Desalination and Water Treatment
www.deswater.com

doi: 10.5004/dwt.2021.27178

224 (2021) 395–406
June

Adsorption of Crystal violet dye from synthetic textile effluents by utilizing wheat bran (*Triticum aestivum*)

Hafiza Amna Haq[a,*], Tariq Javed[a,*], Muhammad Amin Abid[a], Shagufta Zafar[b], Muhammad Imran Din[c]

[a]*Department of Chemistry, University of Sahiwal, Sahiwal 57000, Pakistan, emails: hafizaamnahaq@gmail.com (H.A. Haq), mtariq@uosahiwal.edu.pk (T. Javed), mabid@uosahiwal.edu.pk (M.A. Abid)*
[b]*Department of Chemistry, The Government Sadiq College Women University, Bahawalpur 63000, Pakistan, email: shg_zf@yahoo.com*
[c]*Institute of Chemistry, University of the Punjab Lahore, Pakistan, email: imran.chem@pu.edu.pk*

Received 25 August 2020; Accepted 21 February 2021

ABSTRACT

The present investigation reports the decolorization and subtraction of harmful Crystal violet (basic) dye from the aqueous solution by adsorption on wheat bran (WB). Experiments are performed by monitoring various factors, for instance, granular size of adsorbent (105, 210 and 500 mesh sizes), pH (1–11), duration of contact (5–120 min), amount of wheat bran (0.1–1.0 g), initial dye concentration (300–550 ppm) and temperature (0°C–60°C). The surface study of wheat bran was investigated by Fourier-transform infrared spectroscopy and scanning electron micrograph. The calculations reveal adsorption of Crystal violet (CV) at the surface of WB is directly proportional to exposure time, amount of WB, initial dye concentration and temperature. Three isotherm equations were applied, Freundlich, Langmuir and Dubinin–Radushkevich isotherms, to explore experimental data. The computations indicate that data fits efficiently with the Langmuir model. Optimum uptake capacity was calculated, that is, 116.6 mg g^{-1}. Moreover, the adsorption data were used to calculate the rate constants of pseudo-first-order, pseudo-second-order, liquid film diffusion and intraparticle diffusion. The regression value ($R^2 = 1$) was obtained to confirm the good correlation with pseudo-second-order kinetic equation rather than others observed kinetic equations. To figure out the nature of adsorption, the free energy of adsorption of CV on WB (ΔG), enthalpy (ΔH) and entropy (ΔS) were determined. The numerical results of ΔG, ΔH and ΔS show that adsorption of CV on WB was feasible, spontaneous and endothermic in nature. The maximum removal efficiency of wheat bran towards Crystal violet, that is, 86.57% is observed at optimum conditions, that is, pH 2, 0.6 g of WB, 30 min of contact time and 400 ppm of initial dye concentration. It can be concluded from the experimental results that WB could be effectively employed as a biosorbent for the removal of CV.

Keywords: Adsorption; Crystal violet; Wheat bran; Kinetics; Entropy; Enthalpy

1. Introduction

In recent years, industrial development made a major influence on the environment. The industries such as textile, paper, food, cosmetics, plastic; etc. use dyes to tint the products [1]. Out of these industries, the textile industries are one of the most common and important parts of the world. Textile industries consume an excess of H_2O, the production processes mainly in the staining and dying practices. Moreover, from industrial sectors water discharged from the textile industry is considered as the most

* Corresponding authors.

polluted water [2]. More than 10,000 commercially accessible dyes with more than 7×10^5 tonnes of rinse stuff produced per annum. From correlated industries, it is assessed that 2% of dyes which is produced annually are released in effluents [3]. The expulsion of wastewater containing dyes into the streams and other water bodies affects the aesthetic nature as well as hinders the transmission of light in the water streams and decreases the photosynthetic activity and causes critical complications to the aquatic life and food web [4].

The usage of food colors in different products causes colon, cancer, obesity, high blood pressure, allergies, and may be led to unimaginable reactions [8]. Crystal violet is an eminent cancer-causing poison [5]. Crystal violet (CV) stimulates the eyes sore, queasiness, vomiting, oral herpes [6], cancer [5], jaundice, tissue necrosis, renal failure, everlasting injury to the cornea and oculus [7], dermal irritation, and alimentary tract irritation [5,7]. When ingested it causes peritonitis, weight loss, birth defects, reproductive defects and mutations in genetic material.

Elimination of dyes from effluents can be performed by different methods, that is, physical, chemical and biological processes [9–12]. The chemical and biological methods have disadvantages such as expensive, consumption of large amount of chemicals, incomplete elimination of dyes and production of toxic sludge [12]. The adsorption process offered advantages over other techniques, that is, high efficiency, cheap, selectivity, high level of purification and retrieval of adsorbate and adsorbent [12,13].

Adsorption processes have been employed to eliminate dyes from the waste effluents. The process of adsorption is an applicable method rather than others due to its sludgeless, clean procedure and entirely eliminated dyes even from dilute solution [14]. Two adsorption methodologies are used to eliminate the contaminants from wastewater, that is, batch adsorption and column adsorption methodology. The batch technique is used rather than column because it is easy to apply and provides a simple way to explain factors that effects the adsorption behavior [15].

Adsorption process using solid adsorbents like activated carbon and synthetic resin to adsorb the various types of pollutants from wastewater. Different types of pollutants such as metals, dyes, phenols, insecticides, etc. have been removed by various adsorbents [16]. To reduce the cost of adsorption operation, agro-industrial waste has gained a lot of attention [12]. Recently the applications of economic adsorbents for the dyes and metal ions removal have been investigated [17]. Most conventional and low-cost sorbents have been used to eliminate dyes from effluents such as native clay [18], jute stick powder [19], sawdust [20], oil palm, trunk fiber [21], fly ash [22], guava leaf powder [23], citrus waste [24], barley husk [25], and sugar cane bagasse [26].

So, from the resource sustainability and economic point of view, biomass adsorbents have a high potential to use in pollution control. In Pakistan, wheat is a vital and ample crop. Wheat grain's skin is wheat bran, it is an agricultural bio-product and can be easily obtained from flour mills. It accounts for 40% weight of wheat grains. The predominant composition of wheat bran gave an idea of converting it into sorbent. In the structure of wheat bran, it comprises cellulose, hemicellulose and lignin have a huge amount of hydroxyl (OH) groups. Because of the existence of easily accessible hydroxyl groups, a chain of chemical reactions such as condensation, etherification, and co-polymerization can simply proceed [27]. These fibers also have a large surface area which makes them favorable for their binding with other compounds [28].

The present study investigates the usage of wheat bran which is an agricultural biowaste to adsorb the toxic Crystal violet dye from wastewater. Agricultural biowaste as an adsorbent is very effective because of its low-cost, abundance, and availability [29]. In this work, different factors were applied to study the effect of different parameters towards toxic Crystal violet dye. The novelty of this work is that the wheat bran is employed as an adsorbent is agricultural waste material and is used in an unprocessed form without any physical or chemical treatment. The mechanism and feasibility of this adsorption process have been evaluated by using different kinetic models.

2. Materials and methods

2.1. Preparation of Crystal violet (adsorbate)

Among various kinds of basic dyes, CV is called Basic violet 3. It is an example of cationic dye [30]. The Fig. 1 shows that Crystal Violet is a triarylmethane synthetic dye, having purple color [5].

