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Adsorption of toxic crystal violet dye using rice husk: equilibrium, kinetic, and thermodynamic study

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ABSTRACT

Bio-sorbents have arisen as prospective remediation substantial for the exclusion of colorants. Rice husk, a generally accessible agricultural waste material in Pakistan, was chosen as an adsorbent material for the elimination of synthetic CV tint from a watery solution. The adsorption revisions of mutagenic CV tint from watery solution have been conducted on untreated rice husk by adjusting diverse parameters like adsorbent particle size (105, 210, and 500 mesh sizes), initial dye concentrations (300–450 mg/L), contact interval (5–120 min), pH (1–11), temperature (0°C–50°C) and adsorbent dosage (0.1–1.0 g). Freundlich, Langmuir, and Dubinin–Radushkevich (D–R) adsorption lines were analyzed utilizing the experimental statistics. Freundlich and D–R isotherms fit best with experimental data having R^2 values 0.998 and 0.999, respectively. The pseudo-second-order shows excellent agreement out of all the adsorption kinetics because $R^2 = 1$. Thermodynamic parameters (variation in Gibb's free energy ($\Delta G°$), variation in enthalpy ($\Delta H°$), and variation in entropy ($\Delta S°$)) were also debated and verified. The results indicate that the adsorption process shows feasibility, exothermic behavior, and a positive value of entropy ($\Delta S°$) indicates that randomness prevails the adsorption process in this study. These optimum conditions results in 90.24% of crystal violet dye removal and the maximum adsorption capacity found out was 53.00 mg/g. Applicability of maximum conditions with tap water results in 80.6% removal of CV dye which indicates that rice husk might be able to recycle at a low price and proved effectual adsorbent material for the elimination of crystal violet tint from discarded water.

Keywords: Rice husk; Crystal violet; Thermodynamic; Kinetic; Adsorption isotherm

1. Introduction

In modern eons, industrial developments have marked their impacts on ecological civilization. Voluminous trades are using dyes to color their manufactured products and consume a large volume of water for this purpose. Out of all the industries, the Textile Industry is a common and essential sector that consumes large amounts of water during manufacturing processes. According to an estimation, more than 10,000 different dyes are used in the industries and more than 7×10^5 heaps of synthetic types of dyes are manufactured in the world year after year [1–3]. In Textile Industry, approximately 20,000 tons of synthetic dyes are discharged into the water as effluents every year during the dyeing

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process and finishing operations. This discharge is due to the inefficiencies of dyeing procedures adopted in various industries [3]. It is an estimation that 2% of the dyes are released as waste material from the manufacturing process while 10% is released from the textile industry and other associated industries [4]. Therefore, the disposal of these dyes-based effluents has been a great concern over a few decades.

The release of these dyes adversely affects all living entities in an ecosystem by causing acute threats to health [5]. The uptake of dyes in children of different age groups causes restlessness, irritability, sleep disturbance, and hyperactivity [6]. Out of all the dyes, crystal violet color is mostly identified as a mutagenic and mitotic toxin [7,8], and its mild causes are difficulty in breathing, nausea, vomiting, oral ulceration, jaundice, eyes burn, shock, dermal irritation, and gastrointestinal tract irritation. However, its life-threatening causes are tissue necrosis, kidney failure, cancer, perpetual harm to the arcus senilis and oculus [9]. When it is released in freshwater bodies, it decreases the oxygen content within water causes severe harm to the aquatic environment while it affects the seed germination in the terrestrial environment. As this dye has less biodegradability due to its stable structure so it must be removed from the industrial effluents [10]. Many physical, chemical, and microbial means had been used to take out the CV from colored water like membrane separation, ion exchange, biological degradation [11], etc. However, all these methods are considered very expensive so cannot be used on large scale in emerging countries so they have limited applications in pollution control [10]. Out of all of these methods, the adsorption technique is mostly employed due to its simplicity, eco-friendly nature, high sorption capacity, non-toxicity, a high degree of purification [12], and availability of a large number of adsorbents [13]. This technique could be employed on a large scale because it can process properly large flow rates resulting in high quality of water without any residual contaminants [14]. This method provides an appealing alternative approach, particularly when the adsorbent is readily available and inexpensive [15]. Many researchers have investigated various effective and developed adsorbents for the elimination of numerous categories of tints and metal ions such as biosorption of Pb^{2+}, Cu^{2+}, and Ni^{2+} ions from aqueous medium by using L-cysteine modified montmorillonite-immobilized alginate nanocomposite [16] and use of nanomaterials for dye adsorption [17–19]. Many non-conventional and nanoparticles adsorbents have been used to eliminate dyes from wastewater such as low-cost adsorbent *Chenopodium album* [20], bagasse pith [21], de-oiled soya [22] iron-based metallic organic framework [23], coir pith [24], *Curcuma caesia* based activated carbon [25], hardwood sawdust [26], soy meal hull [27], maize stalk [28], hazelnut shells [29], bottom ash [30] cobalt doped iron-based MOF [13], applications of eggshell and eggshell membrane [31], mesoporous silica (MPS) and MPS-Fe composite [32], modified rice husk (MRH), alginate (ALG) immobilized biomasses, polyvinyl alcohol (PVA), and carboxy methylcellulose (CMC) [33], polymeric biocomposites polypyrrole, polyaniline/starch, polyaniline/chitosan, and polypyrrole/starch [34], manganese nanoparticles synthesized from *Cinnamomum verum* black extract [35], etc.

Rice husk, an unusable and undesirable agricultural waste material in Pakistan, is produced as a by-product in rice milling industries. It is considered as most important agricultural waste material because it is available in large amounts. It represents 20% of the weight bases of the whole rice produced [36]. According to an estimation, the annual production of rice is five hundred million tons in the emerging realms and roughly a hundred million heaps of rice hull is obtained year after year in these countries for consumption. In many republics, rice hull has been used in the formation of blocks which are used in civil construction in the form of panels, and sometimes rice industry uses them itself for the boilers as an alternative energy source [37]. On the other hand, the quantity of rice hull accessible is still in surplus of any native use and is facing discarding issues [38].

