Desalination and Water Treatment
www.deswater.com

doi: 10.5004/dwt.2021.27538

233 (2021) 387–398
September

Adsorption of crystal violet dye by using a low-cost adsorbent – peanut husk

Sohail Abbas[a,*], Tariq Javeed[a,*], Shagufta Zafar[b], Muhammad Babar Taj[c], Ahmad Raza Ashraf[d], Muhammad Imran Din[e]

[a]*Department of Chemistry, University of Sahiwal, Sahiwal 57000, Pakistan, emails: sohailabbas5456@gmail.com (S. Abbas), mtariq@uosahiwal.edu.pk (T. Javeed)*
[b]*Department of Chemistry, The Government Sadiq College Women University, Bahawalpur 63000, Pakistan, email: shg_zf@yahoo.com*
[c]*Division of Inorganic Chemistry, Institute of Chemistry, Islamia University of Bahawalpur, Bahawalpur 63100, Pakistan, email: dr.taj@iub.edu.pk*
[d]*Department of Chemistry, Division of Science and Technology, University of Education Lahore, Pakistan, email: ahmad.raza@ue.edu.pk*
[e]*Institute of Chemistry, University of the Punjab Lahore, Pakistan, email: Imran.chem@pu.edu.pk*

Received 26 August 2020; Accepted 21 June 2021

ABSTRACT

Nowadays, industrial effluent containing textile dyes is considered a major environmental concern. Crystal violet (CV) is one of the vital textile dyes of the triphenylmethane group and it is known for its mutagenic and mitotic poisoning nature so it must be treated. This study aims to evaluate the adsorption potential of peanut husk (PH) towards CV dye removal. Adsorption studies are conducted to study the effects of different parameters on adsorption such as particle size of adsorbent (105, 210, and 500 mesh sizes), initial dye concentration (5–100 mg/L), contact time (5–120 min), pH (1–11), temperature (0–60°C), and adsorbent dosage (0.1–1.0 g). Langmuir, Freundlich, and Dubinin–Radushkevich isotherm models are applied to experimental data for the determination of the nature of adsorption. The kinetic studies have been carried out using the pseudo-first-order, pseudo-second-order, and intra-particle diffusion model for adsorption of CV on PH. Thermodynamic parameters such as changes in Gibb's free energy (ΔG), enthalpy (ΔH), and entropy (ΔS) are also determined. Optimum conditions for maximum removal of toxic CV dye from wastewater on PH includes 210 mesh size, 100 ppm initial dye concentration with 10 min contact time at temperature 30°C using 0.1 g of adsorbent. Alkaline medium favors adsorption of CV onto the surface of PH and its maximum removal is observed at a pH of 8. These optimum conditions result in 90% removal of CV dye from aqueous solution and the maximum adsorption capacity found out was 20.95 mg/g. Applicability of this developed procedure with tap water is 83.16% indicating that the PH is a promising adsorbent for the removal of cationic CV dye from the aqueous solution.

Keywords: Peanut husk; Crystal violet; Thermodynamic; Isotherms; Kinetics

1. Introduction

Nowadays, water pollution is considered a serious issue because it badly affects our lives and is expected to get worse in the upcoming years. Modern industrialization leads to serious environmental concerns and the release of toxic reagents have endangered the natural ecosystem [1]. Many industries are using dyes colors to tint their goods and consume enormous capacities of water for this purpose. Dyes are organic compounds, which may be natural and artificial, that become attached to the surface of the fabric to give it a bright color. The discharged dyeing waste revealed a maximum level of toxicity [2]. The release of wastewater containing dyes into

---

* Corresponding authors.

the streams, rivers, and water bodies affects the aesthetic nature as well as hinders the transmission of light which decreases the photosynthetic activity [3] and causes serious problems for aquatic life and disturbs the food web [4]. Crystal violet (CV) color (tris (4-(dimethylamino) phenyl) methylium chloride) is a triaryl methane synthetic dye [5,6] used as pH indicator, in coloring silk and cotton in the printing ink, in paints, in gram staining to differentiate between gram-positive and gram-negative bacteria [7] and it causes breathing difficulties, eyes burn, nausea, vomiting, oral ulceration [8,9], cancer, jaundice, tissue necrosis, shock, and kidney failure [10], permanent injury to the arcus senilis and oculus, dermal irritation, and gastrointestinal tract irritation [11,12]. The most usual techniques used for the deduction of colorants from discarded water are divided into two methods, physio-chemical and biological methods. However, these methods are exorbitant and cannot rummage-sale by trivial businesses to extravagance the extensive variety of dyes wastewater [13]. Adsorption, a green technology [14], is the best technique for the removal of dyes from wastewater because it is easy to operate, economical, and has a simple design.

Nowadays, the development of economical adsorbents to remove the number of dyes from wastewater has gained a lot of attention. Many conventional and low-cost adsorbents have been used to remove dyes and pollutants from wastewater such as Jute stick powder [15], cattail root [16], peanut hull [17], maize stalk [18], hazelnut shells [19], de-oiled soya [20], pumpkin seed hull [21], broad bean peels [22], metal-based TiO_2 photocatalyst [23], biofunctional magnetic beads [24], nanoplatelets kaolinite [25], TiO_2/kaolinite nanocomposite [26], MnO_2 nanofibrous mesh as photocatalyst [27], olive branches activated carbon [28] and *Musa paradisiaca* peels [29].

Peanut husk is an agricultural waste residue in many countries. The sudden dumping of this agricultural by-product results in disposal issues. The intention of this finding was on the way to explore the potential of PH as an economical, inexpensive, and eco-friendly adsorbent for the removal of toxic CV color from H_2O medium. In addition, it was used without any physical and chemical treatment. This study focused on batch experiments to investigate the adsorption characteristics of target contaminant and toxic CV color onto PH from H_2O medium. The effects of contact phase, pH, and initial concentration of dye, adsorbent measured quantity, and temperature were studied in batch adsorption experiments. The adsorption kinetics, thermodynamic, and isotherms for a CV onto the PH are also discussed.

2. Materials and methods

2.1. Preparation of adsorbate

The stock solution of CV dye (structural formula of crystal violet dye is shown in Fig. 1) was prepared by dissolving 1 g of accurately weighed dye in 1,000 mL of distilled water to obtain 1,000 mL dye solution. To study the effect of different initial dye concentrations, the stock solution was further diluted to make different standard concentrations. All the chemicals (HCl, KOH, NaCl, and KNO_3) used in this study are of analytical grade, highly pure, and were taken from Merck (Germany) and Sigma-Aldrich Chemical Co., (USA). The percentage purity of CV is 99.99%.

2.2. Preparation of adsorbent

The raw PH was collected from the local market of Sahiwal, Pakistan, and was washed thoroughly with water to remove the dirt, dust, and other particles. This washed material was then placed in an oven for 8 h at 60°C. It was then ground in a mill and sieved through three different particle mesh sizes, that is, 105, 210, and 500 mesh sizes.

2.3. Adsorbent characterization

A Fourier transforms infrared (FTIR) spectrophotometer was used to recognize the diverse functional groups present on PH sites and their effects on adsorption. The FTIR of the adsorbent was taken before and after the adsorption of CV dye using a FTIR spectrophotometer. A scanning electron microscope (SEM) was used to analyze the surface morphology and texture of the adsorbent. The SEM analysis is performed by first preparing the sample for which the solid samples are ground in an agate pestle mortar followed by sieving through a sieve of 50 mesh size.

