



Adsorptive removal of toxic methylene blue and crystal violet dyes from aqueous solutions using *Prunus spinosa*: isotherm, kinetic, thermodynamic, and error analysis

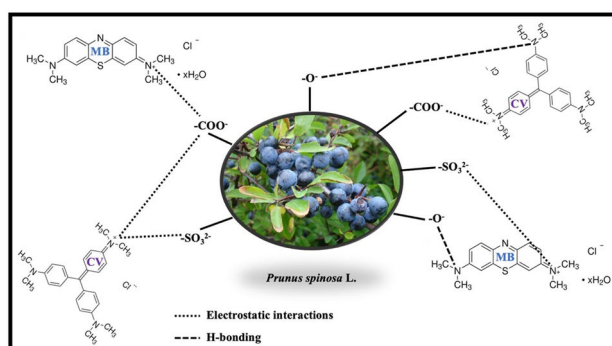
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Abstract

In this study, it was aimed to use *Prunus spinosa* L. fruit pulp as an adsorbent zero-waste and low-cost for the removal of toxic methylene blue (MB) and crystal violet (CV) dyes from aqueous solutions. The adsorbent was characterized utilizing FTIR-ATR, SEM, and pH_{pzc} tests. The pH_{pzc} value of the adsorbent is 4.96. According to optimization experiments, the optimum adsorbent dosage was determined as 0.05 g/50 mL for MB and CV dyes, the optimum pH values were determined as approximately 7 for MB and CV dyes, and the optimum contact time was determined as 45 min for MB and 30 min for CV dyes. The Langmuir model has been used to calculate the maximum adsorption capacities of MB and CV dyes at a temperature of 298 K. The obtained values are 59.59 mg/g for MB and 53.19 mg/g for CV. The experimental data for *Prunus spinosa* L. for both dyes exhibited a *pseudo-second-order* kinetic model. According to error analyses, the reproducibility and applicability of isotherm and kinetic models were investigated. From thermodynamic results, the enthalpy values were calculated as -42.04 kJ/mol for MB and -24.08 kJ/mol for CV dyes, which indicates that the process is exothermic. Also, the Gibbs free energies of MB and CV dyes were determined as -34.20 kJ/mol and -32.33 kJ/mol at 298 K, which indicates the process is spontaneous. Research and comparisons with other adsorbents have demonstrated that *Prunus spinosa* L. is a cost-effective and appealing choice for removing MB and CV dyes from water solutions.

Graphical Abstract



Keywords Adsorption · *Prunus spinosa* L. · Methylene blue · Crystal violet

1 Introduction

The exponential increase in the global population and the improvement in people's living conditions are leading to a higher demand for freshwater worldwide, resulting in the

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depletion of current freshwater resources. As a result of the scarcity of freshwater, around 1.1 billion individuals globally presently do not have access to clean drinking water. This figure is expected to multiply significantly by 2050 when the global population is predicted to reach 10 billion [1, 2]. Ensuring and enhancing water quality has become imperative for the survival and progress of humanity [3, 4]. Annually, a substantial quantity of pollutants, such as heavy metals [5], emerging pollutants [6], pharmaceuticals [7], radioactive wastes [8], and dyes [9], is discharged into the environment, leading to a decline in water quality and posing ecological hazards. Specifically, dye pollution is prominently recognized as one of the most pressing issues among water contaminants. They have extensive utilization in both industrial production and daily life for various purposes including textiles, printing, plastics, leather, and paper. This allows for the creation of a diverse array of items that exhibit vivid hues. Based on the Textile Color Index, over 10,000 distinct textile dyes are manufactured each year, amounting to a total of approximately 700,000 tons [10, 11]. Dyes pose a challenge in terms of treatment and removal from wastewater due to their intricate organic composition. Textile dyes, which are non-biodegradable, can have detrimental effects on the aquatic environment and disrupt its biological balance. Furthermore, they have the potential to augment the concentration of dyes in water, leading to extensive toxicity in aquatic ecosystems and other organisms, while impeding the penetration of light into the aquatic environment [12, 13].

Methylene blue (MB) and crystal violet (CV) are extensively employed cationic dyes for dyeing wood, cotton, paper, and silk. Moreover, the dye structure of MB and CV will remain unaltered in natural surroundings because of their resistant character. MB and CV are acknowledged as significant contaminants in paint effluent due to their detrimental impact on the environment, including decreased photosynthesis, as well as their harmful impacts on human health, such as respiratory distress and skin irritation [14–16]. Hence, it is imperative to eliminate dyes before their release into natural aquatic ecosystems to safeguard the environment and human well-being. Several methods are commonly employed to eliminate water-based dyes, including photocatalytic degradation [17], adsorption [18, 19], electrochemical degradation [20], and coagulation/flocculation [21–23]. Regrettably, the development of secondary waste, as well as inefficiency or complexity, impose limitations on many of these operations. Adsorption techniques are commonly utilized because of their cost-effectiveness, high efficiency, and commercial feasibility [24–26].

Carbonaceous materials are highly cost-effective and efficient adsorbents for removing dyes, and they can be reused multiple times. Especially, activated carbon is the most extensively used adsorbent for the elimination of several

dyes, including MB and CV; yet, it is regarded as prohibitively pricey and challenging to regenerate. Consequently, there is a necessity for alternative, cost-effective, natural, zero-waste adsorbents to render the adsorption process a feasible wastewater treatment technique. In recent years, the adsorption process utilizing biomass waste has been acknowledged as the most economical and viable method for color removal. Consequently, recent years have observed effective utilization of various fruit peels, including orange [27], mango [28], pomelo [29], grapefruit [30], lemon [31], banana [32], watermelon (*Citrullus lanatus*) [33], and dragon fruit (*Hylocereus polyrhizus*) [34] peels, and activated carbon derived from mixed orange peel and watermelon rind [35] for the elimination of colors from aqueous solutions via the adsorption process. High adsorption capabilities can be attained by utilizing inexpensive, environmentally friendly, waste-free, easily accessible, and naturally occurring biomasses [36, 37]. Uddin et al. effectively removed crystal violet and malachite green dyes using rubber seed pericarp biomass modified with sulfuric acid and determined the maximum adsorption capacities as 302.7 and 567.6 mg/g for CV and MG, respectively [25]. Abdulhameed et al. effectively removed CV and MB dyes using microalgae and determined the maximum adsorption capacities as 243.0 and 297.1 mg/g for CV and MB, respectively [38].

