



Bioremoval of crystal violet dye from aqueous solutions using *Physalis Peruviana* calyx: mechanism, biosorption isotherms, kinetic modeling, and thermodynamic analysis

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Abstract

The objective of this study is to examine the potential of the calyx of *Physalis peruviana* (PPC) as a biosorbent for the removal of the highly toxic Crystal violet dye (CV) from aqueous solutions. In order to characterise the biosorbent, a series of analyses were conducted, including FTIR, SEM, EDX, and zero point of charge analyses. The compatibility of the Langmuir, Freundlich, and Dubinin-Radushkevich isotherm models was evaluated in order to assess the biosorption isotherms. The Langmuir isotherm model, which exhibited the highest correlation coefficient ($R^2 = 0.930$), was identified as the most accurate description of the biosorption process. At 25 °C and a natural pH (4.8), the monolayer biosorption capacity was determined to be 144 mg g⁻¹. The biosorption kinetic mechanism was found to align with both the PSO ($R^2 = 0.943$), and the IPD model ($R^2 = 0.990$). The thermodynamic parameters indicated that the biosorption process is heat-absorbing ($\Delta H^\circ > 0$) and spontaneous ($\Delta G^\circ < 0$), and results in an increase in entropy ($\Delta S^\circ > 0$). It was thus determined that biological waste PPC can be evaluated as a cost efficient, renewable and effective biosorbent in CV removal and as an alternative to other sorbents that have been previously reported.

Keywords Biosorption · Cape gooseberry · Crystal violet · Wastewater treatment

1 Introduction

The accelerated pace of industrialization, population growth, unplanned urbanization, and anthropogenic activities have resulted in the release of pollutants, which present a considerable threat to our most vital resource: water. Synthetic dyes represent one of the most pervasive forms of pollution globally, with approximately 800.000 tons of 10.000 distinct types manufactured annually [1]. This is largely attributable to the simplicity of their synthesis and the rapidity of the production process [2]. The use of synthetic dyes and pigments in various industrial sectors, among others textiles, cosmetics, pharmaceuticals, rubber, food processing,

paper, and paint, represents a significant contribution to the field of coloring during production processes. However, due to the inability of these synthetic dyes to form complete bonds with the processed materials, a considerable quantity ultimately finds its way into water sources. This phenomenon brings with it environmental pollution problems that have negative effects especially on aquatic ecosystems. It prevents light from reaching the depths of the water, disrupts the photosynthesis process and causes the extinction of aquatic plants [3]. These synthetic dyes, which possess high chemical stability, low biodegradability, and high toxicity, can inflict substantial damage on the environment and human health if not removed from wastewater using an appropriate method [4]. Crystal violet dye (CV) is a synthetic, positively charged dye classified under the triaryl methane class [5]. It is classified as a synthetic dye due to its chemical composition and properties. In its powdered state, CV exhibits a dark green hue, whereas in solution it displays a purple coloration. It is employed in the textile, printing, and paper industries for dyeing purposes, as well as in veterinary medicine, where it is utilized as a bacterial growth

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inhibitor for Gram staining and as a main ingredient in disinfectants for human skin [6]. Nevertheless, at concentrations down to 1 mg/L in water systems, the widely used CV has been demonstrated to exert cancer, gene damage, birth malformations, and toxic consequences for life forms [7]. In addition, the use of the synthetic CV, which is more toxic than other anionic dyes, has been found to cause adverse effects on the human reproductive, nervous and digestive systems and other organs [8]. It is therefore imperative to identify an efficacious methodology for the removal of these highly deleterious synthetic dyes from water sources.

Significant research to date has emphasized the removal of dyes using a variety of physical and chemical processes, including precipitation [9], membrane-based filtration [10], coagulation-flocculation [11], microextraction [12], ozonation [13], chemical and electrochemical oxidation [14], photocatalytic degradation [15], and adsorption [16, 17]. While these methods are indeed effective in dye removal, they are not without their own set of drawbacks. These include the need for expensive equipment and chemicals, high power requirements, and secondary waste generation, each of which is a limitation for such approaches. The adsorption method has become increasingly popular due to a number of advantages, including being economical and easy to use, flexibility of operation, and not causing secondary pollution [18]. A significant proportion of these advantages can be attributed to the nature of the adsorbents employed. Consequently, recent studies into the removal of dyes have investigated the use of abundant, easily accessible, renewable, and non-toxic plant waste and biomasses as biosorbents. Biosorbents are composed of a variety of compounds, including cellulose, hemicellulose, lignin, and pectin. The functional groups present in these compounds, including carboxyl, carbonyl, hydroxyl, amino, and nitrogroups, can bond with the reactive groups of the dye molecules [19]. The potential of lignocellulosic biosorbents, including *Stipa tenacissima* L [20], *Sphagnum perichaetiale* [8], *Adiantum capillus-veneris* plant [21], *Urtica dioica* leaves [22], *Prunus cerasus* leaves [23], *Bambusa bambos* leaves [24], acacia leaves [25], *Laurus nobilis* L. leaves [7], and *Asplenium scolopendrium* leaves [26], for the removal of CV from water, has been the subject of investigation. Nevertheless, there is a continued requirement for biosorbents that exhibit high adsorption efficiency, are cost-effective, and comply with green chemistry standards, intending to facilitate the removal of pollutants from wastewater without requiring extensive processing. In accordance with the aforementioned trends, this study was conducted with the objective of investigating the removal of CV from aqueous solutions using *Physalis peruviana* calyx (PPC) without any prior

processing. *Physalis peruviana* L., a perennial tropical and subtropical fruit belonging to the *Solanaceae* family, is classified within the *Physalis* genus. It is cultivated and exported to numerous countries, including China, South America, and Colombia [27]. In Türkiye, this fruit, also known as goldenberry or South lantern, is characterized by a yellow-orange coloration, a juicy texture, and a round shape. During its development and maturation, the fruit is protected by a protective structure made of fibers, the calyx, which serves to shield it from pathogens, climatic conditions, and pests. This lignocellulosic structure, which constitutes approximately 5% of the fresh fruit, can be defined as a form of unused plant waste [28].