CV is also known as Gentian violet. Initially; the name Gentian violet was used for methyl violet but recently it is used as an alternative word for Crystal violet. The %age purity of dye used is 99.9%. By adding 1 g of Crystal violet powder in distilled water in a thoroughly washed and dried 1,000 mL measuring flask, 1,000 ppm stock solution was prepared. The total volume of the solution was 1,000 by diluting the CV solution with distilled water equal to the mark.

2.2. Preparation of wheat bran (adsorbent)

Wheat bran is derived from wheat-milling industries. It is usually an abundant and natural material in Pakistan. The Fig. 2 shows that wheat bran (b) is the skin of wheat grains (a). This bran is usually isolated from the wheat in the conversion process of wheat into flour. The present study deals with the adsorption abilities of wheat bran for the removal of toxic Crystal violet dye from wastewater.

2.3. Characterization of wheat bran surface

The characterization of adsorbent is carried out with the help of two instruments: Fourier-transform infrared spectroscopy (FT-IR) and scanning electron microscopy (SEM). FT-IR in the extent of 4,000–5,000 cm^{-1} using potassium bromide (KBr) disc, comprising 1% of finely milled raw wheat bran [31]. SEM was employed to determine the surface morphology and consistency of the wheat bran (WB). The SEM analysis is performed by first preparing the sample for which the solid samples of wheat bran are ground into fine particles. These prepared WB samples were then positioned on double-sided carbon tape present on sample holders.

2.4. Batch adsorption experiment

The extent of uptake of Crystal violet (CV) on wheat bran was investigated by using different parameters. Experiments were performed by varying one limitation at a time while other conditions remain the same. Initial dye concentration before adsorption was determined by UV-Visible spectrophotometer setting at 590 nm wavelength, that is, λ_{max} of CV. After the addition of a suitable amount of adsorbent in a Crystal violet solution, manual shaking was performed. After the attainment of equilibrium, the wheat bran which adsorbed the CV was parted from the solution and the deposit collected was evaluated by means of the UV-Visible spectrophotometer at 590 nm. The percentage adsorption of CV was determined by changing the concentration of CV formerly and afterward adsorption. The equation used to estimate the %age adsorption of CV dye:

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

where A_i is the initial absorbance of dye solution; A_f is the final absorbance of dye solution after adsorption.

The uptake capacity (mg g^{-1}) of adsorbent (wheat bran) was estimated by the following equation:

$$q_t = \frac{\left(C_0 - C_t\right)}{m} V \tag{2}$$

3. Theory

Three isotherm models, that is, Freundlich, Langmuir and Dubinin–Radushkevich (D-R) isotherm models have been described in the present study in order to determine the adsorption equilibria:

3.1. Adsorption isotherms

3.1.1. Freundlich adsorption isotherm

Freundlich adsorption isotherm gave an empirical equation which represent the amount of adsorbate adsorbed on the surface of substance with respect to pressure or concentration at constant temperature.

$$\log \frac{x}{m} = \log k + \frac{1}{n} \log P \tag{3}$$

This is a straight-line equation, a plot of logx/m vs. log$P$ should be a straight t line with slope $1/n$ and intercept log$k$. These curves show the association between adsorption and pressure at lower values. The restriction of the Freundlich isotherm curve is that it failed to guess the adsorption capacity at higher pressure.

3.1.2. Langmuir adsorption isotherm

In 1916, Langmuir proposed another isotherm. It is based on different assumptions, one of which is that the dynamic equilibrium exists between adsorbate, that is, adsorbed gaseous molecules and the free gaseous molecules.

The nonlinear Langmuir isotherm can be linearized into the following expression:

$$\frac{C_{\text{Eq}}}{C_{\text{ad}}} = \frac{1}{bQ} + \frac{C_{\text{Eq}}}{Q} \tag{4}$$

where C_{Eq} is the dyes ions concentration solution (mol L^{-1}) at equilibrium, C_{ad} is the amount adsorbed per unit mass onto wheat bran at equilibrium (mol g^{-1}), constant Q is monolayer adsorption capacity (mol g^{-1}) and b (L mol^{-1}) is related to the energy of adsorption.

3.1.3. D-R adsorption isotherm

In order to classify the physical or chemical adsorption of adsorbate on the adsorbent, the experimental data were subjected to a D-R adsorption isotherm. The non-linear D-R equation can be written as:

$$\ln q_e = \ln q_{\text{DR}} - \beta\varepsilon^2 \tag{5}$$

where β is the activity coefficient, q_{DR} is the theoretical saturation capacity and ε is the Polanyi potential and is given as follow:

$$\varepsilon = RT \ln\left(1 + \frac{1}{C_e}\right) \tag{6}$$

where T is the temperature and R is the general gas constant.

From a value of β, mean sorption energy which is defined as the energy of transfer of one mole of solute from infinity to the surface of the adsorbent and can be calculated with the following formula:

$$\text{SE}_s = \frac{1}{\sqrt{2\beta}} \tag{7}$$

3.2. Adsorption kinetics

Adsorption kinetics is studied to measure the dye uptake rate and adsorption time at constant pressure or concentration and it is used to measure the diffusion of dyes into the apertures of the adsorbent.

Kinetics models which have been utilized to explain the process of adsorption and potential rate-controlling process as follows:

3.2.1. Pseudo-first-order model

This equation is employed to study the adsorption of dyes from an aqueous solution. According to the pseudo-first-order equation, the rate of change of solute uptake with time increases with an increase in the difference of concentration and the extent of solid uptake with time.

This model is represented by the following equation:

$$\frac{dq_t}{dt} = k_1\left(q_e - q_t\right) \tag{8}$$

where k_1 (min^{-1}) is the pseudo-first-order rate constant, q_e and q_t (mg g^{-1}) are the amount of adsorbate adsorbed as per the unit weight of adsorbent at a time "t" in addition to equilibrium.

By directing boundary conditions, the linear form of this model is represented as:

$$\ln\left(q_e - q_t\right) = \ln q_e - k_1 t \tag{9}$$

The graph plotted between $\ln(q_e - q_t)$ vs. t, the value of rate constant k_1 can be calculated from intercept and the value of the slope is determined by "q_e".

3.2.2. Pseudo-second-order kinetic model

This model is applied to study the rate of adsorption. According to this model, the adsorption rate is directly related to the square of a number of unoccupied sites.

$$\frac{dq_t}{dt} = k_2\left(q_e - q_t\right)^2 \tag{10}$$

where k_2 (g mg^{-1} min^{-1}) is the pseudo-second-order constant.

The linearized equation of this model is represented as:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \tag{11}$$

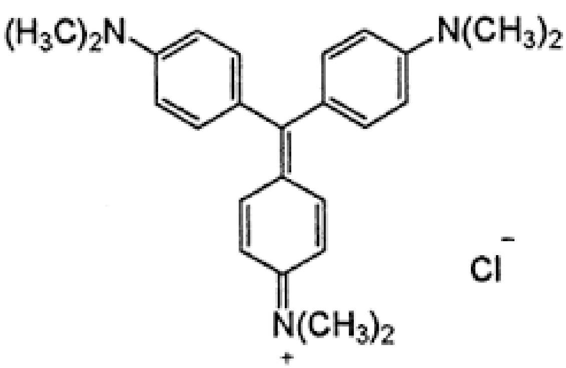

Fig. 1. Structure of Crystal violet.

where q_e and q_t are the amount of adsorbate adsorbed on the surface of substance act as adsorbent at equilibrium and at a time "t" respectively.