Prunus spinosa L., commonly referred to as coyote plum, is a fruit belonging to the *Prunus* genus within the Rosaceae family. The plant thrives in several areas of Turkey, particularly in central, northern, western, and southern Anatolia [39]. *Prunus spinosa* L. has demonstrated its efficacy as a fruit rich in antioxidant compounds and natural pigments. The fruits of this plant are rich in cyanidin-3-o-rutinoside and peonidin-3-o-rutinoside, as well as other abundant antioxidant chemicals. They are frequently employed in the manufacturing of liqueurs and jams, as well as for some therapeutic applications. Following these applications, the residual components of the plant and its fruit can be further utilized as adsorbents through a zero-waste assessment [40, 41]. No literature review yielded any studies on the utilization of this plant as an adsorbent.

The aim and novelty of this study were to effectively and rapidly remove toxic MB and CV dyes from aqueous solutions using low-cost, natural *Prunus spinosa* L. fruit wastes, which are considered zero waste. The primary reasons for choosing this adsorbent are their low cost and environmental friendliness. The adsorbent that was synthesized underwent characterization using FTIR-ATR, SEM, and pH_{pzc} measurement. The optimal conditions for the adsorption of various dyes on the produced adsorbent were found, taking into account factors such as initial pH, contact time, and adsorbent dosage. Subsequently, adsorption experiments were conducted. The experimental experiments provided raw data that were used to apply non-linear Langmuir, Freundlich,

Dubinin-Radushkevich (D-R), and Temkin isotherm models, as well as *pseudo-first-order* and *pseudo-second-order* kinetic models. Experiments were conducted to investigate the process of adsorption at various temperatures, and the associated thermodynamic parameters were computed.

2 Materials and methods

2.1 Chemicals and instrumentation methods

The *Prunus spinosa* L. was collected from the forest in Keşan, Turkey. The crystal violet (CV, $C_{25}H_{30}N_3Cl$, M_w 407.9 mol/g, purity $\geq 90.0\%$, price 135.00 € for 50 g), methylene blue (MB, $C_{16}H_{18}ClN_3S$, M_w 319.9 mol/g, purity 85.0%, price 106.00 € for 25 g), sodium chloride (NaCl, M_w 58.44 mol/g, purity $\geq 99.0\%$, price 33.70 € for 25 g), calcium chloride ($CaCl_2$, M_w 110.9 mol/g, purity $\geq 97.0\%$, price 51.50 € for 500 g), hydrochloric acid (HCl, M_w 36.46 mol/g, purity 37.0%, price 51.70 € for 100 mL), sodium hydroxide (NaOH, M_w 39.99 mol/g, purity $\geq 97.0\%$, price 28.50 € for 25 g), and sodium nitrate ($NaNO_3$, M_w 84.99 mol/g, purity $\geq 99.0\%$, price 66.50 € for 500 g) were purchased from Sigma-Aldrich and Merck, Inc. (Germany).

To determine the functional groups before and after dye adsorption, the Fourier transform infrared-attenuated total reflectance (FTIR-ATR) spectroscopy analyses were conducted using the Nicolet IS10 Thermo FTIR device. The surface morphology of the adsorbent before and after

adsorption was investigated by scanning electron microscopy (SEM) analysis using a Zeiss EVO LS10 device. The solution pH was adjusted using the Ohaus Starter 3100 pH meter.

2.2 Preparation of *Prunus spinosa* L. adsorbent

Fruits of *Prunus spinosa* L. were gathered from a wooded region in Keşan, Turkey. The adsorbent was evaluated within the scope of zero waste. The fruits underwent a thorough washing process using distilled water to eliminate any dust and external contaminants. Subsequently, they were boiled multiple times to eliminate coloring chemicals and impurities present in their structure. The leftover pulp of the fruits was then utilized for adsorption experiments. The objective in this context was to make use of fruit pulps as part of a zero-waste initiative. The pulps were initially air-dried and subsequently fully dried in a vacuum oven at a temperature of 105 °C. Subsequently, the material was pulverized to achieve a particle size of 100 mesh using a grinder. The resulting powder was then stored in a desiccator for use in adsorption investigations. The preparation of adsorbent is illustrated in Fig. 1.

2.3 Batch adsorption experiments

Prunus spinosa L. fruits prepared as adsorbent were used for the adsorption of MB and CV dyes from aqueous solutions. The effects of time (0–70 min), pH of the solution (2–12),