Following a comprehensive review of the extant literature, it is estimated that this study will be among the first of its kind to investigate the biosorption efficiency and applicability of PPC in the removal of synthetic dyes from aqueous solutions. PPC can be utilised as an adsorbent without the necessity for any preliminary treatment, thereby providing an economical and environmentally sustainable alternative to conventional adsorbents due to its low cost and the absence of additional chemicals. A comprehensive characterization of the biosorbent was conducted utilizing FTIR, SEM, EDX, and point of zero charge (pzc) analyses. Furthermore, isotherm, kinetic, thermodynamic, and recovery studies were conducted to evaluate the biosorption performance.

2 Materials and methods

2.1 Chemicals

The CV used in the experiment was obtained in powder form from Sigma-Aldrich, while hydrochloric acid (HCl), sodium hydroxide (NaOH), potassium nitrate (KNO₃), and methanol (CH₃OH) were also sourced from Merck. All chemicals were of analytical reagent grade. The experiments were conducted in duplicate using double-distilled water.

2.2 Adsorbate

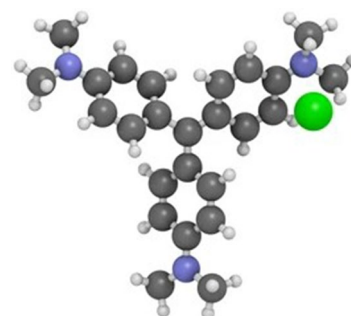
The properties of CV used as sorbate in the experimental procedure are shown in Table 1.

2.3 Preparation of the biosorbent

PPC collected from local gardens in Sivas Center was subjected to purified water to remove all contaminants. Subsequently, the material was subjected to a moisture removal

Table 1 Properties of crystal Violet

Molecular formula	$C_{25}H_{41}ClN_3$
Molar mass	407.99 g/mol
Group	Cationic dye
Apperance	Brilliant Violet
$\lambda_{max}(nm)$	592
IUPAC nomenclature	Tris(4- (dimethylamino)phenyl)methylium chloride

Molecular structure

process conducted in a thermostat-controlled oven at 50 °C for 12 h. PPC, which had been cut into small pieces, was then stored in polypropylene sample containers, to protect it from moisture, until it was utilized in the experimental procedures.

2.4 Characterization of biosorbent

The equilibrium solution concentrations of CV were calculated by measuring the CV absorbance at $\lambda = 592$ nm using a UV-vis spectrophotometer. The functional groups present in the PPC, both before and after biosorption, were identified through Fourier Transform Infrared (FT-IR) analysis.

The surface morphology of the biosorbent was examined before and after biosorption using scanning electron microscopy (SEM) coupled with energy-dispersive X-ray spectroscopy (EDX). The pH was adjusted and the PZC was determined using a pH meter. Thermodynamic studies were conducted using a thermostatic water bath.

2.5 Batch-Phase biosorption method

The CV biosorption onto PPC was analyzed employing the batch mode. Analyses were carried out by adding 50 mg PPC to 10 mL of CV solution at a concentration of 500 mg L⁻¹, natural pH (4.8) and temperature of 25 °C for 24 h. In order to gain insight into the impact of the experimental conditions on the removal of CV, a series of experiments were conducted in 10 mL polypropylene tubes, with varying parameters including initial dye concentration (10–500 mg L⁻¹), PPC amount (1–20 g L⁻¹), time (1–1440 min.), initial dye pH (2–12), and temperature (5, 25, and 40 °C).

The removal percentage of CV (% removal), the equilibrium biosorption of CV (Q , mg g⁻¹), and the recovery rate were determined using Eq.s (1), (2), and (3), respectively.

$$\% R = \left(\frac{C_o - C_e}{C_o} \right) \times 100 \quad (1)$$

$$Q = (C_o - C_e) \cdot \frac{V}{m} \quad (2)$$

$$\% Recovery = \frac{Q_{des}}{Q_{ads}} \times 100 \quad (3)$$

Here, C_o and C_e (mg L⁻¹) represent the initial and equilibrium concentrations of CV, respectively. The variable V (L) denotes the volume of the solution, while the variable m (g) represents the mass of the PPC biosorbent. Furthermore, the quantity of CV adsorbed is represented by the term Q_{ads} (mg g⁻¹), whereas Q_{des} (mg g⁻¹) denotes the amount of CV desorbed.

The pzc value of PPC was determined using the method described in the literature [29]. 0.1 M KNO₃ solutions with pH values ranging from 2 to 12 were prepared. The pH values were recorded as the initial pH (pH_i). Subsequently, 100 mg of PPC biosorbent was introduced to each solution, and the suspensions were agitated at 25 °C for 24 h. After 24 h, the equilibrium pH (pH_f) values of the mixtures were measured [30]. A graph was constructed with the difference between the equilibrium pH (pH_f) and initial pH (pH_i) values (ΔpH) on the y-axis and the initial pH (pH_i) values on the x-axis. The pzc value of the PPC was determined from the point on the graph where ΔpH equals zero.