When t = 0, k_2 is used to measure the initial adsorption rate "h".

$$h = k_2 q_e^2 \tag{12}$$

By the plot of the graph between t/q & t, the value of k_2, initial adsorption rate "h" and "q_e" can be calculated.

3.2.3. Intraparticle diffusion model

This model was developed by Weber and Morris. It is used for measuring the diffusion mechanism and rate-controlling step. It can be expressed as:

$$Q_t = K_i t^{1/2} + C \tag{13}$$

where C is the intercept which represents the effect of boundary layer thickness. K_i (mg g^{-1} min$^{-1/2}$) is an intraparticle diffusion rate constant and its value is estimated from the slope of the rectilinear plot of $q_t/t^{1/2}$.

3.2.4. Liquid film diffusion (Reichenberg) model

The nature of the adsorption through the liquid film diffusion mechanism was confirmed by applying the liquid film diffusion model which is also known as Reichenberg kinetic model developed by Reichenberg in 1953.

$$X = \left(1 - \frac{6}{\pi^2}\right) e^{-\beta_t} \tag{14}$$

where

$$X = \frac{q_t}{q_e} \tag{15}$$

q_t amount of adsorbate adsorbed at a time "t", q_e amount of adsorbate adsorbed at equilibrium [32].

3.3. Thermodynamics of adsorption

In the adsorption process, thermodynamic concerns are essential in order to know the process is spontaneous or

Fig. 2. Wheat grain (a) and wheat bran (b).

not. Gibb's free energy, $\Delta G°$ is an important criterion for the suggestion of spontaneity of a chemical reaction. To know the value of $\Delta G°$, entropy and energy factors must be taken into account. If $\Delta G°$ is negative, it means reaction happens spontaneously.

The free energy of adsorption is given by the following equation:

$$\Delta G° = -RT\ln k_H \tag{16}$$

where $\Delta G°$ = Gibb's free energy change; R = universal gas constant; k_H = adsorption equilibrium constant; T = absolute temperature.

The change in equilibrium constant with temperature can be obtained by applying differentials as follows:

$$\frac{d\ln k_H}{dT} = \frac{\Delta H°}{RT^2} \tag{17}$$

By applying integration, the integrated form of Eq. (17) becomes:

$$\ln k_H = -\frac{\Delta H°}{RT} + Y \tag{18}$$

The equation rearranged to become,

$$-RT\ln k_H = \Delta H° - \mathrm{TRY} \tag{19}$$

To assume, RY = $\Delta S°$; $-RT\ln k_H = \Delta G°$.

Eq. (19) becomes

$$\Delta G° = \Delta H° - T\Delta S° \tag{20}$$

The feasibility, spontaneity and exothermic or endothermic nature of adsorption can be determined in terms of the determination of values of the thermodynamic parameter.

If the value of $\Delta G°$ is negative it confirms the spontaneous nature of the adsorption process.

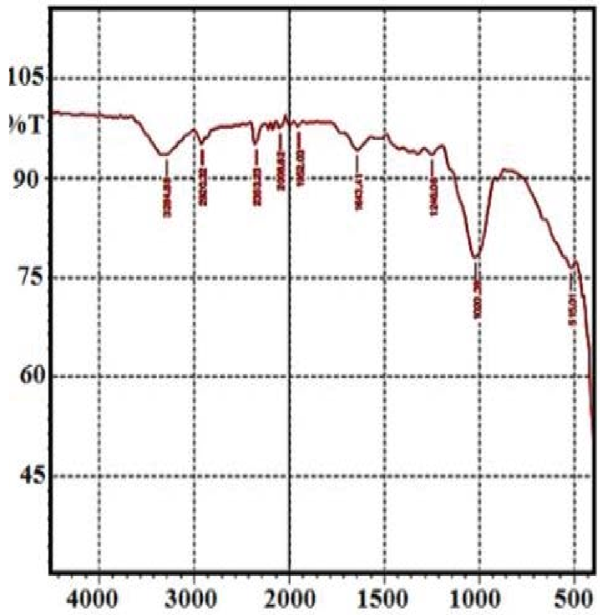

Fig. 3. FT-IR of un-adsorbed wheat bran.

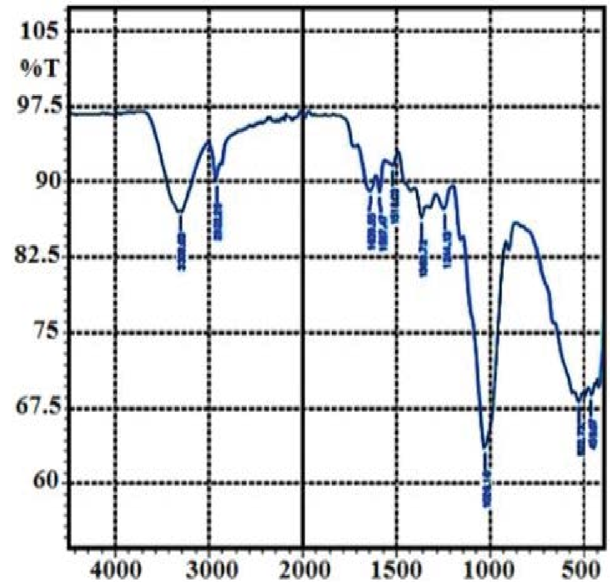

Fig. 4. FT-IR analysis of CV loaded wheat bran.

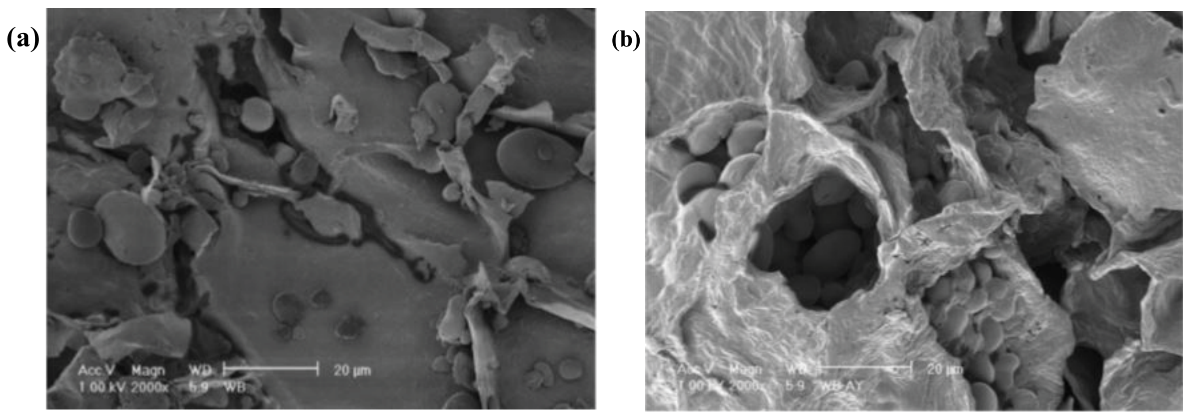

Fig. 5. Scanning electron micrograph of WB (a) before adsorption and (b) after dye adsorption.

$\Delta G°$ = negative (spontaneous process)

If the value of $\Delta H°$ is negative it means the process is exothermic in nature.

$\Delta H°$ = negative (exothermic process)

If the value of $\Delta S°$ is positive it means adsorbent have a greater affinity for solute molecules and suggest that during adsorption some structural changes occur in adsorbent and adsorbate.

