Kinetic, Isotherm and Mechanism Investigations of the Removal of Basic Violet 3 from Water by Raw Spent Coffee Grounds

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This work examines the possibility of removing the crystal violet (a cationic dye), used in dyeing of cotton, wood, and silk, onto untreated coffee waste. The influence of various experimental parameters on the adsorption of crystal violet has been analysed: pH, adsorbent dose and initial dye concentration. The optimum adsorption of crystal violet took place at pH 6 and at lower temperatures. Further, the adsorbent was characterised by Fourier transform infrared (FTIR) spectroscopy. The FTIR analysis revealed the presence of several functional groups that are responsible for the adsorption process. Adsorption equilibrium follows the Langmuir's model with maximum retention of 63.3 mg g^{-1}. The kinetics of the crystal violet adsorption were studied using the pseudo-first order and pseudo-second order equations. Adsorption of the dye can be described by pseudo-second order kinetics, reaching the equilibrium at 40 min. The value of the activation energy shows that adsorption is physisorption. The Weber-Morris model indicates that this adsorption occurs in two steps. Thermodynamic parameters suggest that the adsorption is spontaneous and exothermic.

Keywords: Adsorption, Cationic dye, Spent coffee grounds

INTTRODUCTION

Currently more than 700,000 tons/year of dyes are manufactured [1], 15 to 20% are discharged with the liquid effluent, without any prior treatment [2]. These discharges present a real danger to humans and to the environment due to their low biodegradability. For this reason, colored-effluents require appropriate treatment before being discharged into nature. In this context, a wide variety of physical techniques (adsorption, membrane filtration, precipitation, coagulation, flocculation and decantation), chemical (ion exchange resin, oxidation), and biological

(aerobic and anaerobic treatment) [3] have been employed. Among various techniques, adsorption has proven to be efficient, easy to implement, and inexpensive [4]. Activated carbon is the most widely used adsorbent, because of its interesting adsorption properties, but it is expensive and difficult to regenerate [5].

Research is then directed towards the exploitation of natural materials, agricultural by-products, and some industrial wastes, because of their abundance and low cost [6]. Several studies show that these materials have interesting properties for dyes removal. Such as olive cake waste [7], *Luffa aegyptica* peel [8], Bombax buonopozense [9], almond shells [10], pineapple peelings and coconut shells [11], *Cortaderia selloana* flower spikes [12],

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rice husk [13], potato peel [14], corn cob [15], garlic straw [16], coconut coir dust [17], bananas waste [18] and *Cucumis sativus* peel waste [19].

World coffee production, according to the International Coffee Organisation, is 160 million bags in 2018 (1 bag is 60 kg). Except for a few losses, all these quantities of coffee end up as spent coffee grounds (SCGs) in the rejects. SCGs is an excellent candidate for the adsorption of cationic dyes because it has a high carbon content (cellulose, lignin and hemicelluloses) and is rich in functional groups such as hydroxyl carboxyl and phenols [20]. In addition, the use of SCGs as an adsorbent requires little or no treatment.

The SCGs have been used for bioenergy, bioactive compounds and materials, and for adsorption of several heavy metals [21]. However, studies of the use of SCGs as an adsorbent for basic dyes are rare.

The present study is part of this perspective and consists of testing SCGs to remove a cationic dye widely used in the textile industry, which is crystal violet. It also aims to optimize their retention capacity by studying the effects of operating parameters.

MATERIALS AND METHODS

Adsorbent Preparation and Characterization

The spent coffee grounds were collected from a coffee shop in Meknes City (Morocco). The collected SCGs were washed thoroughly with hot distilled water (60 °C), until a neutral pH was reached, and then they were dried in an oven at 105 °C for 24 h. The dried SCGs were sieved to obtain a grain size of fewer than 250 μm. The product was stored in a clean and dry place. The surface chemistry of SCGs was studied by determining the pH at the point zero charge (pH$_{PZC}$), and the surface functions.

The pH$_{pzc}$ was determined by the salt addition technique: a mass of 0.2 g of SCGs was introduced into a series of tubes each containing 40 ml of NaCl solution (0.1 M). The pH was adjusted using a solution of HCl (0.1 M) and NaOH (0.1 M) as required. The pH values of the supernatant in each tube were designated as pH$_i$. The samples were agitated for 24 h at 200 rpm. After settling, the pH values of the supernatant in each tube were measured and designated as pH$_f$. The pH$_{PZC}$ was obtained from the plot of ΔpH (= pH$_f$ - pH$_i$) *vs.* pH$_i$ at ΔpH = 0.

Chemical groups present on the SCGs surface were characterised by Fourier transform infrared (FTIR) spectroscopy using a Fourier transform infrared spectrometer (Shimadzu, JASCO 4100). The samples were prepared in KBr discs from very well dried mixtures of about 4% (w/w). The FTIR spectra were recorded from 4000 to 400 cm^{-1} by an accumulation of at least 64 scans with a resolution of 4 cm^{-1} per sample.

Adsorbate Dye

The dye considered in this study is a crystal violet (CV) with very high purity (98%) and a C.I. index of 42,555. Its molecular structure is shown in Fig. 1 and its main characteristics are presented in Table 1. It has been used without any prior purification. A stock solution of 400 mg l^{-1} was prepared by dissolving 400 mg of dye in 1L of distilled water. The colored solutions of different concentrations used in this study were prepared by dilution with distilled water.

Adsorption Experiments

Adsorption experiments were carried out in a batch mode. The various experimental conditions are shown in Table 2. A precisely weighed quantity of adsorbent is introduced into a volume (40 ml) of the CV of C$_0$ concentration. The initial solution pH was adjusted using 0.1 M HCl and 0.1 M NaOH solutions. The reaction mixtures were stirred at 600 rpm, using a heated magnetic stirrer, at an adjustable temperature, for a specified time. At the end of each experiment the colored solution was separated from the adsorbent by centrifugation at 3000 rpm for 20 min. The absorbance of the supernatant solution was measured using a UV/visible spectrometer (Shimadzu, UV-1240), at the wavelength corresponding to the maximum CV absorbance (λ_{max} = 590 nm). The residual dye concentration C$_t$ in the reaction mixture was calculated using a previously drawn calibration curve.

The amount of adsorbed CV q$_t$ (mg g^{-1}), and the removal percentage R$_t$ (%) were determined by the following Eqs. (1) and (2) [22]:
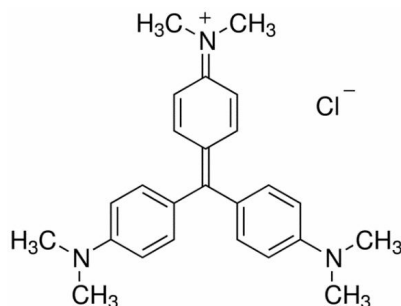
$$q_t = \frac{(C_0 - C_t).V}{m} \qquad (1)$$

Fig. 1. Chemical structure of crystal violet.

