

Aloe vera biomass containing cellulosic moieties used as sustainable adsorbents for the removal of crystal violet dye from aqueous solution

Akil Ahmad^{a,b,*}, David Lokhat^{a,*}, Mohd. Rafatullah^b, Asma Khatoon^c,
Siti Hamidah Mohd Setapar^c

^aDepartment of Chemical Engineering, Howard College Campus, University of KwaZulu Natal, Durban 4041, South Africa, emails: akilchem@yahoo.com (A. Ahmad), lokhat@ukzn.ac.za (D. Lokhat)

^bSchool of Industrial Technology, Universiti Sains Malaysia, Penang 11800, Malaysia

^cSchool of Chemical and Energy Engineering, Universiti Teknologi Malaysia, Johor 81310, Malaysia

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ABSTRACT

A chemically treated *Aloe vera* adsorbent was prepared for the removal of hazardous crystal violet (CV) dye from an aqueous system. The chemically modified adsorbent and the adsorbent after uptake of CV dye were characterized by Fourier-transform infrared spectroscopy and scanning electron microscopy. Various physico-chemical parameters such as pH (2–10), contact time (15–180 min), adsorbent dosage (0.05–0.5 g), initial dye concentration (50–400 mg L⁻¹), and temperature (30°C–60°C) were investigated. These parameters were found to have a significant influence on the adsorption process. The maximum adsorption capacity of CV was found at pH 9. Adsorption isotherms (Langmuir, Freundlich and Temkin) and kinetic parameters (pseudo-first-order, pseudo-second-order and intraparticle diffusion) have been applied to the experimental data. The adsorption of CV onto treated *Aloe vera* was best represented by the Langmuir isotherm and followed the pseudo-second-order kinetic model. Thermodynamic calculations of free energy, enthalpy and entropy were carried out. These calculations showed that the adsorption process is spontaneous, endothermic and results in increased randomness in the adsorbent/adsorbate interface. *Aloe vera* waste has been applied as potential low-cost adsorbent for the removal of dyes from water and wastewater.

Keywords: *Aloe vera* waste; Cellulosic moieties; Crystal violet; Adsorption isotherm; Kinetic parameter; FTIR

1. Introduction

The lack of access to clean drinking water in the developing world is a persistent problem. The demand for clean water resources has become increasingly urgent throughout the world, owing mainly to the rapid growth in the global population. Water is the most essential and vital resource for the survival of all plants, human beings and other living organisms on earth. Major water contaminants having organic and inorganic moieties include insecticides, pesticides, coloring dyes, industrial solvents, heavy metals, fertilizers, industrial discharges, etc [1–4]. These pollutants are

highly toxic and carcinogenic in nature. Dyes are commonly employed from many industrial fields such as textiles, paper, cosmetics, plastics, rubber etc., to color the various commercial products. Due to the use of these color compounds, a large amount of toxic, colored wastewater is produced and discharged into surrounding water bodies.

Crystal Violet (CV) is a triphenylmethane dye (chemical formula: C₂₅N₃H₃₀Cl) which is extensively employed in many industrial applications, such as coloring cotton and silk, as a pH indicator, gram staining to classify bacteria, in paints, in printing ink and so on. The toxic effect of this dye can be harmful to animals and humans either through direct interaction or by ingestion and inhalation [5]. Because of the complicated chemical structure (Fig. 1) of CV, it is very

* Corresponding authors.

challenging to remove the chemical from wastewaters by conventional methods, e.g. chemical precipitation and biological treatment.

Various procedures, for example ion exchange, flocculation, coagulation, precipitation, biosorption, photo-oxidation, photocatalysis, and electrochemical membrane-filtration techniques, have been employed to remove dye from water and wastewater. [6–10]. Apart from the aforementioned techniques, adsorption has been considered as a very simple, efficient and cheap process used for the removal of dye from wastewater [11–13]. Many plant based waste materials have been used as potential sources to develop economical adsorbents. Numerous plant based waste materials have been reported as suitable for the adsorption process, namely agricultural waste [14], olive cake waste [15], corn stalks [16], sunflower piths [17], rice straw [18], banana and orange peels [19], pineapple waste [20], *Punica granatum* shell [21] amongst others. The nature of these waste materials plays a significant role in their efficacy for dye removal from wastewater. Therefore, improvement in the adsorbents prepared from locally sourced waste materials still needs to be explored, in particular their effectiveness for the removal of organic dyes from wastewater.

Aloe vera is a thick, fleshy, green or grey-green coloured plant with a short stem (60–100 cm). Generally it is found in tropical regions throughout the world. It is cultivated for ornamental, agricultural and medicinal purposes [22,23]. *Aloe vera* raw material sales are estimated to be up to \$70–90 million globally according to “The International Aloe Science Council (IASC)”. The Aloe Council of South Africa was established in 2006 with the aim to promote the *Aloe vera* product in the commercial market. Different types of *Aloe vera* species are cultivated in almost all the provinces of South Africa. It is an available, cheap and eco-friendly bio-material. Therefore, *Aloe vera* waste can be used as potential biosorbents for the removal of inorganic and organic contaminants from wastewater.

In the current work, chemically treated *Aloe vera* waste was selected as a potential adsorbent for removal of CV dye from solution. Batch experiments were performed

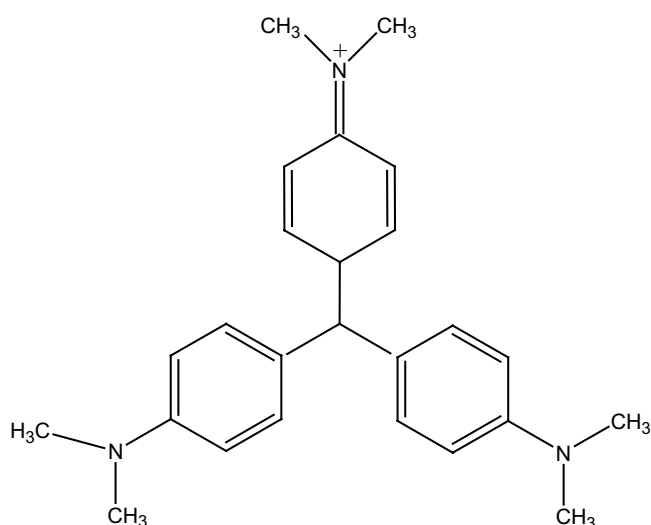


Fig. 1. Chemical structure of Crystal Violet (CV).

to determine the adsorption capacity and investigate the effectiveness of *Aloe vera* waste as an adsorbent. Various aspects of the adsorption process such as equilibrium, thermodynamics and kinetics were investigated. Operating parameters including contact time, initial CV concentration and pH were varied and their effect on the sorption performance was determined. Different kinetic models (pseudo-first-order, pseudo-second-order and interparticle diffusion) and adsorption isotherms (Langmuir, Freundlich and Temkin) for CV adsorption onto *Aloe vera* were also investigated. The mechanism of dye adsorption onto the surface of the adsorbent was also discussed.