Agricultural waste materials are continuously being searched for the removal of dyes from wastewater because of their carbonaceous nature possessing high content of silica, cellulose, and hemicellulose [39], and high affinity toward molecules due to the presence of diverse functional groups. Besides, agro-waste materials do not require modification or rather few modifications. The rice husk belongs to these agro-waste materials so to resolve its dumping issue and to utilize its use for wastewater treatment this study was conducted. The intention of this revision stayed to examine the possibility of using rice husk as an adsorbent material for the elimination of crystal violet dye from watery solution by adsorption. Based on methodology there are two techniques, that is, batch or column techniques which are used to remove dyes from wastewater. The batch technique has been employed in this study as it provides a simple way to optimize diverse adsorption parameters [40]. Diverse adsorption parameters including the outcome of adsorbent amount, contact period, pH, initial dye adsorption, and temperature on CV dye using RH were premeditated. Adsorption isotherms, kinetics, and thermodynamic parameters were likewise discussed and reported.

2. Materials and techniques

2.1. Adsorbate

Crystal violet (CV), an adsorbate, also called Aniline violet and Gentian Violet was taken from Sigma-Aldrich (United States) and utilized without any purification. It has molecular formulation $C_{25}H_{30}ClN_3$ (with molecular mass 407.979 g/mol) with CAS Number 208-953-6 and color index number 32675. The configuration of the CV tint is exposed in Fig. 1. The percentage purity of crystal violet is 99.99%. Ordinary resolution of crystal violet tint was made by running 1 g of accurately weighed tint in 1,000 mL of doubly purified H_2O to obtain 1,000 mL dye solution. To check the adsorption factor such as the consequence of different preliminary dye concentrations, the stock solution was diluted further to make different standard concentrations. Standardization curvature for this tint was made by copying the absorbance standards for a series of recognized concentrations of colorant solution at precise wavelength, that is, 590 nm to acquire maximum absorbance of the dye.

2.2. Adsorbent

Rice husk in this work was acquired locally. For the formation of the powdered husk, it was ground initially

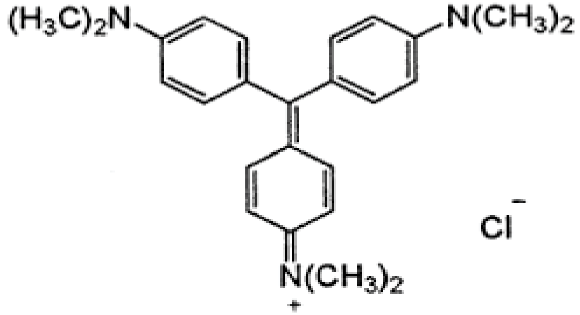

Fig. 1. Structure of Crystal Violet dye molecule.

and then was homogenized using a food blender for 15 min. 210 mesh particle size was collected by passing the substantial material across the steel strainer of 210 mesh size. Afterward, these grounded hulls were packed in bottles (made up of polyethylene) having great solidity and used devoid of somewhat physical or chemical handling.

2.3. Characterization of adsorbent

Fourier transform infrared (FTIR) spectrophotometer detected and identified the different functional groups existing on rice husk surface and their effects taking place during adsorption phenomena. The FTIR of the rice hull was reserved before the adsorption of crystal violet dye. The rice husk was encapsulated with potassium bromide spectroscopic grade and the solid translucent disk was obtained by mixing the rice husk in a piston's compartment of a hydraulic propel having a compression force of 16 kPa/cm^2. Then the FTIR spectrum was observed and recorded with wavenumbers ranging from 4,000 to 500 cm^{-1}. Scanning electron microscopy (SEM) of rice husk was used to analyze its texture and surface morphology. In SEM analysis, the sample is prepared firstly by grinding the solid sample in agate pestle mortar, and secondly, this prepared sample was sieved through a 50 mesh size. This sample was then placed on carbon tape (double-sided) present on sample holders. Further, this prepared sample was placed in an automatic ion sputtering device to cover the sample with a thin layer of gold. The SEM images and energy dispersive X-rays spectroscopy (EDX) studies were carried out using an SEM machine.

2.4. Batch adsorption studies

These experiments were operated to improve numerous parameters of adsorption for instance influence of pH, amount of adsorbent dosage, contact time, different concentrations of crystal violet solution, and temperature. All batch experiments were performed in 250 mL Erlenmeyer flasks by keeping the preset amount of adsorbent in a known volume of crystal violet solution. Then the contents of this solution are kept in an orbital shaker for some time to ensure proper shaking. The aqueous phase was separated by centrifugation followed by filtration and the amount of solution was ascertained before and after equilibrium by optimizing instrumental parameters for crystal violet dye. The formula used to calculate the % age removal is:

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

where A_i is the initial absorbance of adsorbate on adsorbent and A_f is the final absorbance of adsorbate on the adsorbent. The volume of CV tint adsorbed on the surface at time t is evaluated as of mass balance equation:

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

where q_t (mg/g) represents the magnitude of CV dye adsorbed on RH adsorbent at time t. C_0 (mg/L) shows the intensity of small quantity in the watery solution initially, C_t (mg/L) shows the intensity or dilution of solute at a specific time "t", V in the equation represents the capacity of solution taken in L, and m displays the extent of adsorbent taken in grams.

3. Theory

In requisition to determine the adsorption equilibria three adsorption isotherm representations, that is, Langmuir, Freundlich, and D–R isotherms have been discussed in the present study.

3.1. Adsorption isotherms

3.1.1. Freundlich adsorption isotherm

Freundlich adsorption isotherm is experiential figuring that portrays the heterogeneous adsorption of adsorbate going on the shallow destinations of an adsorbent. The undeviating equation of Freundlich isotherm is given as:

$$\log C_{\text{ad}} = \log K + \frac{1}{n} \log C_{\text{Eq}} \tag{3}$$

where C_{ad} is the sum of CV tint adsorbed at equilibrium time taken in mole per gram, C_{Eq} is the CV concentration at equilibrium time taken in mol L^{-1}, and K and $1/n$ are the constants in Freundlich equation, K symbolize adsorption capability and n determines the strength of adsorption.