Table 1. Chemical Properties and Characteristics of Crystal Violet

Generic name	Crystal violet
Chemical formula	$C_{25}H_{30}N_3Cl$
Molecular weight (g mol^{-1})	407.98
Type of dye	Cationic
λ_{max} (nm)	590 nm
Chemical safety	

Table 2. Effect of Parameters on the Adsorption Process

	Parameters				
	pH	Concentration dye (mg l^{-1})	Adsorbent dosage (g l^{-1})	Time (min)	Temperature (°C)
Effect of pH	2-12	100	2	50	25
Effect of adsorbent dosage	6	100	0.1- 7	50	25
Effect of time	6	100	2	0-120	25
Effect of temperature	6	100	2	50	25-50

$$R_t = \frac{(C_0 - C_t).100}{C_0} \qquad (2)$$

where C_0 and C_t are the CV initial concentration and concentration (mg l^{-1}) at the time t, V is the solution volume (L), and m is the adsorbent mass (g).

Kinetics and Isotherms Modeling

In order to understand the mechanism of CV adsorption on the SCGs, the kinetic data were analysed by the linear forms of the pseudo-first order and pseudo-second order kinetic models, as well as the intra-particle diffusion model. On the other hand, the modeling of the adsorption equilibrium was undertaken by the non-linear forms of Langmuir, Freundlich, and Temkin isotherms. The validity of the kinetic models and isotherms were confirmed by the coefficient of determination (R^2). All the corresponding equations are summarised in Table 3.

The K_L value of the Langmuir adsorption isotherm is used to determine the separation factor R_L, given by Eq. (3):

$$R_L = \frac{1}{1 + K_L C_0} \qquad (3)$$

The value of R_L is used to predict the favorability of the adsorption process: adsorption is favorable when $0 < R_L < 1$, linear when $R_L = 1$, unfavorable when $R_L > 1$, and irreversible when $R_L = 0$.

Where q_t (mg g^{-1}) and q_e (mg g^{-1}) are the quantities of adsorbed dye at the time t and at equilibrium, k_1 (min^{-1}) and k_2 (g mg^{-1} min^{-1}) are the constants of pseudo-first order and pseudo-second order models, respectively. k_d and C are the intra-particle diffusion rate constant and thickness of the boundary layer, respectively. C_e (mg l^{-1}) is the equilibrium concentration; q_m (mg g^{-1}) is the maximum adsorption capacity; K_L (l mg^{-1}) is the Langmuir constant; K_F (mg g^{-1}) (l mg^{-1})$^{1/n}$ and n are the Freundlich constants. A and b are the Temkin constants, R is the universal gas constant (8.314 J mol^{-1} K^{-1}), and T is the absolute temperature in Kelvin.

Thermodynamic Parameters

The thermodynamic behavior of CV adsorption on SCGs was evaluated by the thermodynamic parameters:

Gibbs free energy ($\Delta G°$), enthalpy ($\Delta H°$), and entropy ($\Delta S°$). These parameters were calculated using the following equations [22]:

$$\ln(K_D) = \frac{\Delta S°}{R} - \frac{\Delta H°}{RT} \qquad (4)$$

where K_D is the distribution coefficient:

$$K_D = \frac{C_0 - C_e}{C_e} \qquad (5)$$

$$\Delta G° = \Delta H° - T\Delta S° \qquad (6)$$

RESULTS AND DISCUSSION

Effect of Operating Parameters

Effect of pH. The influence of the initial pH on the adsorption was studied in the range of pH 2-12. Figure 2 shows that the amount retained by the adsorbent is closely related to the initial pH value. The retention rate is appreciable for pH values between 6 and 9, with a retention peak around pH = 6. Above pH = 10, a drop-in efficacy was observed. A similar trend in the effect of pH was observed for the adsorption of basic red on sawdust [28]. In order to elucidate the effect of pH on the adsorbent surface charge, the determination of the point of zero charge or pH$_{PZC}$ was carried out. The pH$_{PZC}$ is very important in the adsorption phenomenon, especially when the forces of electrostatic are involved in the mechanisms, which is the case for biomass [29]. Figure 2 shows that the pH$_{PZC}$ of the SCGs is 5.3. This value is comparable to that found by Min-Suk Kimin [30] for cadmium adsorption onto SCGs. The overall surface charge is positive for solutions with a pH below this value, and it is negative when the pH is above pH$_{PZC}$. As the dye used is alkaline, its dissolution releases positively charged ions. This explains why retention is most noticeable when the pH is above 5.3. Nevertheless, this loss of CV removal, as the pH increases, shows that the reaction is rather complex and far from being a simple electrostatic attraction between opposite charge species. Elbariji *et al.* [31] have reported that the hydroxide functions of cellulose and lignin, in the presence of NaOH, are transformed into alcoholate functions. This hypothesis suggests that if the medium

Table 3. The Equations of the Models Used in this Work

Kinetic models		Ref.
Pseudo-first order	$\ln(q_e - q_t) = \ln q_e - k_1 t$	[23]
Pseudo-second order	$\dfrac{t}{q_t} = \dfrac{1}{k_2 q_e^2} + \dfrac{1}{q_e} t$	[24]
Weber and Morris	$q_t = k_{id} \, t^{\frac{1}{2}} + C_i$	[25]
Isotherm models		
Langmuir	$q_e = \dfrac{q_m K_L C_e}{1 + K_L C_e}$	[26]
Freundlich	$q_e = K_F \, C_e^{\frac{1}{n}}$	[26]
Temkin	$q_e = \dfrac{RT}{b} \ln(A C_e)$	[27]

becomes very alkaline, competition is likely between Na^+ cations, which are smaller and more mobile than those of the dye, preventing them from accessing the surface of the adsorbent.

Effect of adsorbent dose. The influence of the adsorbent dose was studied in the range of 0.1-7 g l^{-1}, for an initial CV concentration of 100 mg l^{-1}. The curve in Fig. 3 shows that a dose of 2 g l^{-1} of SCGs can remove 90% of the dye. Above this dose, the elimination rate remains unchanged due to saturation of the active adsorption sites [32]. Similar results have been reported on the removal of the CV dye by Anatolian black pine [33]. In the following, we will work with adsorbent dose of 2 g l^{-1}.

Adsorption Isotherms

The isotherms of CV adsorption on SCGs were studied at an initial concentration range of 0-400 mg l^{-1}. The experimental points obtained are shown in Fig. 4. The non-linear forms of the Langmuir, Freundlich and Temkin models were used to modeling the adsorption equilibrium.