$\Delta S°$ = positive (greater affinity between adsorbent and adsorbate)

4. Results and discussion

4.1. Characterization of adsorbent

In the FT-IR spectrum, the CV adsorbed on wheat bran was observed by comparing it with un-adsorbed wheat bran. The Fig. 4 reveals that there is a decrease in the amide group at 459 and 522 cm^{-1} and the hydroxyl (OH) group extending at 3,308 cm^{-1} peak. The extensive adsorption is due to the carboxylic acid, lignin, alcohol, phenolic groups present in pectin and cellulose, it reveals the occurrence of hydroxyl groups on the exterior of wheat bran employed for the adsorption CV dye. Variation in the adsorption maxima of two spectra (Figs. 3 and 4) indicates the adsorption of CV pigment at the surface of wheat bran [20].

SEM analysis is a key tool for illustrating the surface morphology and main physical properties of adsorbents. It is advantageous for analyzing the particle figure, sponginess and suitable size distribution of adsorbent. Before dye adsorption (Fig. 5a), it confirms an irregular and rough surface morphology. After dye adsorption (Fig. 5b), the surface of wheat bran is covered with dye molecules.

Elemental analysis was performed with an EA 1108 Fison's instrument [31].

Table 1
Chemical characteristics of WB used in the experiment

Chemical characteristics	Percentage %
Moisture content	6.40
Water soluble components	20.89
Insoluble components	72.34
Ash	2.58
Total loss of ignition	88.45
Carbon content	44.59
Hydrogen content	6.56

4.2. Effect of pH

The alkalinity of dye solution greatly impacts the adsorptive behavior of the adsorbent. The H^+ ions modify the surface charge of adsorbate and adsorbent. From acidic to basic pH values 1–11, the adsorption phenomenon of CV dye on the surface of wheat bran was assessed.

From experimental work in Fig. 6, it is concluded that the maximum adsorption of CV on wheat bran at pH 2, the %age removal of dye was 92.51% by keeping other conditions constant throughout the experiment [31]. Fig. 6 shows that by forwarding towards the basicity, the adsorption process decreases gradually and minimum at pH 11.

The point of zero charges of biomass is 2 [33]. At this pH, the surface of the adsorbent is neutral, from experimental trials it became clear the maximum %age of dye (92.51%) has been removed at this pH value of 2. This can be explained by the fact that at low pH 2 maximum adsorption of CV dye may be due to interactions such as hydrogen bonding and van der Waals forces. Also, the pK value of CV is 8.6 so, pH 2 lies under the pH values in which the surface of the adsorbent is neutral and resultantly positively charged CV dye molecules adsorbed on the uncharged adsorbent surface by the formation of non-ionic chemical

Table 2
Isotherm parameters and their correlation coefficient for the adsorption of CV onto WB

Isotherms	Isotherm correlation coefficients of adsorption		
Freundlich adsorption isotherm	n	K_f (mg g^{-1})	R^2
	0.38	999,856.5	0.9923
Langmuir adsorption isotherm	q_0 (mg g^{-1})	b (dm^3 mol^{-1})	R^2
	116.94	6.632×10^{-5}	0.9952
Dubinin–Radushkevich isotherm	β (kJ^2 mol^{-2})	E_s (kJ mol^{-1})	R^2
	1.8563	0.532	0.9939

Table 3
First and second-order parameters for the adsorption of CV onto WB

Pseudo-first-order kinetics parameters				Pseudo-second-order kinetics parameters			
$q_{e,\mathrm{cal}}$ (mg g^{-1})	$q_{e,\mathrm{exp}}$ (mg g^{-1})	k_1 (mg g^{-1} min^{-1})	R^2	$q_{e,\mathrm{cal}}$ (mg g^{-1})	$q_{e,\mathrm{exp}}$ (mg g^{-1})	k_2 (mg g^{-1} min^{-1})	R^2
0.025	6.645	1.29	0.563	6.645	6.644	7.55	1

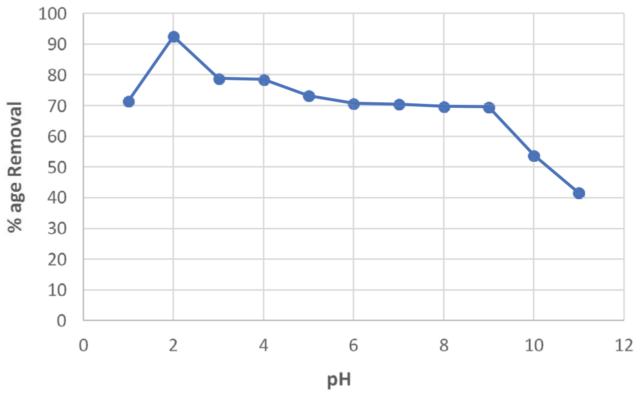

Fig. 6. Plot between pH of the solution and %age removal of the dye.

Table 4
Thermodynamic data and parameters for CV adsorption onto wheat bran

Temperature	ΔG	ΔH	ΔS
(K)	(kJ mol⁻¹)	(kJ mol⁻¹)	(JK⁻¹ mol⁻¹)
273	–0.866		0.0066
283	–0.956		0.0067
293	–0.965		0.0065
303	–0.984	0.959	0.0064
313	–0.989		0.0062
323	–1.00		0.0060
333	–1.033		0.0059

complexes with the functional groups of adsorbents. Hence ionic pairs have formed that aids in maximum adsorption of CV dye molecules [34]. So, pH 2 was maintained in the next experiments.

4.3. Effect of adsorbent dosage

In order to explore the effect of adsorbent dosage, the amount of wheat bran is varied by keeping all the other conditions constant. Adsorbent dosage greatly influences the removal capacity of dye by the adsorbent. There is a rapid rise in the exclusion of dye by aggregating the amount of wheat bran. It is due to the accessibility of surface area by increasing the concentration of wheat bran.

The figure shows that %age removal is directly related to the adsorbent dosage. As the removal proficiency from 0.1 to 0.5 g was increased from 78.35% to 97.04%. Beyond this, there is no considerable rise in adsorption of dye it may be due to overcrowding of WB particles directed to the covering of WB sites [32]. The graph in Fig. 7 shows that there is no prominent increase of CV adsorption beyond 0.6 g of wheat bran. So, in the next experiments, the amount of wheat bran remains 0.6 g.

4.4. Effect of contact time

To evaluate the adsorption procedure, contact time is one of the significant parameters. In this experiment, different ranges of contact time were selected, that is, from 5 to 120 min. From Fig. 8, it became clear that contact time for the maximum exclusion of Crystal violet dye takes place at 120 min with 89.73% adsorption efficiency. Though, at 30 min the removal percentage was 87.25%. So, there is no considerable change in the uptake of CV dye after 30 min [35,36]. A contact time of 30 min was preferred for the next study. It is evident from Fig. 8 that the adsorption percentage of dye was directly related to the contact time. The exclusion process was very fast in the first 5 min because of the presence of vacant adsorption sites on WB for adsorption. That's why there is no significant rise in adsorption by increasing the time due to the unavailability of vacant adsorption sites.

4.5. Effect of dye concentration

By varying the dye concentration (300–550 ppm) and by keeping all the other factors constant, the effect of dye concentration on adsorption phenomena is studied. It is evident from the plot in Fig. 9 that %age removal is inversely proportional to the dye concentration. The removal efficiency of CV decreases from 96.4% to 83.8% by increasing the concentration from 300 to 550 ppm. The decrease in % removal is due to the overfilling of adsorption places on the surface of WB by escalating the CV concentration. At low concentrations, there are vacant adsorption sites accessible for the adsorption of CV dye [35]. So, results indicate that the adsorption is well reliant on initial dye concentration.