3 Results and discussion

3.1 Characterization studies of PPC

FTIR spectra of PPC functional compounds before and after biosorption are depicted in Fig. 1. The strong broad peak detected around 3270 cm^{-1} can be ascribed to the stretching of hydroxyl (-OH) and amino (N-H) groups in alcohols, phenols, and carboxylic acids [8]. The doublet peaks detected at 2918 and 2850 cm^{-1} are thought to originate from the stretching of C-H bonds [31]. The peaks detected at 1730 and 1608 cm^{-1} can be ascribed to the carbonyl (C=O) stretching of hemicellulose and the aromatic C=C stretching of lignin's aromatic groups, respectively [32]. The peaks detected at 1412 and 1369 cm^{-1} are ascribed to the C-H bending in -CH_2 and -CH_3 ,

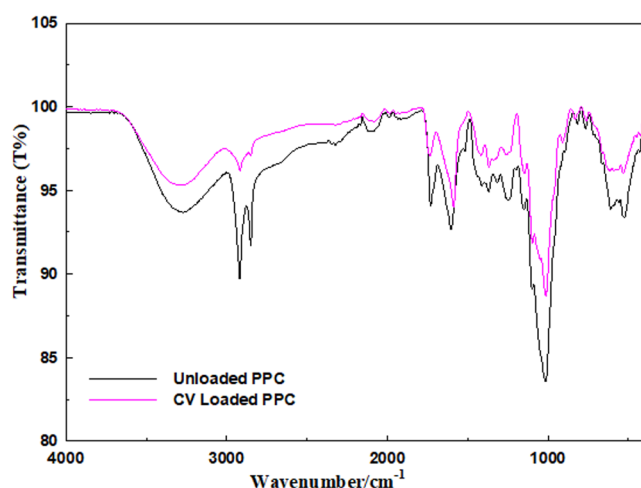


Fig. 1 FTIR spectra of PPC and CV-loaded PPC

originating from aromatic structures. The sharp and intense peak at 1098 cm^{-1} is due to C-O-C stretching vibrations [33]. When the FTIR spectra for CV-loaded PPC and raw PPC were examined, a decrease in the intensity of the peaks and differences in the positions of the peaks were detected. The aforementioned structural alterations suggest that functional groups including O-H , C-C , C=O , N-H , and C-O are actively engaged in the removal of CV molecules throughout the biosorption process and that there is a chemical interaction between the CV molecules and these groups.

SEM analysis was conducted to observe the surface morphology of the PPC biosorbent before and after CV biosorption. The results are presented in Fig. 2(a-b). Prior to the CV biosorption process, the surface of the PPC biosorbent was detected to exhibit a wrinkled and heterogeneous structure. The presence of such a structure in PPC indicates that it has a high biosorption capacity for CV molecules (Fig. 2a). In Fig. 2b, after CV biosorption, the surface of the PPC biosorbent is seen to have undergone a complete transformation. The wrinkled structure detected before biosorption has been smoothed out as the dye molecules coated the surface. The modified structures result from the effective adsorption of CV molecules, which engage with the functional groups present on the PPC surface. Additionally, the EDX spectra obtained before and after biosorption further support these findings (Fig. 2a and b). Before biosorption, the elemental analysis of PPC revealed the presence of C, O, Cl, K, and Mg elements. (Fig. 2a). Figure 2b illustrates the EDX spectrum of PPC following biosorption, which reveals the presence of 11.68% N. The detection of N, a constituent of CV, in the EDX spectrum, after biosorption provides compelling evidence of the biosorption process.

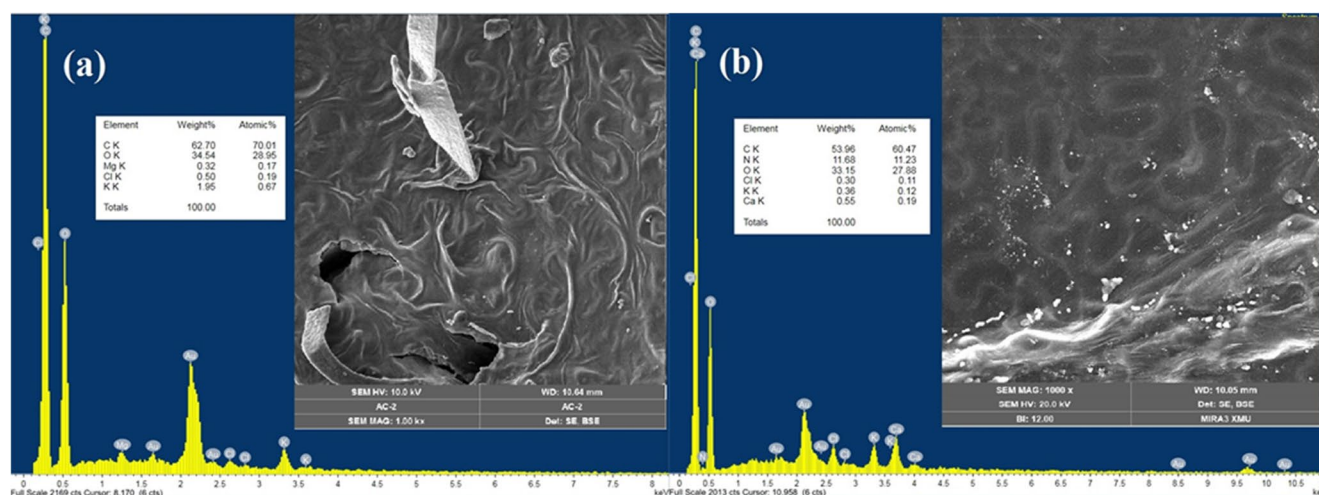


Fig. 2 SEM images and EDX spectra (a) PPC (b) CV biosorbed PPC

3.2 Impact of pH_{pzc} and pH on PPC biosorption

The impact of pH on CV removal using PPC was investigated by varying the initial pH values and the results are shown in Fig. 3.