Figure 4 shows the non-linear curves of these models, and Table 4 gives the calculated constants of these three models. These results indicate that the Langmuir model best reflects the adsorption of the dye on SCGs. The equilibrium parameter RL is equal to 0.010 ($0 < R_L < 1$), indicating that adsorption is favourable. The coefficient of determination R^2 is also the best compared to the other models used ($R^2 = 0.999$). This indicates that the retention of CV on the SCGs is monolayer at homogeneous adsorption sites with no interaction between the adsorbed cations of the dye. The maximum CV adsorption capacity on SCGs ($q_m = 63.3$ mg g^{-1}) is comparable to those reported in the literature for different adsorbents, as shown in Table 5.

Adsorption Kinetics

The results of the kinetics obtained are shown in Fig. 5. The equilibrium time of CV adsorption by SCGs for the four temperatures is 40 min. The curves show that CV adsorption is slightly temperature-dependent. An increase in temperature has a negative effect on adsorption, indicating
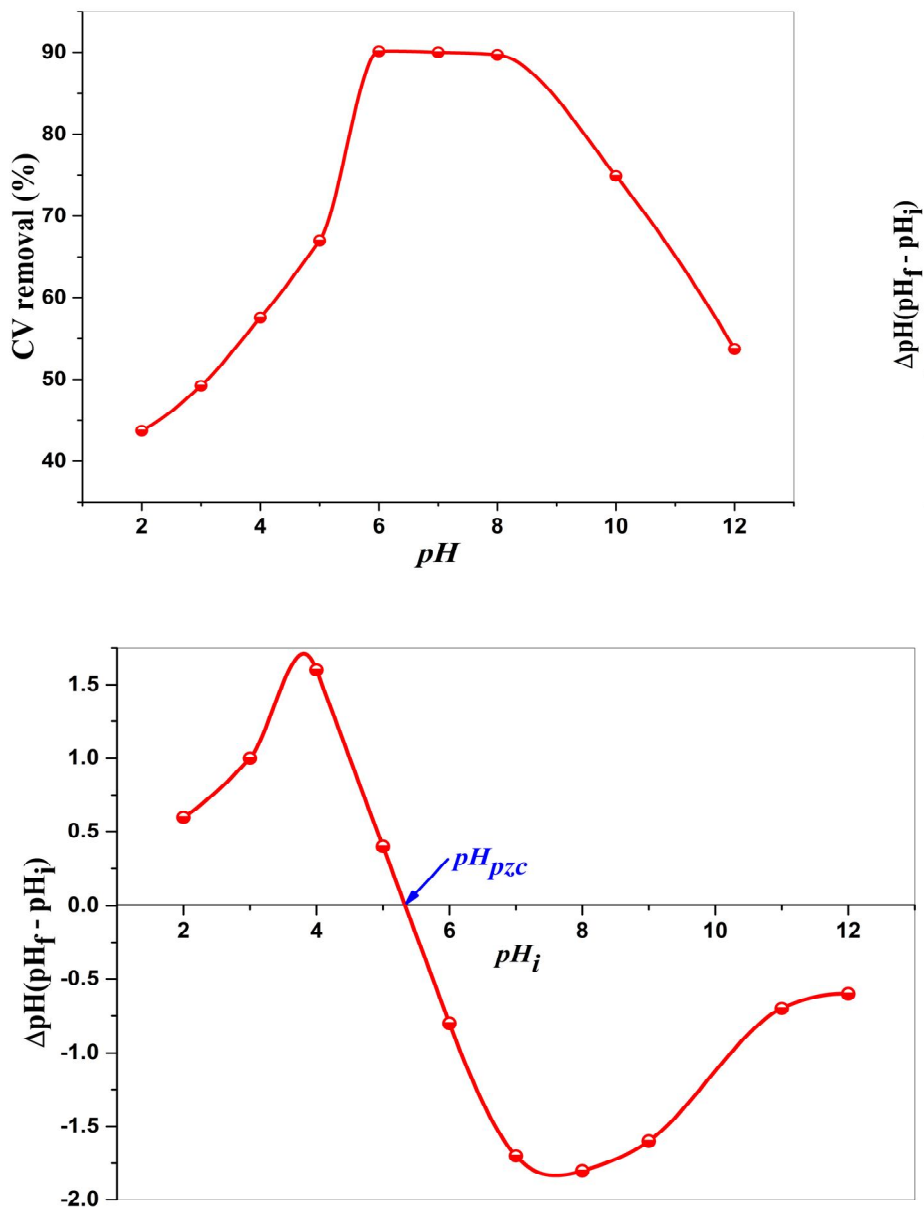
Fig. 2. The effect of pH and determination of pH_{PZC} (adsorbent dose = 2 g l^{-1}; time = 50 min; temperature 25 °C; V = 40 ml; stirring rate = 400 rpm).

that the process is exothermic [27]. For all temperatures, adsorption takes place rapidly during the first few moments, due to the availability of sites on the adsorbent surface. Over time, the adsorption efficiency decreases, due to the progressive decrease in the number of free sites, on the adsorbent surface [22].

In order to modeling the kinetics and to understand the mechanism of adsorption, the experimental points were analysed by two models, namely the pseudo-first order (PFO) and pseudo-second order (PSO) models. To identify the most suitable model, the experimental data were analysed using the coefficient of determination (R^2). The
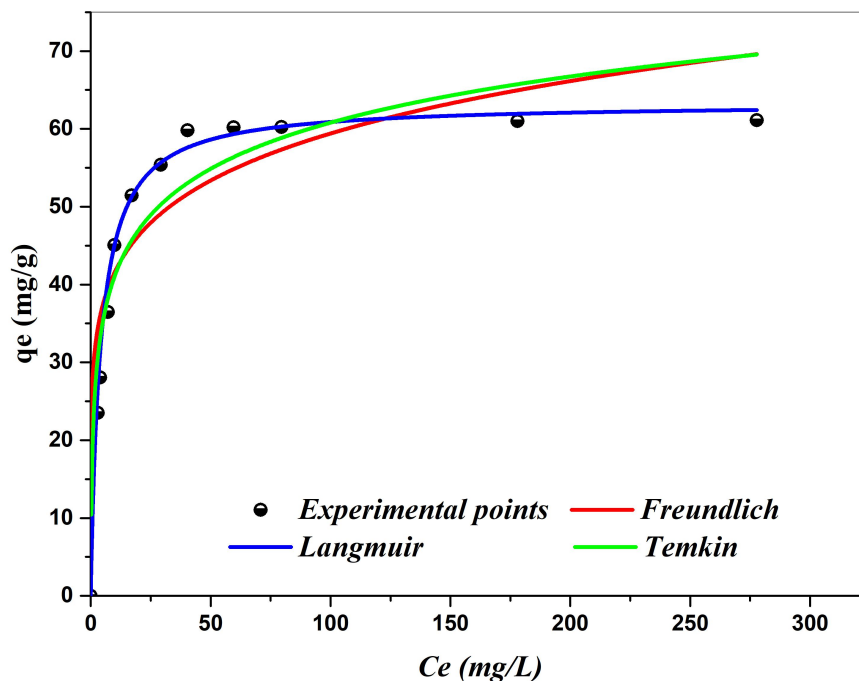
Fig. 4. Isotherm plots for CV adsorption on SCGs at 25 °C.

