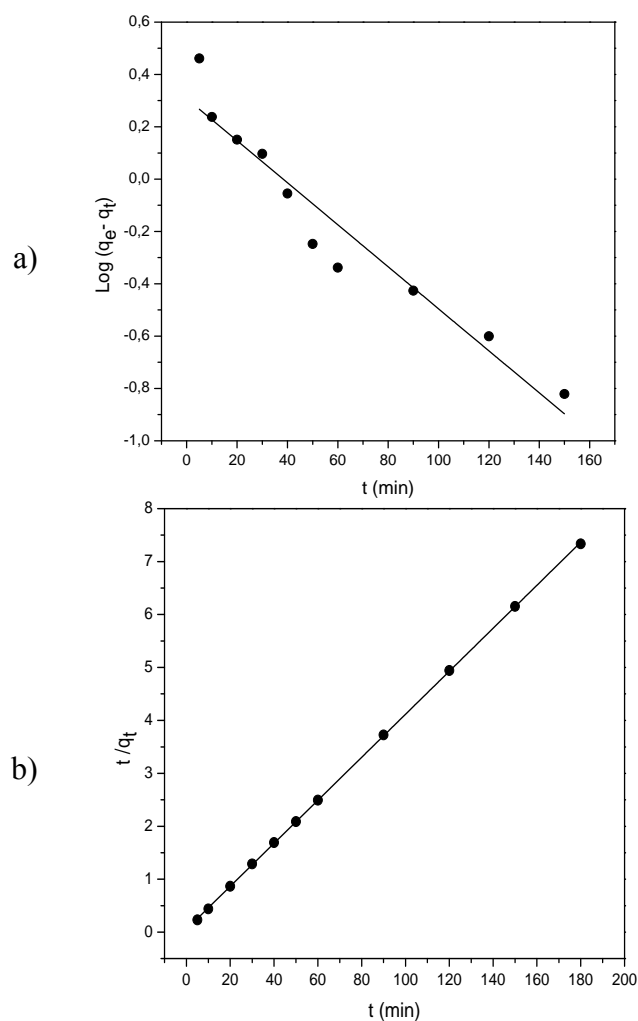


Figure 11. Kinetic models for biosorption of CV onto DS:
a) pseudo-first-order; b) second-first-order,
 $C_0 = 100 \text{ mg}\cdot\text{L}^{-1}$, $d = 4 \text{ g}\cdot\text{L}^{-1}$, $\text{pH} = 5.46$, $s = 50 - 100 \mu\text{m}$, $T = 20^\circ\text{C}$

All kinetics parameters determined from these curves and the values of the correlation coefficient r^2 are collected in Table 1.

Table 1. Kinetic parameters for biosorption of CV onto DS

$q_{e,\text{exp}} [\text{mg}\cdot\text{g}^{-1}]$	Pseudo-first-order model		
	$q_{e,\text{cal}} [\text{mg}\cdot\text{g}^{-1}]$	$K_1 [\text{min}^{-1}]$	r^2
24.53	2.02	0.018	0.931
	Pseudo-second-order model		
	$q_{e,\text{cal}} [\text{mg}\cdot\text{g}^{-1}]$	$K_2 [\text{g}\cdot\text{mg}^{-1}\cdot\text{min}^{-1}]$	r^2
	25.01	0.030	0.999

We conclude that the second order model gives a better description of the kinetic of the biosorption of CV on DS versus to first-order model.

Biosorption isotherms

The adsorption process was carried out at different temperatures from 20 to 50 °C with initial concentration of CV varying from 50 to 800 mg·L⁻¹. To ensure full equilibration, a shaking time of 60 min was used for all concentrations of CV in this study with 4 g·L⁻¹ of biosorbent dosage. The equilibrium data obtained of the biosorption of CV onto DS were analyzed using isotherm models: Langmuir, Freundlich and Temkin.