2.4. Optimization of pH

The effect of pH is an imperative consideration in the adsorption studies of dyes. Different pH values ranging from 1 to 11 were investigated during the experiment. The pH of the CV dye solution was attuned by using 0.1 M HCl or 0.1 M KOH solution, respectively. The effect of pH (1–11) was observed by keeping the following conditions constant: concentration of adsorbate 10 ppm, the volume of solution 10 mL, adsorbent dosage 0.25 g, contact time of 20 min including 10 min of shaking in an orbital shaker, and a centrifugation speed of 3,000 rpm for 3 min.

2.5. Optimization of adsorbent dosage

The upshot of adsorbent dosage for the deduction of CV concentration (30 ppm) of known volume (20 mL) was carried out with different amounts of adsorbent at pH 2 with a contact time of 10 min including 5 min of shaking in an orbital shaker. A similar procedure for batch adsorption study was employed.

2.6. Optimization of the contact period

The upshot of the contact period (5, 10, 20, 30, 40, 50, 60, 80, 100, and 120 min) was carried out with 0.5 g of adsorbent in 20 mL of dye solution (400 ppm). The effects of the contact period were investigated at pH 2 with 5 min of shaking in an orbital shaker.

2.7. Optimization of initial dye concentration

Different concentrations of CV solution, that is 100, 150, 200, 250, 300, 350, 400, and 450 ppm were observed by keeping the following parameters constant like the amount of CV solution 20 mL in flasks, amount of adsorbent 0.5 g, contact period of 30 min including 5 min of shaking.

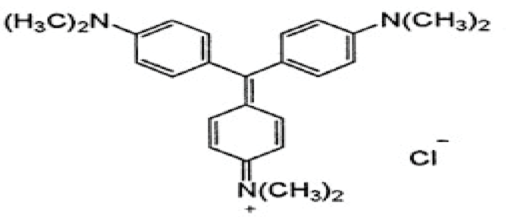


Fig. 1. Structure of crystal violet dye.

Table 1
Freundich isotherm parameters

Adsorbate	Crystal violet
Adsorbent	Peanut husk
K_f (mg/g)	4,194
n (L/g)	2.14
R^2	0.95

2.8. Optimization of temperature

Different temperatures (0–60°C) were selected to study the removal of dyes from an aqueous solution. All optimized conditions were used for the deduction of dyes, that is, 400 ppm concentration of CV solution, 0.5 g of adsorbent, contact time 30 min, and shaking time 5 min at pH 2.

2.9. Batch adsorption study

The batch adsorption experiments were conducted to optimize the above parameters of adsorption. All batch trials were conceded in 250 mL Erlenmeyer flasks by keeping the fixed amount of adsorbent in a known volume of CV solution. Then the contents of this solution are kept in an orbital shaker to ensure proper shaking. The aqueous phase was separated by filtration and centrifugation and the amount of dye solution was determined before and after equilibrium by optimizing instrumental parameters for CV dye. A blank solution was also made and run in the same way. The removal efficiency is calculated by:

$$\%\text{ age removal} = \frac{A_i - A_f}{A_i} \times 100 \tag{1}$$

where A_i is the preliminary concentration taken in milligram per liter and A_f is the concluding concentration taken in mg/L.

3. Results and discussions

3.1. Characterization of adsorbent

The morphological characterization of PH was observed by making use of the scanning electron microscopy (SEM) (Quanta 200 FEI) combined with an energy-dispersive X-ray as shown in Figs. 2 and 3, respectively. The SEM images revealed a fiber structure of PH and showed a partial linkage among the fibers which results in the creation of pores of different sizes. Pores of bigger sizes on the surface of rice husk were also evident, which were more heterogeneous and the formation of slopes and grooves on the surface, increased surface area providing large surface sites for retention of dyes ion. The SEM analysis shows that the surface of the PH is rough and heterogeneous due to the presence of a large number of protrusions inside the surface of the adsorbent. Dye adsorbed on these surface sites resulting in the loss of surface porosity. Elemental analysis of PH was carried out, to determine the percentage weight of chemical compositions available on the surface of PH, through energy dispersive spectrometer (EDX) analysis as shown in Fig. 3. The results are grouped in the following table showing elements with their weight and atomic %. According to the table, the highest amounts corresponded to carbon (54% weight and 61% atomic) and oxygen (24.33% weight and 20.54% atomic) which proves the organic nature of the adsorbent. To identify the major functional groups present on the surface of PH, FTIR spectra were recorded in the mid-IR (infrared) region in the range of 4,000 to 400 cm^{-1} by BRUKER (Vertex70) as mentioned in Fig. 4. FTIR spectra for the PH

Table 2
Langmuir isotherm parameters

Adsorbate	Crystal violet
Adsorbent	Peanut husk
Q_0 (mg/g)	20.95
b (dm^3 mol^{-1})	1.03
R^2	0.85

Table 3
D–R isotherm parameters

Adsorbate	Crystal violet
Adsorbent	Peanut husk
β (kJ^2 mol^{-2})	−0.613
ε^2 (kJ mol^{-1})	1.63
R^2	0.94

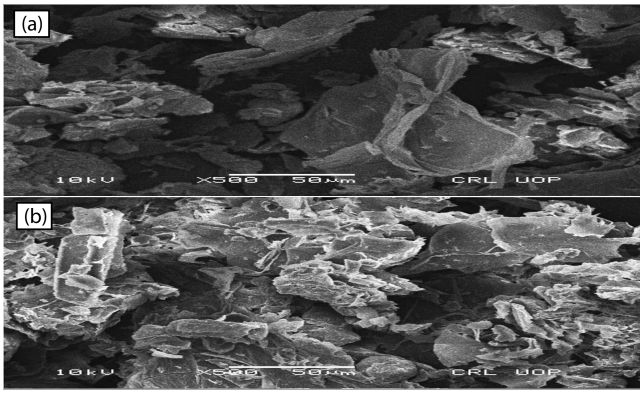
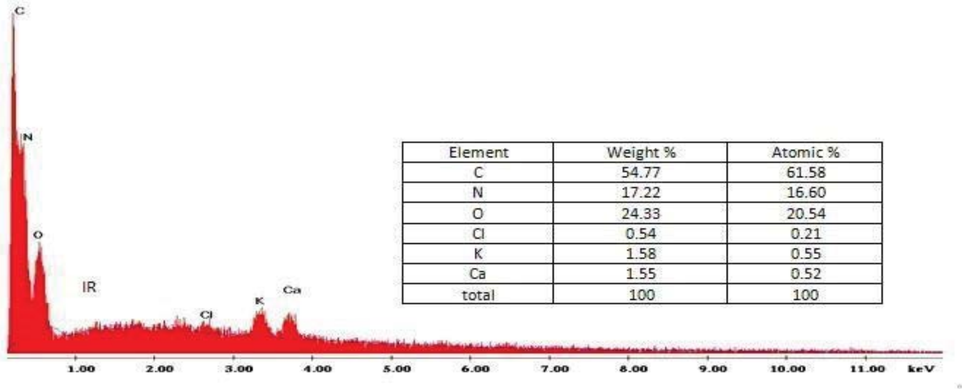


Fig. 2. SEM Images of PH: (a) before adsorption and (b) after adsorption.



Element	Weight %	Atomic %
C	54.77	61.58
N	17.22	16.60
O	24.33	20.54
Cl	0.54	0.21
K	1.58	0.55
Ca	1.55	0.52
total	100	100

Fig. 3. EDX analysis of pH.

displayed several peaks that exhibited different functional groups. The broad and intense peak around 3,310 cm^{-1} corresponds to O–H stretching vibrations and a peak at 2,917 cm^{-1} shows C–H stretching vibrations indicated the presence of methyl and methylene groups, respectively. The peak at 1,742 cm^{-1} represented C=O stretching vibrations. The peaks at 1,628 cm^{-1} and 1,509 cm^{-1} correspond to C=C stretching vibrations, the other peak at 1,260 cm^{-1} represented CH bending vibration, and the characteristic peak at 1,024 cm^{-1} corresponds to the CO stretching vibrations.