Table 4. Isotherm Constants for CV Adsorption on SCGs at 25 °C

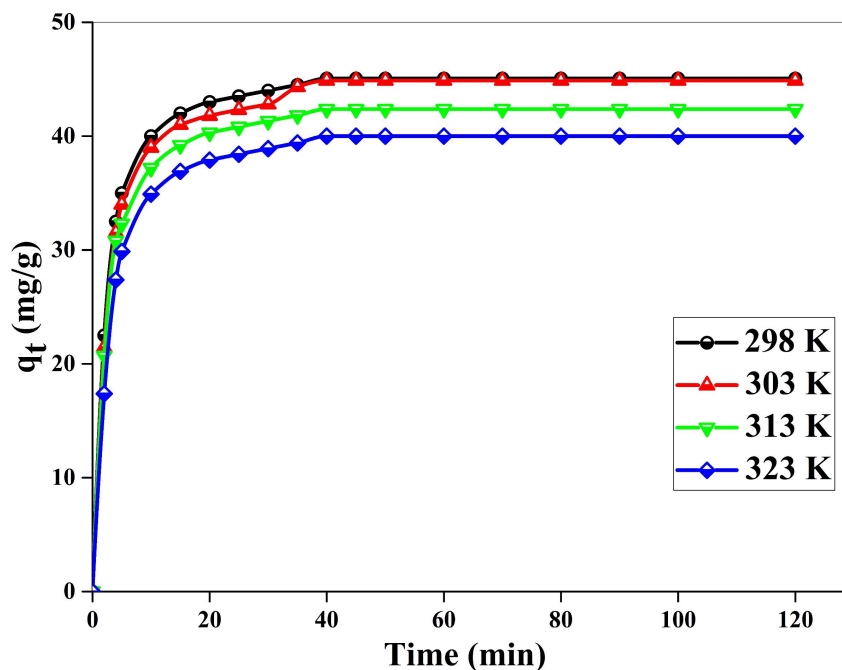| Isotherm	Parameters
Langmuir	
q_m (mg g^{-1})	63.3
K_L (l mg^{-1})	0.249
R_L	0.010
R^2	0.999
Freundlich	
K_F (mg g^{-1}) (l mg^{-1})$^{1/n}$	29.1
n	0.155
R^2	0.876
Temkin	
A (l g^{-1})	12.2
B	8.560
R^2	0.918

Fig. 5. Effects of contact time and temperature on the adsorption of CV on SCGs (pH = 6; C_0 = 100 mg l^{-1}; V = 40 ml; adsorbent dose = 2 g l^{-1}; stirring rate = 400 rpm)

Table 5. Comparison of the Equilibrium Capacity for CV onto the other Different Adsorbents

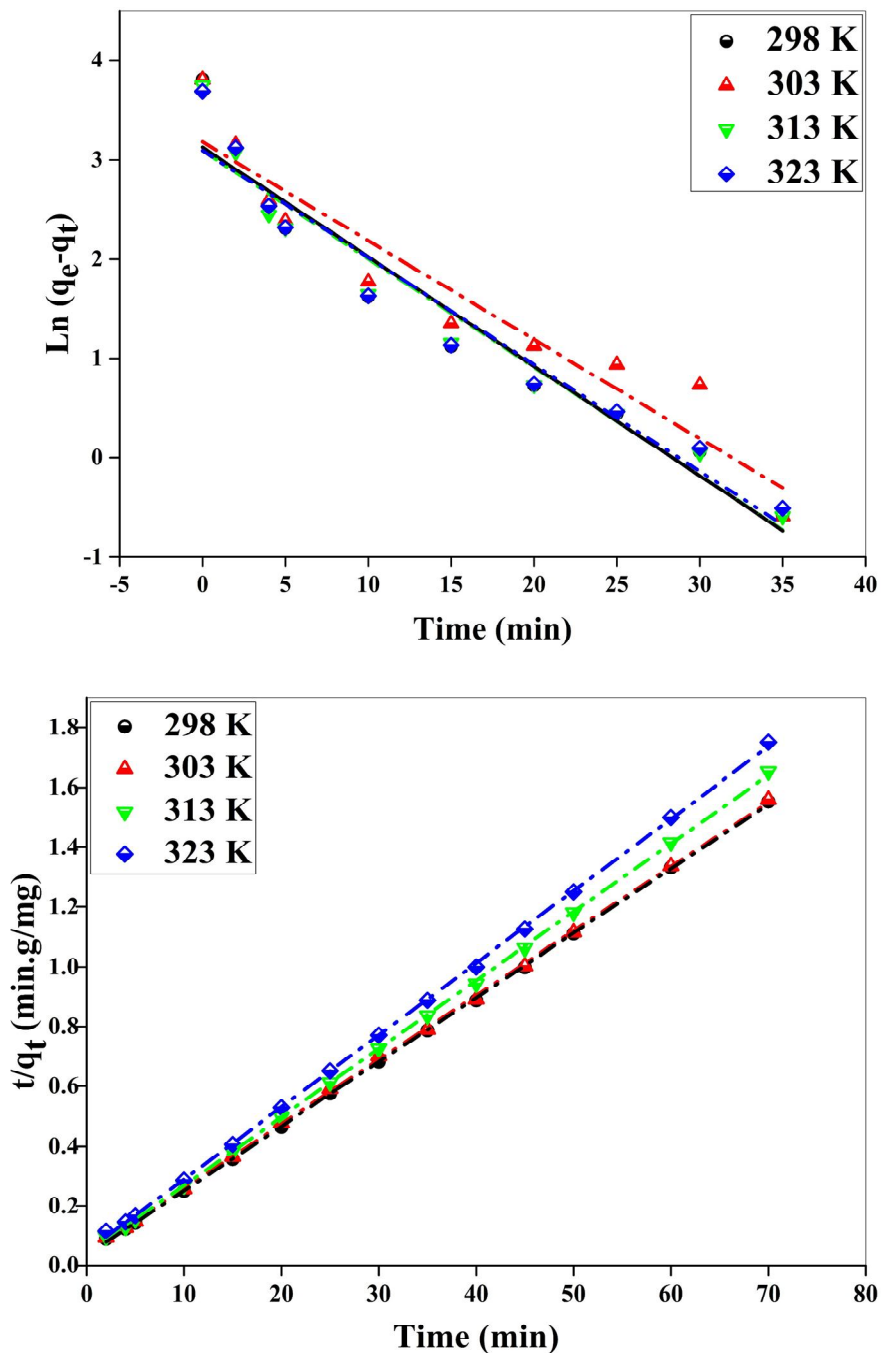| Adsorbent	q_m (mg g^{-1})	Ref.
SCGs	63.3	This work
Anatolian black pine	12.4	[33]
Spathodea campanulata leaves	12.7	[34]
Kaolin KM 20	23.6	[35]
Epichlorohydrin modified corncob	71.4	[36]
Commercial activated carbon	22.7	[37]
Almond shells	1.1	[38]
Date Palm Fibre	0.3	[39]
NaOH-modified rice husk	44.9	[40]
Bottom ash	6.9	[41]