4.6. Effects of temperature

Temperature is a significant factor to study the adsorption process, it determines that the process is either exothermic or endothermic. It is also used to study the other thermodynamic parameters, that is, the process is either spontaneous or non-spontaneous and it is used to calculate the entropy value. As the graph (Fig. 10) shows that there is a direct relationship between the temperature and %age removal. Percentage removal increases gradually from 85.5% to 86.5% by raising the temperature from 0°C to 60°C.

The results indicate that the process is occurred by absorbing the heat (endothermic), that is, the uptake of CV dye increases with the increase in temperature [37]. The temperature has influenced the removal of dyes by

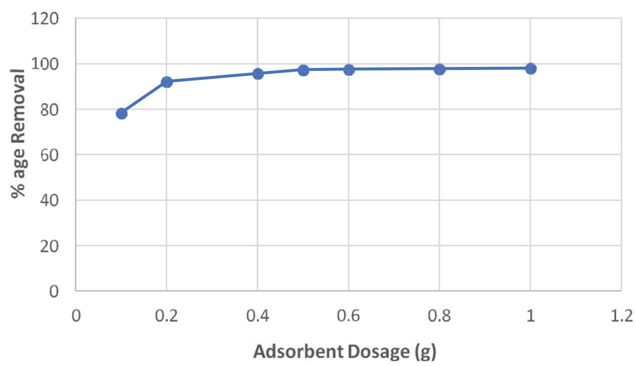

Fig. 7. Plot between %age removal and adsorbent dosage (g).

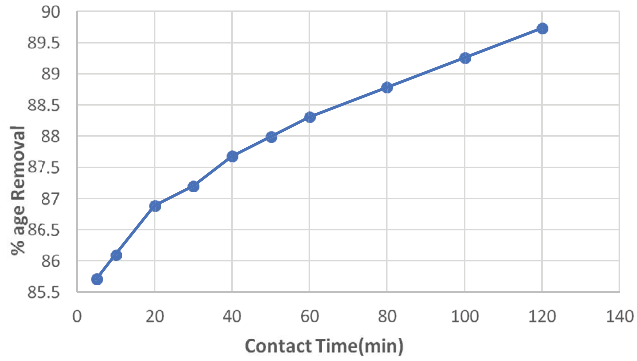

Fig. 8. Plot between %age removal and contact time (min).

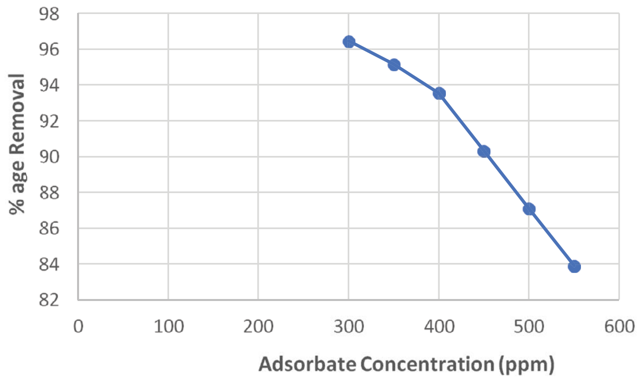

Fig. 9. Plot between %age removal and adsorbate concentration (ppm).

changing the solubility of dyes and the interactions of molecules [38].

4.7. Adsorption isotherms

The three most frequently used adsorption isotherm equations, that is, Freundlich, Langmuir and D-R isotherms were applied from equilibrium data which is obtained from initial dye concentration. These three adsorption isotherms were mostly employed.

4.7.1. Freundlich adsorption isotherm

The Freundlich equation is an empirical equation that is used for the representation of adsorption data. It is mathematically defined as follows:

$$C_{\text{ad}} = KC_{\text{ad}}^{1/n} \tag{21}$$

The logarithmic form of the Freundlich equation can be written as:

$$\log C_{\text{ad}} = \log K + \frac{1}{n}\log C_{\text{Eq}} \tag{22}$$

where C_{ad} (mol g^{-1}) = amount of CV adsorbed at equilibrium, C_{Eq} (mol L^{-1}) = CV dye concentration at equilibrium, K and $1/n$ = Freundlich constant.

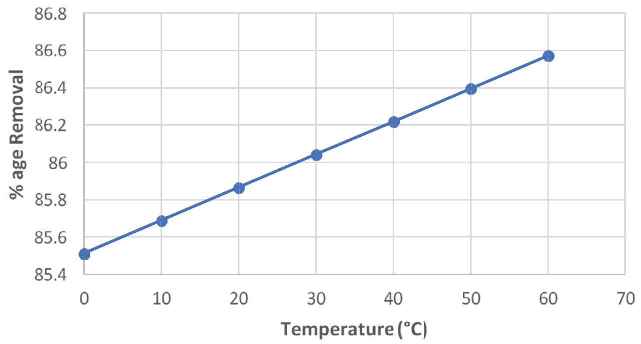

Fig. 10. Plot between %age removal and temperature (°C).

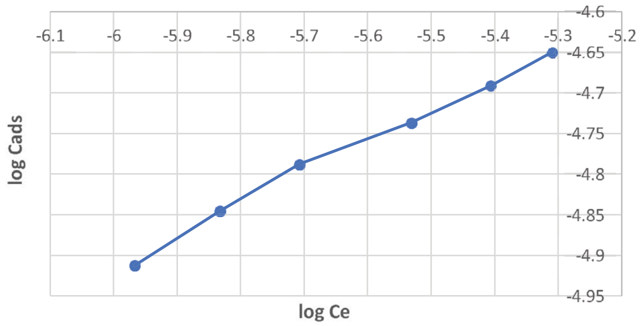

Fig. 11. Freundlich adsorption isotherm for adsorption of CV on wheat bran.

TThe Fig. 11 shows the Freundlich isotherm for the adsorption of CV on wheat bran. It is distinct from the plot and regression value (0.9923) that the experimental data fit best with the Freundlich adsorption isotherm.

4.7.2. Langmuir adsorption isotherm

The linearized expression for b and q_e was obtained from the slopes and intercepts of the linear plots of C_e/C_{ad} vs. C_e (Fig. 12) whereas the reported parameters are listed in Table. The maximum adsorption capacity of CV on wheat bran is found to be 116.94 mg g^{-1} by Langmuir isotherm.

4.7.3. D-R isotherm model

In order to classify the physical or chemical adsorption of adsorbate on the adsorbent, the experimental data were subjected to D-R adsorption isotherm. The non-linear D-R equation can be written as:

$$\ln q_e = \ln q_{\text{DR}} - \beta\varepsilon^2 \tag{23}$$

The D-R isotherm model for the adsorption of CV on WB is depicted in Fig. 13. The D-R isotherm parameters are computed and summarized in Table 2. From the high values of the correlation coefficient, as shown in Table 2, the D-R isotherm was found to be the best fit for the exclusion of CV on WB. The value of E calculated is 0.53 kJ mol^{-1} as shown in Table 2 indicating that the adsorption process of CV on WB is physisorption.