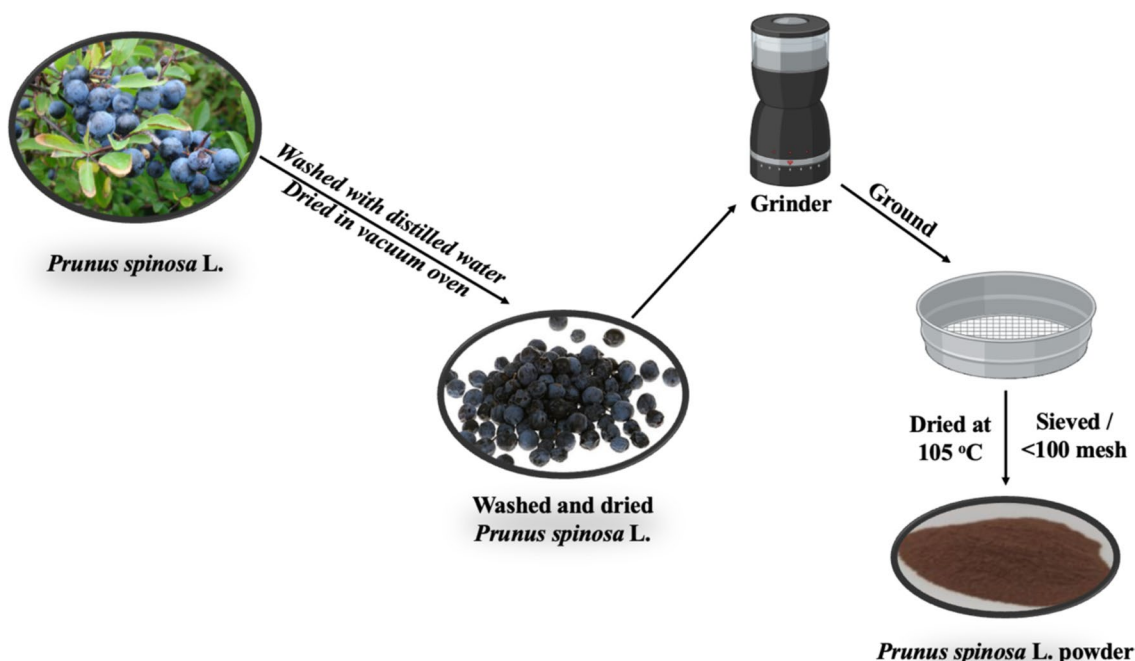


Fig. 1 The preparation of *Prunus spinosa* L. as adsorbent

initial dye concentration (10–50 mg/L), and adsorbent dosage (0.01–0.20 g) were investigated and optimized to determine the maximum adsorption capacity. The pH of the dye solutions was modified using 0.1 M NaOH and 0.1 M HCl solutions. Once the equilibrium time was reached, the sample solutions were subjected to centrifugation at a speed of 9000 rpm for 5 min. The residual dye concentration was subsequently measured using a UV–vis spectrophotometer (Peak Analyzer C-7200) at a wavelength of 663 nm for MB dye and 591 nm for CV dye. The equilibrium adsorption capacity and adsorption percentage values of the adsorbent for MB and CV dyes were calculated by the following equations [42, 43]:

$$q_e(\text{mg/g}) = (C_o - C_e) \times \frac{V}{m} \quad (1)$$

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

In these equations, q_e is the adsorption capacity in equilibrium (mg/g), C_o and C_e are the initial and equilibrium dye concentration (mg/L), V is the volume of the dye solution (L), and m is the amount of adsorbent (g).

An experiment was conducted to examine the impact of NaCl and CaCl_2 salts on the efficiency of removing MB and CV using *Prunus spinosa* L. The salt concentrations used ranged from 0.01 to 1.00 mol/L, and the experiment was conducted under optimal adsorption conditions.

The zero-charge point (pH_{pzc}) was found by preparing 50 mL of a 0.1 M NaNO_3 solution in several flasks, where the pH of the solution was adjusted to the necessary values. Each flask was supplemented with 0.2 g of *Prunus spinosa* L. The solution was agitated for a duration of 48 h, and the final pH value (pH_{final}) was documented. Subsequently, the pH_{pzc} was determined as the point of intersection between the graph depicting the initial pH ($\text{pH}_{\text{initial}}$) and ΔpH ($\text{pH}_{\text{final}} - \text{pH}_{\text{initial}}$) and the origin line [44].

2.4 Error analysis

Nonlinear regression was used to analyze equilibrium systems using experimentally collected data. The investigative data was examined and fitted to specified models using a non-linear least-square approach implemented in Microsoft Excel software. The quality of the fit was evaluated using statistical metrics such as SSE (sum of squared errors), ARE (absolute relative error), RMSE (root mean square error), SD (standard deviation), χ^2 (chi-squared), sum of absolute errors (EABS), and derivative of Marquardt's percent standard deviation (MPSD). These metrics were considered the main criteria for assessment. Statistical parameters and mathematical calculations were given as follows [45–48]:

$$\text{SSE} = \sum_{i=1}^n (q_{e,\text{exp}} - q_{e,\text{cal}})^2 \quad (3)$$

$$\text{ARE} = \frac{100}{n} \sum_{i=1}^n \left| \frac{q_{e,\text{exp}} - q_{e,\text{cal}}}{q_{e,\text{exp}}} \right| \quad (4)$$

$$\text{RMSE} = \sqrt{\frac{1}{n-2} \sum_{i=1}^n (q_{e,\text{exp}} - q_{e,\text{cal}})^2} \quad (5)$$

$$\text{SD} = \sqrt{\frac{1}{n} \sum_{i=1}^n (q_{e,\text{cal}} - q_{e,\text{exp}})^2} \quad (6)$$

$$\chi^2 = \sum_{i=1}^n \frac{(q_{e,\text{exp}} - q_{e,\text{cal}})^2}{q_{e,\text{cal}}} \quad (7)$$

$$\text{EABS} = \sum_{i=1}^n |q_{e,\text{cal}} - q_{e,\text{exp}}| \quad (8)$$

$$\text{MPSD} = \sum_{i=1}^n \left[\frac{(q_{e,\text{exp}} - q_{e,\text{cal}})}{q_{e,\text{exp}}} \right]^2 \quad (9)$$

In these equations, $q_{e,\text{cal}}$ and $q_{e,\text{exp}}$ are the calculated and experimental adsorption capacity in mg/g, respectively.

3 Results and discussion

3.1 Characterization of *Prunus spinosa* L.

FTIR-ATR spectra were generated to detect the presence of functional groups on the surface of *Prunus spinosa* L. that could potentially interact with MB and CV dye molecules. FTIR-ATR spectra of the samples before and after adsorption processes are given in Fig. 2. The spectrum of *Prunus spinosa* L. showed –OH stretchings (3281 cm^{-1}), CH_3 and CH_2 stretchings (2916 and 2849 cm^{-1}), C=O stretchings (1608 cm^{-1}), C=C stretchings (1439 cm^{-1}), O–C–O stretchings (1246 cm^{-1}), and S=O stretchings (1031 cm^{-1}) [49, 50]. The provided data indicates the presence of functional groups, including –OH, –COOH, and SO_3^{2-} , on the surface of *Prunus spinosa* L. Furthermore, there were changes in certain peaks following the adsorption process. The adsorption of MB dye caused the –OH stretchings peak at 3281 cm^{-1} to shift to 3294 cm^{-1} . Similarly, the C=O stretchings' peak at 1608 cm^{-1} shifted to 1601 cm^{-1} , the C=C stretchings' peak at 1439 cm^{-1} shifted to 1440 cm^{-1} , the O–C–O stretchings' peak at 1246 cm^{-1} shifted to 1247 cm^{-1} , and the S=O stretchings' peak at 1031 cm^{-1} shifted to 1035 cm^{-1} . After the CV dye was adsorbed, the peak at 3281 cm^{-1} shifted to 3293 cm^{-1} , the peak at 1608 cm^{-1} changed to 1610 cm^{-1} ,