Fig. 6. The plots of pseudo-first order and pseudo-second order model for CV on SCGs for different temperatures.

representation of the models is summarised in Fig. 6, and the values of the different kinetic parameters are given in Table 6. It is clear from Table 6 that the PSO model describes well the experimental points for all temperatures, leading to equilibrium adsorption capacity values (q_{cal}) that are in perfect agreement with those found experimentally

Table 6. The Pseudo-first Order and Pseudo-second Order Adsorption Rate Constants Obtained at Different Temperatures

T (°K)	Pseudo-first-order kinetic model				Pseudo-second-order kinetic model		
	$q_{e,exp}$ (mg g^{-1})	$q_{e,cal}$ (mg g^{-1})	k_1 (min^{-1})	R^2	$q_{e,cal}$ (mg g^{-1})	k_2 (g mg^{-1} min^{-1})	R^2
298	45.06	22.79	0.110	0.936	45.79	0.017	0.999
303	44.88	24.05	0.115	0.906	45.75	0.022	0.999
313	42.38	22.06	0.122	0.942	43.09	0.026	0.999
323	40.00	22.03	0.125	0.941	40.77	0.030	0.999

(q_{exp}). Moreover, this result is confirmed by the values of the coefficient of determination R^2 which is very close to 1. From the pseudo-second order rate constant k_2, the activation energy E_a for adsorption of CV onto SCGs was determined using the Arrhenius Eq. (4) [27]:

$$\ln(K_2) = \ln(A) - \frac{E_a}{RT} \qquad (7)$$

where k_2 is the pseudo-second order rate constant (g mg^{-1} min^{-1}), A is the Arrhenius constant (min^{-1}), E_a is the activation energy (KJ mol^{-1}), R is the universal gas constant (8.314 J mol^{-1} K^{-1}) and T is the temperature (K).

E_a was obtained by plotting $\ln(k_2)$ *vs.* $1/T$ (the figure is not shown). From the slope, the value of E_a is 17 kJ mol^{-1}. The activation energy is less than 40 kJ mol^{-1}, suggesting a physisorption mechanism [42].

The Weber-Morris intraparticle model was tested to study the process of external and internal diffusion of CV on the adsorbent surface. The representation of q_t *vs.* $t^{0.5}$ for the kinetic data is given in Fig. 7. For the four temperatures, we notice that each curve has two line segments indicating that the adsorption process takes place in two steps, the first step is fast, corresponding to the first line segment, which is attributed to external diffusion. The second with the lowest intra-particle diffusion rate constant is related to the intraparticle diffusion. These lines do not pass through the origin, indicating that intraparticle diffusion is not the only

limiting step [43].

Adsorption Thermodynamic

The thermodynamic study is represented by the plot of $ln(K_D)$ *vs.* $1/T$ (Fig. 8). Values of ΔH° and ΔS° were obtained from the slope and the intersection with the origin. The thermodynamic parameters are grouped in Table 8. The results confirm the exothermic nature of the process (ΔH° negative). The negative values of ΔG° and ΔS° indicate that the adsorption of CV on SCGs is spontaneous and that the adsorption is accompanied by a decrease in the disorder [44]. This observation is similar to the results obtained when CV was adsorbed onto black tea leaves [45] where the adsorption process was found to be exothermic.

Adsorbent Characterisation by Fourier Transform Infrared (FTIR) Spectroscopy

The FTIR spectra of the SCGs, recorded between 400 and 4000 cm^{-1}, are shown in Fig. 9. The spectra show a wide band centred at 3432 cm^{-1}, related to the O-H bond stretching vibration of hydrogen bonds of alcohols and phenols [20]. The two bands at 2934 and 2852 cm^{-1} are allocated to the symmetrical and asymmetric C-H stretching of the aliphatic chains. The thin band around 1740 cm^{-1} is attributed to the stretching vibration of the carbonyl group C=O of aldehydes, ketones, lactones, carboxylic acids and aliphatic esters [20]. The bands around 1644 cm^{-1}, 1465, 1242, and 1379 cm^{-1} indicate the presence of CO and COO$^-$
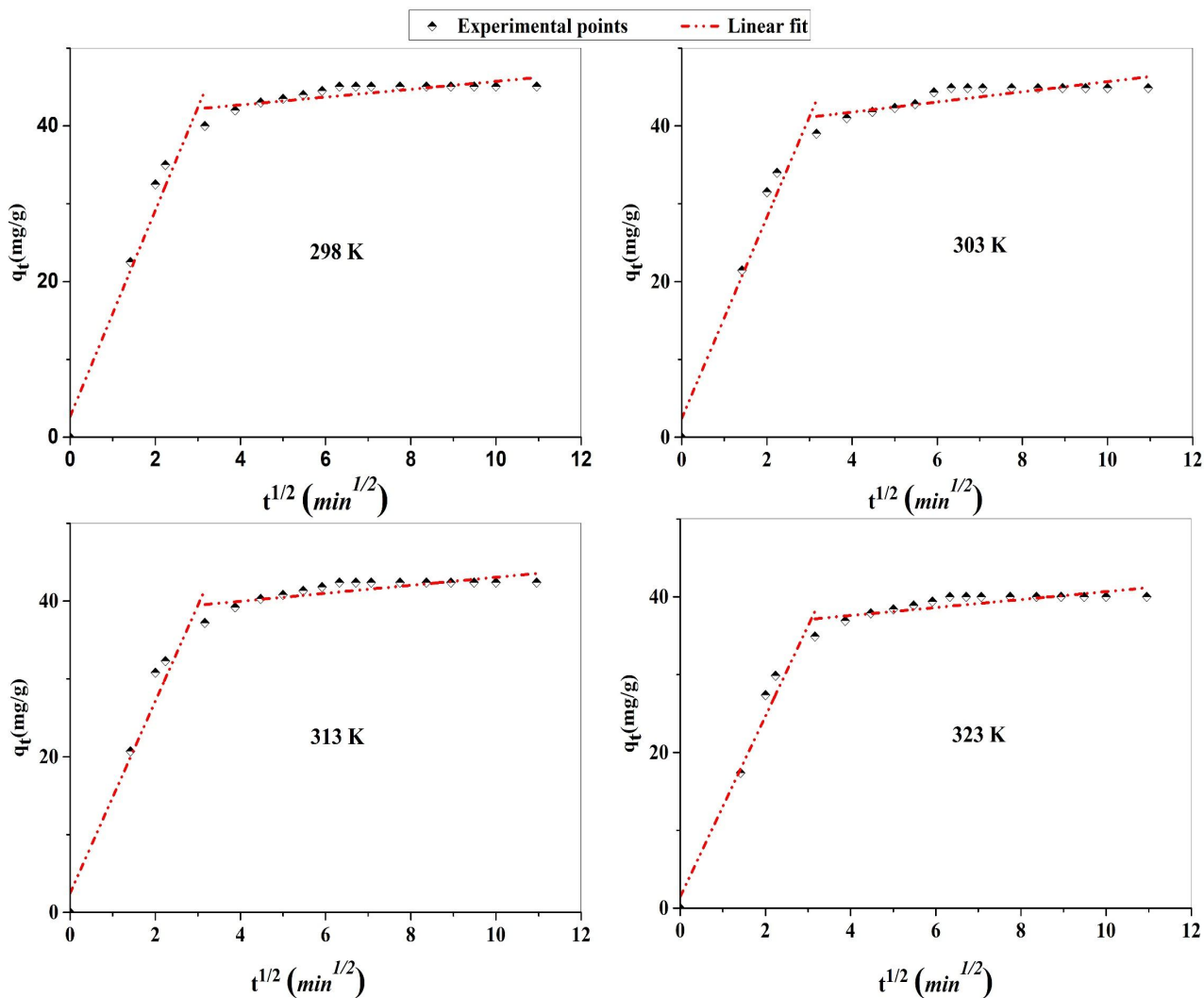
Fig. 7. Intraparticle diffusion plot for the CV adsorption on SCGs for different temperatures.