2. Materials and methods

2.1. Materials

CV {Tris(4-(dimethylamino)phenyl)methylium chloride; molar mass: 407.979 g mol⁻¹; molecular formula: C₂₅N₃H₃₀Cl} was obtained from Sigma Aldrich (Germany). Analytical grade reagents were used without further purification and were obtained from Sigma-Aldrich (Germany) and Fluka (Germany). A standard solution with a concentration of 1,000 ppm CV in distilled water was prepared. Various concentrations of the CV solution were synthesized by the dilution of the standard solution with additional distilled water. These solutions were used as the adsorbate. The pH of the various solutions was modified using NaOH (0.1 M) and HCl (0.1 M), respectively. Demineralized water (DMW) was used throughout the experimental work.

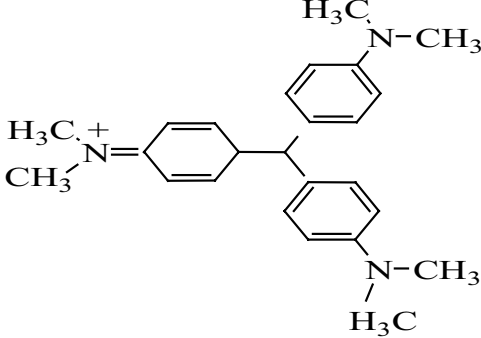
2.2. Preparation of biosorbents

Aloe vera leaves were collected from the Glenmore area, Durban, South Africa. Untreated *Aloe vera* leaves were washed 2–3 times with distilled water to eliminate the dirt and sediment materials. Afterwards these leaves were sliced into small pieces and the flesh was removed. The thick epidermis or skin portion was collected and sun dried for 2 d. Afterwards these samples were placed in an oven at 80°C for 48 h. Dehydrated materials were ground in a mortar and pestle and sieved to obtain a sample of 150–250 mm particle size. Particle size 150–250 mm adsorbents were used for the adsorption experiments. Sulfuric acid (H₂SO₄) and zinc chloride (ZnCl₂) in a ratio of 1:1 was used to treat the biomass materials for the activation of functional groups present in adsorbents [24]. 25 g of powdered *Aloe vera* leaf was soaked in the prepared solution overnight. Afterwards the materials were filtered and washed many times with deionised water to eliminate extra acid present in the biomass. After washing, the material was dried in an oven for 24 h at 80°C and used for additional application in the adsorption process. Finally, chemically treated *Aloe vera* biosorbent was used to study the various physico-chemical parameters. The relevant physical and structural properties of CV and *Aloe vera* are presented in Table 1.

2.3. Characterization of adsorbents

Fourier-transform infrared spectroscopy (FTIR) spectra of acid treated and CV saturated *Aloe vera* biosorbent were

Table 1
Various chemical and physical properties of adsorbent and adsorbate

<i>Aloe vera</i>	Properties
Family	Liliaceae
Botanical name	<i>Aloe barbadensis</i>
Structure	Thick and green fleshy, lance-shaped leaves
Origin	Mainly found in Africa, Mexico, South and central America, India, Australia, Iran and Caribbean
Chemical constituent	Approx. 75 biologically active compounds includes, polysaccharides, sugars, mannose, chitin, lignin, saponins, enzymes, minerals, salicylic acids and amino acids
Medicinal application	Antioxidant, anticancer, anti-inflammatory, anti-diabetic and anti-ageing properties
Chemical structure	
Chemical formula	$C_{25}H_{30}N_3Cl$
Wave length (nm)	590
IUPAC name	Tris(4-(dimethylamino)methyl) methyl cation chloride
Molecular weight (g mol ⁻¹)	407.979
Melting point (°C)	205
Solubility	Soluble in water, chloroform, alcohol (partially soluble), glycerol (partially soluble), insoluble in ether

measured using an FTIR Spectrometer Nexus-670 (Nicolet, USA) operating at a wavelength of 500–4,000 cm⁻¹ with a resolution of ±4.0 cm⁻¹. Some potential changes were observed on the surface of *Aloe vera* before and after saturation with CV by scanning electron microscopy (SEM) analysis on a ZEISS LEO 1450 SEM, USA. The specific surface area and pore size of acid activated *Aloe vera* adsorbent was analysed using a Brunauer–Emmett–Teller analyser (ASAP 2010, Micrometrics Inc., USA).

2.4. Batch adsorption studies

Batch studies of the adsorption process were performed in a vessel comprising 0.2 g of adsorbent and 100 mL solution of CV (concentration range from 50–400 mg L⁻¹). This vessel was placed in a water bath shaker set at 200 rpm. The influence of pH on the sorption properties of the prepared biosorbents was investigated in the range of 2–12, with pH changes being effected by adjustment using the relevant buffer solutions. In addition, the contact time at a constant initial CV concentration of 100 mg L⁻¹ was varied between 15.0–180 min in order to optimize this parameter for the CV removal from the test solution. A UV-vis spectrophotometer was employed to determine the final concentration of CV in the supernatants after the sorption tests. The equilibrium capacities of biosorption and % removal of CV onto treated

Aloe vera powdered material were calculated according to the following expressions:

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

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

where C_0 represents the initial concentration and C_e is final concentration of CV in the test solution. V represents the volume in (L) and M denotes biosorbent mass (g).

3. Results and discussion

3.1. Characterization

The SEM micrographs were recorded for both unsaturated and CV saturated *Aloe vera* waste, which is presented in Fig. 2. It was clearly observed that some surface alteration occurred in the dye saturated sample. As shown in Fig. 2a, the surface of *Aloe vera* waste are porous. However, after adsorption of CV onto *Aloe vera* surface, the morphology has been changed and pores are filled completely, verified the CV adsorption on the surface of adsorbent (Fig. 2b).