Langmuir isotherm model

The Langmuir isotherm assumes that sorption occurs at specific homogeneous sites within the biosorbent, that the capacity of the biosorbent is finite and that the adsorption process is a monolayer [29]. The linearized form of the Langmuir equation is as follows:

$$\frac{C_e}{q_e} = \frac{1}{q_m K_L} + \frac{C_e}{q_m} \quad (5)$$

where: K_L (L·mg⁻¹) is the Langmuir constant and q_m (mg·g⁻¹) is the maximum amount of adsorbate retained on the medium used. The essential characteristics of Langmuir isotherm can be expressed in terms of a dimensionless parameter balance R_L which is defined by:

$$R_L = \frac{1}{1 + K_L C_0} \quad (6)$$

where: C_0 is the initial concentration of the biosorbate (mg·L⁻¹). The R_L value indicates the mode sorption isotherm process, if the process is unfavorable ($R_L > 1$) or linear ($R_L = 1$) or favorable ($0 < R_L < 1$) or irreversible ($R_L = 0$).

Freundlich isotherm model

The Freundlich isotherm is suitable for heterogeneous surface [30]. The Freundlich eqn. is linearized as follows:

$$\ln q_e = \ln K_F + \frac{1}{n} \ln C_e \quad (7)$$

where: K_F ((mg·g⁻¹) (L·mg⁻¹)^{1/n}) and n are Freundlich constants, which are related to the capacity and intensity of the biosorption, respectively.

Temkin isotherm model

The Temkin isotherm suggests that sorption energy decreases as the degree of completion of the sorption at centers of an adsorbent is increased [31]. The linearized form of the Temkin equation is as follows:

$$q_e = B \ln K_T + B \ln C_e \quad (8)$$

where: K_T (L·mg⁻¹) and B are Temkin constants.

The results obtained are shown in Figure 12 (a, b, c).