Table 7. Constants of the Intraparticle Diffusion Model

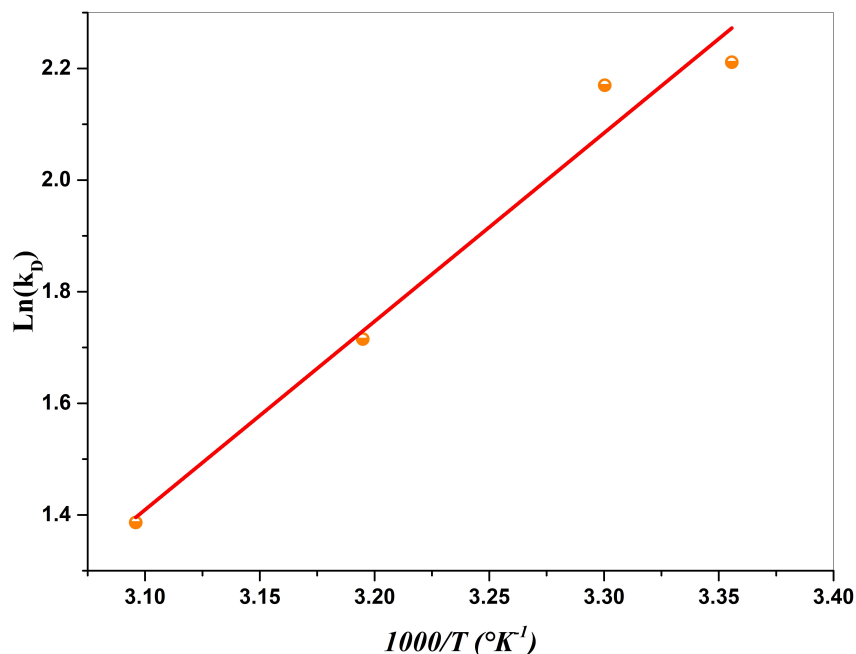|	Step1			Step2		
T	k_{d1}	C_1	R^2	k_{d2}	C_2	R^2
(°K)	(mg min^2 g^{-1})			(mg min^2 g^{-1})		
298	13.25	2.65	0.976	0.50	40.69	0.920
303	12.93	2.40	0.941	0.65	39.17	0.956
313	12.34	2.45	0.975	0.51	37.92	0.923
323	11.60	1.45	0.983	0.51	35.57	0.928

Fig. 8. The plot of *ln (K_D) vs. 1/T*.

Table 8. Thermodynamic Parameters for the Adsorption of CV on SCGs

Temperature (K)	$\Delta H°$ (kJ mol^{-1})	$\Delta S°$ (J mol^{-1} K^{-1})	$\Delta G°$ (kJ mol^{-1})	R^2
298			-5.626	
303	-28.06	-75.28	-5.250	0.988
313			-4.497	
323			-3.745	

groups on the surface of adsorbent [20]. Other bands appear between 1200-1000 cm^{-1} are attributed to the stretching vibration of the C-O group of esters, phenols, ethers, anhydrous and carboxylic acids[20].

CONCLUSIONS

The objective of this study was to test the potential of SCGs as an adsorbent to remove a cationic dye. The FTIR adsorbent, for a solution of 100 mg l^{-1}, is 2 g l^{-1}, and the optimal pH value is around 6. The increase in temperature slightly disadvantages adsorption, indicating the exothermic nature of the process. The adsorption equilibrium was analysed by the non-linear forms of Langmuir, Freundlich and Temkin models. The adsorption data were better adapted to the Langmuir isotherm, and the maximum biosorption capacity was 63.3 mg g^{-1}. Biosorption kinetics were studied at four temperatures using pseudo-first and
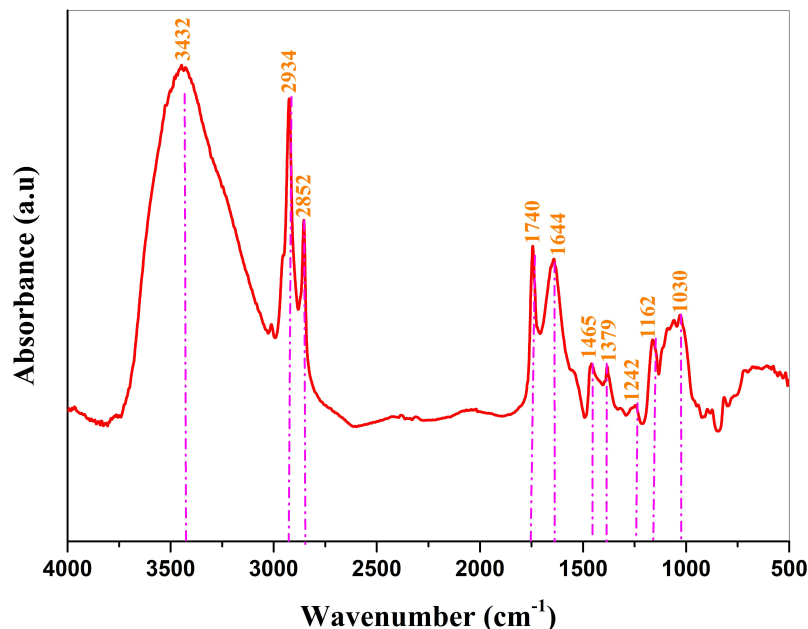
Fig. 9. The FTIR spectra of SCGs.

pseudo-second order kinetic models. The data for all four temperatures were followed by the pseudo-second order kinetic model. The intraparticle diffusion model plots, for the four temperatures, showed that the adsorption process takes place in two steps and that intraparticle diffusion is not the only limiting step. Thermodynamic parameters ($\Delta G°$, $\Delta H°$, $\Delta S°$) also indicated that CV adsorption on SCGs is feasible, spontaneous and exothermic in nature. These results clearly show that SCGs can be promoted as an effective and inexpensive adsorbent for removing CV from the aqueous solutions.