The FTIR investigation was carried out for the determination of functional groups that exist on the *Aloe vera* surface before and after adsorption of CV dyes. The FTIR peak of the *Aloe vera* is presented in Fig. 3. As shown in Fig. 3a, two broad and strong peaks were appeared around 3,401.68 and 3,117.74 cm^{-1} , which were mainly ascribed to amine ($-\text{NH}$) and hydroxyl ($\text{O}-\text{H}$) groups and for the cellulosic part of the *Aloe vera* materials. The peak present at 2,927 cm^{-1} was attributed to the CH band of the methyl group. Furthermore, the sharp peaks appearing at 1,770 and 1,616 cm^{-1} may be due to the carbonyl band of un-ionized carboxylate extending carboxylic acids, and the C–O band of the carboxylic functional group. The peak at 1,569 cm^{-1} in the spectrum of *Aloe vera* may be due to the C=C bond of aromatic rings. The peak at 1,421 cm^{-1} correlates to the twisting vibration of CH_2 group. The peaks present in the range from 1,317 to 947 cm^{-1} may be assigned either to C–H bending vibrations or O–H bending and extending. In Fig. 3b, a strong new peak present at 1,242.66 cm^{-1} , allocated to the C–N group belonging to CV dye, confirms that CV dyes adsorb on the surface of *Aloe vera* adsorbents. As displayed in Fig. 3b, the CV loaded *Aloe vera* functional groups are moderately affected with regards to the peak positions and intensities. A shift was noticed from the range of 10–39 cm^{-1} for OH, COO^- and CO stretching vibrations, indicative of their active part in electrostatic interaction/H-bonding with CV dyes. Similar results were reported by Akar et al. and Lata et al. [25,26].

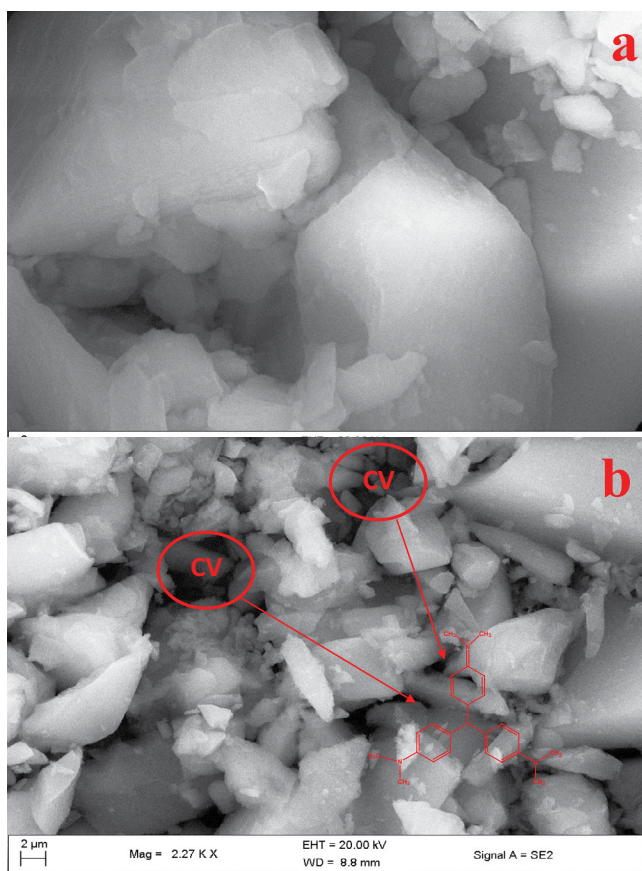


Fig. 2. SEM micrograph of *Aloe vera* (magnification: 2.27 K): (a) before adsorption and (b) after adsorption of CV.

Aloe vera powder was chemically treated with Sulfuric acid (H_2SO_4) and Zinc chloride (ZnCl_2) in a ratio of 1:1. From the results, the specific surface area of acid treated *Aloe vera* powder was $11.05 \text{ m}^2 \text{ g}^{-1}$. According to International Union of Pure and Applied Chemistry (IUPAC), pore size of materials can be classified into three major categories: as micropores (diameter (d) < 20 Å), mesopores (20 Å < d < 500 Å) and macropores (d > 500 Å). According to Barrett–Joiner–Helenda method, the average pore diameter of *Aloe vera* powder was 89.67 Å which indicates that the chemically treated *Aloe vera* powder has mesopores.

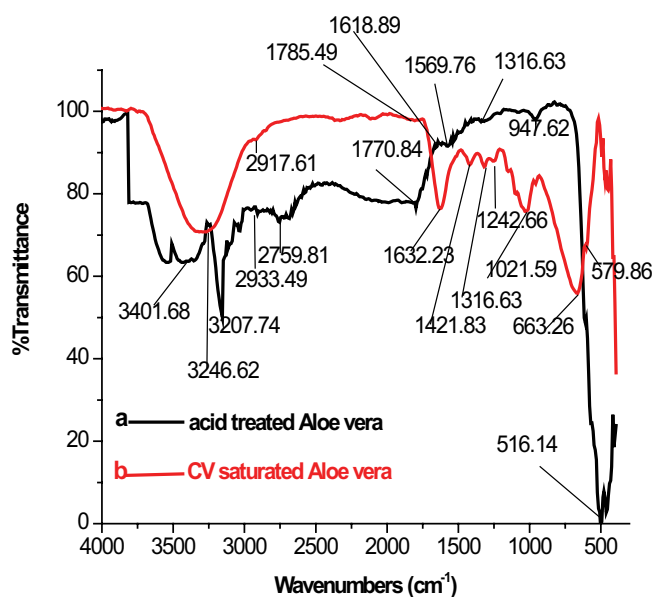


Fig. 3. FTIR Spectra of *Aloe vera*: (a) before adsorption and (b) after adsorption of CV.

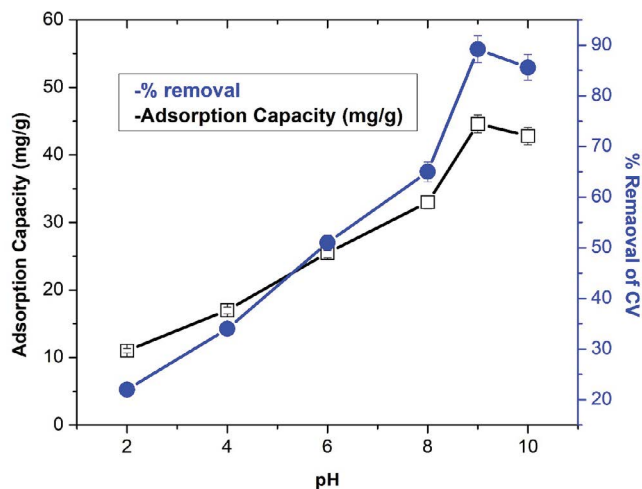


Fig. 4. Effect of solution pH on CV adsorption onto *Aloe vera* (experimental condition: CV concentration: 100 ppm; temperature: 30°C; time: 120 min and amount of adsorbent: 0.2 g).