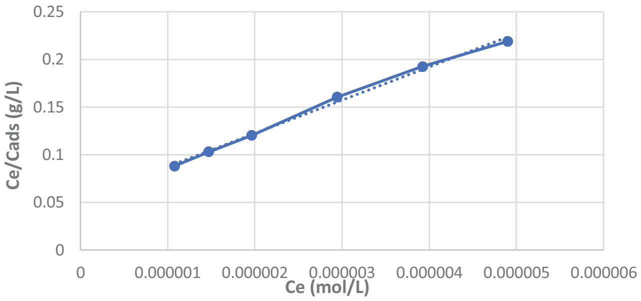

Fig. 12. Langmuir adsorption isotherm for adsorption of CV on WB.

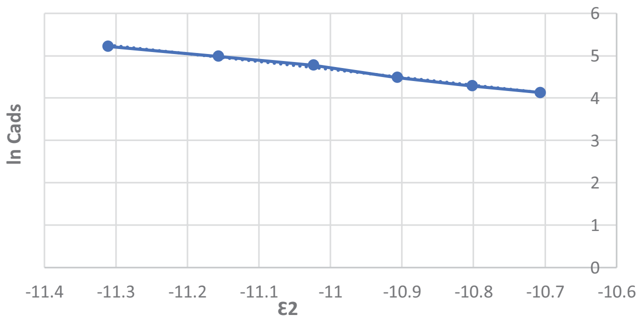

Fig. 13. D-R isotherm for the adsorption of CV on WB.

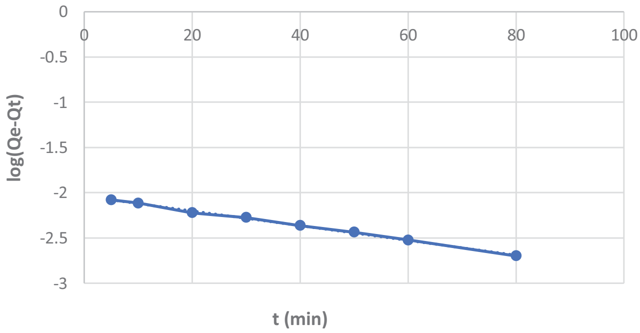

Fig. 14. Pseudo-first-order kinetic model for adsorption of CV on WB.

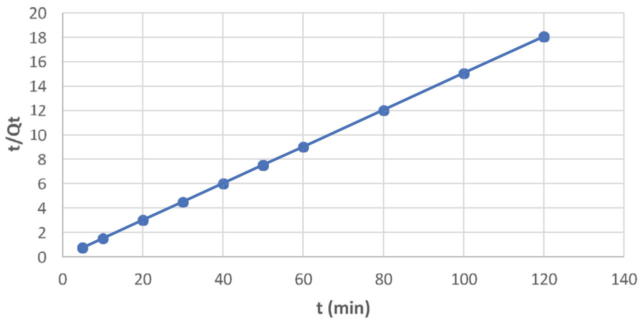

Fig. 15. Pseudo-second-order kinetic model for adsorption of CV on WB.

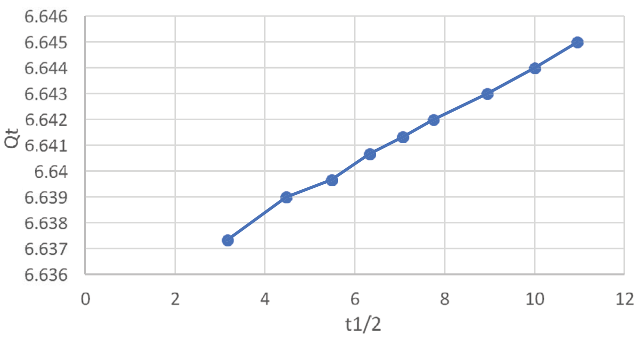

Fig. 16. Intraparticle diffusion model for adsorption of CV on WB.

4.8. Adsorption kinetics

The four kinetic models were employed to inspect the reaction ways and potential rate-determining steps of the adsorption of CV on to wheat bran are as follows:

4.8.1. Pseudo-first-order kinetic model

Based on the plot (Fig. 14), it can be concluded that there is a lack of correlation between the experimental q_e value (6.645) and the q_e value calculated from the graph (0.025 mg g^{-1}) as well as a low R^2 value (0.5603).

4.8.2. Pseudo-second-order kinetic model

Now the plot (Fig. 15) and their parameters in Table 3 shows that there is an accurate relationship between the experimental q_e (6.645 mg g^{-1}) and the q_e calculated from the plot (6.64 mg g^{-1}) as well as high R^2 (1) as a contrast to first-order kinetics. Thus, the adsorption of CV on WB actually obeys pseudo-second-order reaction kinetics [32,35].

4.8.3. Intraparticle diffusion model

In a batch adsorption organization, there is an opportunity for intraparticle pore diffusion of adsorbate ions (CV), which may be a rate-limiting step. To explore the probability of intraparticle diffusion opposition affecting the adsorption process. The model is given as:

$$q_t = K_i t^{1/2} + C \tag{24}$$

According to the equation, the plot (Fig. 16) of q_t vs. $t^{1/2}$. It should be a straight line when this mechanism obeys the intraparticle diffusion model. However, the current study of CV on WB illustrates that although intraparticle diffusion model (R^2 = 0.9974) elaborates in the adsorption process.

4.8.4. Liquid film diffusion model

By applying this model, the nature of the adsorption through liquid film diffusion mechanism was established which is also known as Reichenberg kinetic model developed by Reichenberg in 1953. The plot of β vs. t for the adsorption of CV on WB is a straight line exposed in Fig. 17 having R^2 value of 0.9956. The inability of the plot to pass through the origin shows that the estimate of the

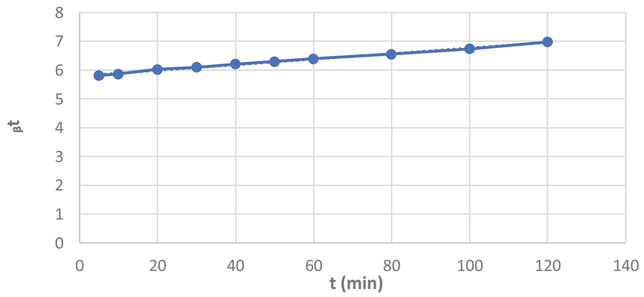

Fig. 17. Liquid film diffusion model for the adsorption of CV on WB.

Reichenberg model will have limited applicability in the adsorption of CV dye on wheat bran.

4.9. Thermodynamic studies

The linear Van't Hoff equation plot for the adsorption of CV on WB is depicted in Fig. 18. The thermodynamic parameters are presented in Table 4. Negative $\Delta G°$ values (Table 4) indicate the feasibility and spontaneous nature of CV dye adsorption onto wheat bran.

The positive ΔH values obtained for the adsorption of CV on WB approve the endothermic nature of the adsorption process [35]. The value of ΔS is positive it means adsorbent have a greater affinity for solute molecules and suggest that during adsorption some structural changes occur in the CV and WB [32].

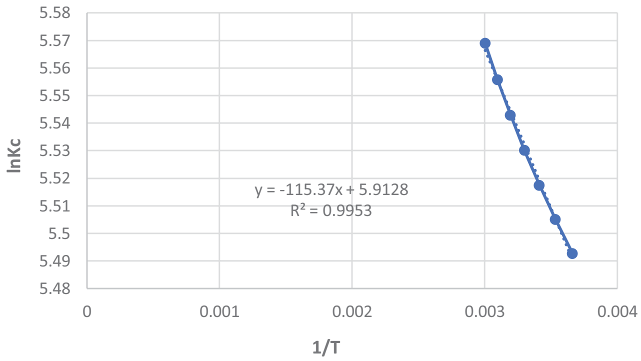

Fig. 18. Van't Hoff plot for the adsorption of CV on WB.