As seen in Fig. 3, the adsorption rate increased between pH 2 and 6. However, there was no significant change in the adsorption rate between pH 6 and 12 and it was fixed. It was found that the maximum adsorption of PPC occurred around pH: 6.0.

This phenomenon can be explained by the cationic character of CV. At low pH values, the high number of H_3O^+ ions causes a decrease in the number of negatively charged centers on the biosorbent while simultaneously increasing the number of positively charged surface areas. In this case, the biosorption of cationic CV decreases.

The increase in pH values increases the number of negative charges on the PPC surface. This promotes the biosorption of cationic CV. In the study, it was determined that the biosorption of CV did not show a significant change in the pH range of 6 to 12 and could be considered constant in this range. According to previous studies, this process can be attributed to the fact that at high pH levels, CV dye molecules can transform into hydroxides and thus the biosorption of CV by the active sites of the PPC biosorbent is not enhanced [34]. At basic pH values, the number of negative surfaces on the PPC surface increases. This supports the biosorption of cationic CV. These findings are in agreement with the results in the literature on CV removal [35–37].

CV removal using PPC increases with increasing pH values. This situation can be related to the pH_{pzc} value. The pH_{pzc} value of PPC was found to be 4.03 using the solid addition method (Fig. 3). It has been demonstrated that at pH values exceeding PPC's pH_{pzc} value, the negative charge density of PPC increases noticeably. At $\text{pH}_{\text{pzc}} < \text{pH}$ values, the biosorbent surface is negatively charged due to

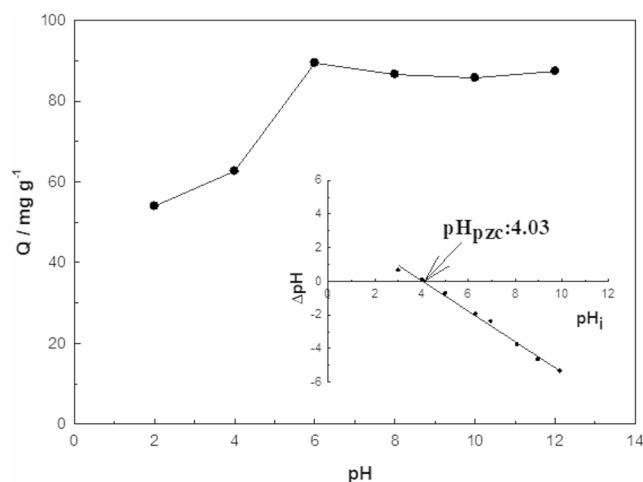


Fig. 3 Impact of pH on biosorption and pH_{pzc} for PPC

the high OH^- concentration in the solution. This supports the binding of cationic CV molecules with electrostatic attraction forces. At pH values below the pH_{pzc} value of PPC, i.e. at $\text{pH}_{\text{pzc}} > \text{pH}$ values, the biosorbent surface is positively charged due to the high H_3O^+ ion concentration in the solution. The increase in the positive charge density on the surface of PPC causes a repulsive force between the cationic CV molecules and the surface. Consequently, the biosorption of cationic CV decreases.

3.3 Impact of PPC dose on biosorption efficiency

In the biosorption process, optimizing the biosorbent dosage is essential for achieving the optimum biosorption capacity. Another aim of biosorbent dosage optimization is to reduce the cost of the biosorbent [38, 39]. Figure 4 illustrates the impact of varying biosorbent dosages ($1\text{--}20\text{ g L}^{-1}$) on the biosorption amount (mg/g) and percentage removal in 500 mg/L CV solutions. Increasing the PPC dosage from 0.01 g to 0.2 g caused the percentage removal to increase from 79% to 88% and the biosorption amount to decrease from 415 mg/g to 25 mg/g (Fig. 4). An increase in biosorbent dosage results in a higher percentage removal, which is due to the gradual enhancement of active sites or functional surface groups on the biosorbent [40]. The reduction in biosorption can be assigned to an increase in the number of sites that support biosorption while the concentration of CV remains constant, and an inability to saturate these sites to their full capacity. Given that no notable alteration in the percentage removal was discerned for biosorbent dosages exceeding 0.05 g/L, this quantity was deemed to represent the optimal biosorbent dosage.

3.4 Biosorption isotherms

Biosorption isotherm studies are conducted to explain the fundamental interaction between the biosorbent and

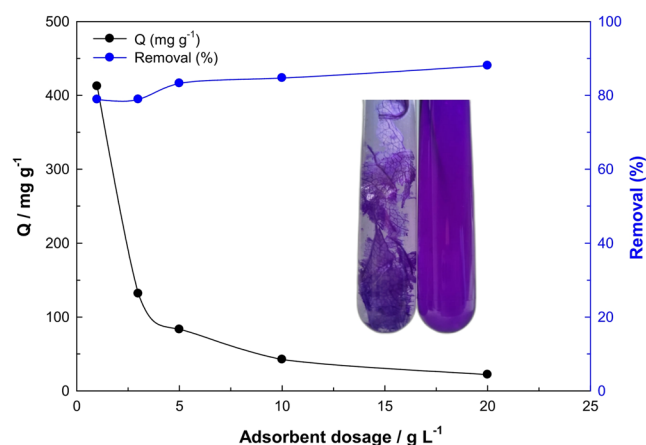


Fig. 4 Impact of PPC dose on biosorption

biosorbent after biosorption equilibrium under constant temperature and pressure, as well as to describe the biosorption mechanism. This research utilized Langmuir, Freundlich, and Dubinin–Radushkevich adsorption isotherms to model experimental data to characterize the affinity interactions between PPC and CV (Fig. 5) [41].