3.2. Influence of pH and pH_{PZC}

The influence of solution pH on the CV dyes adsorption onto chemically treated *Aloe vera* was measured in the range of pH 1–10 as presented in Fig. 4. The process of adsorption is strongly influenced by the solution pH, which could be owing to a surface charge change of the adsorbents as well as ionization of dye molecules. Adsorption of CV dye onto *Aloe vera* was increased with solution pH and the highest biosorption capacity was found at pH 9, but slightly decreases when pH is further increased. The maximum adsorption capacity as observed in basic medium may be due to more negative charge (hydroxyl group) present on the adsorbent surface. Similar results were observed by other authors in the literature [27]. The adsorption of CV onto *Aloe vera* can be attributed to Van der Waals, electro static, H-bonding and $n-\pi$ interactions. In a basic medium, more negative hydroxyl ($-\text{OH}$) groups occurs, which present at the surface of *Aloe vera* adsorbents are likely to be interacting with positively charged $+\text{N}-\text{CH}_3$ of CV dyes. In other words, it may be because of electrostatic interaction among positively charged amine group of CV dyes and negatively charged adsorbents surface. Another possibility of interaction is H-bonding which occurs between nitrogen and oxygen containing functional group of *Aloe vera* surface and CV dyes. Several earlier papers have also considered the pH effect on the adsorption of CV over different adsorbents. The maximum pH for CV adsorption was reported to be in the range of 8–9 [28,29].

The point zero charge (PZC) is a physical phenomenon of adsorption and stated as pH when the surface charge of adsorbent is zero. The pH_{PZC} depends on different factors like the nature of adsorbents, temperature, impurity content and adsorption efficiency of electrolytes. This experiment was carried out by the following solid adding technique [30]. Exactly 50 mL of 0.01 M solution of KNO_3 was transferred

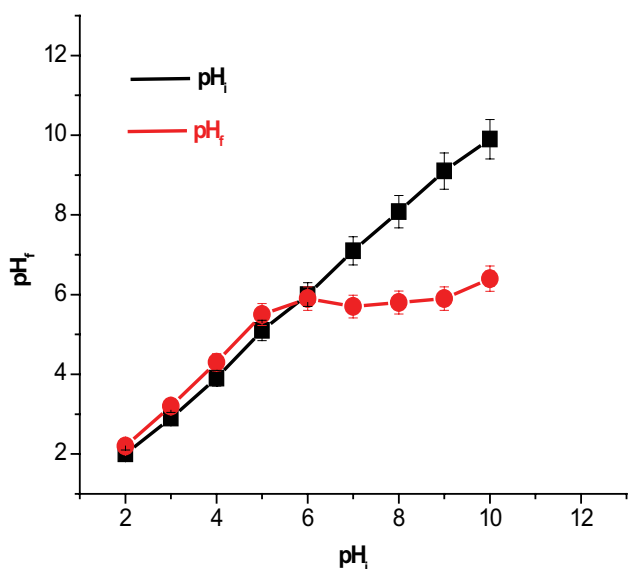


Fig. 5. Initial vs. final pH plot for the determination of pH_{zpc} of *Aloe vera* (experimental condition: CV concentration: 100 ppm; temperature: 30°C; time: 120 min and amount of adsorbent: 0.2 g).

to a flask and the solution pH was adjusted (within the range 2–10) by using the solutions of 0.1 M HCl or NaOH. Afterwards, 0.5 g of *Aloe vera* material was put into each flask. This solution was stirred with the help of a magnetic stirrer and the final pH of solution was noted after 24 h. A curve was plotted between pH_i and pH_f (Fig. 5). From the curve it was detected that the solution pH was more than the isoelectric point (pH_{PZC} 6) and therefore an accumulation of negative charge on the *Aloe vera* surface occurred in abundant amount, which favored the adsorption of positively charged dye [31].

3.3. Influence of dosage on CV biosorption

The amount of dosage (0.05–0.5 g) was varied to examine the influence of adsorbent amount on adsorption of CV. Experimental conditions for this study (dye concentration 100 ppm, 30°C, 90 min, and pH 9.0) were maintained constant. From the results, it was found that with adsorbent amount increases from 0.05 to 0.5 g, the % removal increased from 15.26% to 91% (Fig. 6). This may be possible only owing to enhancement in surface area and adsorbent active sites [32,33]. However, further increase in amount of adsorbent resulted in no further increase in the removal (%), which may be due to the capacity of available binding positions and accumulation of adsorbate molecules [21,34]. From these findings, it was concluded that there is initially an increase in % CV removal with an increase in the amount of adsorbent, which reaches a plateau and then remains constant after further increase of the dosage amount.

3.4. Desorption of dye

Regeneration of CV saturated adsorbent was carried out using different acids (hydrochloric acid, nitric acid, sulfuric acid and acetic acid). For desorption studies, 0.1 g of adsorbents was used for adsorption of CV dyes of concentration 50 mg L^{-1} . After adsorption, dye saturated adsorbent was

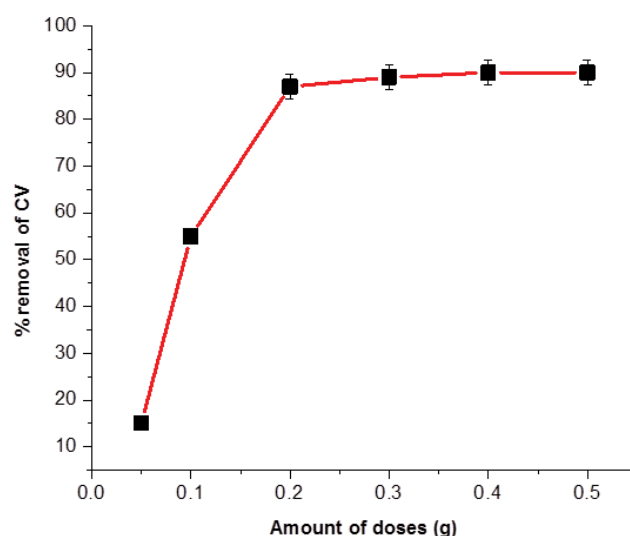


Fig. 6. Effect of adsorbent dosage on CV removal onto *Aloe vera* (experimental condition: CV concentration: 100 ppm; temperature: 30°C; time: 90 min and pH: 9).

fixed in a column (1 × 30 cm). The column was washed with distilled water to remove the unadsorbed CV dye from *Aloe vera* waste. 20 mL (0.1 M) of each acid was used to elute the dye from adsorbents. Results show that 57%, 63%, 72% and 43% dye were desorbed using four different acids such as hydrochloric acid, nitric acid, sulfuric acid and acetic acid, respectively. In this study, sulfuric acid shows better efficiency as compared to other acids used.