3.2. Optimization of pH

The pH of the system plays an imperative role in the adsorptive uptake of adsorbate molecules (CV dye) as it affects the surface properties of adsorbent (PH) and the ionization or dissociation of adsorbate molecules. As such the adsorption behavior of CV on PH is studied over the different pH ranges. It is evident from Fig. 5 that when the aqueous solution of CV was treated with pH, it was found that 94% removal occurs at pH 2 and 76% removal occurs at pH 8 [30]. Fig. 5 shows that the percentage removal of dye on PH decreases after pH 8. Hence, it can be concluded that the acidic pH of dyes favored its adsorption on the PH.

3.3. Optimization of adsorbent measured quantity

The influence of adsorbent dose on CV by PH was inspected in the array of 0.1–1.2 g while keeping other parameters of adsorption constant. The percentage removal

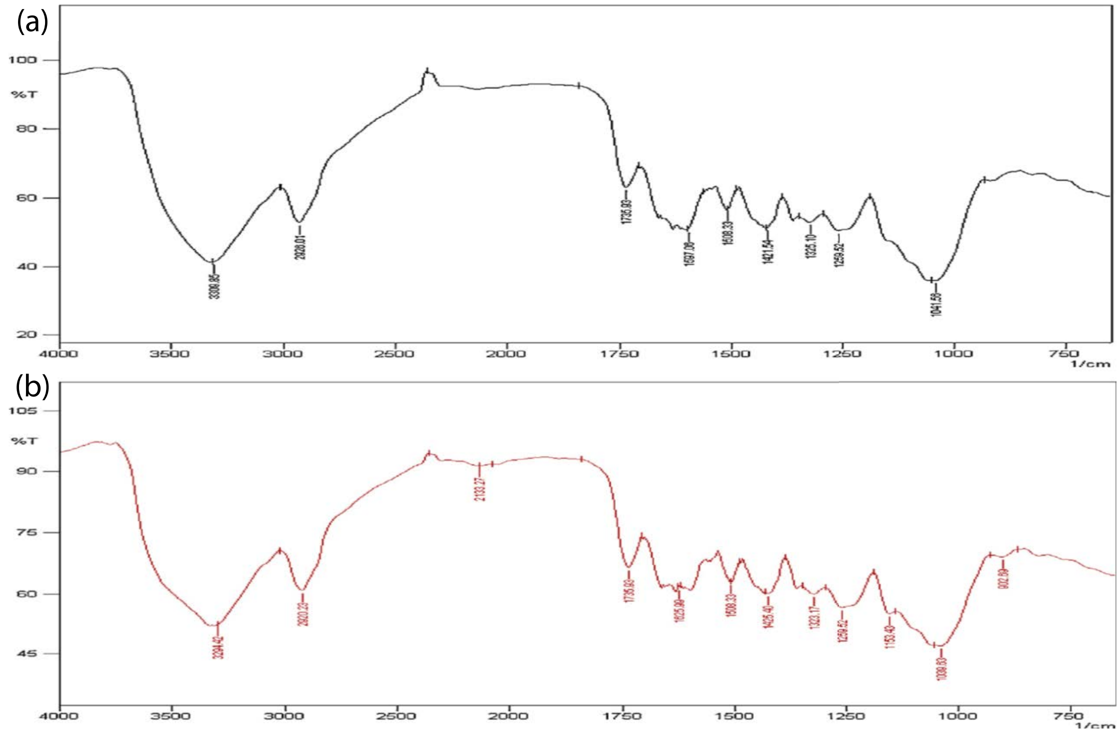


Fig. 4. FTIR spectra of peanut husk (a) before adsorption and (b) after adsorption.

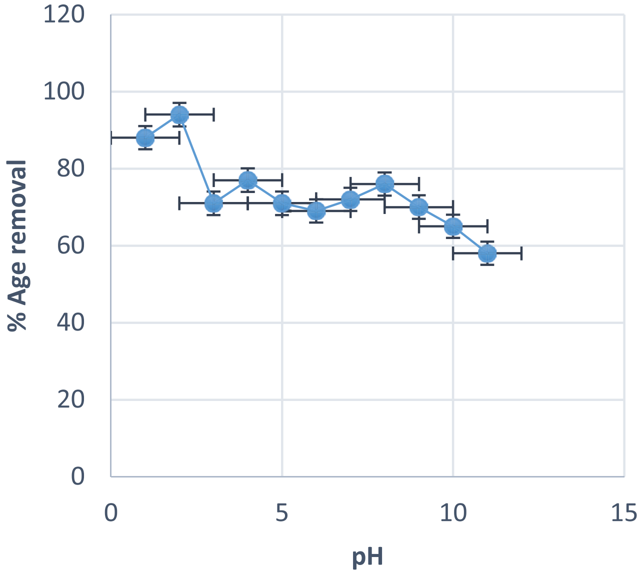


Fig. 5. Optimization of pH.

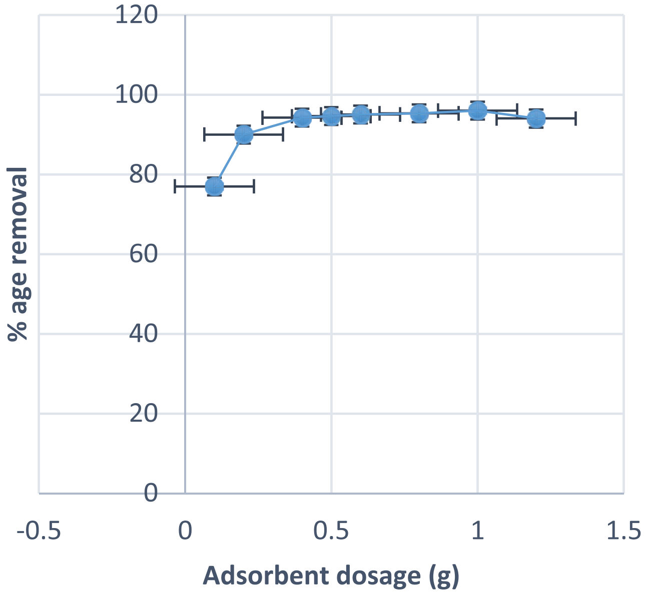


Fig. 6. Optimization of adsorbent dosage.

of 77 to 94.6 takes place by fluctuating the adsorbent measured quantity from 0.1 to 0.5 g. The intensification in percentage removal of CV dye on PH may be due to an increase in the exterior area of adsorbent, enhancing the number of adsorption spots available for adsorption as testified [31,32]. The effects of adsorbent dose on percentage removal of dye is shown in Fig. 6.

3.4. Optimization of adsorbate concentration

Fig. 7 shows that intensification in adsorbate concentration results in a reduction in percentage removal of CV on PH. The removal efficiency of CV dye decreased from 95.33 to 83.19 by increasing concentration from 100–400 mg/L. The reduction in percentage removal with the upsurge in adsorbate concentration is due to the saturation of adsorbent spots on the exterior of the adsorbent. At a low concentration of dye, there will be unoccupied binding sites at the adsorbent surface, and with increases in initial dye concentration, there will be insufficient binding sites that result in a decrease percentage removal of dye. The results indicated that the adsorption of CV is much dependent on adsorbate concentration.