3.1.2. Langmuir adsorption isotherm

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

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

where C_{Eq} is the dye concentration taken in mol L^{-1} at equilibrium, C_{ad} demonstrations 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.

3.1.3. Dubinin–Radushkevich adsorption isotherm

The experimental facts were laid open to Dubinin–Radushkevich (D–R) adsorption isotherm so that the adsorption of adsorbate on adsorbent can be classified into physical or chemical adsorption. The D–R equation is written as follows:

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

And ε is given as follow:

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

where T shows the temperature taken in Kelvin (K), R shows the general gas constant (in a general gas equation). The mean sorption energy might be proposed by using the subsequent formula:

$$E_s = \frac{1}{\sqrt{2\beta}} \tag{7}$$

where E_s shows the mean sorption energy. The nature of adsorption is differentiated through its value.

3.2. Adsorption kinetics

To review the appliance of adsorption procedure, four different kinetic pattern or models, that is, pseudo-first-order kinetic model, pseudo-second-order kinetic model, intraparticle diffusion model, and liquid film diffusion models have been developed.

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 of the difference in concentration and the extent of solid uptake with time [41,42].

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 ($\mathrm{min^{-1}}$) is the pseudo-first-order rate constant, q_e and q_t (mg/g) are the amount of adsorbate adsorbed as per the unit weight of adsorbent at 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, k_1 the value of the rate constant 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 the number of unoccupied sites.

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

where k_2 (g $\mathrm{mg^{-1}\ min^{-1}}$) is a pseudo-second-order constant. The linearized equation of this model is represented as:

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

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

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

By plotting a graph between t/q_t and t, the value of k_2 initial adsorption rate "h" and "q_e" can be calculated.

3.2.3. Intra particle 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 that indicates the effect of boundary layer thickness. K_i (mg $\mathrm{g^{-1}\ min^{-1/2}}$) is an intra-particle diffusion rate constant and its value is estimated from the slope of a rectilinear plot of $Q_t/t^{1/2}$. If the plot of Q_t vs. $t^{1/2}$ gives a straight line passes through the origin then the intraparticle diffusion is the sole rate-controlling step while if the plot of $Q_t/t^{1/2}$ appears in the form of multilinear plots then two or more steps will influence the adsorption process such as film diffusion and intraparticle diffusion model.

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

$$X = \frac{Q_t}{Q_e} \tag{15}$$

where X is the amount of adsorbate adsorbed at time/amount of adsorbate adsorbed at equilibrium.

3.3. Thermodynamics of adsorption

Adsorption includes the following thermodynamic considerations like variations in Gibb's free energy, entropy, and enthalpy that are used to authorize the feasibility and description of adsorption for the adsorbate–adsorbent system. These thermodynamic parameters are determined with the help of equations. Gibb's free energy is determined as:

$$\Delta G^\circ = -RT\ln K_c \tag{16}$$

where $\Delta G°$, the alteration in Gibbs free energy is measured in kJ/mol might be determined from the above equation. R symbolizes the general gas constant having a value of 1.985 cal/°C and T signifies absolute temperature taken in Kelvin (K), K_c, an equilibrium constant determined with the help of the following equation:

$$K_c = \frac{C_{Ae}}{C_e} \tag{17}$$

where C_{Ae} is the mass of the adsorbate onto adsorbent at the rate of equilibrium taken in mg per liter and C_e shows the evenness concentration of the adsorbate solution taken in milligram per liter. The Van't Hoff equation is expressed with the following relation between entropy and enthalpy:

$$\ln K_{ads} = \frac{\Delta S°}{R} - \frac{\Delta H°}{RT} \tag{18}$$

where $\Delta H°$ displays the variation in enthalpy in kJ/mol and $\Delta S°$ is the alteration in entropy in J/mol/K. The values of enthalpy and entropy are determined from the slope and intercept by plotting the graph between $\ln K_{ads}$ and $1/T$. The relationship between them helps to attain the thermodynamics parameters values. The negative or undesirable estimates of Gibb's free energy specify the impulsive character and viability of the adsorption procedure.

4. Results and discussions

4.1. Description of rice hull

The chemical composition of rice husk by component, elemental, and proximate analysis has been reported by weight was found. The component analysis of rice husk shows the percentage composition of cellulose 35.1%, hemicellulose 29.6%, lignin 18.9%, and ash 16.9% by weight while the elemental analysis of rice husk shows the percentage composition of oxygen 49.3%, carbon 44.6%, and hydrogen 5.6%. The proximate analysis of rice husk represents the percentage composition of volatiles 59.5%, mineral ash 17.1%, and moisture 7.9% by weight. A SEM is a powerful technique for investigating the surface texture, composition, crystalline structure, and properties [43]. The samples of the rice hull were shielded employing a narrow coating of gold to make it conductive and an electron speed up the voltage of 20 kV was put into operation. The surface of RH was investigated before and after adsorption. The apparent surface of the rice hull before adsorption was uneven and irregular with many loops and humps [44] and after adsorption, it becomes smooth and regular. The composition of rice husk was determined with X-ray fluorescence spectrum and the results show that powdered RH substantial have pronounced values of silica and carbon equivalent to 3.78% and 47.29% of the entire mass of the substantial RH, respectively. Additional metals such as arsenic, zirconium, copper, and lead are also existing but in a very small quantity in the RH substantial. The FTIR spectra of rice husk before adsorption were used to determine the vibrational frequencies of functional assemblies existing on the surface. The spectra of RH were observed in the range of 400–4,000 cm^{-1}. The FTIR spectrum of RH (Fig. 4) shows functional groups of SieOeSi (1,084 cm^{-1}), SieH (767 and 467 cm^{-1}), CO stretching band (1,699 cm^{-1}), and SieOH and OH (3,000 and 3,700 cm^{-1}) broadband [45].