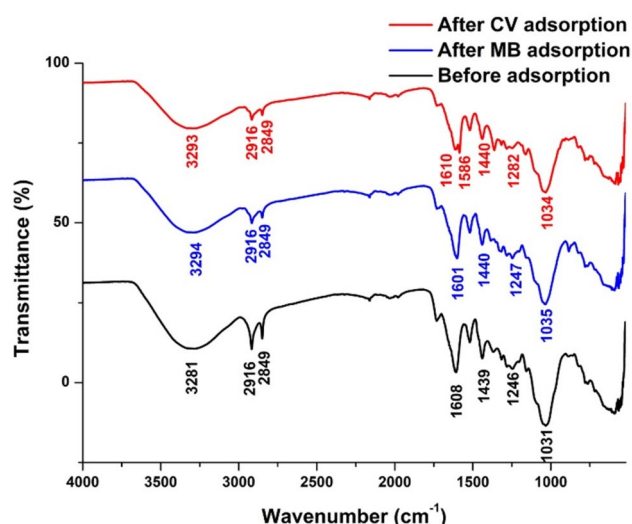


Fig. 2 The FTIR-ATR spectra of *Prunus spinosa* L. before and after adsorption (wavenumber range 4000–600 cm⁻¹)

the peak at 1439 cm⁻¹ shifted to 1440 cm⁻¹, the peak at 1246 cm⁻¹ shifted to 1282 cm⁻¹, and the peak at 1031 cm⁻¹ shifted to 1034 cm⁻¹. This phenomenon was ascribed to the electrostatic interactions occurring between the dye molecules and the surface functional groups of the adsorbent. Additionally, the emergence of a novel peak at 1586 cm⁻¹ following the adsorption of CV dye can be ascribed to the presence of the C-N functional group inside the CV dye molecules [51, 52]. This suggests that the adsorption procedure was successful.

SEM images of *Prunus spinosa* L. before and after adsorption of MB and CV dyes were depicted in Fig. 3. Based on the images, it was noted that the adsorbent exhibited a rough, disordered, and fragmented surface. Following the adsorption of MB and CV dyes, a denser surface morphology was observed. This phenomenon can be explained by the colonization of the pores and cavities of *Prunus spinosa* L. by MB and CV dye molecules.

3.2 Optimum physicochemical parameters

3.2.1 Influence of adsorbent dosage on adsorption performance

MB and CV dyes exhibit distinct molecular architectures and possess unique characteristics. Adsorbents exhibit distinct adsorption mechanisms for different types of contaminants, and the affinity between pollutants and adsorbents varies [32, 42, 53]. To establish the ideal dose of *Prunus spinosa* L. for the adsorption process, we examined the impact of varying amounts of adsorbent on the percentage and capacity of adsorption. Figure 4a displays the outcomes of the impact of adsorbent dosage on MB and CV dye solutions. As the dose

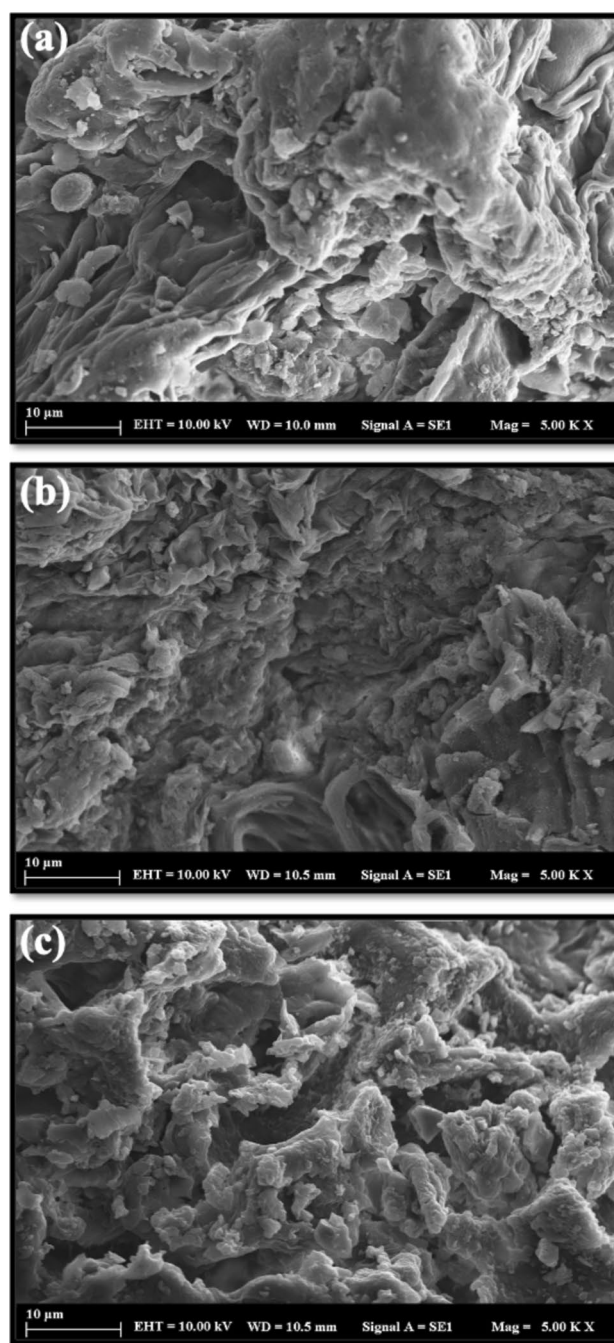


Fig. 3 The SEM images of *Prunus spinosa* L. before (a) and after MB (b) and CV (c) dye adsorption (WD 10.0–10.5, Mag 5.00 KX, EHT 10.00 kV, size 10 μm)

of *Prunus spinosa* L. adsorbent increased, the percentage of adsorption for MB and CV dyes grew gradually, whereas the adsorption capacity declined gradually. When the concentration of dyes is kept constant, any surplus of the *Prunus spinosa* L. adsorbent will build up in the solution. Conversely, the quantity of unoccupied adsorption locations will rise when there is reduced interaction between the adsorbent