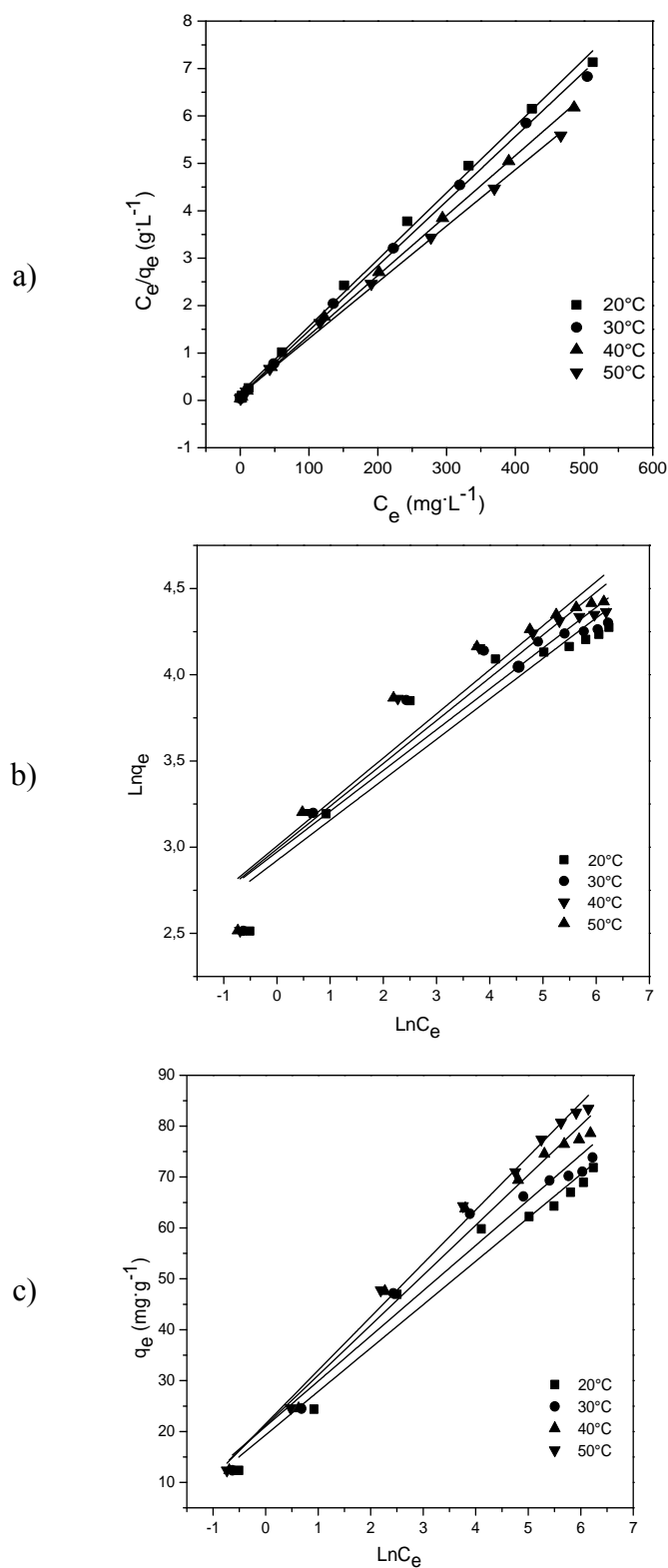


Figure 12. Isotherms for biosorption of CV onto DS:

a) Langmuir, b) Freundlich, c) Temkin,

$C_0 = 50 - 800 \text{ mg}\cdot\text{L}^{-1}$, $t = 60 \text{ min}$, $d = 4 \text{ g}\cdot\text{L}^{-1}$, $\text{pH} = 5.46$, $s = 50 - 100 \mu\text{m}$

The isotherm constants of each model were calculated and presented in Table 2.

Table 2. Isotherms parameters for biosorption of CV onto DS

T [°C]	Langmuir			
	K _L [L·mg ⁻¹]	q _m [mg·g ⁻¹]	R _L	r ²
20	0.091	71.42	0.013 - 0.180	0.997
30	0.121	76.92	0.010 - 0.141	0.998
40	0.114	83.33	0.011 - 0.149	0.999
50	0.054	90.89	0.022 - 0.270	0.998
T [°C]	Freundlich			
	K _F [(mg·g ⁻¹)(L·mg ⁻¹) ^{1/n}]	1/n	r ²	
20	18.57	0.234	0.904	
30	19.53	0.236	0.901	
40	19.86	0.248	0.914	
50	20.20	0.255	0.925	
T [°C]	Temkin			
	K _T [L·mg ⁻¹]	B	r ²	
20	9.64	8.53	0.974	
30	10.54	8.89	0.971	
40	8.65	9.82	0.984	
50	7.50	10.50	0.993	

Analysis of these results showed that the biosorption of CV on DS fits Langmuir isotherm with a well higher correlation, compared to Freundlich and Temkin isotherms, reflecting that the biosorption sites on the surface of DS is evenly distributed.

According to a Langmuir adsorption isotherm, the q_m for CV is calculated for different temperatures (71.42, 76.92, 83.33 and 90.90 mg·g⁻¹ at 20, 30, 40 and 50 °C, respectively). The maximum biosorption of CV on DS increases with increasing the temperature, exhibiting the endothermic nature of the biosorption process, favorable because the equilibrium parameter R_L is always between 0 and 1.

Thermodynamic biosorption

The thermodynamic behavior of the adsorption of CV on DS was evaluated by thermodynamic parameters gift variation of the free energy ΔG , enthalpy ΔH and entropy ΔS . These parameters are calculated from the following equations:

$$\Delta G = -R T \ln K_0 \quad (9)$$

$$K_0 = \frac{C_b}{C_s} \quad (10)$$

$$\Delta G = \Delta H - T \Delta S \quad (11)$$

$$\ln K_0 = \frac{\Delta S}{R} - \frac{\Delta H}{R T} \quad (12)$$

where: R is the constant of perfect gases 8.314 (J·mol⁻¹·K⁻¹), T is the absolute temperature (K), K_0 is the distribution coefficient, C_b is the equilibrium dye

concentration on the biosorbent ($\text{mg}\cdot\text{L}^{-1}$) and C_s is the equilibrium dye concentration in solution ($\text{mg}\cdot\text{L}^{-1}$) [32].