4.2. Influence of particle size of adsorbent

A fixed amount of adsorbent in three different available mesh sizes which are 105, 210, and 500 particle sizes were investigated for the exclusion of 10 ppm crystal violet solution (10 mL) by keeping other constraints constant, that is, adsorbent dosage, dye concentration, contact time, and pH. The outcomes are publicized within Fig. 2. Here, it might be perceived that the particle size of 500 mesh size showed very low percentage removal as compared to other mesh sizes. Generally speaking, an increase in particle size increases the superficial area of adsorbent that results in higher percentage exclusion of dye or tint from prepared solution as from 105 to 210 mesh size [46]. However, the adsorption phenomena are also affected by many other factors such as porosity, specific area, and chemical affinity, etc. Therefore, all experiments within this study are performed with rice husk of 210 mesh size based on experimental results mentioned in Fig. 2.

4.3. Influence of pH

According to a fact, the pH value of a solution has a great stimulus upon the adsorptive approval of adsorbate particles (CV dye) that might be owed to its effects on the surface of rice husk and the ionizing process or breakdown of adsorbate particles [47]. As such the adsorption characteristics of CV on rice husk are studied over the pH range 1–11. The pH was maintained with 0.1 N HNO_3 and 0.1 N KOH (Fig. 3). It is clear from the figure that when the solution of CV treated with RH, it was found that 99% removal occurs at pH 2 [46] and 82% removal occurs at pH 8 [48]. The percentage removal of dye on rice husk decreases

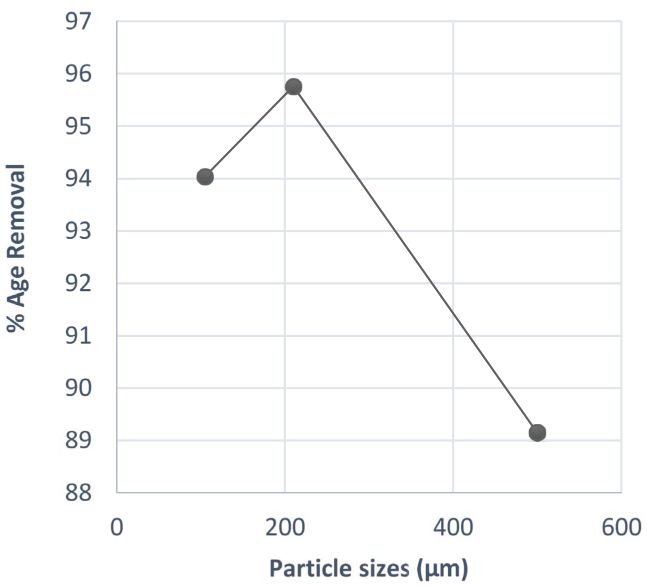

Fig. 2. Influence of particle size of RH on CV adsorption.

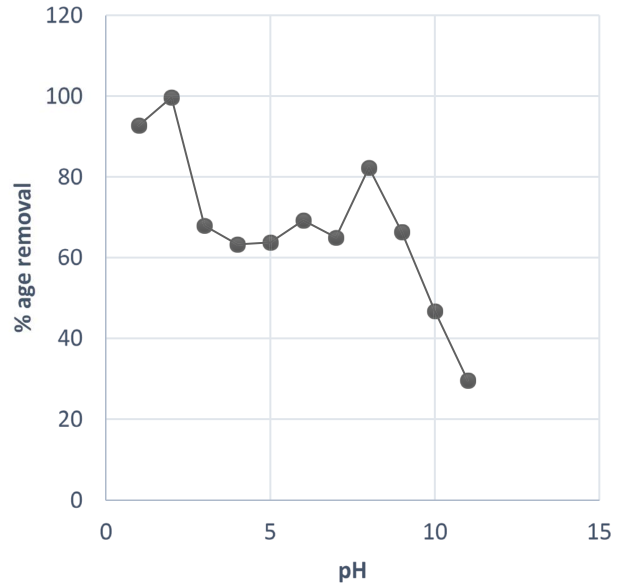

Fig. 3. Influence of pH on CV adsorption.

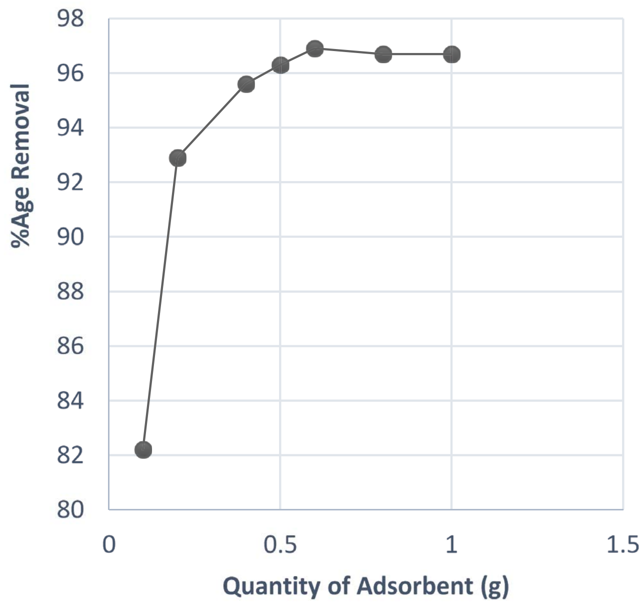

Fig. 4. Outcome of adsorbent amount on of CV by RH.

after pH 8 can be seen in the figure. Solution pH has influenced both upon the exterior compulsory spots of the RH adsorbent and on aqueous chemistry [39]. In acidic pH protonation of CV takes place and this protonation results in three positively charged nitrogen atoms which then combine with the negatively charged surface of rice husk easily. At higher pH, the protonation of CV decreases which in turn results in decreases in % age removal. As crystal violet is a cationic dye that exists as a positively charged ion in an aqueous solution. Subsequently, for the charged species, the degree of adsorption onto the surface of RH is dependent upon the surface charge of the adsorbent that depends upon solution pH. The point of zero charges of the biomass is 1.3 [49,50]. When the solution pH is greater than the pH of the point of zero charges, the surface of RH becomes negatively charged with more functional groups on its surface available for bonding. At pH > 1.3 electrostatic attractions take place between positively charged dye and negatively charged rice husk surface. As the maximum removal takes place up to pH 2 so this pH is further employed in the optimization of other parameters of adsorption.