3.5. Influence of contact time

Contact time effect for the CV adsorption onto *Aloe vera* adsorbents is shown in Fig. 7. The experiments were carried out ranging from 15 to 180 min, under the same conditions of 30°C, pH 9.0, 0.2 g adsorbent dose, and the initial concentrations of CV was from 50 to 400 mg L⁻¹. Initially the uptake rate of CV by *Aloe vera* adsorbents increases with contact time and the solution concentration. This may be attributed to the better driving force for adsorption by concentration gradient with the initial concentration of CV increases [35,36]. As shown in the temporal curve, the adsorbate uptake is initially quick but this steadily decelerates until a

condition of equilibrium is reached. During the early stages, a large amount of free surface positions are accessible for adsorption. After some duration, the number of vacant sites is reduced and those that remain are hard to access owing to repulsive forces working among the solute particles on the bulk and solid phases. The highest removal of CV onto *Aloe vera* adsorbent was obtained after 90 min contact time and found constant after the equilibrium was reached. Once the equilibrium condition was attained, the sorption of CV was constant with further increases in time. Therefore, it was considered that a lengthier treatment may not have any beneficial effect on the behaviour of the adsorbent. With the increase in the initial CV concentration between 50 and 400 mg L⁻¹, an increase in adsorption capacity was observed onto *Aloe vera* from 16.26 to 47.59 mg g⁻¹. As shown in Fig. 7, it was found that at high concentrations the fractional CV adsorption onto *Aloe vera* is low; while at low concentrations dye uptake is fast initially, representing the fast reaction on surface. The initial concentration of CV has a significant influence on the level and frequency of uptake of CV on *Aloe vera* adsorbent. Similar results have been reported for adsorption of CV onto Date Stone [28] and water hyacinth [29].

3.6. Kinetic studies

For the prediction of rate of adsorption, a study of kinetic parameters is helpful and gives important data regarding the efficacy of adsorption [37]. For kinetics experiment of CV adsorption onto *Aloe vera*, 0.2 g of bio sorbents was added to a 100 mL solution of initial CV concentration of 100 mg L⁻¹, at 30°C temperature and at pH-9.

In this study, the rate of CV adsorption onto *Aloe vera* surface according to the pseudo-first-order [38], pseudo-second-order kinetic [39] and Weber-Morris diffusion models [40] were investigated. The pseudo-first-order kinetic models with linear equation can be represented as:

Pseudo-first-order model:

$$\log(q_e - q_t) = \log q_e - \frac{k_1 t}{2.303} \quad (3)$$

where q_e represents the solute amount adsorbed at equilibrium per unit weight of adsorbent (mg g⁻¹) and q_t represents the amount of solute adsorbed at any time (mg g⁻¹) and k_1 (min⁻¹) is the rate of constant. All the kinetic parameters values were measured from linear plots $\log(q_e - q_t)$ vs. t and are shown

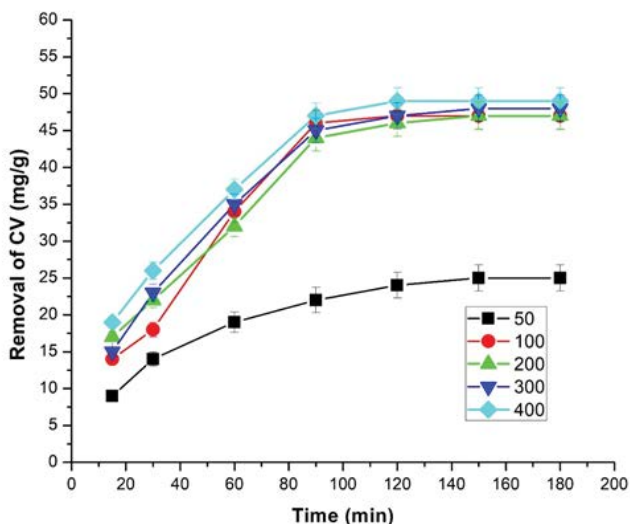


Fig. 7. Effect of contact time on CV removal onto *Aloe vera* (experimental condition: CV concentration: 50–400 ppm; temperature: 30°C; pH: 9 and amount of adsorbent: 0.2 g).

Table 2

Pseudo-first-order, pseudo-second-order and intraparticle diffusion models for the adsorption of CV onto *Aloe vera* (experimental conditions: CV concentration: 100–400 ppm; temperature: 30°C; pH: 9 and amount of adsorbent: 0.2 g)

Initial concentration ppm	Pseudo-first-order kinetic			Pseudo-second-order kinetic			Intraparticle diffusion		
	q_e (mg g ⁻¹)	k_1 (min ⁻¹)	R^2	q_e (mg g ⁻¹)	k_2 (g mg ⁻¹ min ⁻¹)	R^2	k_{id} (min ^{1/2})	C	R^2
50	18.67	1.5869	0.784	23.56	0.0027	0.957	4.927	8.856	0.772
100	30.90	1.3011	0.844	45.66	0.0013	0.989	5.741	10.367	0.819
200	37.34	1.1264	0.873	47.82	0.0034	0.972	5.924	11.652	0.856
300	41.85	1.0847	0.796	43.57	0.0017	0.969	6.153	10.558	0.732
400	39.93	1.2793	0.905	40.87	0.0023	0.982	5.868	9.747	0.805

in Table 2. From the result, the value of R^2 is very low, so the pseudo-first-order kinetic model was rejected.

Therefore, the pseudo-second-order model was further investigated for the kinetic data. The linearized equation for pseudo-second-order is stated as:

Pseudo-second-order model:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \tag{4}$$

Herein, q_t represents the amount of CV dye adsorbed (mg g^{-1}) at specified time t (min), q_e represents the CV amount adsorbed at equilibrium (mg g^{-1}) and k_2 represents the pseudo-second-order constant rate for adsorption ($\text{g mg}^{-1} \text{min}^{-1}$). The values of the kinetic parameters for pseudo-second-order were calculated from linear plots (t/q_t) vs. t . The values obtained for kinetic factors are tabulated in Table 2. From the findings, the coefficient correlation (R^2) values were observed to be much higher for pseudo-second-order as compared to pseudo-first-order. These values show that adsorption of CV onto *Aloe vera* is better represented by pseudo-second-order kinetics. Similar findings for the adsorption of CV have been presented by Porkodi and Kumar and Ahmad, [41,42].