According to eqn. (12), the parameters ΔH and ΔS can be calculated from the slope and intercept of the plot of $\ln K_0$ vs. $1/T$. The results obtained are shown in Figure 13.

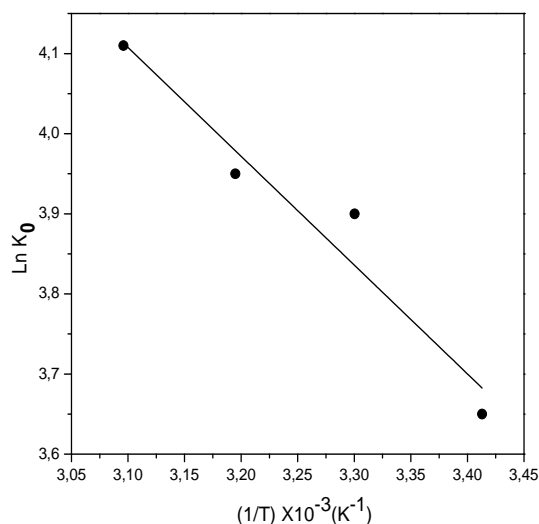


Figure 13. Plot of $\ln K_0$ versus $1/T$ for biosorption of CV onto DS:
 $t = 60 \text{ min}$, $d = 4 \text{ g}\cdot\text{L}^{-1}$, $C_0 = 100 \text{ mg}\cdot\text{L}^{-1}$, $\text{pH} = 5.46$, $s = 50 - 100 \mu\text{m}$

The values of ΔG , ΔH , ΔS and r^2 for the biosorption of CV on DS are given in Table 3.

Table 3. Thermodynamic parameters for biosorption of CV onto DS

T [K]	$\Delta G [\text{kJ}\cdot\text{mol}^{-1}]$	$\Delta H [\text{kJ}\cdot\text{mol}^{-1}]$	$\Delta S [\text{J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}]$	r^2
293	-8.80	11.28	69.12	0.944
303	-9.82			
313	-10.29			
323	-11.03			

The negative values of ΔG (-8.80, -9.82, -10.29, -11.03 $\text{kJ}\cdot\text{mol}^{-1}$) indicates that biosorption is favorable and spontaneous [33]. The positive value of ΔH (11.28 $\text{kJ}\cdot\text{mol}^{-1}$) suggests the endothermic nature of this biosorption [34], while the positive value of ΔS (69.12 $\text{J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$) indicates the increasing randomness at the solid/liquid interface during the biosorption of CV onto DS [35].

Comparison of different low cost biosorbents

The data presented in Table 4 compares the maximum monolayer biosorption capacity of some biosorbents used for the removal of CV, and we clearly note the good behavior of our biosorption DS.

Table 4. Comparison of maximum monolayer biosorption capacity of CV by some biosorbents

Biosorbent	q_m [mg·g ⁻¹]	Reference
Esparto grass fibers	43.47	[36]
Pineapple leaf powder	78.22	[37]
Cyperus rotundus	85.11	[38]
Formosa papaya seed powder	85.99	[39]
Palm kernel fiber	78.90	[40]
Breadfruit skin	145.80	[41]
Tea dust	175.40	[42]
Chitosan hydrogel beads	76.90	[43]
Jackfruit leaf powder	43.39	[44]
Date stones	90.89	This study