The Langmuir isotherm model is employed to describe physical and chemical biosorption occurring in a homogeneous and monolayered manner on the surface of the biosorbate. All active sites exhibit the same biosorption energy [42]. The nonlinear Langmuir Eq. is given in (4).

$$Q = \frac{K_L \cdot X_m \cdot C_e}{1 + K_L \cdot C_e} \quad (4)$$

Freundlich isotherm is a common empirical formula based on experimental data that describes the adsorption behavior of organic pollutants and heavy metals on various adsorbents [43]. The Freundlich Eq. is represented as follows (5).

$$Q = K_F \cdot C_e^\beta \quad (5)$$

The Dubinin–Radushkevich (D-R) model assumes that the pore distribution of the adsorbent adheres to a Gaussian energy distribution. It is also applied to explain physical and chemical adsorption processes occurring in multilayers [44, 45]. The D-R model is represented by the Eq.s below (6–8). The E_{DR} determined for biosorption indicates the nature of the adsorption process, whether it occurs chemically or physically. An E_{DR} value of 8–16 kJ mol^{−1} suggests that the adsorption process is predominantly chemical, while an E_{DR} value less than 8 kJ mol^{−1} implies that the adsorption is predominantly physical.

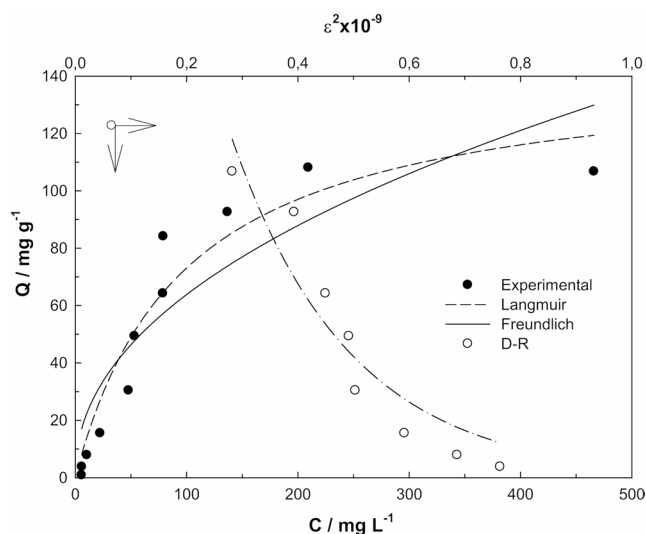


Fig. 5 Biosorption isotherms

$$Q = X_{DR} \cdot e^{-K_{DR} \cdot \epsilon^2} \quad (6)$$

$$\epsilon = R \cdot T \ln \left(1 + \frac{1}{C_e} \right) \quad (7)$$

$$E = \frac{1}{\sqrt{2K_{DR}}} \quad (8)$$

The isotherm parameters are provided in Table 2. A comparison of the correlation coefficients of the isotherms reveals that the R^2 value for the Langmuir model (0.930) is higher than that of the Freundlich model (0.821). Accordingly, the data indicate that the biosorption process is better represented by the Langmuir model, which assumes a single-layer adsorption on a homogeneous, pore-distributed surface [31]. The maximum biosorption capacity for PPC was calculated to be 144 mg g^{−1}, and the K_L value was determined to be 1.48 L mg^{−1}. The positive value of the equilibrium constant K_L indicates a strong sorption affinity between the biosorbate and the biosorbent [46]. The Freundlich isotherm model yielded $K_F = 7.61$ and $\beta = 0.462$. With $K_F > 1$ and $0 < \beta < 1$, these values indicate a strong interaction between PPC and CV molecules, confirming the suitability of the biosorption process [47]. The E_{DR} value for biosorption, calculated from the D-R model, is 10.3 kJ mol^{−1}. This value suggests that the biosorption process of CV molecules onto PPC is of a chemical nature.

A review of the existing literature reveals that various biosorbents have been investigated for the removal of CV. A comparison of the biosorption capacities of some of these biosorbents is provided in Table 3 for the reader's convenience. The results demonstrate that the biosorption capacity of PPC for CV removal is more promising than that of many other biosorbents.

3.5 Biosorption kinetics

In the field of biosorption design, the utilization of biosorption kinetic models is a prevalent practice, facilitating the determination of biosorption capacity and affinity. These properties are subject to influence by the contact time between the biosorbate and the biosorbent [52]. To determine the biosorption mechanism of CV molecules onto the surface of PPC, the experimental data were analyzed using the Pseudo-first-order kinetic (PFO) model, the

Table 2 Biosorption isotherm parameters

Langmuir	Freundlich	D-R
$X_m/\text{mg g}^{-1}$	K_F	X_{DR}
144	7.61	447
$K_L/\text{L mg}^{-1}$	β	$-K_{DR} \times 10^9$
1.48	0.462	4.72
R^2	R^2	R^2
0.930	0.821	0.885
		$E_{DR}/\text{kJ mol}^{-1}$
		10.3

Table 3 Comparison of biosorption capacities of various adsorbents for CV removal