To investigate the diffusion mechanism of CV onto *Aloe vera*, the Weber-Morris intraparticle diffusion model was examined. This is represented as:

$$q_t = k_{id} t^{1/2} + C \tag{5}$$

Herein q_t denotes the adsorbed amount (mg g^{-1}) at time t (min), k_{id} represents the diffusion constant rate ($\text{mg g}^{-1} \text{min}^{-1/2}$) and C is a constant (mg g^{-1}). The k_{id} , C and R^2 values were calculated from the slope of plot q_t vs. $t^{1/2}$ as represented in Fig. 8 and data presented in Table 2. The results demonstrate the multi-linearity for adsorption of CV onto *Aloe vera*, that

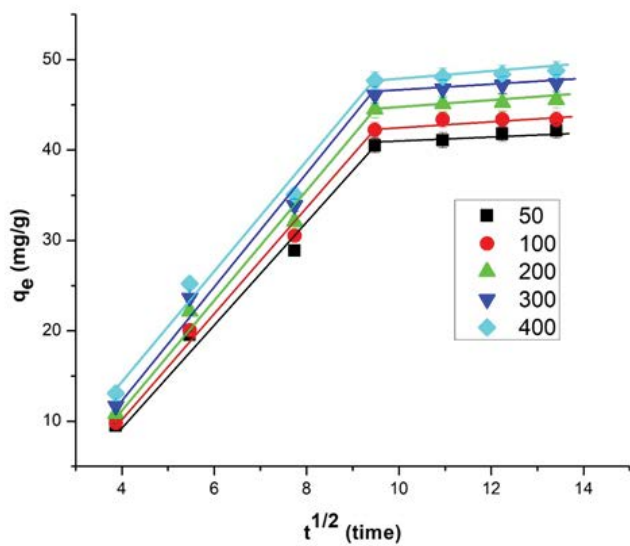


Fig. 8. Intraparticle diffusion kinetic plot for CV adsorption onto *Aloe vera* (experimental condition: CV concentration: 50–400 ppm; temperature: 30°C; pH: 9 and amount of adsorbent: 0.2 g).

is, more than one rate determining step was implicated in process of adsorption. The range of the first linear portion is ascribed to film diffusion (external diffusion) of CV onto the surface of *Aloe vera* and the region of the second linear portion represents CV diffusion into the particle. The plot presented in Fig. 8 affirmed that there are more than on critical step. From the origin some deviation is observed which shows that diffusion through the film and intraparticle diffusion were implicated in the adsorption process [43].

3.7. Adsorption isotherm

The properties of surface, adsorbate and adsorbent affinity have been categorized by employing three frequently used isotherm models viz., Langmuir [44], Freundlich [45] and Temkin [46] which are representative of the most suitable models for the adsorption process. The influence of initial CV concentration on the CV adsorption onto *Aloe vera* adsorbents is shown in Fig. 9. The Langmuir model speculates that the process of adsorption takes place at equal and homogeneous positions on the adsorbents and covers up to a monolayer of the adsorbate onto the adsorbents surface. Secondly, Freundlich model is used to discuss the nonideal adsorption on heterogenous surfaces and multilayer adsorption which is denoted by the factor of heterogeneity $1/n$. The adsorption of CV dyes onto *Aloe vera* was investigated at various concentrations ranging from 50 to 400 mg L^{-1} with fixed amount of adsorbents. The result reveals that analyse uptake increases with increasing concentration of CV dye. The enhancement in the capacity of adsorption relating to the concentration of CV may be due to the higher driving forces for mass transfer. The linearized form of Freundlich, Langmuir and Temkin isotherm are stated as:

$$\frac{C_e}{q_e} = \frac{1}{q_m b} + \frac{C_e}{q_m} \tag{6}$$

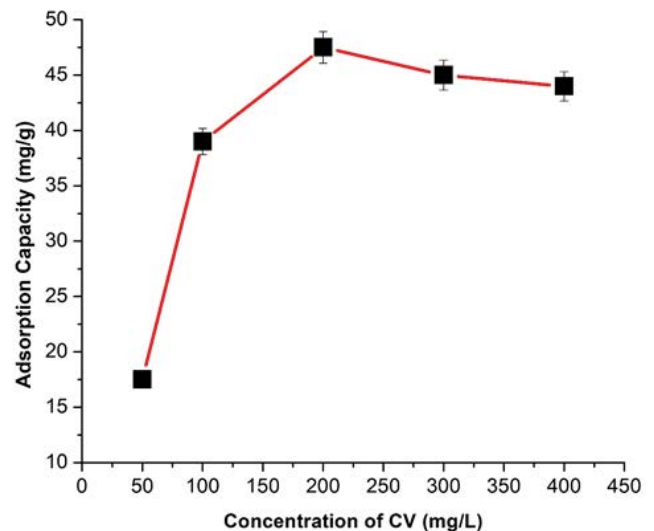


Fig. 9. Effect of initial concentration on CV adsorption onto *Aloe vera* (experimental condition: time: 90 min; temperature: 30°C; pH: 9 and amount of adsorbent: 0.2 g).

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

$$q_e = B \ln A + B \ln C \quad (8)$$

where C_e represents the CV concentration at equilibrium (mg L^{-1}), q_e represents the biosorbed equilibrium amount (mg g^{-1}) and q_m and b represents the Langmuir constants associated to biosorption capacity and biosorption of energy, respectively. A plot of C_e vs. C_e/q_e for Langmuir isotherm should be a linear line with an intercept $1/bq_m$ and slope $1/q_m$. K_F and $1/n$ are associated to the Freundlich capacity of adsorption and factors of heterogeneity. A plot of $\ln q_e$ vs. $\ln C_e$ for Freundlich isotherm should be a linear line with an intercept of $\ln K_F$ and a slope of $1/n$. A represents the binding constant with equilibrium (L mg^{-1}) and B is interrelated to the biosorption of heat. A plot of q_e vs. $\ln C_e$ gives a linear line from the curve. The values were recorded from the slope and intercept of their respected plots of the isotherm. All the isotherm values with parameters are presented in Table 3. The coefficient of correlation (R^2) of the Langmuir isotherm is comparatively high (0.9930) compared to the Freundlich (0.9870) and Temkin (0.777) correlation coefficient values. From the findings, it was found that the Langmuir isotherm was best fitted with high experimental regression coefficient

(R^2) values as obtained by linearized isotherms. Therefore, this result was confirmed that the CV adsorption onto *Aloe vera* surface occurs via a monolayer and homogeneously with no CV transmission and constant energy and in the surface plane.