CONCLUSIONS

This study shows that dates stones can be used successfully for the biosorption of crystal violet from aqueous solution. The biosorption of CV onto DS was found to increase with an increase in biosorbent dosage, contact time, temperature, initial *pH* of the solution and decrease with increase in biosorbent particle size. The experimental data were evaluated by Langmuir, Freundlich and Temkin isotherms. Equilibrium data were well fitted to Langmuir isotherm model. The kinetic model of pseudo-second-order fits very well with this dynamic biosorption. The thermodynamic calculations indicated the feasibility, spontaneity and endothermic nature of the sorption process and increased randomness in the biosorbent/solution interface. Finally the various results obtained indicated that the chosen adsorbent for this study was efficient and could be used as an economical sorbent for the industrial effluents.

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REFERENCES

1. Zollinger, H.: *Color Chemistry: Syntheses, Properties, and Applications of Organic Dyes and Pigments*, VCH, Cambridge, **1987**;
2. Vaidya, A.A., Datye, K.V.: Environmental pollution during chemical processing of synthetic fibers, *Colourage*, **1982**, 14, 3-10;
3. Hameed, B.H., Ahmad, A.A.: Batch adsorption of methylene blue from aqueous solution by garlic peel, an agricultural waste biomass, *Journal of Hazardous Materials*, **2009**, 164 (2-3), 870-875;
4. Turner, G.P.A.: *Introduction to Paint Chemistry and Principles of Paint Technology*, 3rd edition, Chapman and Hall, London, New York, **1988**;
5. Kadirvelu, K., Kavipriya, M., Karthika, C., Radhika, M., Vennilamani, N., Pattabhi, S.: Utilization of various agricultural wastes for activated carbon preparation and application for the removal of dyes and metal ions from aqueous solutions, *Bioresource Technology*, **2003**, 87 (1), 129-132;