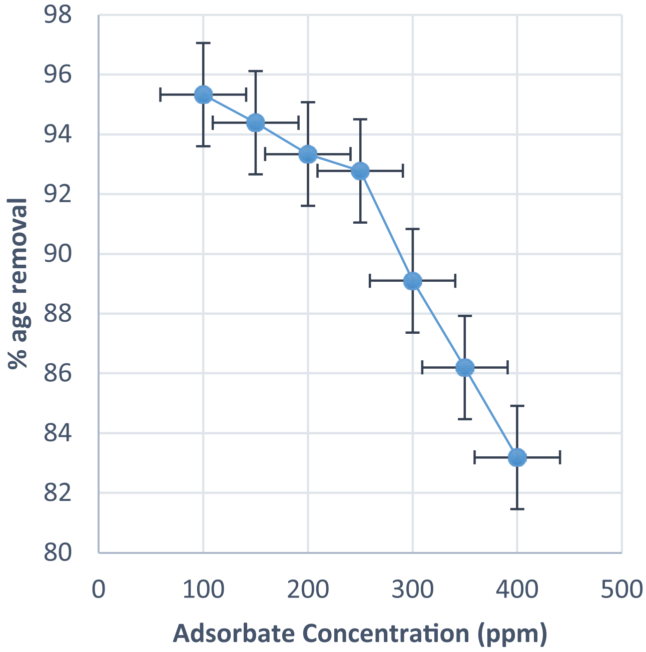


Fig. 7. Optimization of adsorbate concentration.

3.5. Optimization of the contact period

The upshot of the contact period on CV dye using PH adsorbent is depicted in Fig. 8 at 40°C. It can be perceived that there is a rapid deduction of CV color in the first 40 min after which there is slight removal because all the adsorbent sites available are fully occupied by the CV dye. It is evident from Fig. 8 that 89.7 to 84.7 percentage removal of CV occurs using PH as an adsorbent. The optimum contact time chosen from the experiment is 30 min which is kept constant in further experiments. The present observations are in common agreement with other observations of investigators [33,34].

3.6. Optimization of temperature

To investigate the upshot of temperature on the deduction of CV dye using PH, experiments were conducted by ranging the temperature from 0°C to 50°C. It was observed that the removal of CV bring into being was 77% to 89% keeping other parameters constant. The results have been shown in Fig. 9. This figure revealed that the upturn in temperature would increase the agility of ions of dyes and produces a puffiness upshot within the interior assembly of adsorbent that enables the outsized molecules of dyes to penetrate further [30]. The increase in percentage

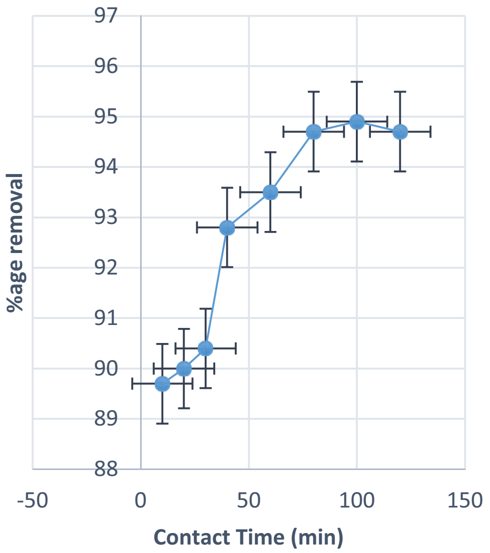


Fig. 8. Optimization of contact time.

removal of CV dye by increase in temperature is might be owed to extra collaboration between CV colorant and PH.

3.7. Absorption isotherms

The interaction between the adsorbate and adsorbent can be explained by adsorption isotherms. The Langmuir, D–R, and Freundlich adsorption isotherm describe the behavior of CV dye. The Freundlich adsorption isotherm is grounded upon the assumption that the adsorption course takes place on the dissimilar surface depending upon the interaction between adsorbed molecules while Langmuir adsorption isotherm is built on the supposition that it includes the formation of a structurally homogeneous adsorbent and monolayer coverage having no interaction between adsorbate molecules. In command to regulate the character of adsorption phenomena, whichever physical or chemical process, the D–R isotherm model is used. The equations of Freundlich Langmuir and non-linear equation of D–R isotherms are given as respectively:

$$\log C_{\mathrm{ad}} = \log K + \frac{1}{n}\log C_{\mathrm{Eq}} \tag{2}$$

$$\frac{C_{\mathrm{Eq}}}{C_{\mathrm{ad}}} = \frac{1}{bQ} + \frac{C_{\mathrm{Eq}}}{Q} \tag{3}$$

$$\ln q_e = \ln q_{\mathrm{DR}} - \beta\varepsilon^2 \tag{4}$$

where C_{ad} is the sum of CV tint adsorbed at the time of equilibrium taken in mole per gram, C_{Eq} is the CV concentration at the time of equilibrium taken in mol L^{-1} and K and $1/n$ are the constants in Freundlich equation, K symbolizes adsorption capability and n determines the strength of adsorption. C_{Eq} is the dye concentration solution taken in mol L^{-1} at equilibrium, C_{ad} demonstrates the magnitude of CV adsorbed for every unit mass onto rice husk at the stage of equilibrium taken in mole per gram. The constant Q shows the adsorption capacity of the monolayer taken in mole per gram and "b" taken in liter per mole shows the energy of adsorption. q_{DR} (mg/g) is the Dubinin–Radushkevich maximum monolayer adsorption capacity, β (mol²/J²) is a constant (mean sorption energy (β) is the energy of transferral of one mole of solute from infinity to the surface of an adsorbent [35]. K_f is the Freundlich constant interrelated to bonding energy and n is the adsorption intensity or heterogeneous factor in Eq. (1). C_{Eq} is the dyes ions concentration solution (mol L^{-1}) at equilibrium, C_{ad} is the sum adsorbed per component or unit mass onto rice husk at equilibrium (mol per g), constant Q is the monolayer adsorption capability (mol g^{-1}), and b (L mol^{-1}) is allied to the energy of adsorption in the equation.

In the case of the Langmuir isotherm model, a straight line is attained by plotting a graph among C_e (mg L^{-1})/q_e (mg g^{-1}) and C_e (mg L^{-1}) from which slope and intercept can be calculated. For the Freundlich isotherm model, a graph is plotted between $\ln q_e$ and $\ln C_e$ and the value of slope $1/n$ provides us the value of 'n' and intercept $\ln K_F$ gives the value of K_F. The value of "n" gives us information about

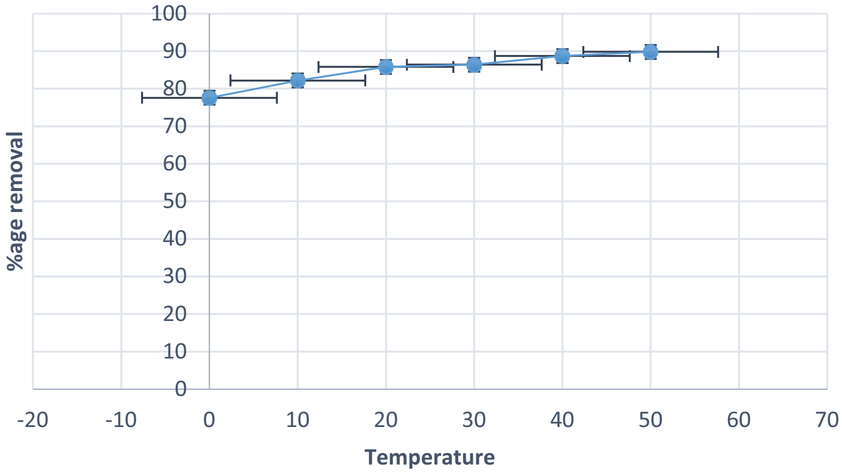


Fig. 9. Optimization of temperature.

the adsorption process, that is, when the value of '*n*' is greater than unity, it shows that adsorption progresses to a greater amount. The value of '*n*' fluctuates from 1 to 10^{19} [36].