The adsorption of CV was also demonstrated by Vermeulen criteria [47] and correlated with the characteristics of Langmuir adsorption isotherm. The Vermeulen principles are represented by a dimensionless separation factor " R_L ", which is expressed as:

$$R_L = \frac{1}{(1 + bC_0)} \quad (9)$$

where C_0 (mg L^{-1}) represents the initial CV concentration and b (L mg^{-1}) represents Langmuir constant. The R_L value demonstrates the isotherms shape. This can be expressed either: $R_L = 1$ (linear biosorption), $R_L > 1$ (unfavorable biosorption), $0 < R_L < 1$ (encouraging biosorption), and $R_L = 0$ (irretrievable adsorption). The R_L values were found to be in the range from 0.0019 to 0.0154 for CV adsorption which shows that the adsorption process was promising. A comparison of capacity of biosorption and other parameters of *Aloe vera* and other adsorbents used for CV removal are tabulated in Table 4.

Table 3

Adsorption isotherm parameters for the adsorption of CV onto *Aloe vera* (experimental conditions: time: 90 min; temperature: 30°C; pH: 9 and amount of adsorbent: 0.2 g)

Adsorption isotherm	Adsorption of Crystal Violet (CV) onto <i>Aloe vera</i> leaf adsorbents			
Langmuir	q_m (mg g^{-1})	b (L mg^{-1})	R^2	R_L
	44.84	1.2730	0.9930	0.0019–0.0154
Freundlich	K_F (mg g^{-1}) (L mg^{-1}) $^{-1/n}$	$1/n$	R^2	
	53.21	1.9841	0.9870	
Temkin	A (L mg^{-1})	B	R^2	
	24.54	16.22	0.777	

Table 4

Comparison of adsorption capacities and other parameters of various adsorbents for CV

Adsorbents	Adsorption capacity	Contact time	Concentration range	pH	Temperature range	References
Sulfuric acid carbonized tendu waste (TLR-CM)	22.47 mg g^{-1}	240 min	150 mg L^{-1}	3	–	[48]
Composite of <i>Typha latifolia</i> activated carbon	0.269 mg g^{-1}	60 min	20–100 mg L^{-1}	9	32°C–72°C	[49]
Jalshakti® super absorbent	12.9 mg g^{-1}	60–90 min	0.20–0.60 g L^{-1}	6.5	27°C	[50]
Jute fiber carbon	27.99 mg g^{-1}	6 h	10–40 mg L^{-1}	8.0	30°C	[41]
Leaf biomass of <i>Calotropis procera</i>	4.14 mg g^{-1}	60 min	10–50 mg L^{-1}	9.0	30°C	[51]
Coniferous Pinus bark powder hydroxides	32.78 mg g^{-1}	2 h	10–50 mg L^{-1}	8	30°C–50°C	[42]
NaOH-modified rice husk	44.87 mg g^{-1}	3 h	50 mg L^{-1}	8	20°C–40°C	[52]
Coir pith	24.75 mg g^{-1}	5 h	20–100 mg L^{-1}	NA	27°C	[53]
<i>Aloe vera</i> leaf waste	44.84 mg g^{-1}	90 min	50–400 mg L^{-1}	9.0	30°C–60°C	This study

3.8. Determination of thermodynamic parameters

To investigate the thermodynamic parameters (such as enthalpy change (ΔH°), standard free energy change (ΔG°) and entropy change (ΔS°)) for the removal of CV were evaluated by using the following equations:

$$\Delta G^\circ = -RT \ln K_c \quad (10)$$

$$\ln K_c = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT} \quad (11)$$

Herein T (K) represents the absolute temperature; R (value-8.314 J mol⁻¹ K⁻¹) represents the universal constant of gas while K_c represents the coefficient of distribution. A linear graph $\ln K_c$ vs. $1/T$ was plotted and entropy change (ΔS°) and enthalpy change (ΔH°) values were measured from the intercept and slope of linear plot for the CV adsorption onto *Aloe vera* at different temperatures, which is presented in Fig. 10. From Table 5, the ΔG° value differs from -3.975 to -9.557 kJ mol⁻¹ with temperature rising from 303 to 333 K. The negative ΔG° value shows the spontaneous nature of the process with high efficiency of adsorption of CV onto *Aloe vera*. The positive ΔH° value proves the process

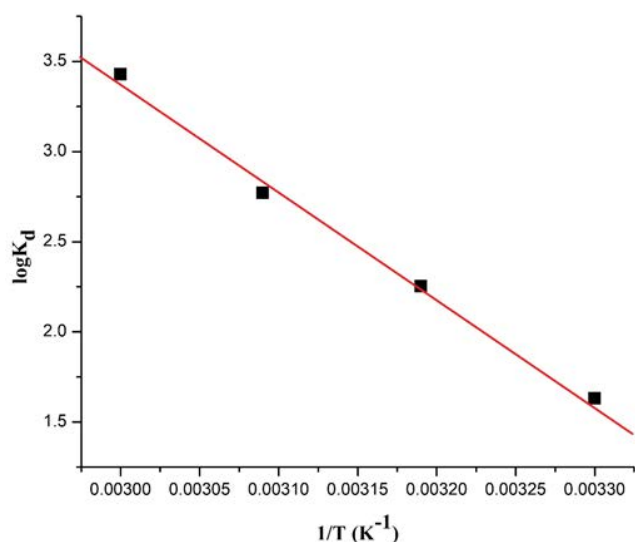


Fig. 10. Plot of $\log K_d$ vs. $1/T$ for CV adsorption onto *Aloe vera* (experimental condition: CV concentration: 100 ppm; time: 90 min; pH: 9 and amount of adsorbent: 0.2 g).

Table 5

Values of thermodynamic parameters for Crystal Violet (CV) adsorption onto *Aloe vera* (experimental condition: CV concentration: 100 ppm; time: 90 min; pH: 9 and amount of adsorbent: - 0.2 g)

Temperature (K)	ΔG° (kJ mol ⁻¹)	ΔH° (kJ mol ⁻¹)	ΔS° (kJ mol ⁻¹ K ⁻¹)	R^2
303	-3.975			
313	-5.714			
323	-7.393	11.83	33.58	0.998
333	-9.557			

of adsorption is naturally endothermic. On the other hand, positive ΔS° values proved the growth in disorderness at solid adsorbent/adsorbate interface of solution during the CV adsorption process onto *Aloe vera* [28]. The energy correlated with various physical forces such as hydrophobic bond forces (5 kJ mol⁻¹), Van der Waals forces (4–10 kJ mol⁻¹), coordination interchange (40 kJ mol⁻¹), hydrogen bond forces (2–40 kJ mol⁻¹), dipole bond forces (2–29 kJ mol⁻¹) and chemical forces (>60 kJ mol⁻¹) [54]. In this work, ΔH° was noted to be 11.83 kJ mol⁻¹ and it affirmed that physical forces were responsible for biosorption of CV onto *Aloe vera*.