6. Jin, Y., Row, K.H.: Adsorption isotherm of ibuprofen on molecular imprinted polymer, *Korean Journal of Chemical Engineering*, **2005**, 22 (2), 264-267;
7. Danish, M., Hashim, R., Ibrahim, M.N.M., Sulaiman, O.: Optimized preparation for large surface area activated carbon from date (*Phoenix dactylifera* L.) stone biomass, *Biomass and Bioenergy*, **2014**, 61, 167-178;
8. Sun, X.F., Xu, F., Sun, R.C., Fowler, P., Baird, M.S.: Characteristics of degraded cellulose obtained from steam-exploded wheat straw, *Carbohydrate Research*, **2005**, 340 (1), 97-106;
9. Bouchelta, C., Medjram, M.S., Bertrand, O., Bellat, J.-P.: Preparation and characterization of activated carbon from date stones by physical activation with steam, *Journal of Analytical and Applied Pyrolysis*, **2008**, 82 (1), 70-77;
10. Al-Ghouti, M.A., Hawari, A., Khraisheh, M.: A solid-phase extractant based on microemulsion modified date pits for toxic pollutants, *Journal of Environmental Management*, **2013**, 130, 80-89;
11. Sain, M., Panthapulakkal, S.: Bioprocess preparation of wheat straw fibers and their characterization, *Industrial Crops and Products*, **2006**, 23 (1), 1-8;
12. Sao, K., Khan, F., Pandey, P.K., Pandey, M.: Equilibrium isotherm study for removal of Mn (II) from aqueous solutions by using novel bioadsorbent *Tinospora cordifolia*, *Advances in Research*, **2016**, 6 (4), 1-11;
13. Kumar, R., Ahmad, R.: Biosorption of hazardous crystal violet dye from aqueous solution onto treated ginger waste (TGW), *Desalination*, **2011**, 265 (1-3), 112-118;
14. El Khomri, M., Lacherai, A., El Messaoudi, N., Bentahar, S., Ezahri, M.: Retention of methylene blue on an agro-source material, *International Journal of Engineering Research & Technology*, **2014**, 3 (8), 1657-1663;
15. Ouajai, S., Shanks, R.A.: Composition, structure and thermal degradation of hemp cellulose after chemical treatments, *Polymer Degradation and Stability*, **2005**, 89 (2), 327-335;
16. Essabir, H., Hilali, E., Elgharad, A., El Minor, H., Imad, A., Elamraoui, A., Al Gaoudi, O.: Mechanical and thermal properties of biocomposites based on polypropylene reinforced with nutshells of argan particles, *Materials & Design*, **2013**, 49, 442-448;
17. Arrakhiz, F.Z., El Achaby, M., Benmoussa, K., Bouhfid, R., Essassi, E.M., Qaiss, A.: Evaluation of mechanical and thermal properties of pine cone fibers reinforced compatibilized polypropylene, *Materials & Design*, **2012**, 40, 528-535;
18. Albano, C., Gonzalez, J., Ichazo, M., Kaiser, D.: Thermal stability of blends of polyolefins and sisal fiber, *Polymer Degradation and Stability*, **1999**, 66 (2), 179-190;
19. Chakraborty, S., Chowdhury, S., Saha, P.D.: Adsorption of crystal violet from aqueous solution onto NaOH-modified rice husk, *Carbohydrate Polymers*, **2011**, 86 (4), 1533-1541;
20. El Haddad, M., Slimani, R., Mamouni, R., Laamari, M.R., Rafqah, S., Lazar, S.: Evaluation of potential capability of calcined bones on the biosorption removal efficiency of safranin as cationic dye from aqueous solutions, *Journal of the Taiwan Institute of Chemical Engineers*, **2013**, 44 (1), 13-18;
21. Alkan, M., Doğan, M.: Adsorption kinetics of victoria blue onto perlite, *Fresenius Environmental Bulletin*, **2003**, 12 (5), 418-425;
22. Asfour, H.M., Fadali, O.A., Nassar, M.M., El-Geundi, M.S.: Equilibrium studies on adsorption of basic dyes on hardwood, *Journal of Chemical Technology and Biotechnology. Chemical Technology*, **1985**, 35 (1), 21-27;
23. Wang, X.S., Zhou, Y., Jiang, Y., Sun, C.: The removal of basic dyes from aqueous solution using agricultural by products, *Journal of Hazardous Materials*, **2008**, 157 (2-3), 374-385;
24. Malik, P.K.: Use of activated carbon prepared from sawdust and rice-husk for adsorption of acid dyes: a case study of Acid Yellow 36, *Dyes and Pigments*, **2003**, 56 (3), 239-249;
25. Noreen, S., Bhatti, H.N., Nausheen, S., Sadaf, S., Ashfaq, M.: Batch and fixed bed adsorption study for the removal of Drimarine Black CL-B dye from aqueous solution using a lignocellulosic waste: A cost affective adsorbent, *Industrial Crops and Products*, **2013**, 50, 568-579;
26. Barka, N., Abdennouri, M., El Makhfouk, M.: Removal of methylene blue and eriochrome black T from aqueous solutions by biosorption on *Scolymus hispanicus* L.: Kinetics, equilibrium and thermodynamics, *Journal of the Taiwan Institute of Chemical Engineers*, **2011**, 42 (2), 320-326;
27. Lagergren, S.: About the theory of so-called adsorption of soluble substances (in German), *Kungliga Svenska Vetenskapsakademiens Handlingar*, **1898**, 24 (4), 1-39;
28. Ho, Y.S., McKay, G.: Pseudo-second order model for sorption processes, *Process Biochemistry*, **1999**, 34 (5), 451-465;