Funding Sources

Conflict of Interest

On behalf of all the authors, the corresponding author states that there is no conflict of interest.

REFERENCE

[1]   Bencheqroun, Z.; El Mrabet, I.; Kachabi, M.; *et al.*, Removal of basic dyes from aqueous solutions by adsorption onto Moroccan clay (Fez city). *Mediterr J. Chem.* **2019**, *8*, 158-167. DOI: 10.13171/10.13171/ MJC8319050803HZ.

[2]   Chraibi, S.; Allouch, M.; Boukhlifi, F.; Alami, M., Study of the effect of solid waste reinforcing on the thermal behavior of a nanocomposite. *J Chem.***2014**, *5*, 490-493.

[3]   Gebrati, L.; El Achaby, M.; Chatoui, H.; *et al.*, Inhibiting effect of textile wastewater on the activity of sludge from the biological treatment process of the activated sludge plant. *Saudi J. Biol. Sci.* **2019**, *26*, 1753-1757. DOI: 10.1016/j.sjbs.2018.06.003.

[4]   Katheresan, V.; Kansedo, J.; Lau, S. Y., Efficiency of various recent wastewater dye removal methods: A review. *J. Environ. Chem. Eng.* **2018**, *6*, 4676-4697. DOI:10.1016/j.jece.2018.06.060.

[5]   Rosales, E.; Meijide, J.; Pazos, M.; Sanromán, M. A., Challenges and recent advances in biochar as low-cost biosorbent: From batch assays to continuous-flow systems. *Bioresour Technol.* **2017**, *246*, 176-192. DOI: 10.1016/j.biortech.2017.06.084.

[6]   De Gisi, S.; Lofrano, G.; Grassi, M.; Notarnicola, M., Characteristics and adsorption capacities of low-cost

sorbents for wastewater treatment: A review. *Sustain Mater. Technol.* **2016**, *9*, 10-40. DOI: 10.1016/j.susmat.2016.06.002.

[7] Toumi, K. H.; Benguerba, Y.; Erto, A.; *et al.*, Molecular modeling of cationic dyes adsorption on agricultural Algerian olive cake waste. *J. Mol. Liq.* **2018**, *264*, 127-133. DOI: 10.1016/j.molliq.2018.05.045.

[8] Mashkoor, F.; Nasar, A., Preparation, characterization and adsorption studies of the chemically modified Luffa aegyptica peel as a potential adsorbent for the removal of malachite green from aqueous solution. *J. Mol. Liq.* **2019**, *274*, 315-327. DOI: 10.1016/j.molliq.2018.10.119.

[9] Achour, Y.; Khouili, M.; Abderrafia, H.; *et al.*, DFT investigations and experimental studies for competitive and adsorptive removal of two cationic dyes onto an eco-friendly material from aqueous media. *Int. J. Environ. Res.* **2018**, *12*, 789-802. DOI: 10.1007/s41742-018-0131-x.

[10] Göksu, A.; Tanaydin, M. K., Determination of optimum conditions of crystal violet dye adsorption on almond shells. *AIP Conf. Proc.* **2017**, *1833*, 1-4. DOI: 10.1063/1.4981762.

[11] Ndifor-Angwafor, N. G.; Kuete Tiotsop, I. H.; Tchuifon, Tchuifon, D. R.; *et al.*, Biosorption of amaranth red in aqueous solution onto treated and untreated lignocellulosic materials (pineapple peelings and coconut shells). *J. Mater. Environ. Sci.* **2017**, *8*, 4199-4212. DOI:10.26872/jmes.2017.8.12.441.

[12] Jia, Z; Li, Z; Ni, T; Li, S., Adsorption of low-cost absorption materials based on biomass (Cortaderia selloana flower spikes) for dye removal: Kinetics, isotherms and thermodynamic studies. *J. Mol. Liq.* **2017**, *229*, 285-292. DOI: 10.1016/j.molliq.2016.12.059.

[13] Shalaby, N. H.; Ewais, E. M. M.; Elsaadany, R. M.; Ahmed, A., Rice husk templated water treatment sludge as low cost dye and metal adsorbent. *Egypt J. Pet.* **2017**, *26*, 661-668. DOI: 10.1016/j.ejpe.2016.10.006.

[14] Lairini, S.; El Mahtal, K.; Miyah, Y.; *et al.*, The adsorption of crystal violet from aqueous solution by using potato peels (Solanum tuberosum): Equilibrium

and kinetic studies. *J. Mater. Environ. Sci.* **2017**, *8*, 3252-3261.

[15] Miyah, Y.; Lahrichi, A.; Idrissi, M., Removal of cationic dye-methylene bleu- from aqueous solution by adsorption onto corn cob powder calcined. *J. Mater. Environ. Sci.* **2016**, *7*, 96-104.

[16] Kallel, F.; Chaari, F.; Bouaziz, F.; *et al.*, Sorption and desorption characteristics for the removal of a toxic dye, methylene blue from aqueous solution by a low cost agricultural by-product. *J. Mol. Liq.* **2016**, *219*, 279-288. DOI: 10.1016/j.molliq.2016.03.024.

[17] Etim, U. J.; Umoren, S. A.; Eduok, U. M., Coconut coir dust as a low cost adsorbent for the removal of cationic dye from aqueous solution. *J. Saudi Chem. Soc.* **2016**, *20*, S67-S76. DOI: 10.1016/j.jscs.2012.09.014.

[18] Ahmad, T.; Danish, M., Prospects of banana waste utilization in wastewater treatment: A review. *J. Environ Manage.* **2018**, *206*, 330-348. DOI: 10.1016/j.jenvman.2017.10.061.

[19] Leal, T. W.; Lourenço, L. A.; Scheibe, A. S.; *et al.*, Adsorptive treatment of hazardous methylene blue dye from artificially contaminated water using cucumis sativus peel waste as a low-cost adsorbent. *J. Environ. Manage.* **2018**, *6*, 235-253. DOI: 10.1016/j.gsd.2017.06.005.

[20] Anastopoulos, I.; Karamesouti, M.; Mitropoulos, A. C.; Kyzas, G. Z., A review for coffee adsorbents. *J. Mol Liq.* **2017**, *229*, 555-565. DOI: 10.1016/j.molliq.2016.12.096.

[21] McNut, J.; He, Q. (Sophia)., Spent coffee grounds: A review on current utilization. *J. Ind. Eng. Chem.* **2019**, *71*, 78-88. DOI: 10.1016/j.jiec.2018.11.054.