5. Comparison of wheat bran with other sorbents

Table 5 summarizes the comparison of the maximum CV adsorption capacity of various adsorbents including unmodified WB. The comparison shows that WB has a higher adsorption capacity compared to other than reported adsorbents.

Table 5
Comparison of CV adsorption capacity of WB with another low-cost sorbent

Sorbents	q_{max} (mg g^{-1})	References
Coniferous pinus bark powder	32.78	[35]
Rice bran	42.25	[39]
Calotropis procera leaf	4.14	[40]
Orange peel	14.3	[41]
Sugarcane dust	3.8	[42]
Neem sawdust	3.8	[43]
Wheat bran	116.94	This study

6. Experiment performed with tap water

Tap water contains various cations and anions as compared to de-ionized water. In this practical, CV solution was prepared with tap water to check the applicability of this adsorption procedure conducted with wheat bran as an adsorbent at optimum factors, that is, pH 2, 0.6 g of wheat bran (WB), 400 ppm CV concentration, 30 min of interaction time and 60°C temperature. As presented in Table 6, the removal efficiency obtained was 85.6% confirms that this procedure has future prospects to clean the CV containing waste water.

Table 6
Removal efficiency of CV on WB using tap water

Amount of adsorbent	0.6 g
Initial dye concentration	400 mg L^{-1}
Contact time	30 min
Shaking time	5 min
Temperature	60°C
Removal efficiency	85.6%

7. Conclusion

The present research reveals that WB as a low-cost agricultural waste is significantly effective for the adsorption of CV from textile effluents. WB was analyzed by FT-IR and SEM instruments. Batch adsorption experiments were performed with finely ground WB, passed through 210 mesh sizes. Different factors can affect the adsorption process experimented, that is, pH of dye solution, amount of adsorbent, duration of contact, initial dye concentration and Temperature. The adsorption phenomena of CV on WB are directly proportional to the pH of the solution, contact time, amount of adsorbent, initial dye concentration in addition to temperature and inversely proportional to initial dye concentration. It means by increasing the pH of CV solution, duration of contact between adsorbate and adsorbent, adsorbent dosage and temperature uptake of CV solution increases and it decreases by increasing the increasing initial dye concentration.

Optimum conditions from the batch adsorption studies come out to be at 2 pH, 0.6 g of adsorbent, 30 min of contact time, using 400 ppm of initial dye concentration for the maximum uptake of CV, that is, 86.57%, from effluents using WB. The adsorption process obeys the pseudo-second-order model having Regression value $R^2 = 1$. The Langmuir model efficiently explains the experimental data, calculates the CV uptake value, that is, 116.94 mg g^{-1}. Thermodynamic quantities such as free energy of adsorption ΔG, enthalpy ΔH and entropy ΔS have considered it explains that the

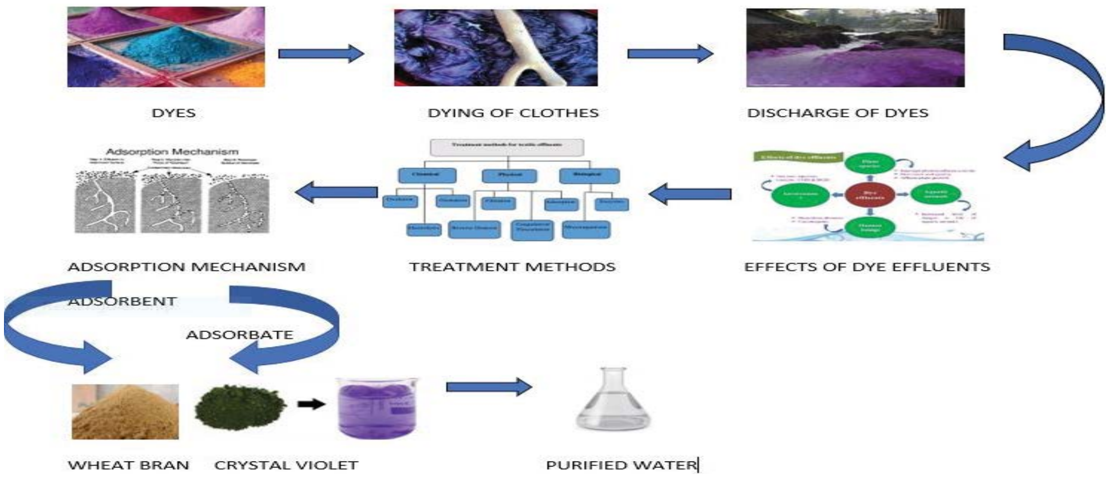

Fig. 19. Pictorial representation of the procedure, that is, removal of toxic dye Crystal violet from wastewater by using economical adsorbent wheat bran.

procedure is spontaneous, endothermic and there is a strong interaction between adsorbate and adsorbent respectively which is cheap and easily accessible material, substitute for more expensive adsorbents used for dye removal in wastewater treatment methods. Fig. 19 reveals the pictorial representation of the procedure.

Acknowledgment

I would like to express my deep and sincere gratitude to my research supervisor, Dr. Tariq Javed for giving me the opportunity to do research and providing invaluable guidance throughout this research.