Biosorbents	pH	Biosorption capacities (mg g ⁻¹)	Ref.
<i>Daucus carota</i> pomace	3	27	[48]
<i>Ficus religiosa</i> leaves	9	2.4	[48]
Date palm leaves	-	37.73	[49]
<i>Bambusa bambos</i> leaves	10	30	[24]
<i>Rauvolfia tetraphylla</i> leaves	7	37.12	[50]
Chestnut shell	6.8	57.8	[51]
<i>Adiantum capillus-veneris</i> leaves	3	18.51	[21]
PPC	4.8	144	This study

Pseudo-second-order kinetic (PSO) model, and the Intraparticle Diffusion (IPD) model [53]. The PFO kinetic model posits that the adsorption rate is governed by the difference between the instantaneous adsorption capacity and the equilibrium adsorption capacity. The PSO kinetic model suggests that the adsorption process is influenced by both the characteristics of the biosorbent and the solute molecules [54]. The Eq.s representing the PFO (9–10) and PSO (11–12) models are as follows.

$$Q_t = Q_e (1 - e^{-kt}) \quad (9)$$

$$H_1 = k_1 \cdot Q_e \quad (10)$$

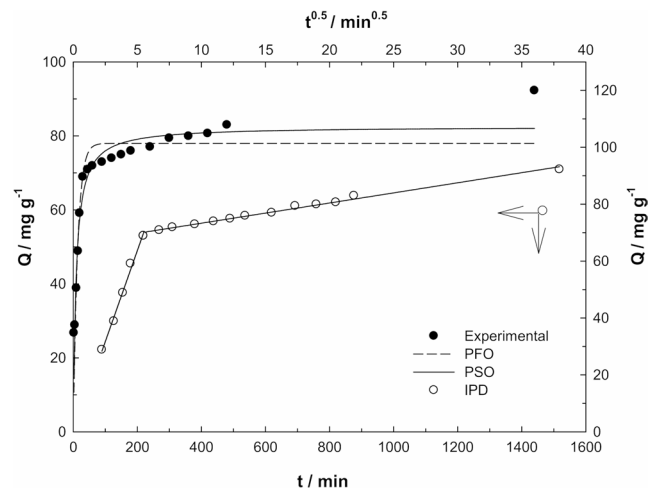
$$Q_t = t / [k_2 \cdot Q_e^2] + \left[\frac{1}{Q_e} \right] \cdot t \quad (11)$$

$$H_2 = k_2 \cdot Q_e \quad (12)$$

The IPD model proposed by Weber-Morris describes the adsorption mechanism and rate controlling step. The Eq. is given below (13).

$$Q_t = k_i \cdot t^{0.5} \quad (13)$$

Figure 6 illustrates the compatibility of the models employed for the removal of CV onto the PPC biosorbent, while Table 5 presents the determined kinetic parameters. It was established that the quantity of biosorbed CV exhibited a rapid increase with the duration of contact until the 180th minute, after which a deceleration was detected, reaching equilibrium at the 240th minute. In the initial phase, which occurs rapidly, the CV molecules are distributed throughout all active centres. The effectiveness of an adsorption model in describing experimental data is generally assessed through the correlation coefficient (R^2) values. When R^2 nears unity, the model's predictions align more closely with the detected data, aiding in the

**Fig. 6** Biosorption kinetics

evaluation of both the process mechanism and the model's capability to be applied to the system [55]. A comparison of the R^2 of the PFO and PSO models presented in Table 4 revealed that the R^2 value for the PSO model (0.943) is closer to unity, indicating that it is more consistent with the biosorption process. In addition, the close match between the theoretical Q_t and the experimental Q_e values for the PSO model strengthens the view that the biosorption follows the PSO model. As a result, the biosorption of CV molecules onto the PPC surface can be considered as a chemical process. As seen in Fig. 6, the Q - $t^{0.5}$ graph plotted for the IPD kinetic model indicates that the biosorption process progresses in two parts. The first slope represents the rapid transfer of CV molecules to the surface of the biosorbent, while the second slope corresponds to the IPD until equilibrium is reached [56]. It was detected that the curves obtained from the graph are not linear and do not intersect the origin. This suggests that the rate-limiting process involves additional processes along with intraparticle diffusion [57]. These findings suggest that the biosorption kinetics are consistent with the mechanisms described by the PSO and IPD models.

3.6 Biosorption thermodynamics

Thermodynamic studies conducted in biosorption processes provide insights into how temperature changes affect the process. Therefore, the biosorption of CV onto PPC was evaluated at 5 °C, 25 °C and 40 °C. Enthalpy change (ΔH°),

Table 4 Parameters of kinetic models

Crystal Violet	(k_1, k_2, k_3) $\times 10^3$	R^2	Q_t	Q_e	$H \times 10^4$
PFO	73,9	0,894	83,4	78,5	5764
PSO	1,39	0,943	83,4	83,2	9576
IPD	232	0,990	-	-	-

Gibbs free energy (ΔG°) and entropy change (ΔS°) provide information about the energy changes during the biosorption. The mathematical Eq.s used to obtain these parameters are given in Eqs. (14–17).

$$K_d = \frac{Q}{C_e} \quad (14)$$

$$\ln K_D = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT} \quad (15)$$

$$\Delta G^\circ = -RT \ln(K_d) \quad (16)$$

$$\Delta G^\circ = \Delta H^\circ - T \Delta S^\circ \quad (17)$$

The ΔH° and ΔS° parameters were determined from the slope and intersection values obtained from the linear graph of $\ln K_D$ versus $1/T$ (Fig. 7). ΔG° change values for temperatures of 278, 298, and 313 K were calculated using the Eq [17]. The thermodynamic parameters are listed in Table 5. The positive ΔH° value (12.9 kJ mol^{-1}) is an indication that CV biosorption on PPC is an endothermic process. In addition, the positive ΔS° value (150 J/mol K) indicates that the randomness at the interface between the PPC and the CV is increasing. The negative ΔG° values (-28.8 , -31.8 , $-34.1 \text{ kJ mol}^{-1}$) detected at elevated temperatures indicate that the biosorption process occurs rapidly and spontaneously.