4.4. Influence of RH adsorbent dose

Adsorbent dose, a noteworthy factor, affects the adsorption procedure greatly via influencing the adsorption dimensions. For that reason, the impact of adsorbent dosage upon CV through rice husk remained studied in the range of 0.1–1.0 g while keeping other adsorption parameters constant. The percentage exclusion of 82.2–93.6 takes place by changing the adsorbent dosage from 0.1 to 0.5 g (Fig. 4). The increase in percentage exclusion of CV colorant on rice husk might be owed to rise in superficial locates of rice husk supplementing the number of adsorption places accessible for the adsorption phenomena as conveyed [46]. Further increase in adsorbent dosage from 0.5 to1.0 g does not result in significant amputation of CV colorant through prepared normalized solution [51,52]. The increase in adsorbent dosage at a constant concentration of dye and volume may results in filling of all adsorbent sites due to particle interaction that results in accumulation or aggregation of the particles [48]. Such aggregations may go-ahead to reduce the capacity of the rice husk Therefore the following experiment was conducted further with the constant amount of rice husk, that is, 0.5 g.

4.5. Influence of adsorbate concentration

The percentage exclusion of dyes from aqueous media is greatly dependent upon the concentration of adsorbate, that is, the initial concentration of dye. The influence of adsorbate concentration relies upon the instantaneous relation amongst the CV dye and the accessible binding positions of the RH surface. The effect of the concentration of dye (100–450 mg/L) has been observed by keeping all the other adsorption parameters constant. It is evident from the figure that an increase in adsorbate concentration results in a decline in percentage removal of CV on rice husk. The percentage removal of CV dye decreased from 96.35% to 86.49% by increasing concentration from 100 to 450 mg/L (Fig. 5). The decline in percentage elimination through an increase in adsorbate concentration is due to the unavailability of sites on the exterior of the rice hull [52]. When the concentration of dye is low, there would be uninhabited binding positions next to the adsorbent external, and if this initial concentration of colorant upsurges there will be insufficient binding sites which result in decrease percentage removal of dye. The results prove that the adsorption procedure of CV is much dependent on its concentration. These observations are closely related to the reported observation [53] where a decrease in percentage removal occurred by increasing initial dye concentration.

4.6. Influence of contact time

The consequences of contact time on CV colorant using RH substantial are depicted in Fig. 6. It can be perceived easily that there is the rapid removal of CV dye in the first 30 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. 6 that 67% to 86.6% removal of CV occurs using RH as an adsorbent [51,52]. 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 [54]. The increase in the extent of removal of CV with the increase in contact time is due to that it formed a monolayer on the RH surface.

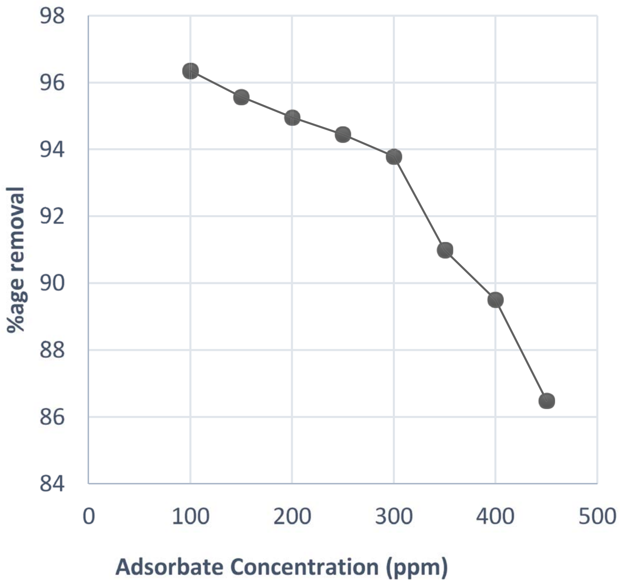

Fig. 5. Outcome of adsorbate concentration.

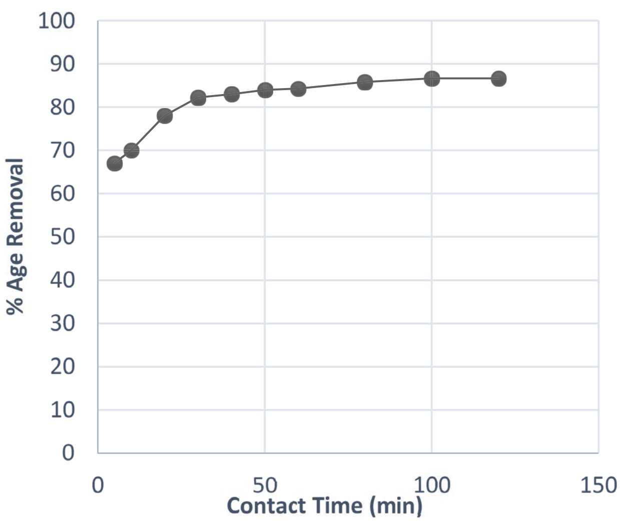

Fig. 6. Outcome of contact time on CV using RH.

4.7. Influence of temperature

Temperature, an important parameter, serves as an indicator as to whether the adsorption is an endothermic or an exothermic process. In demand to observe the consequences of temperature upon the percentage removal of CV dye using rice husk, experiments were conducted by ranging the temperature from 0°C to 50°C. It was detected that the removal of CV was found to be 83%–95% keeping other adsorption parameters fixed. The results can be seen in Fig. 7. This Fig. 7 revealed that the increase in temperature will raise the movement of ions of CV dye and a swelling effect will be produced within the structure of the rice husk that will permit the saturation of large molecules of dyes further in the rice husk [47]. The temperature influences the removal of dyes by changing the solubility of dyes and the interactions of molecules [55]. The rise in percentage exclusion of CV colorant by an upsurge in temperature is might be the more interaction between CV dye (adsorbate) and rice husk surface.