29. Langmuir, I.: The adsorption of gases on plane surfaces of glass, mica and platinum, *Journal of the American Chemical Society*, **1918**, 40 (9), 1361-1403;
30. Freundlich, H.M.F.: Over the adsorption in solution (in German), *Zeitschrift für Physikalische Chemie*, **1906**, 57 (A), 385-470;
31. Temkin, M.J., Pyzhev, V.: Recent modifications to Langmuir isotherms, *Acta Physicochimica URSS*, **1940**, 12, 217-222;
32. El Haddad, M., Regti, A., Slimani, R., Lazar, S.: Assessment of the biosorption kinetic and thermodynamic for the removal of safranin dye from aqueous solutions using calcined mussel shells, *Journal of Industrial and Engineering Chemistry*, **2014**, 20 (2), 717-724;
33. Güzel, F., Saygılı, H., Saygılı, G.A., Koyuncu, F.: Decolorisation of aqueous crystal violet solution by a new nanoporous carbon: Equilibrium and kinetic approach, *Journal of Industrial and Engineering Chemistry*, **2014**, 20 (5), 3375-3386;
34. Secula, M.S., Cagnon, B., Crețescu, I., Diaconu, M., Petrescu, S.: Removal of an acid dye from aqueous solutions by adsorption on a commercial granular activated carbon: Equilibrium, kinetic and thermodynamic study, *Scientific Study & Research Chemistry & Chemical Engineering, Biotechnology, Food Industry*, **2011**, 12 (4), 307-322;
35. Ofomaja, A.E., Ho, Y.-S.: Effect of temperatures and pH on methyl violet biosorption by *Mansonia* wood sawdust, *Bioresource Technology*, **2008**, 99 (13), 5411-5417;
36. Lafi, R., Hamdi, N., Hafiane, A.: Study of the performance of Esparto grass fibers as adsorbent of dyes from aqueous solutions, *Desalination and Water Treatment*, **2015**, 56 (3), 722-735;
37. Chakraborty, S., Chowdhury, S., Saha, P.D.: Insight into biosorption equilibrium, kinetics and thermodynamics of crystal violet onto *Ananas comosus* (pineapple) leaf powder, *Applied Water Science*, **2012**, 2 (2), 135-141;
38. Suyamboo, B.K., Srikrishnapuram, R.: Biosorption of crystal violet onto *Cyperus rotundus* in batch system: kinetic and equilibrium modeling, *Desalination and Water Treatment*, **2014**, 52 (19-21), 3535-3546;
39. Pavan, F.A., Camacho, E.S., Lima, E.C., Dotto, G.L., Branco, V.T.A., Dias, S.L.P.: Formosa papaya seed powder (FPSP): Preparation, characterization and application as an alternative adsorbent for the removal of crystal violet from aqueous phase, *Journal of Environmental Chemical Engineering*, **2014**, 2 (1), 230-238;
40. El-Sayed, G.O.: Removal of methylene blue and crystal violet from aqueous solutions by palm kernel fiber, *Desalination*, **2011**, 272 (1-3), 225-232;
41. Lim, L.B.L., Priyantha, N., Mansor, N.H.M.: *Artocarpus altilis* (breadfruit) skin as a potential low-cost biosorbent for the removal of crystal violet dye: equilibrium, thermodynamics and kinetics studies, *Environmental Earth Sciences*, **2015**, 73 (7), 3239-3247;
42. Khan, M.M.R., Rahman, M.W., Ong, H.R., Ismail, A.B., Cheng, C.K.: Tea dust as a potential low-cost adsorbent for the removal of crystal violet from aqueous solution, *Desalination and Water Treatment*, **2016**, 57 (31), 14728-14738;
43. Pal, A., Pan, S., Saha, S.: Synergistically improved adsorption of anionic surfactant and crystal violet on chitosan hydrogel beads, *Chemical Engineering Journal*, **2013**, 217, 426-434;
44. Saha, P.D., Chakraborty, S., Chowdhury, S.: Batch and continuous (fixed-bed column) biosorption of crystal violet by *Artocarpus heterophyllus* (jackfruit) leaf powder, *Colloids and Surfaces B: Biointerfaces*, **2012**, 92, 262-270.