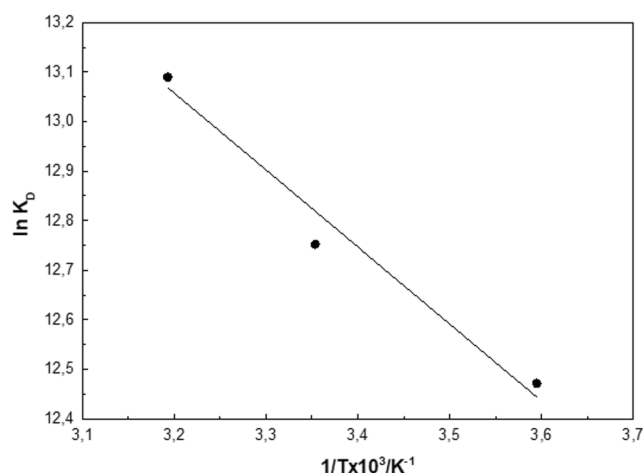


Fig. 7 Biosorption thermodynamics

Table 5 Thermodynamic parameters

Temperature	ΔH°	ΔG°	ΔS°	R^2
5	12.9	-28.8	150	0.977
25		-31.8		
40		-34.1		

3.7 Biosorption mechanism

Based on the findings of the experimental studies, a diagram was prepared showing the possible mechanism of CV biosorption onto PPC (Fig. 8). The mechanism of biosorption process of PPC biomaterial can be attributed to active groups contained in biomaterial. FT-IR spectra of PPC were studied to identify these active centers. The strong flat stretching peak detected at approximately 3270 cm^{-1} in FT-IR spectrum of PPC indicates the presence of free or hydrogen bonded (-OH) and amino (N-H) groups (alcohols, phenols and carboxylic acids) such as pectin, cellulose and lignin [8]. The peak detected at 1730 cm^{-1} is the stretching vibration of C = O bond originating from carboxylic groups assigned to carboxylic acids or their esters [32]. The peak detected at 1608 cm^{-1} can be assigned to the formation of symmetric stretching vibrations of aromatic -COO- belonging to aromatic groups of lignin [31]. FT-IR spectrum of PPC clearly reveals that the biosorbent has abundant carboxyl and hydroxyl groups. The adsorption of cationic CV molecules onto PPC is probably due to electrostatic attraction interactions with these groups.

In the CV removal process, the solution pH at which adsorption occurs is of critical importance and sheds light on the mechanism of the biosorption. The solution pH value changes the surface charge of the PPC from positive to negative. The PPC, which has a pHpzc value of 4.03, attracts the cationic dye at $\text{pH} < \text{pHpzc}$ and repels it at $\text{pH} > \text{pHpzc}$. At $\text{pH} < 4.03$, the surface of the PPC is positively charged. Cationic CV molecules are protonated at acidic pH values. In this case, electrostatic repulsion occurs between the positively charged PPC surface and the protonated CV molecules.

At $\text{pH} > 6.0$, the PPC surface becomes negatively charged due to the presence of OH^- ions. At the same time, deprotonation occurs in the CV at basic pH values. However, the cationic part of the dye may still be present. This causes electrostatic attraction with the negatively charged PPC surface and relatively lower adsorption efficiency is detected. Figure 3 supports the findings that adsorption efficiency decreases at $\text{pH} > 6.0$.

In general, maximum adsorption efficiency is observable at $\text{pH} \approx 6.0$. Because at this pH value, the adsorbent surface is largely negatively charged. In addition, the CV is protonated and cationic. The electrostatic attraction between the surface and the dye molecules is quite large and the biosorption efficiency is high. At this pH value, electrostatic interactions, H-bonds and π - π interactions occur between the CV molecules and the surface functional groups of the PPC. H-bonds are formed between the nitrogen atoms of the CV and the H atoms of the hydroxyl and carboxyl groups of the PPC. Electrostatic interactions are detected between the