4.8. Adsorption isotherms

Three adsorption isotherm representations namely, the Langmuir, Freundlich, Dubinin–Raduskevich (D–R), adsorption isotherm were put on to discuss the affiliation among the CV concentration remain in liquid and that adsorbed upon the rice husk's exterior. Fig. 8 shows the Freundlich isotherm of CV adsorption on rice husk. It is clear from the plot and the value of correlation coefficient (0.9989) that the experimental data best described with Freundlich adsorption isotherm in this study. A Freundlich isotherm constant "n", whose value was calculated and comes out to be greater than 1 indicates the adsorption of crystal violet colorant upon RH is a promising procedure. The plot and the parameter's value of Freundlich isotherm show its adequacy for CV adsorption on RH showing that adsorption principally happened on the diverse surface of rice husk [56–58]. Similar results have been reported for the adsorption of CV by coffee husk [46,51].

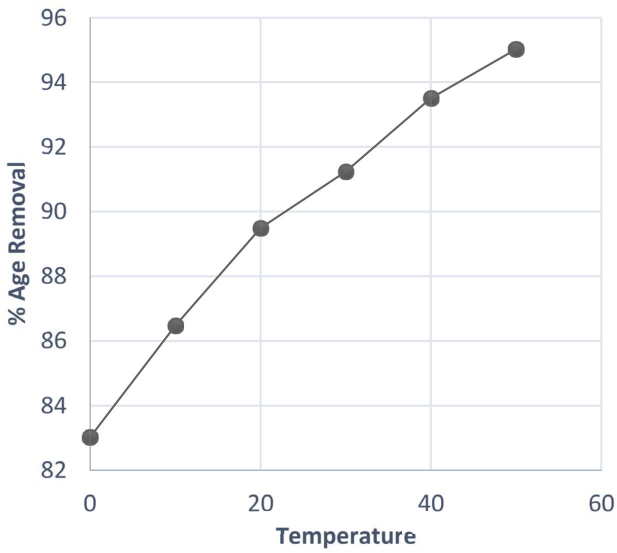

Fig. 7. Outcome of temperature on CV on RH.

The Langmuir isotherm model for the CV adsorption on RH is made known in Fig. 9. The Langmuir isotherm constants have been calculated which showed the Langmuir model was found to be appropriate for CV adsorption utilizing RH powder. Furthermore, the maximum CV colorant sorption capacity of rice husk bring into being was 53 mg/g. The Dubinin–Radushkevich model for CV adsorption on RH is represented in Fig. 10. The D–R isotherm has a high value of correlation coefficient, that is, 0.9994 so it can be concluded that both Freundlich and D–R isotherms are appropriate for CV adsorption on RH. The value of E_s comes out from calculations is 1.12 kJ/mol revealing that the adsorption study of CV adsorption on RH is physisorption in nature as E_s the calculated value is not as much as 8 kJ/mol.

4.9. Adsorption kinetics

The four kinetical models, that is, pseudo-first-kinetical order, pseudo-second-kinetical order, intra-particle diffusion model, and liquid film diffusion models were directed for the investigation of the possible rate-determining step and reaction pathways of CV adsorption on the rice husk. Based on the established plot of pseudo-first-kinetical order (Fig. 11) and the parameters' values, it can be stated that there is no correlation between experimental q_e value, that is, 399.9 mg/g, and the value of q_e calculated from the graph, that is, 0 mg/g as well as having a low R^2 value, that is, 0.946. Therefore, it might be resolved from the above figure, experimental statistics, and the parameters of pseudo-first-order

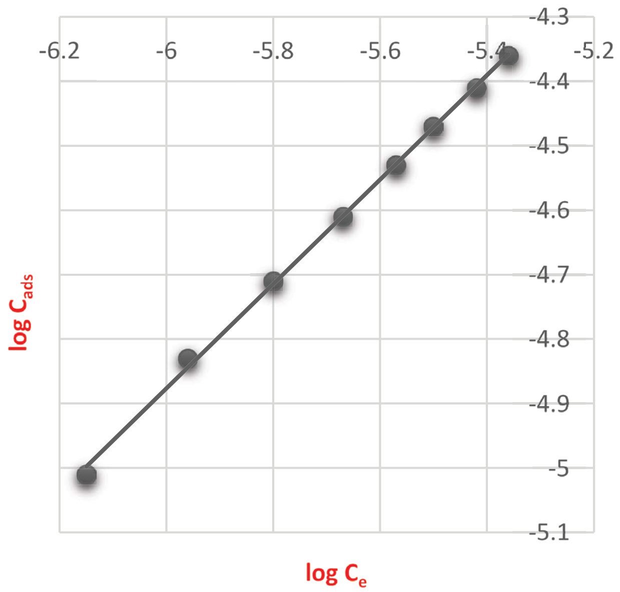

Fig. 8. Freundlich isotherm of CV on RH.

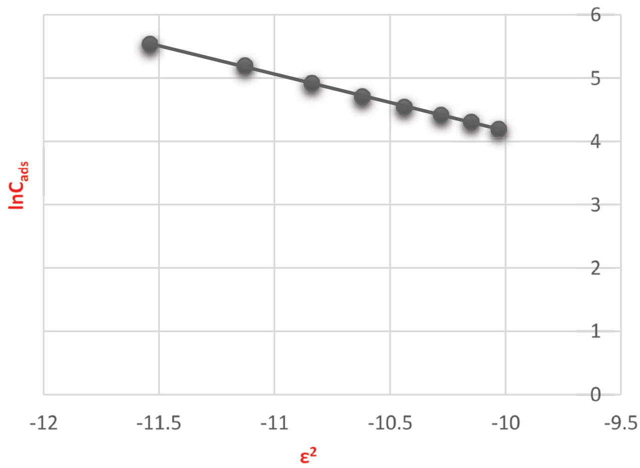

Fig. 10. D–R adsorption model.