[22] Loulidi, I.; Boukhlifi, F.; Ouchabi, M.; *et al.*, Adsorption of crystal violet onto an agricultural Waste residue: Kinetics, isotherm, thermodynamics, and mechanism of adsorption. *Sci. World J.* **2020**, *2020*, 1-9. DOI: 10.1155/2020/5873521.

[23] Arami, M.; Limaee, N. Y.; Mahmoodi, N. M., Evaluation of the adsorption kinetics and equilibrium for the potential removal of acid dyes using a biosorbent. *Chem. Eng. J.* **2008**, *139*, 2-10. DOI: 10.1016/j.cej.2007.07.060.

[24] Loulidi, I.; Boukhlifi, F.; Ouchabi, M.; *et al.*,

Adsorptive removal of chromium(VI) using walnut. *Res. J. Chem. Environ.* **2019**, *23*, 25-32.

[25] Hameed, B. H., Spent tea leaves: A new non-conventional and low-cost adsorbent for removal of basic dye from aqueous solutions. *J. Hazard. Mater.* **2009**, *161*, 753-759. DOI: 10.1016/j.jhazmat.2008.04.019.

[26] Ouallal, H.; Dehmani, Y.; Moussout, H.; *et al.*, Kinetic, isotherm and mechanism investigations of the removal of phenols from water by raw and calcined clays. *Heliyon.* **2019**, *5*, e01616. DOI: 10.1016/j.heliyon.2019.e01616.

[27] Aazza, M.; Ahlafi, H.; Moussout, H.; Maghat, H., Adsorption of metha-nitrophenol onto alumina and HDTMA modified alumina: Kinetic, isotherm and mechanism investigations. *J. Mol. Liq.* **2018**, *268*, 587-597. DOI: 10.1016/j.molliq.2018.07.095.

[28] Belaid, K. D.; Kacha, S., Étude cinétique et thermodynamique de l'adsorption d'un colorant basique sur la sciure de boisStudy of the kinetics and thermodynamics of the adsorption of a basic dye on sawdust. *Rev. des Sci. l'eau.* **2012**, *24*, 131. DOI: 10.7202/1006107ar.

[29] Bakatula, E. N.; Richard, D.; Neculita, C. M.; Zagury, G. J., Determination of point of zero charge of natural organic materials. *Environ. Sci. Pollut. Res.* **2018**, *25*, 7823-7833. DOI: 10.1007/s11356-017-1115-7.

[30] Kim, M. S.; Kim, J. G., Adsorption characteristics of spent coffee grounds as an alternative adsorbent for cadmium in solution. *Environ-MDPI.* **2020**, *7*, 1-12. DOI: 10.3390/environments7040024.

[31] Elbariji, S.; Elamine, M.; Eljazouli, H.; *et al.*, Traitement et valorisation des sous-produits du bois. Application à l'élimination des colorants industriels. *Comptes Rendus Chim.* **2006**, *9*, 1314-1321. DOI: 10.1016/j.crci.2006.05.006.

[32] Boukhlifi, F.; Bencheikh, A., Characterization of natural biosorbents used for the depollution of waste water. *Ann. Chim. Sci. des Materiaux.* **2000**, *25*, 153-160. DOI: 10.1016/s0151-9107(00)88722-x.

[33] Gemici, B. T.; Ucun Ozel, H.; Ozel, H. B., Adsorption behaviors of crystal violet from aqueous solution using Anatolian black pine (Pinus nigra Arnold.): kinetic and equilibrium studies. *Sep. Sci. Technol.*

2019, *0*, 1-9. DOI: 10.1080/01496395.2019.1577268.

[34] Ravikumar, M.; King, P., Equilibrium, kinetic and thermodynamic studies of congo red biosorption from textile wastewater using spathodea campanulata leaves. *Rasayan J. Chem.* **2019**, *12*, 2318-2327. DOI: 10.31788/RJC.2019.1244034.

[35] Yap, P. S.; Priyaa, V., Removal of crystal violet and acid green 25 from water using kaolin. *IOP Conf Ser Mater Sci Eng.* **2019**, *495*. DOI: 10.1088/1757-899X/495/1/012052.

[36] Song, Y.; Peng, R.; Chen, S.; Xiong, Y., Adsorption of crystal violet onto epichlorohydrin modified corncob. *Desalin Water Treat.* **2019**, *154*, 376-384. DOI: 10.5004/dwt.2019.24067.

[37] Abbas, M.; Harrache, Z.; Trari, M., Removal of gentian violet in aqueous solution by activated carbon equilibrium, kinetics, and thermodynamic study. *Adsorpt. Sci. Technol.* **2019**, *37*, 566-589. DOI: 10.1177/0263617419864504.

[38] Goksu, A.; Tanaydin, M. K., Adsorption of hazardous crystal violet dye by almond shells and determination of optimum process conditions by taguchi method. *Desalin Water Treat.* **2017**, *88*, 189-199. DOI: 10.5004/dwt.2017.21364.

[39] Alshabanat, M.; Alsenani, G.; Almufarij, R., Removal of crystal violet dye from aqueous solutions onto date palm fiber by adsorption technique. *J. Chem.* **2013**, *2013*. DOI: 10.1155/2013/210239.

[40] Chakraborty, S.; Chowdhury, S.; Das Saha, P., Adsorption of crystal violet from aqueous solution onto NaOH-modified rice husk. *Carbohydr. Polym.* **2011**, *86*, 1533-1541. DOI: 10.1016/j.carbpol.2011.06.058.

[41] Mittal, A.; Mittal, J.; Malviya, A.; *et al.*, Adsorption of hazardous dye crystal violet from wastewater by waste materials. *J. Colloid Interface Sci.* **2010**, *343*, 463-473. DOI: 10.1016/j.jcis.2009.11.060.

[42] Theme, S., New poly ether ether ketones containing phosphorus. *ASIA-PACIFIC J. Chem. Eng.* **2010**, *7*, 236-249. DOI: 10.1002/apj.

[43] Bouaziz, F.; Koubaa, M.; Kallel, F.; *et al.*, Adsorptive removal of malachite green from aqueous solutions by almond gum: Kinetic study and equilibrium isotherms. *Int. J. Biol. Macromol.* **2017**, *105*, 56-65.

DOI: 10.1016/j.ijbiomac.2017.06.106.

[44] Singh, N. B; Nagpal, G.; Agrawal, S.; Rachna, Water purification by using adsorbents: A Review. *Environ. Technol. Innov.* **2018**, *11*, 187-240. DOI: 10.1016/ j.eti.2018.05.006.

[45] Abul Hossain, M., Adsorption of crystal violet on used black tea leaves from acidic solution: equilibrium, thermodynamic and mechanism studies. *Int. J. Sci.* **2015**, *1*, 31-39. DOI: 10.18483/ijsci.849.