3.9. Adsorption mechanism

There are several factors that can influence the adsorption behavior of adsorbents. These include the molecular structure and size of the dye, surface characteristics of the sorbents, H-bonding and steric effects, electrostatic/Van der Waals interactions etc. Positively charged amine group are present in the structure of CV dye which is a cationic dye. In basic pH, surface of *Aloe vera* has more negative charges due to presence of hydroxide (OH⁻) which favors the interaction of positively charged molecules of CV dye. The FTIR analysis of *Aloe vera* showed that hydroxyl, amine and carboxylic groups are present in abundance on the adsorbent surface. Presence of hydroxyl group on the surface of adsorbents, its oxygen part can interact with nitrogen atom of dye functionality which forms the H-bonding between CV dye and *Aloe vera* adsorbent and responsible for the removal of CV dye from aqueous solution. From the FTIR spectra, a red shift was noticed from the range of 10–39 cm⁻¹ for OH, COO⁻, and CO stretching vibrations, indicative of their active part in electrostatic interaction/H-bonding with CV dyes. The CV adsorption onto the *Aloe vera* may be owing to electrostatic attraction/H-bonding, which is shown in Fig. 11. Heibati et al. [55] also reported that the COO⁻, -OH, -HN-N group present on *Aloe vera* and +N-CH₃ groups of CV were participated in the adsorption process.

4. Conclusion

The removal of positively charged CV onto chemically treated *Aloe vera* agricultural waste (H₂SO₄:ZnCl₂) was studied using a batch procedure. The following conclusions can be drawn from the results:

- The CV adsorption onto *Aloe vera* was greatly influenced by pH of test solution. The maximum adsorption (89.2%) was observed at pH 9. The highest removal of dye was found in

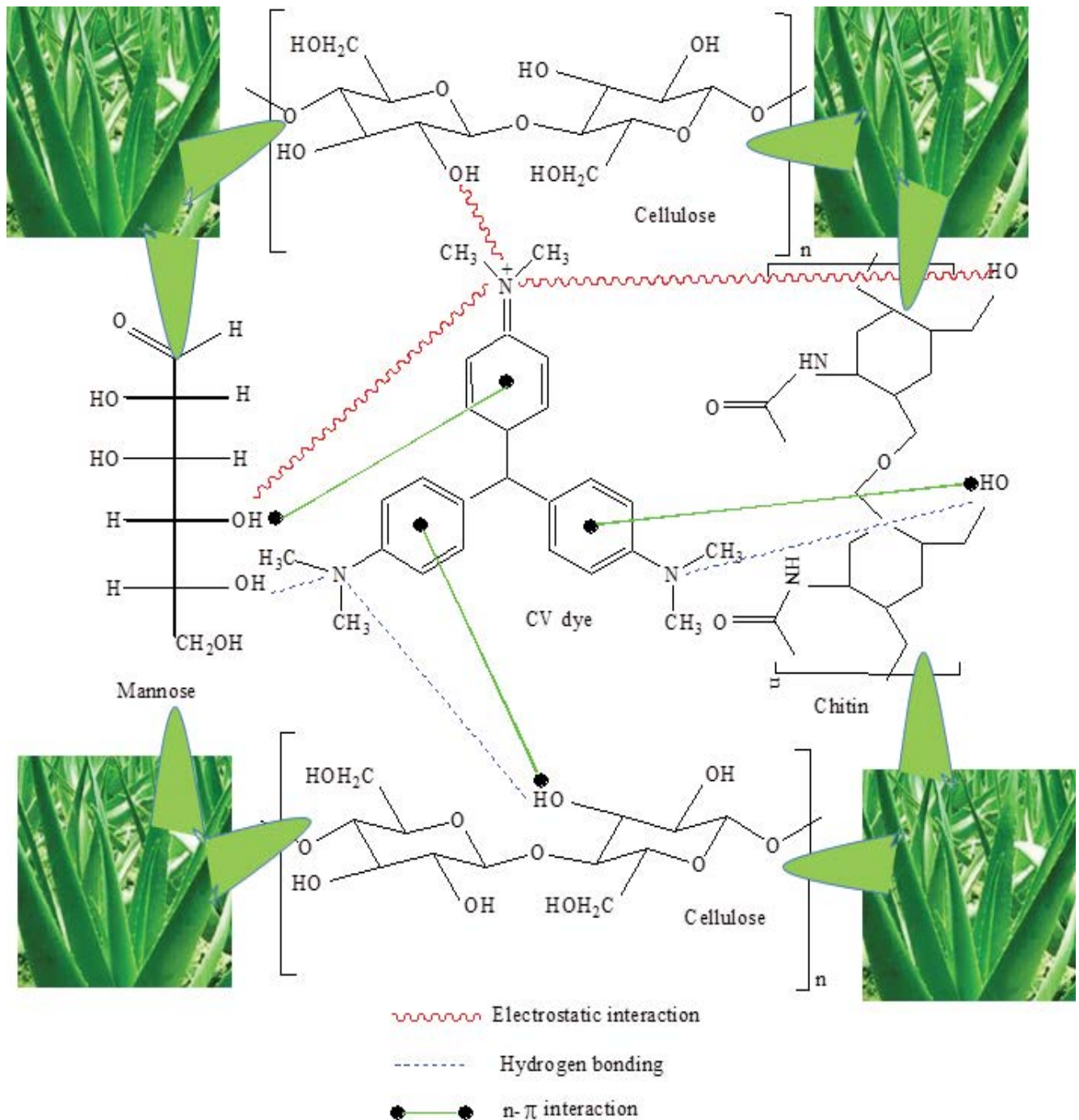


Fig. 11. Proposed mechanism of CV adsorption onto *Aloe vera*.

a basic medium which may be due to the electrostatic interaction among cationic part of dye and negatively charged adsorbent surface, hydrogen bonding and $n-\pi$ interactions.

- Various functional groups are present in *Aloe vera* such as Carboxylic (COO^-) and hydroxyl (OH) functional groups which are vital for the removal of CV from aqueous solution.
- From the results, the Langmuir model best represented the data experimental data, demonstrating homogeneous

and monolayer adsorption, and following a pseudo-second-order kinetic model.

- Thermodynamic investigations showed that CV adsorption onto *Aloe vera* were naturally spontaneous and endothermic. The ΔH° and ΔS° values are $11.83 \text{ kJ mol}^{-1}$ and $33.58 \text{ kJ mol}^{-1} \text{ K}^{-1}$, respectively.
- The *Aloe vera* material is a potential, promising, alternative, cheap and effective adsorbent for the removal of CV from wastewater.

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