From the graphical representation and table showing parameters of Freundlich (Fig. 10), Langmuir (Fig. 11), and D–R (Fig. 12) isotherm, it can be observed that the experimental data is best described by Freundlich and D–R isotherms as reflected by their correlation coefficients. The value of correlation coefficient for Freundlich isotherm comes out to be 0.95 (very close to unity) while in the case of the Langmuir isotherm model its value is 0.85 (less than Freundlich isotherm) which confirms that data fits best to Freundlich isotherm model, that is, the adsorption of CV occurs on the heterogeneous surface of the PH. Moreover, the value of n is greater than 1 indicates that the process of CV adsorption on PH is favorable and the value of E_s calculated displays that this process is physisorption in nature. Results of Freundlich, Langmuir and D–R isotherm parameters are given in Tables 1–3, respectively.

3.8. Adsorption kinetics

Four kinetic models, that is, pseudo-first-order kinetics, pseudo-second-order kinetics, intra-particle diffusion model, and liquid film diffusion model were applied to investigate the reaction passage ways and probable rate-determining stage of the adsorption of CV on to PH. The rectilinear form of the pseudo-first-order kinetic model is given as:

$$\ln\left(q_e - q_t\right) = \ln q_e - K_f t \quad (5)$$

where q_e is the value of the extent of dye (adsorbate) adsorbed for every unit mass on the adsorbent at equilibrium. q_t is the value of the amount of dye adsorbed for every unit mass on the adsorbent at various time intervals. K_1 is the pseudo-first-order adsorption rate constant taken per minute. When $\ln(q_e - q_t)$ is plotted against t (min) then we get a straight line graph and slope K_f besides intercept

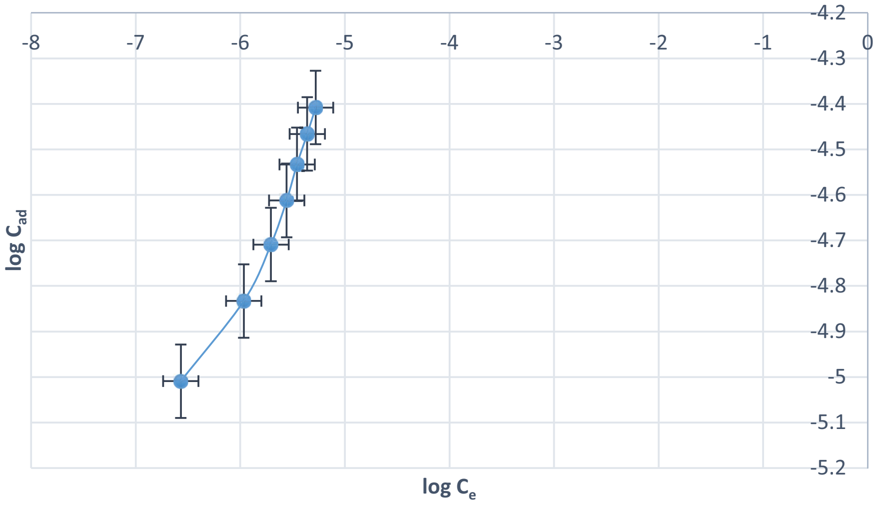


Fig. 10. Freundlich adsorption isotherm.

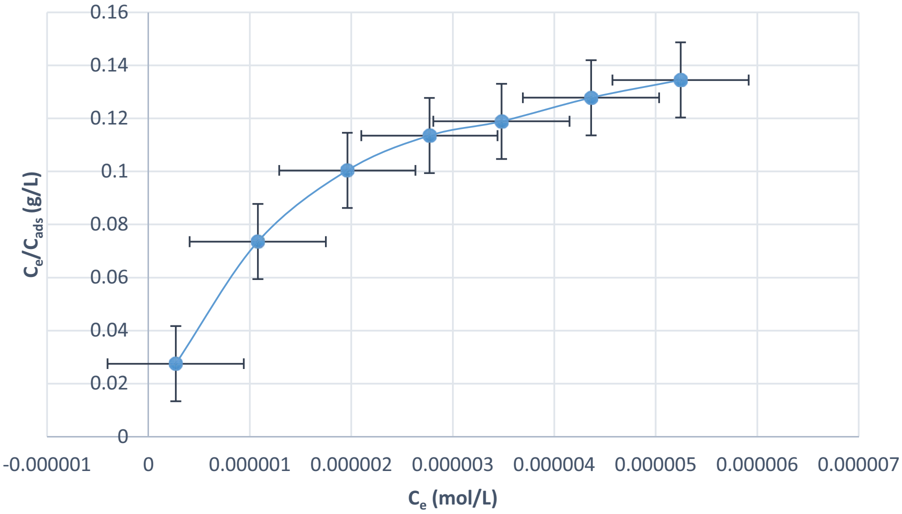


Fig. 11. Langmuir adsorption isotherm.

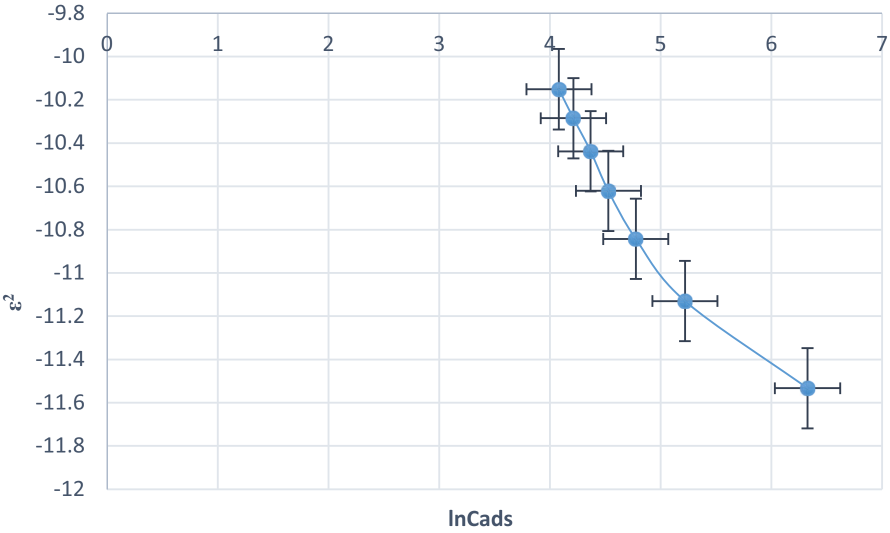


Fig. 12. D–R isotherm for CV adsorption on PH.

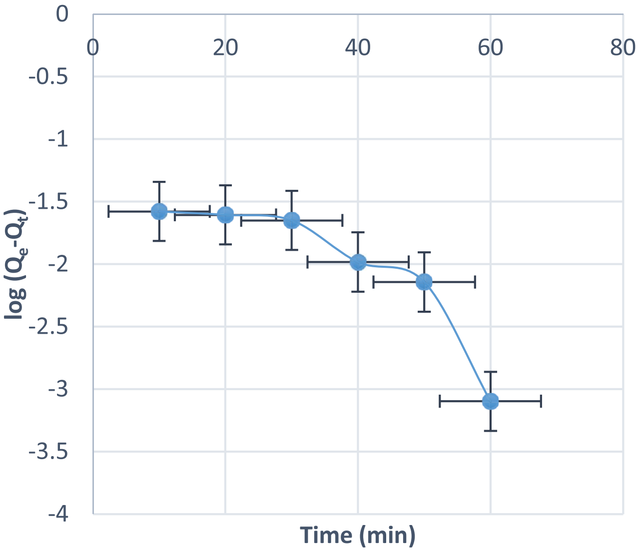


Fig. 13. Pseudo-first-order kinetic model.