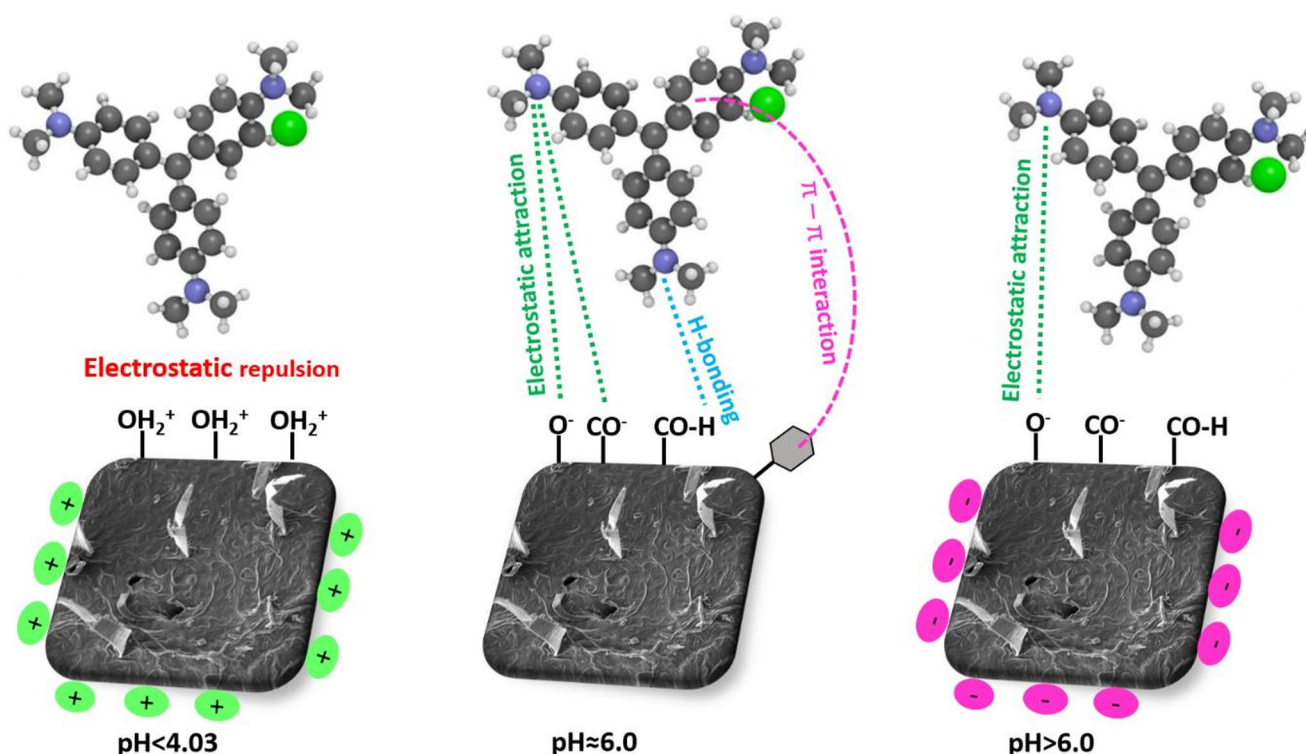


Fig. 8 Possible biosorption mechanism for the biosorption process of CV onto PPC

N groups of the CV and the O atoms of the hydroxyl and carboxyl groups of the PPC. $\pi-\pi$ interactions occur between the benzene ring of the CV molecules and the C-C group of the PPC. In the light of all this information, the possible mechanism of the biosorption of CV onto the PPC surface is schematically envisaged in Fig. 9.

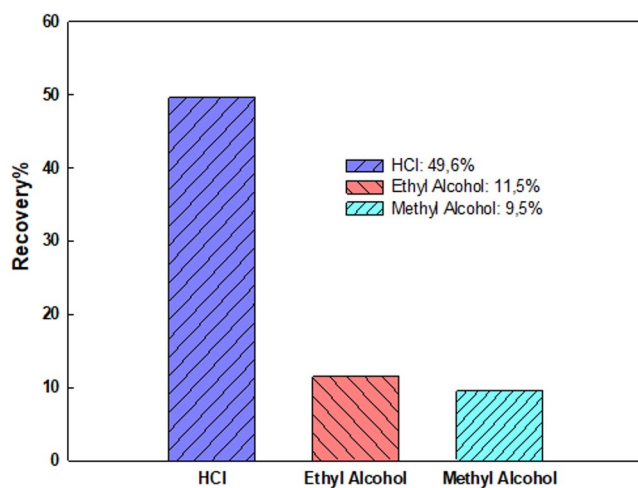


Fig. 9 The recovery rates of different solvents for the desorption of PPC

3.8 Recovery

The ability of a biosorbent to be reused is a key factor in assessing its stability. Desorption studies were conducted to identify the optimal desorption agent for effective use in multiple reusability cycles. Consequently, desorption experiments were conducted five times, utilising HCl, methanol, and ethanol solutions to recover CV molecules from the surface of the PPC. The recovery percentage values for desorption solutions are presented in Fig. 9. The analysis revealed that CV can be desorbed from PPC biosorbent, with the highest recovery achieved using HCl (49.6%) and the lowest recovery detected with methanol (23%). The findings demonstrate that PPC biosorbent represents an environmentally benign and affordable alternative biosorbent for the removal of CV.

4 Conclusion

The aim of this study was to determine the potential of *Physalis peruviana* calyx as a non-toxic, low-cost and effective biosorbent for the removal of CV from aqueous solution. In order to evaluate the experimental data, the Freundlich, Langmuir, and D-R isotherm models were applied. It thus

emerged that the Langmuir isotherm model was the most consistent with the biosorption process, as evidenced by the higher correlation coefficient. The Langmuir model was employed to calculate the maximum biosorption capacity for a single layer, which was determined to be 144 mg g^{-1} at 25°C and $\text{pH} \cong 4.8$. This value was reported to be higher than that of many biosorbents reported in the literature. The E_{DR} value of 10.3 kJ mol^{-1} , established through the D-R isotherm, suggests that the biosorption process is of a chemical. FTIR, SEM, and EDX analyses conducted prior to and following the biosorption process provided evidence of the interaction between the functional groups on the surface of the PPC biosorbent and the CV molecules. The kinetic profile of CV biosorption on a PPC biosorbent was observed to be aligned with the PSO and IPD kinetic models. Thermodynamic analysis parameters suggested that the biosorption process is both heat-absorbing and occurs spontaneously. Additionally, it was determined that randomness increased during CV uptake of PPC biosorbent. The study's findings showed that PPC biosorbent in lignocellulosic structure is an effective option for CV removal. PPC can be used as an adsorbent without the need for pretreatment, and its low cost and absence of additional chemicals make it an economically and environmentally sustainable alternative to conventional adsorbents.

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Declarations

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