References

[1] M.A.M. Salleh, D.K. Mahmoud, W.A.W.A. Karim, A. Idris, Cationic and anionic dye adsorption by agricultural solid wastes: a comprehensive review, Desalination, 280 (2011) 1–13.
[2] S. Şen, G.N. Demirer, Anaerobic treatment of real textile wastewater with a fluidized bed reactor, Water Res., 37 (2003) 1868–1878.
[3] B. Koumanova, P. Peeva, S.J. Allen, Variation of intraparticle diffusion parameter during adsorption of *p*-chlorophenol onto activated carbon made from apricot stones, J. Chem. Technol. Biotechnol., 78 (2003) 582–587.
[4] P. Mahajan, S. Singla, J. Kaushal, Phytoremediation of heavy metals using *Brassica juneca*-a review, 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] 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.
[7] V.K. Gupta, Suhas, Application of low-cost adsorbents for dye removal – a review, J. Environ. Manage., 90 (2009) 2313–2342.
[8] J. Mittal, Permissible synthetic food dyes in India, Resonance – J. Sci. Educ., 25 (2020) 567–577.
[9] A.H. Jawad, S.S.A. Norrahma, B.H. Hameed, K. Ismail, Chitosan-glyoxal film as a superior adsorbent for two structurally different reactive and acid dyes: adsorption and mechanism study, Int. J. Biol. Macromol., 135 (2019) 569–581.
[10] A. Oussalah, A. Boukerroui, A. Aichour, B. Djellouli, Cationic and anionic dyes removal by low-cost hybrid alginate/natural bentonite composite beads: adsorption and reusability studies, Int. J. Biol. Macromol., 124 (2019) 854–862.
[11] I. Tahira, Z. Aslam, A. Abbas, M. Monim-ul-Mehboob, S. Ali, A. Asghar, Adsorptive removal of acidic dye onto grafted chitosan: a plausible grafting and adsorption mechanism, Int. J. Biol. Macromol., 136 (2019) 1209–1218.
[12] H.N. Bhatti, Y. Safa, S.M. Yakout, O.H. Shair, M. Iqbal, A. Nazir, Efficient removal of dyes using carboxymethyl cellulose/alginate/polyvinyl alcohol/rice husk composite: adsorption/desorption, kinetics and recycling studies, Int. J. Biol. Macromol., 150 (2020) 861–870.
[13] S. Soni, P.K. Bajpai, J. Mittal, C. Arora, Utilisation of cobalt doped iron based MOF for enhanced removal and recovery of methylene blue dye from waste water, J. Mol. Liq., 314 (2020) 113642, 10.1016/j.molliq.2020.113642.
[14] I. Anastopoulos, I. Pashalidis, A.G. Orfanos, I.D. Manariotis, T. Tatarchuk, L. Sellaoui, A. Bonilla-Petriciolet, A. Mittal, A. Núñez-Delgado, Removal of caffeine, nicotine and amoxicillin from (waste)waters by various adsorbents. A review, J. Environ. Manage., 261 (2020) 110236, doi: 10.1016/j.jenvman.2020.110236.
[15] C. Arora, S. Soni, S. Sahu, J. Mittal, P. Kumar, P.K. Bajpai, Iron based metal organic framework for efficient removal of methylene blue dye from industrial waste, J. Mol. Liq., 284 (2019) 343–352.
[16] A. Mittal, J. Mittal, Chapter 11 – Hen Feather: A Remarkable Adsorbent for Dye Removal, S.K. Sharma, Ed., Green Chemistry for Dyes Removal from Wastewater: Research Trends and Applications, 2015.
[17] A. Bhatnagar, A.K. Jain, A comparative adsorption study with different industrial wastes as adsorbents for the removal of cationic dyes from water, J. Colloid Interface Sci., 281 (2005) 49–55.
[18] S. Nausheen, H.N. Bhatti, K. Arif, J. Nisar, M. Iqbal, Native clay, $MnFe_2O_4$/clay composite and bio-composite efficiency for the removal of synthetic dye from synthetic solution: column versus batch adsorption studies, Desal. Water Treat., 187 (2020) 219–231.
[19] 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.
[20] V.K. Garg, R. Gupta, A.B. Yadav, R. Kumar, Dye removal from aqueous solution by adsorption on treated sawdust, Bioresour. Technol., 89 (2003) 121–124.
[21] B.H. Hameed, M.I. El-Khaiary, Batch removal of malachite green from aqueous solutions by adsorption on oil palm trunk fibre: equilibrium isotherms and kinetic studies, J. Hazard. Mater., 154 (2008) 237–244.

[22] P. Pengthamkeerati, T. Satapanajaru, O. Singchan, Sorption of reactive dye from aqueous solution on biomass fly ash, J. Hazard. Mater., 153 (2008) 1149–1156.
[23] V. Ponnusami, S. Vikram, S.N. Srivastava, Guava (*Psidium guajava*) leaf powder: novel adsorbent for removal of methylene blue from aqueous solutions, J. Hazard. Mater., 152 (2008) 276–286.
[24] H.N. Bhatti, N. Akhtar, N. Saleem, Adsorptive removal of methylene blue by low-cost *Citrus sinensis* bagasse: equilibrium, kinetic and thermodynamic characterization, Arabian J. Sci. Eng., 37 (2012) 9–18.
[25] I.-u. Haq, H.N. Bhatti, M. Asgher, Removal of solar red BA textile dye from aqueous solution by low-cost barley husk: equilibrium, kinetic and thermodynamic study, Can. J. Chem. Eng., 89 (2011) 593–600.
[26] S. Noreen, H.N. Bhatti, M. Iqbal, F. Hussain, F.M. Sarim, Chitosan, starch, polyaniline and polypyrrole biocomposite with sugarcane bagasse for the efficient removal of Acid Black dye, Int. J. Biol. Macromol., 147 (2020) 439–452.
[27] Q.-Q. Zhong, Q.-Y. Yue, Q. Li, X. Xu, B.-Y. Gao, Preparation, characterization of modified wheat residue and its utilization for the anionic dye removal, Desalination, 267 (2011) 193–200.
[28] Y. Zhang, G.H. Huang, C.J. An, X.Y. Xin, X. Liu, M. Raman, Y. Yao, W.X. Wang, M. Doble, Transport of anionic azo dyes from aqueous solution to gemini surfactant-modified wheat bran: synchrotron infrared, molecular interaction and adsorption studies, Sci. Total Environ., 595 (2017) 723–732.
[29] M. Kadhom, N. Albayati, H. Alalwan, M. Al-Furaiji, Removal of dyes by agricultural waste, Sustainable Chem. Pharm., 16 (2020) 100259, doi: 10.1016/j.scp.2020.100259.
[30] 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.
[31] V.K. Gupta, R. Jain, S. Varshney, Removal of Reactofix golden yellow 3 RFN from aqueous solution using wheat husk—an agricultural waste, J. Hazard. Mater., 142 (2007) 443–448.
[32] T. Javed, Sorption of heavy metal ions on low rank Pakistani coal, Desal. Water Treat., 92 (2017) 291–300.
[33] P.P. Kyi, J.O. Quansah, C.-G. Lee, J.-K. Moon, S.-J. Park, The removal of Crystal violet from textile wastewater using palm kernel shell-derived biochar, Appl. Sci., 10 (2020) 2251, doi: 10.3390/app10072251.
[34] E.D. Morales-Álvarez, C.M. Rivera-Hoyos, N. González-Ogliastri, R. Rodríguez-Vázquez, R.A. Poutou-Piñales, C.E. Daza, A.M. Pedroza-Rodríguez, J.C. Salcedo-Reyes, Partial removal and detoxification of Malachite Green and Crystal violet from laboratory artificially contaminated water by *Pleurotus ostreatus*, Univ. Sci., 21 (2016) 259–285.
[35] V.K. Verma, A.K. Mishra, Dye removal by sawdust based adsorbent, Pollut. Res., 24 (2005) 97–99.
[36] C.K. Enenebeaku, N.J. Okorocha, U.E. Enenebeaku, B.I. Onyeachu, Removal Crystal violet dye by adsorption onto *Picrilima nitida* stem bark powder: kinetics and isotherm studies, IOSR J. Appl. Chem. (IOSR-JAC), 9 (2016) 14–23.
[37] 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.
[38] K.K. Pandey, G. Prasad, V.N. Singh, Use of wallstronite for the treatment of Cu(II) effluent, Water Res., 19 (1989) 869–872.
[39] X.S. Wang, J.P. Chen, Biosorption of Congo red from aqueous solution using wheat bran and rice bran: batch studies, Sep. Sci. Technol., 44 (2009) 1452–1466.
[40] H. Ali, S.K. Muhammad, Biosorption of Crystal violet from water on leaf biomass of *Calotropis procera*, Int. J. Environ. Sci. Technol., 1 (2008) 143–150.
[41] G. Annadurai, R.-S. Juang, D.-J. Lee, Use of cellulose-based wastes for adsorption of dyes from aqueous solutions, J. Hazard. Mater., 92 (2004) 263–274.
[42] S.D. Khattri, M.K. Singh, Colour removal from dye wastewater using sugarcane dust as an adsorbent, Adsorpt. Sci. Technol., 17 (1999) 269–282.
[43] S.D. Khattri, M.K. Singh, Colour removal from synthetic dye wastewater using a bioadsorbent, Water Air Soil Pollut., 120 (2009) 283–294.