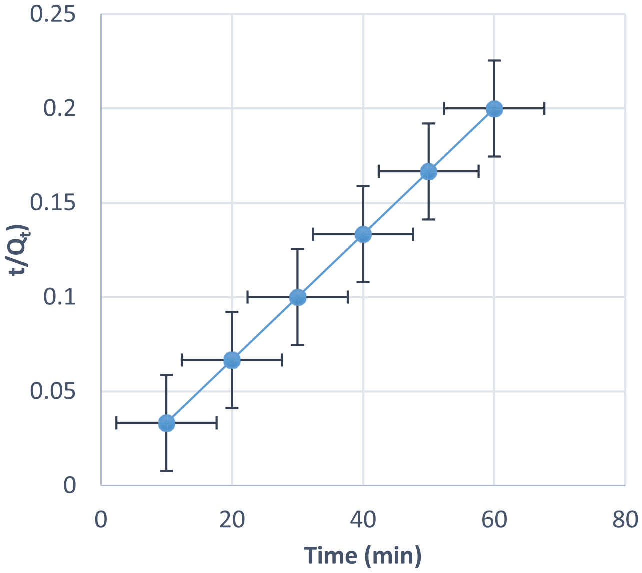


Fig. 14. Pseudo-second-order kinetic model.

q_e can be calculated from this graph [36]. The undeviating form of the pseudo-second-order kinetic equation is as follows;

$$\frac{t}{q_t} = \frac{1}{K_2 q_e^2} + \frac{1}{q_e} t \tag{6}$$

where q_e and q_t are the amount of adsorbate adsorbed on the surface of substance act as adsorbent at equilibrium and at the time '*t*', respectively. A graph of t/q_t (min g mg^{-1}) against t (min) gives a straight line from which slope and intercept can be calculated [36]. As perceived in the below table that the premeditated q_e (303.0303 mg/g) well agrees with the experimental q_e (299.9376 mg/g) and also the linear regression coefficient has a higher value than the pseudo-first-order kinetic equation (R^2 = 0.99). Thus, the adsorption of CV on PH follows pseudo-second-order reaction kinetics indicating the chemical nature of the process [37]. Analogous second-order kinetics has also been informed for CV adsorption on groundnut shells [38]. The intraparticle diffusion model is given as,

$$Q_t = K_i t^{\frac{1}{2}} + C \tag{7}$$

where q_e (mg/g) is the expanse of adsorbate adsorbed at the time '*t*'. *C* is the thickness of layer (*I*). K_i (mg g^{-1} min$^{-1/2}$) is the intraparticle diffusion constant whose values are evaluated using the gradient of an undeviating plot of q_t as opposed to $t^{1/2}$. According to the equation, the conspiracy

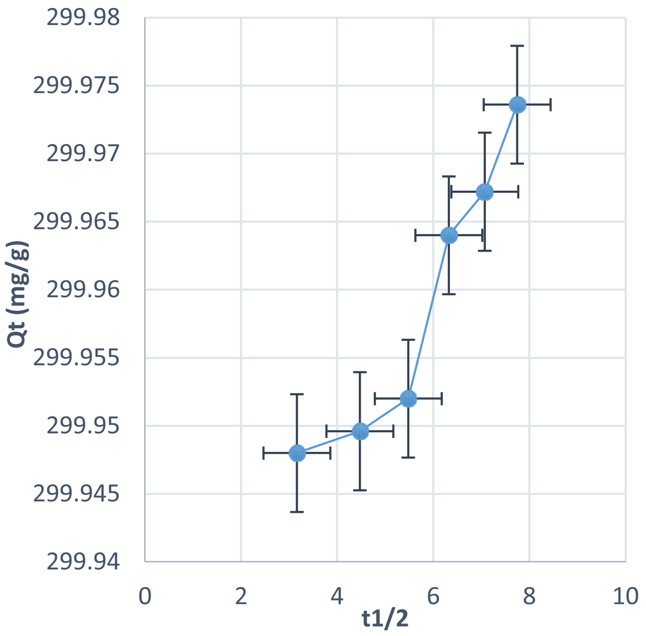


Fig. 15. Intra-particle diffusion kinetical model.

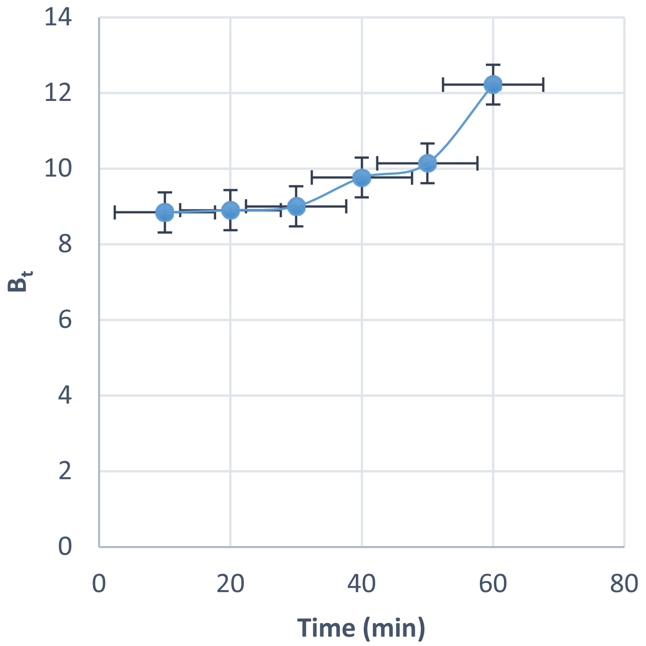


Fig. 16. Liquid film diffusion model.

of q_t as opposed to $t^{1/2}$ should be a conventional line when the adsorption mechanism keeps an eye on the intraparticle diffusion model. A graph is plotted between q_t and $t_{0.5}$ and a straight line of the graph will be obtained from which slope K_{id} and intercept 'I' can be obtained [36]. In the case of the intra-particle diffusion model, a linear graph demonstrates that only the intraparticle diffusion model is involved in the adsorption procedure and zero intercept shows that this model is a rate-limiting step. Some boundary layer management involvement also confirms when a line of the graph is non-zero showing that the intraparticle diffusion model is not only a rate-controlling step but other kinetic models are also engaged in the managing of adsorption level [35]. However, the present study of CV on RH suggests that even though the intraparticle diffusion model (R^2 = 0.9344) is included in the adsorption course, but it is not the individual rate-controlling step, and roughly additional mechanisms also perform their title part. The liquid film diffusion model is given as;

$$X = \left(1 - \frac{6}{\pi^2}\right)e^{-\beta t} \tag{8}$$

where X is the amount of adsorbate adsorbed at time 't'/volume of adsorbate adsorbed at equilibrium. The regression coefficient value from the plot is 0.7828 and the line is not passing through the origin, that is, non-zero intercept indicates that the Reichenberg model has limited applicability in this adsorption process and also that many other different mechanisms are involved in explaining the adsorption process rather than a single model.

The results of pseudo-first-order, pseudo-second-order, intra-particle diffusion and liquid film model are shown in Figs. 13–16, respectively. A comparison of studied kinetic models is given in Table 4. From Table 4, it is noticeable that the current adsorption process follows the pseudo-second-order (PSO) kinetic model since its value of regression coefficient is highest (0.99) and very close to unity as compared to other models, that is, pseudo-first-order (PFO) kinetic model and liquid film diffusion model. Additionally, there is a good agreement between calculated and experimental Q_e (mg/g) in the case of the pseudo-second-order kinetic model which confirms that data fits best to the pseudo-second-order model.