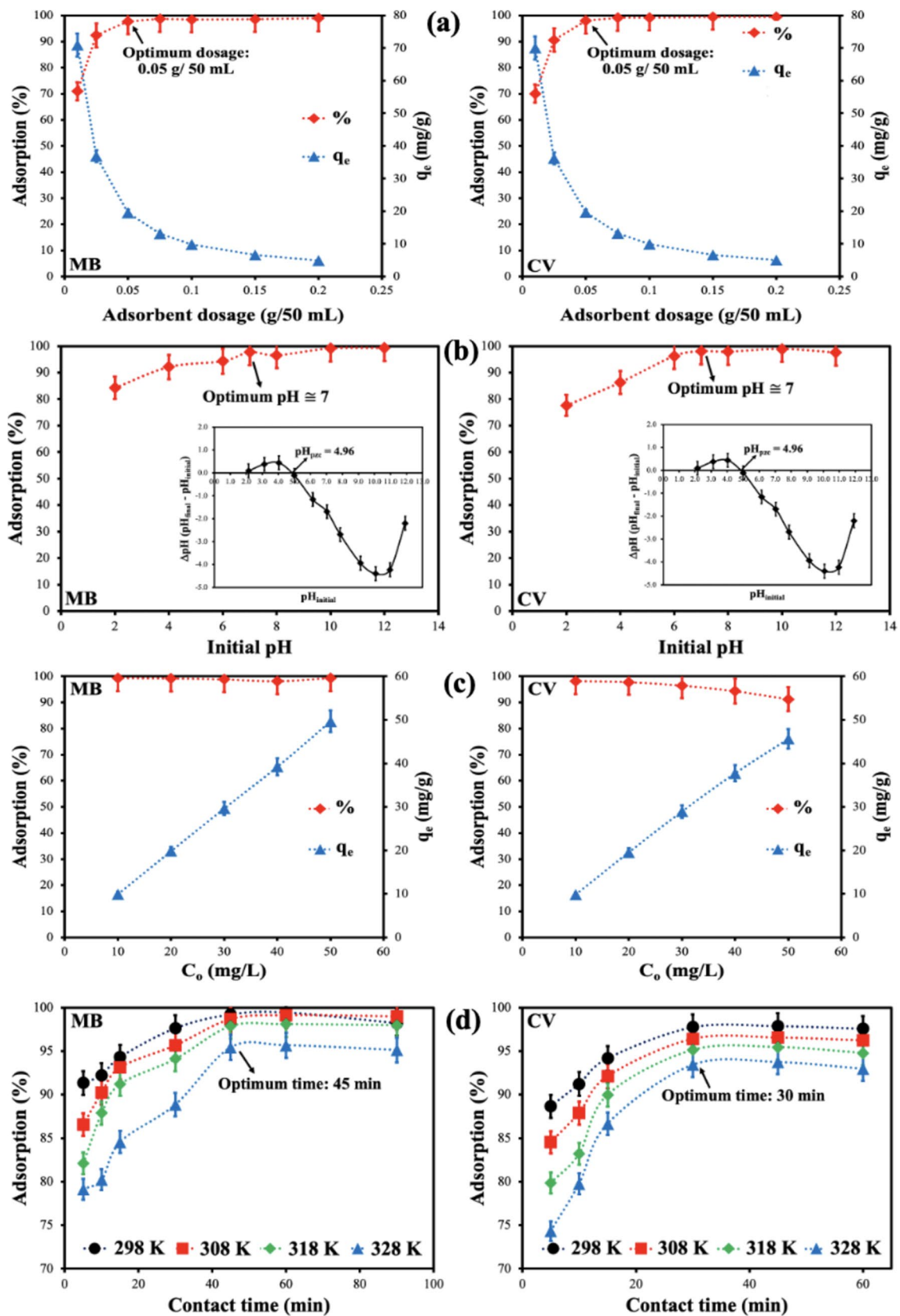


Fig. 4 The influence of optimum physicochemical parameters: **a** adsorbent dosage (initial concentration 20 mg/L; agitation rate 120 rpm; contact time 45 min for MB and 30 min for CV dyes; initial pH 7), **b** initial pH (initial concentration 20 mg/L; agitation rate 120 rpm; contact time 45 min for MB and 30 min for CV dyes; adsorbent dosage 0.05 g/50 mL), **c** initial concentration (adsorbent dosage 0.05 g/50 mL; agitation rate 120 rpm; contact time 45 min for MB and 30 min for CV dyes; initial pH 7), **d** contact time (initial concentration 20 mg/L; agitation rate 120 rpm; adsorbent dosage 0.05 g/50 mL; initial pH 7)

and pollutant for each unit of weight. When the quantity of adsorbent added to the solution surpasses the ideal amount, the active sites of the adsorbent cannot be fully utilized, resulting in a reduction in adsorption capacity. After careful evaluation of the adsorbent's efficiency, the ideal amount of adsorbent for the following adsorption studies was found to be 0.05 g/50 mL for MB and CV dyes.

3.2.2 Influence of solution pH on adsorption performance

The pH of dye solutions has an impact on the surface charge and dissociation of functional groups in the active regions of the adsorbent, as well as the different types of pollutant molecules present. An investigation was conducted to determine the impact of the initial pH on the adsorption process of MB and CV dyes onto *Prunus spinosa* L. The findings are presented in Fig. 4b. Furthermore, the pH_{pzc} graph was depicted similarly. The pH_{pzc} value of *Prunus spinosa* L. was determined to be 4.96 through experimental tests. The data suggests that the adsorption of cationic dyes is more efficient when the pH is higher than 4.96. Conversely, when the pH is below this number, the adsorption process is not as successful. When the pH is less than the pH_{pzc} , the MB and CV dyes in water exist as positively charged ions that are not bound to any other molecules. At this pH, the adsorbent surface will undergo protonation due to acidic circumstances, resulting in a loss in its ability to adsorb the dyes. In this scenario, it contends with MB and CV dyes for H^+ / H_3O^+ adsorption sites, resulting in a reduction in adsorption capability. If the pH is greater than the pH_{pzc} , increasing the pH will increase the amount of negatively charged groups on the surface of the adsorbent. In this scenario, the adsorption of cationic dyes will be more efficient. This event occurs as a result of the decrease in the repulsive force between the dye molecules and the surface molecules of the adsorbent [54–56]. Figure 4b clearly shows that the ideal pH value for both paints is about 7.