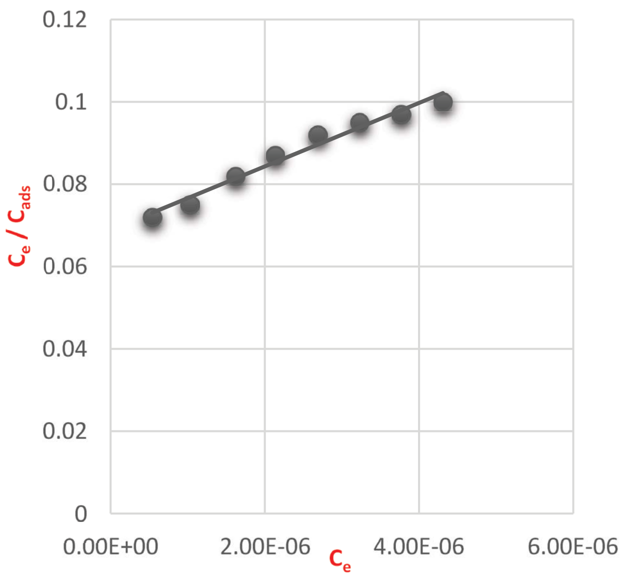

Fig. 9. Langmuir isotherm of CV on RH.

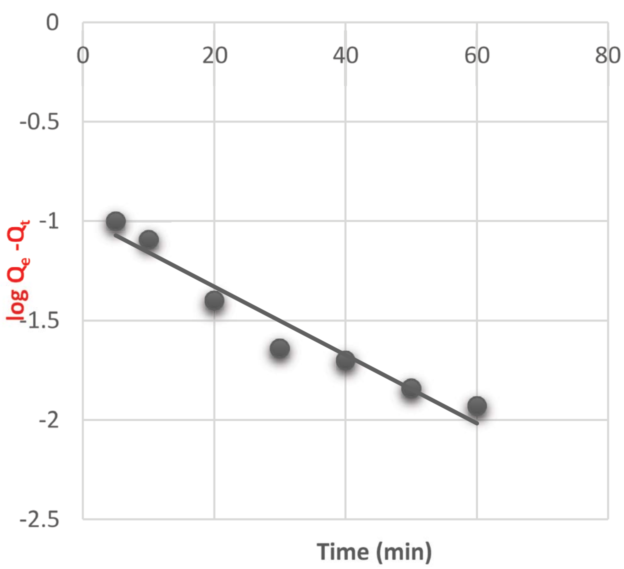

Fig. 11. Pseudo-first-order kinetic model.

calculated for CV on to RH that it is not a favorable model in the present study. The plot of t/q_t against t is represented in Fig. 12. Conflicting toward the pseudo-first-kinetical order, the kinetics data best fits with the pseudo-second-kinetical order showing an excellent undeviating curve with an extraordinary corresponding coefficient, R^2. According to the calculations, the intended q_e (400 mg/g) agree with the experimental q_e (399.932 mg/g) and also the linear regression coefficient has a higher value than the first-order kinetical equation (R^2 = 1.00). Thus, it proves that the adsorption of CV on RH follows a pseudo-second-order kinetical model [46,51,52]. The analogous effect has also been informed for CV dye adsorption on NMRH [44]. According to the equation, if the plot of Q_t vs. $t^{1/2}$ shows a conventional route then the adsorption mechanism will follow the intra-particle diffusion model shown in Fig. 13.

However, the present study of CV on RH entails that even though the intra-particle diffusion model (R^2 = 0.9344) involves in this adsorption course, however, this is not the rate-controlling step and some other procedures are also involved in the adsorption mechanism. The graph drawn between β and t for the adsorption of crystal violet on RH is a straight line shown in Fig. 14 having an R^2 value of 0.9378. The plot is unable to pass through the origin showing the limitation of the Reichenberg model in the applicability procedure of CV dye adsorption on rice husk. Several mechanisms played their role in adsorption so it could be concluded that the adsorption phenomenon cannot be determined by a single model.

4.10. Thermodynamic study

The plot of rectilinear Van't Hoff equality for the adsorption of crystal violet dye on RH is represented in Fig. 15. Negative denominations of ΔG° indicate impulsive character and the probability of CV colorant adsorption onto rice husk [51]. The negative ΔH° values obtained for CV adsorption on rice husk confirm the exothermic character of the adsorption course [51,52]. The extent of enthalpy (ΔH°) possibly indicates the sort of adsorption procedure. If the heat progressed throughout physical adsorption has the same order of magnitude as the heat of condensation that is 2.1–20.9 kJ/mol then the process will be physical adsorption while the chemical adsorption is in the following range, that is, 80–200 kJ/mol. Therefore, CV adsorption on RH is may be physical adsorption (–17.87 kJ/mol). While the positive values of entropy (ΔS°) point out that the randomness of molecules increased during this adsorption process.

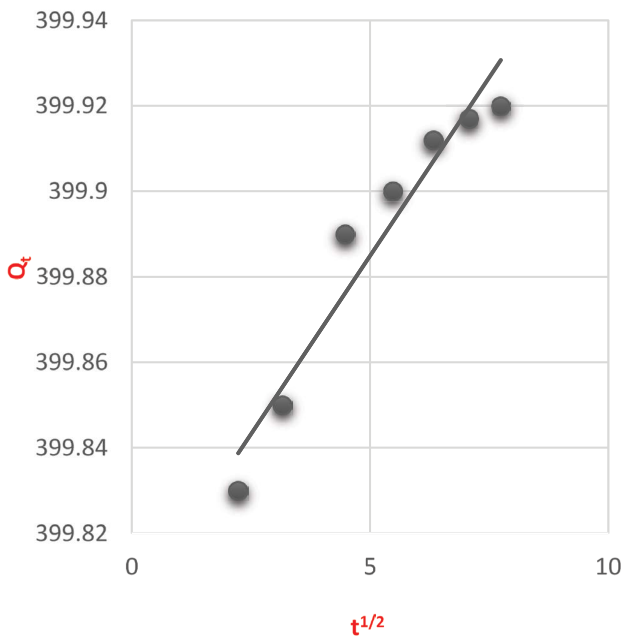

Fig. 13. Intra-particle diffusion kinetical model.