3.9. Thermodynamic study

The thermodynamic considerations like modification in Gibb's free energy $\Delta G°$, enthalpy $\Delta H°$, and entropy $\Delta S°$ were ascertained employing the subsequent equation. The $\Delta G°$ is expressed as follows:

$$\Delta G° = -RT\ln K_c \tag{9}$$

where R is the general gas constant, T is the entire temperature, and K_{ads} is the equilibrium constant of adsorbent whose value is calculated. The Van't Hoff equation is expressed with the following relation between entropy and enthalpy.

$$\ln K_{\text{ads}} = \frac{\Delta S°}{R} - \frac{\Delta H°}{RT} \tag{10}$$

where $\Delta H°$ displays the variation in enthalpy having unit kJ/mol and $\Delta S°$ is the alteration in entropy having unit J/mol K. The quantities of enthalpy and entropy are determined from the slope and cut off by plotting the graph of $\ln K_{\text{ads}}$ contrasted with $1/T$. The relationship between them is used to obtain the thermodynamics parameters values. The slope of the graph gives us the value of ΔH and the intercept gives the value of ΔS [35].

Table 4
Kinetic models and their parameters

Pseudo-first-order	Q_e (mg/g)	Q_e (mg/g)	R^2
kinetical model	Experimental	Calculated	0.94
	300	0.00	
Pseudo-second-order	Q_e (mg/g)	Q_e (mg/g)	R^2
kinetical model	Experimental	Calculated	0.99
	300	303.03	
Liquid film diffusion	C (mg/g)	K (min)$^{-1}$	R^2
model	7.67	0.06	0.78

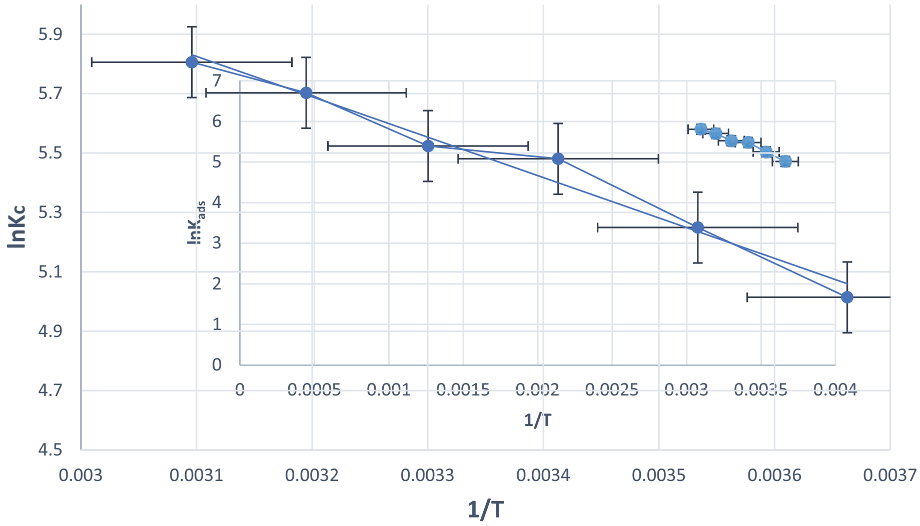


Fig. 17. A plot of Van't Hoff equation.

Fig. 17 refers to the linear Van't Hoff equation conspiracy for the CV adsorption on PH. The thermodynamic parameters are presented in Table 5. Negative $\Delta G°$ values (Table 5) signpost the achievability and extemporaneous nature of CV dye adsorption onto PH. The negative $\Delta H°$ values authorize the exothermic character of the adsorption course while its extent indicates that the process is physio sorption in nature. The ΔS is positive indicates the increase in randomness of molecules during the adsorption process.

3.10. Effect of common salts

In addition to dyes, several salts are also utilized in the dyeing process and the presence of these salts is also a parameter that affects the attraction between adsorbate CV dye and untreated PH. The experiment was conducted by using two salts NaCl and KNO_3 in a range of solution concentrations ranging from 0.1 to 0.5 M. The results indicated that the presence of these salts in the solution decreases the solubility of the dye in water which results in increased absorption on the PH surface [39].

Table 5
Parameters of thermodynamic study

Temperature (K)	ΔG (kJ/mol)	ΔH (kJ/mol)	ΔS (kJ/mol K)
273	−0.833	−11.31	0.08
283	−0.872		
293	−0.911		
303	−0.918		
313	−0.948		
323	−0.965		

4. Conclusion

This revision intended to probe the potential of PH as an economical and biodegradable adsorbent for the degradation and deduction of toxic CV dye from an aqueous medium. Concentration data from the experiment is analyzed using various isotherm models to govern the finest isotherm model in the adsorption process. The three recurrently used adsorption isotherms equations: Freundlich, Langmuir, and D–R equations were verified via equilibrium statistics acquired from the preliminary dye concentration study. Out of all these models, Freundlich and D–R models describe the adsorption process well. The experimental data was applied to four kinetic models, that is, pseudo-first-order, pseudo-second-order, intra-particle diffusion model, and liquid film model. This kinetic study displayed that the facts are finest to the pseudo-second-order kinetic model whose regression coefficient value is 1.00 (greater than other models studied). Negative $\Delta G°$ values indicate the practicality and extemporaneous nature of CV dye adsorption onto PH. The negative values of ΔG° with an upturn in temperature suggest that minor temperature brings about the adsorption at ease. The negative ΔH° values obtained for the adsorption of CV on PH confirm the exothermic nature of the adsorption phenomena. While the positive values of ΔS° pointing out the haphazardness during the adsorption process.

Acknowledgment

I would like to thank the Creator of all worlds, Allah Almighty, all praises for Him, for giving me the strength to complete this project. I would also like to thank my advisors, Dr. Tariq Javed, for encouraging me to think out of the box, for providing me with all the answers to my every query, no matter how small or otherwise, and for guiding and supporting me throughout the project.

References

[1] M. Iqbal, *Viciafaba* bioassay for environmental toxicity monitoring: a review, Chemosphere, 144 (2016) 785–802.

[2] M. Abbas, M. Adil, S. Ehtisham-ul-Haque, B. Munir, M. Yameen, A. Ghaffar, M. Iqbal, *Vibrio fischeri* bioluminescence inhibition assay for ecotoxicity assessment: a review, Sci. Total Environ., 626 (2018) 1295–1309.

[3] F. Çiçek, D. Özer, A. Özer, A. Özer, Low cost removal of reactive dyes using wheat bran, J. Hazard. Mater., 146 (2007) 408–416.

[4] P. Mahajan, S. Singla, J. Kaushal, Phytoremediation of heavy metals using *Brassica juneca*: a review, J. Chem. Eng. Sci. Appl., 2 (2016) 157–173.

[5] S. Mani, R.N. Bharagava, Exposure to crystal violet, its toxic, genotoxic and carcinogenic effects on environment and its degradation and detoxification for environmental safety, Rev. Environ. Contam. Toxicol., 237 (2016) 71–104.

[6] M. Sardar, M. Manna, M. Maharana, S. Sen, Remediation of Dyes from Industrial Wastewater Using Low-Cost Adsorbents Green Adsorbents to Remove Metals, Dyes and Boron from Polluted Water, Springer, Cham, 49, 2017, pp. 377–403.

[7] A. Ahmad, D. Lokhat, M. Rafatullah, A. Khatoon, S.H.M. Setapar, Aloe vera biomass containing cellulosic moieties used as sustainable adsorbents for the removal of crystal violet dye from aqueous solution, Desal. Water Treat., 170 (2019) 337–348.