3.2.3 Influence of initial concentration on adsorption performance

An investigation was conducted to analyze the impact of the concentrations of MB and CV dyes on the process of

adsorption. The outcomes of this analysis are presented in Fig. 4c. As the quantity of target dye molecules rises, the percentage of *Prunus spinosa* L. adsorption drops, while the adsorption capacity steadily increases. This outcome could be attributed to the low initial concentration of dye molecules and the insufficiently saturated binding sites of *Prunus spinosa* L. Moreover, an elevated concentration of dye molecules intensifies the force that propels the barrier to mass transfer between the adsorbent and the solution. This also enhances the probability of dye molecules coming into contact with *Prunus spinosa* L., which is highly advantageous for the elimination of dye molecules [57, 58].

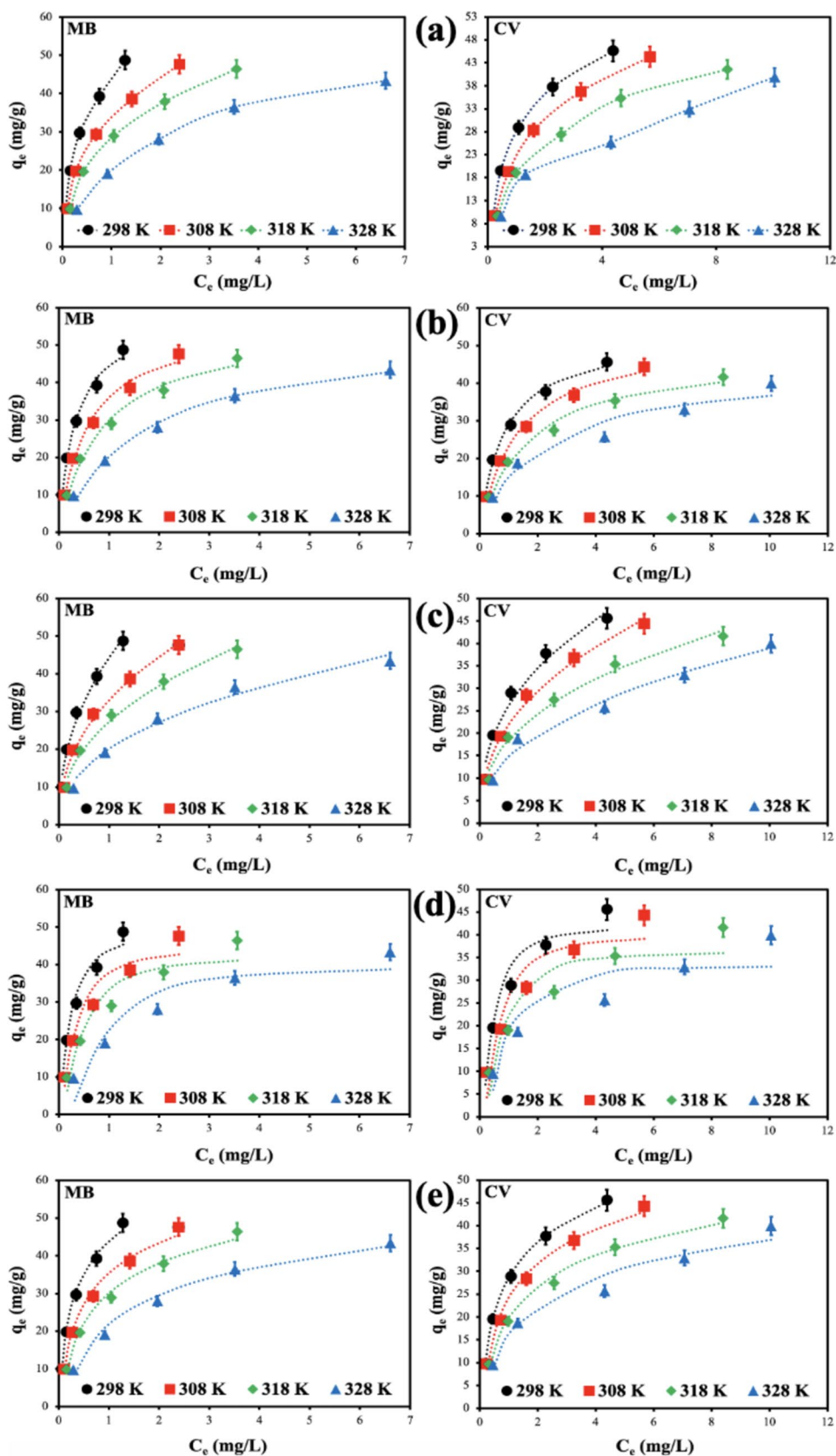
3.2.4 Influence of contact time on adsorption performance

A research investigation was carried out to examine the impact of varying contact durations on the adsorption of MB and CV dyes on *Prunus spinosa* L. The findings are presented in Fig. 4d. The process of *Prunus spinosa* L. absorbing dye molecules can be divided into three distinct stages: an initial rapid increase in adsorption, followed by a slower increase accompanied by a fall in the proportion of adsorption, and finally reaching a steady equilibrium phase. The longer the themes last, the greater the chance for interaction with dye molecules due to the active components in the structure of *Prunus spinosa* L. The dye molecules form chemical bonds with several adsorption active sites in *Prunus spinosa* L. During the later phases of adsorption, as the active sites of adsorption become increasingly filled, the repulsive force between the dye molecules in the solution and the dye molecules within *Prunus spinosa* L. intensifies. Over time, the rate of adsorption decreases and reaches a condition of equilibrium. According to the results shown in Fig. 4d, the ideal duration for achieving adsorption equilibrium in the study of MB dye is 45 min, whereas for CV dye, it is 30 min. Based on the data, the adsorption of MB and CV dyes by *Prunus spinosa* L. occurs quickly. Furthermore, it has been noted that the adsorption percentage for both dyes progressively diminishes as the temperature rises, suggesting that the adsorption process is exothermic.