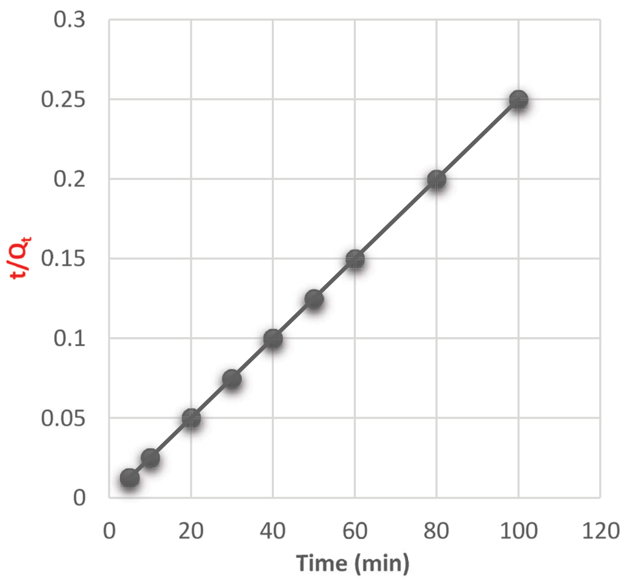

Fig. 12. Pseudo-second-order kinetic model.

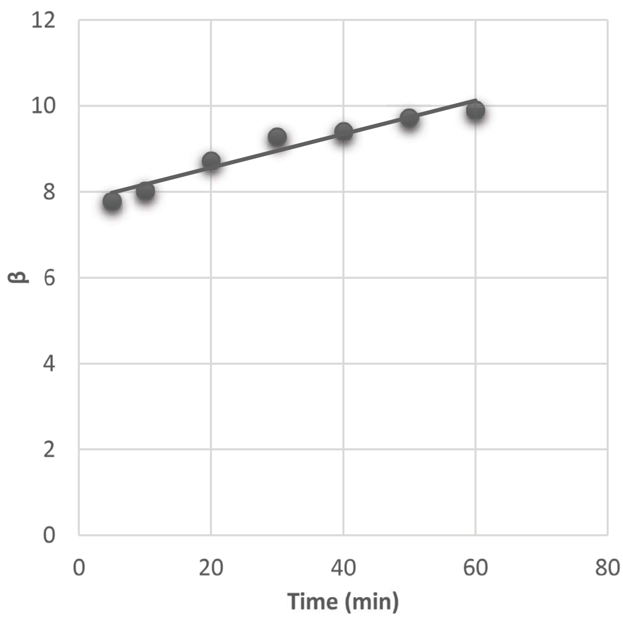

Fig. 14. Liquid film diffusion model.

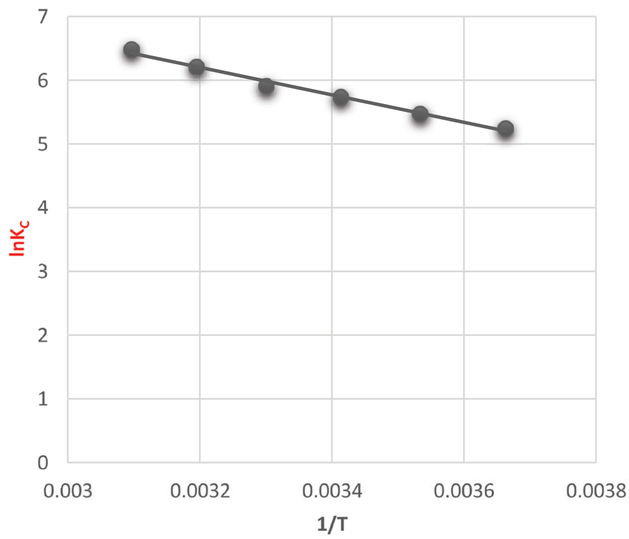

Fig. 15. Van't Hoff plot for CV adsorption on RH.

4.11. Appraisal of RH employing other sorbents

Table 1 sums up the appraisal of the thoroughgoing crystal violet adsorption capabilities of many adsorbents together with unmodified RH. This appraisal displays that rice husk has developed a value of q_e compared to previously reported adsorbents. Moreover, the rice husk loaded with CV dye can be used as fuel in boilers after drying. The ash of RH produced in boilers is used to form the flame lumps, consequently, disposal of crystal violet could be made possible and done with a chemical fixation procedure. The disposal of RH substantial ensures the energy retrieval and the innocuous dumping of crystal violet dye from an aqueous medium. Thus, the use of RH as an adsorbent is thought to be an economic attempt because of its mandatory and needy utilization for wastewater treatment processes.

5. Conclusion

This revision demonstrates that the RH is an efficient substance for the elimination of CV colorant from an aqueous medium. The batch adsorption method was adopted to observe the consequence of various factors of adsorption includes pH, adsorbent prescribed amount, contact period of adsorption, initial concentration of dye, and temperature, and the conditions were optimized one by one. The highest percentage removal of CV dye was observed at 30 min contact time, having a temperature of 30°C and adsorbent dosage of 5 g. Also, the dye adsorption was found to be exceedingly reliant on the pH of a solution. CV dye was optimally adsorbed on the RH surface at pH 2. Out of three models, Freundlich, and D–R models describe the adsorption process well showing that adsorption occurs on the heterogeneous surface and its nature is physisorption. The kinetic study exposed that the investigational and observed facts fit satisfactorily with the pseudo-second-order kinetical model whose regression coefficient value is 1.00 (greater than all four models studied). Negative values of $\Delta G°$ indicate the feasibility and spontaneous nature of adsorption and $\Delta H°$ values point out the exothermic character of CV adsorption on rice hull. While the positive values of entropy ($\Delta S°$) indicate that the randomness of molecules increases during this adsorption course. The maximum adsorption capacity value, that is, q_e on RH was compared with many other adsorbents and was found to be comparatively better. So, it can be concluded from the above results that RH could be employed as a promising, low price, effective substance for the elimination of colors and dyes from wastewater.

Table 1
Comparison of CV adsorption capabilities of many adsorbents together with unmodified RH

Sorbents	q_{max} (mg/g)	References
Coniferous pinus bark powder	33.1	[59]
Rice bran	42.28	[60]
Calotropis procera leaf	4.15	[61]
Orange peel	14.4	[62]
Sugarcane dust	3.7	[63]
Neem sawdust	3.7	[64]
Jute fiber carbon	28	[65]
Skin almond	85.49	[66]
Coir pith	2.58	[67]
Treated coir pith	95	[68]
Sugarcane fiber	10.46	[69]
RH	53.00	[This study]

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