[8] S.M. Yakout, M.S. Ali, Removal of the hazardous crystal violet dye by adsorption on corncob-based and phosphoric acid-activated carbon, Part. Sci. Technol., 33 (2015) 621–625.

[9] W. Yao, W. Zhu, Y. Wu, X. Wang, T. Jianati, Removal of crystal violet dye from wastewater by solidified landfilled sludge and its modified products, Pol. J. Environ. Stud., 24 (2015) 777–785.

[10] Z.U. Zango, S.S. Imam, Evaluation of microcrystalline cellulose from groundnut shell for the removal of crystal violet and methylene blue, J. Nanosci. Nanotechnol., 8 (2018) 1–6.

[11] F.A. Pavan, S.L. Dias, E.C. Lima, E.V. Benvenutti, Removal of Congo red from aqueous solution by a nilinepropylsilica xerogel, Dyes Pigm., 76 (2008) 64–69.

[12] V.K. Gupta, Suhas, Application of low-cost adsorbents for dye removal: a review, J. Environ. Manage., 90 (2009) 2313–2342.

[13] A. Wathukarage, I. Herath, M.C.M. Iqbal, M. Vithanage, Mechanistic understanding of crystal violet dye sorption by woody biochar: implications for wastewater treatment, Environ. Geochem. Health, 41 (2019) 1647–1661.

[14] A.A. Oyekanmia, Z.D. Ab Aziz Abdul Latiff, R.M.S.R. Mohamedb, N.A. Ab Azizb, N. Ismaila, M. Rafatullaha, K. Hossaina, Adsorption of pollutants from palm oil mill effluent using natural adsorbents: optimization and isotherm studies, Desal. Water Treat., 169 (2019) 181–190.

[15] I.D. Mall, V.C. Srivastava, N.K. Agarwal, I.M. Mishra, Adsorptive removal of malachite green dye from aqueous solution by bagasse fly ash and activated carbon-kinetic study and equilibrium isotherm analyses, Colloids Surf., 264 (2005) 17–28.

[16] G.C. Panda, S.K. Das, A.K. Guha, Jute stick powder as a potential biomass for the removal of congo red and rhodamine B from their aqueous solution, J. Hazard. Mater., 164 (2009) 374–379.

[17] Z. Hu, H. Chen, F. Ji, S. Yuan, Removal of Congo Red from aqueous solution by cattail root, J. Hazard. Mater., 173 (2010) 292–297.

[18] R. Gong, Y. Sun, J. Chen, H. Liu, C. Yang, Effect of chemical modification on dye adsorption capacity of peanut hull, Dyes Pigm., 67 (2005) 175–181.

[19] V. Meyer, F.H.H. Carlsson, R.A. Oellermann, Decolourization of textile effluent using a low-cost natural adsorbent material, Water Sci. Technol., 26 (1992) 1205–1211.

[20] M. Doğan, H. Abak, M. Alkan, Biosorption of methylene blue from aqueous solutions by hazelnut shells: equilibrium, parameters and isotherms, Water Air Soil Pollut., 192 (2008) 141–153.

[21] V.K. Gupta, A. Mittal, L. Krishnan, J. Mittal, Adsorption treatment and recovery of the hazardous dye, Brilliant Blue FCF, over bottom ash and de-oiled soya, J. Colloid Interface Sci., 293 (2006) 16–26.

[22] B.H. Hameed, M.I. El-Khaiary, Removal of basic dye from aqueous medium using a novel agricultural waste material: pumpkin seed hull, J. Hazard. Mater., 155 (2008) 601–609.

[23] S. Ghosh, A.P. Das, Modified titanium oxide (TiO_2) nanocomposites and its array of applications: a review, Toxicol. Environ. Chem., 97 (2015) 491–514.

[24] H. Li, Z. Li, T. Liu, X. Xiao, Z. Peng, L. Deng, A novel technology for biosorption and recovery hexavalent chromium in wastewater by bio-functional magnetic beads, Bioresour. Technol., 99 (2007) 6271–6279.

[25] M.M. Alaqarbeh, M.W. Shammout, A.M. Awwad, Nano platelets kaolinite for the adsorption of toxic metal ions in the environment, Chem. Int., 6 (2020) 49–55.

[26] A. Awwad, M. Amer, M. Al-aqarbeh, TiO_2-kaolinite nanocomposite prepared from the Jordanian Kaolin clay: adsorption and thermodynamics of Pb(II) and Cd(II) ions in aqueous solution, Chem. Int., 6 (2020) 168–178.

[27] M. Rahmat, A. Rehman, S. Rahmat, H.N. Bhatti, M. Iqbal, W.S. Khan, A. Nazir, Highly efficient removal of crystal violet dye from water by MnO_2 based nano fibrous mesh/photocatalytic process, J. Mater. Res. Technol., 8 (2019) 5149–5159.

[28] A.M. Alkherraz, A.K. Ali, K.M. Elsherif, Removal of Pb(II), Zn(II), Cu(II) and Cd(II) from aqueous solutions by adsorption onto olive branches activated carbon: equilibrium and thermodynamic studies, Chem. Int., 6 (2020) 11–20.

[29] N.E. Ibisi, C.A. Asoluka, Use of agro-waste (*Musa paradisiaca* peels) as a sustainable biosorbent for toxic metal ions removal from contaminated water, Chem. Int., 4 (2018) 52–59.

[30] B. H.Hameed, M.I. El-Khaiary, Sorption kinetics and isotherm studies of a cationic dye using agricultural waste: broad bean peels, J. Hazard. Mater., 154 (2008) 639–648.

[31] V.K. Verma, A.K. Mishra, Kinetic and isotherm modeling of adsorption of dyes onto rice husk carbon, Global NEST J., 12 (2010) 190–196.

[32] R. Ahmad, Studies on adsorption of crystal violet dye from aqueous solution onto coniferous pinus bark powder (CPBP), J. Hazard. Mater., 171 (2009) 767–773.

[33] A. Saeed, M. Sharif, M. Iqbal, Application potential of grapefruit peel as dye sorbent: kinetics, equilibrium and mechanism of crystal violet adsorption, J. Hazard. Mater., 179 (2010) 564–572.

[34] A. Chham, E. Khouya, M. Oumam, A.K. Abourriche, S. Gmouh, S. Mansouri, H. Hannache, The use of insoluble mater of Moroccan oil shale for removal of dyes from aqueous solution, Chem. Int., 4 (2018) 67–77.

[35] J. Tariq, K. Nasir, M.L. Mirza, Kinetics, equilibrium and thermodynamics of cerium removal by adsorption on low-rank coal, Desal. Water Treat., 89 (2017) 240–249.

[36] C.K. Enenebeaku, N.J. Okorocha, U.E. Enenebeaku, B.I. Onyeachu, Removal of crystal violet dye by adsorption onto

Picrilima nitida stem bark powder: kinetics and isotherm studies, IOSR J. Appl. Chem., 9 (2016) 1423, doi: 10.9790/5736-0908011423.

[37] M. Laissaoui, Y. Elbatal, I. Vioque, G. Manjon, Adsorption of methylene blue on bituminous schists from Tarfaya-Boujdour, Chem. Int., 3 (2017) 343–352.

[38] V.K. Verma, A.K. Mishra, Effectiveness of rice husk carbon for the removal of colour, Asian J. Microbiol. Biotechnol. Environ. Sci., 6 (2004) 221–222.

[39] A.K. Akinola, A.M. Umar, Adsorption of crystal violet onto adsorbents derived from agricultural wastes: kinetic and equilibrium studies, J. Appl. Sci. Environ. Manage., 19 (2015) 279–288.