3.3 Adsorption isotherm studies

The adsorption isotherm was employed to investigate the correlation between cationic dyes and adsorbent molecules [59, 60]. Figure 5a displays the isotherm curves depicting the relationship between the equilibrium concentration of dye molecules and the amount of material adsorbed at equilibrium. Figure 5a shows that based on Giles' isotherm classification [61], the adsorption process for MB dye at 298 K corresponds to the L1 isotherm type, while for CV dye, it corresponds to the L2 isotherm type. As the temperature rises, it can be concluded that the isotherm curves for both

Fig. 5 The isotherm curves (a) of MB and CV dyes onto *Prunus spinosa* L. and non-linear isotherm curves (contact time 45 min for MB dye and 30 min for CV dye; agitation rate 120 rpm; adsorbent dosage 0.05 g/50 mL; initial pH 7); (b) Langmuir, (c) Freundlich, (d) D-R, and (e) Temkin



dyes adhere to the L2 type. Furthermore, it was shown that the adsorption capacity diminishes as the temperature rises, suggesting that the adsorption process is exothermic for both dyes. An investigation was conducted to examine the interaction between MB and CV dye molecules and the adsorbent molecules of *Prunus spinosa* L. Four different non-linear isotherm models, including Langmuir [62], Freundlich [63], Dubinin-Radushkevich (D-R) [64], and Temkin [65], were utilized for this purpose. These isotherm models were utilized to examine the equilibrium isotherms of adsorption, compute the maximum adsorption capacity, and ascertain the adsorption energy. The non-linear equations for the Langmuir, Freundlich, D-R, and Temkin isotherm models are as follows:

$$q_e = \frac{q_m \times K_L \times C_e}{1 + K_L \times C_e} \quad (10)$$

$$q_e = K_F \times C_e^{(1/n)} \quad (11)$$

$$q_e = q_{D-R} \times e^{-\beta \times (R \times T \times \ln(1 + \frac{1}{C_e}))^2}; E_{D-R} = (2\beta)^{-0.5} \quad (12)$$

$$q_e = \frac{R \times T}{b_T} \times \ln(K_T \times C_e) \quad (13)$$

In these equations, q_m is the maximum adsorption capacity (mg/g), and K_L is the Langmuir constant (L/mg). If the K_L value is the range between 0 and 1, the adsorption process occurs favorably. K_F and “ n ” values are the Freundlich constants. Adsorption is classified as chemical when the value of “ n ” is less than one, and as physical when the value of “ n ” is larger than one. q_{D-R} is the theoretical adsorption capacity (mg/g), ϵ is the Polanyi potential, and E_{D-R} is the adsorption energy (kJ/mol). If this value is lower than 8 kJ/mol, the adsorption occurs physically. On the other hand, if this value is higher than 16 kJ/mol, the adsorption occurs chemically. b_T is the Temkin constant, which is associated with the maximum binding energy (kJ/mol), and K_T is the empirical Temkin constant, which is linked with the balanced binding constant.

The Langmuir isotherm model is a quantitative model used to determine the adsorption characteristics of monolayer adsorbate molecules on the external surface of the adsorbent. The isothermal model is utilized to explain homogenous adsorption, assuming that every molecule possesses a consistent activation energy [66–72]. Figure 5b displays the non-linear Langmuir graph, illustrating the relationship between C_e and q_e for both dyes, as indicated by the equality. The isotherm parameters were calculated from Fig. 5b, and the outcomes are presented in Table 1. Table 1 shows that the Langmuir model was used to compute the maximum adsorption capacities of *Prunus spinosa* L. for

MB and CV dyes. The values obtained were 59.59 mg/g for MB and 53.19 mg/g for CV, both at a temperature of 298 K. The discrepancy in adsorption capabilities between the two dyes is due to the CV dye molecule being larger compared to the MB dye molecule and having a less strong affinity for the active components of *Prunus spinosa* L. Furthermore, it was shown that the adsorption capacity diminishes for both dyes as the temperature rises, suggesting that the adsorption process is exothermic.

Table 2 displays a comparative analysis of the dye adsorption capacities of biomass, to similar ones documented in the literature. Table 1 illustrates the high effectiveness of *Prunus spinosa* L. in this study as an adsorbent. These microbeads are distinguished by their inherent and environmentally friendly features. In this situation, it has the potential to be an effective adsorbent for removing positively charged pollutants.

The Freundlich isotherm model is employed to elucidate the adsorption properties of heterogeneous surfaces and is commonly utilized in diverse heterogeneous systems for highly reactive substances, particularly organic chemicals or activated carbon [78, 79]. Equation (11) was utilized to create non-linear graphs between C_e and q_e for both dyes. The outcomes are displayed in Fig. 5c. The isotherm parameters were computed from these non-linear graphs and are documented in Table 1. According to the data presented in Table 1, the values of “ n ” for both paints varied from 2.219 to 2.518. Given that the value of “ n ” falls within the range of 1–10, it can be concluded that the adsorption process is favorable for both dyes. Furthermore, the analysis of the correlation coefficients has demonstrated that the Langmuir isotherm model is appropriate for the adsorption of MB and CV dyes on *Prunus spinosa* L. This conclusion is based on the strong correlation coefficients observed.

The D-R isotherm model is frequently employed to describe the adsorption mechanism on a heterogeneous surface, using a Gaussian energy distribution. This method does not rely on the assumption of a uniform surface or a consistent adsorption potential. Instead, it is used to calculate the average free energy of adsorption [80, 81]. Non-linear graphs were constructed between the variables C_e and q_e for MB and CV dye molecules, based on the principle of Eq. (12). The outcomes of this analysis are presented in Fig. 5d. The isotherm parameters were derived from these non-linear graphs and are documented in Table 1. In addition, adsorption energies were calculated using “ β ” values obtained from the gradient of linear graphs. The E_{D-R} values for MB and CV dyes have been found to fall within the range of 1.692 and 3.672 kJ/mol. Given that these values are below 8 kJ/mol, it was noted that the adsorption process takes place through physical means for both dyes.

The Temkin isotherm model is derived from the adsorption heat that arises from the interactions between the

Table 1 Non-linear isotherm parameters and various error functions for the adsorption of MB and CV dyes on *Prunus spinosa* L. (contact time 45 min for MB dye and 30 min for CV dye; agitation rate 120 rpm; adsorbent dosage 0.05 g/50 mL; initial pH 7)

Temperature (K)	Methylene blue				Crystal violet			
	298	308	318	328	298	308	318	328
Non-linear Langmuir isotherm								
$q_m(\text{mg/g})$	59.59	56.38	55.48	53.60	53.19	52.97	48.03	44.30
$K_L(\text{L/g})$	2.978	1.785	1.175	0.6079	1.187	0.7729	0.6253	0.4758
r^2	0.9976	0.9961	0.9949	0.9910	0.9982	0.9935	0.9947	0.9979
SSE	8.326	14.05	11.44	4.506	4.117	5.996	9.719	34.54
ARE	4.516	6.997	6.897	4.649	3.271	5.287	6.645	10.83
$RMSE$	1.666	2.164	1.952	1.225	1.171	1.414	1.799	3.393
SD	1.290	1.676	1.512	0.9493	0.9074	1.095	1.394	2.628
χ^2	0.2699	0.5685	0.5519	0.4231	0.1479	0.3778	0.5672	1.413
$EABS$	5.939	8.288	7.511	3.402	4.281	5.148	6.289	11.92
$MPSD$	0.0114	0.0288	0.0327	0.0334	0.0061	0.0268	0.0373	0.0717
Non-linear Freundlich isotherm								
$K_F(\text{mg/g}).(\text{L/g})^{1/n}$	44.43	33.06	27.24	20.08	26.09	21.87	18.42	14.68
n	2.219	2.303	2.304	2.335	2.489	2.372	2.518	2.363
r^2	0.9986	0.9987	0.9985	0.9986	0.9988	0.9985	0.9988	0.9999
SSE	13.01	8.849	7.462	13.19	21.21	9.728	8.852	9.613
ARE	8.081	7.118	6.578	7.331	10.54	6.922	6.968	6.494
$RMSE$	2.082	1.718	1.577	2.097	2.659	1.801	1.718	1.791
SD	1.613	1.330	1.222	1.625	2.059	1.395	1.331	1.387
χ^2	0.7909	0.5899	0.4878	0.6172	1.179	0.5622	0.5076	0.5153
$EABS$	6.531	5.514	5.356	7.342	9.244	6.098	6.164	6.339
$MPSD$	0.0833	0.0627	0.0513	0.0525	0.1294	0.0556	0.0503	0.0292
Non-linear Dubinin-Radushkevich isotherm								
$q_{D-R}(\text{mg/g})$	48.92	44.47	42.38	39.60	42.03	40.04	36.49	33.42
$E_{D-R}(\text{kJ/mol})$	3.672	3.131	2.662	1.793	2.392	1.981	1.844	1.692
r^2	0.9983	0.9981	0.9971	0.9908	0.9979	0.9946	0.9967	0.9989
SSE	28.34	59.38	74.69	92.08	52.40	82.89	91.38	107.7
ARE	9.074	12.69	16.14	21.55	12.96	19.47	19.92	19.64
$RMSE$	3.074	4.449	4.989	5.541	4.179	5.256	5.519	5.991
SD	2.381	3.446	3.865	4.291	3.237	4.072	4.275	4.641
χ^2	1.194	2.819	4.854	16.79	2.823	8.986	7.368	5.495
$EABS$	10.87	14.63	16.92	18.27	14.04	18.14	18.86	20.15
$MPSD$	0.0633	0.1428	0.2373	0.5319	0.1488	0.3773	0.3421	0.2694
Non-linear Temkin								
$K_T(\text{L/mg})$	32.73	20.90	14.05	7.361	12.71	9.142	7.614	5.743
$b_T(\text{J/mol})$	196.5	219.4	231.7	248.6	220.1	234.6	270.1	299.9
r^2	0.9999	0.9999	0.9999	0.9999	0.9999	0.9999	0.9999	0.9999
SSE	6.496	9.156	8.834	8.394	0.4218	5.511	4.901	22.76
ARE	4.554	4.977	5.629	6.661	1.082	5.182	4.381	6.752
$RMSE$	1.472	1.767	1.716	1.673	0.3749	1.355	1.278	2.754
SD	1.139	1.353	1.329	1.295	0.2904	1.051	0.9899	2.134
χ^2	0.2567	0.3419	0.3948	0.5102	0.0171	0.3209	0.2313	0.7659
$EABS$	5.402	6.052	6.179	6.176	1.225	4.909	4.476	8.426
$MPSD$	0.0144	0.0178	0.0232	0.0349	0.0009	0.0221	0.0141	0.0322

molecules of the adsorbent and adsorbate [82, 83]. Figure 5e displays the Temkin isotherm graph for the dye-*Prunus spinosa* L. system at various temperatures. The

isotherm parameters derived from these non-linear graphs are presented in Table 1. The Temkin isotherm constants for the MB dye were calculated as 196.5, 219.4, 231.7, and

Table 2 Comparison of dye adsorption capacities of *Prunus spinosa* L. with other adsorbents reported in the literature

Adsorbent	q_m (mg/g)	Dye	Ref
<i>Prunus spinosa</i> L	59.59	MB	This study
<i>Prunus spinosa</i> L	53.19	CV	This study
Mango peel	277.8	MB	[73]
Pomelo peels	133.0	MB	[74]
OPWRAC	137.8	CV	[35]
<i>Leonurus cardiaca</i> L	125.6	CV	[75]
Raw pine leaf biomass	36.88	MB	[76]
<i>Raphanus caudatus</i> biomass	48.70	CV	[77]
<i>Raphanus caudatus</i> biomass	19.00	RhB	[77]

248.6 kJ/mol at temperatures of 298, 308, 318, and 328 K, respectively. However, it was established that the CV dye exhibits values of 220.2, 234.6, 270.1, and 299.9 kJ/mol at temperatures of 298, 308, 318, and 328 K, respectively. It was noted that the adsorption of MB and CV dyes likewise conforms to the Temkin isotherm in this particular example.

The q_e values obtained from the Langmuir, Freundlich, D-R, and Temkin isotherm models, along with the experimental q_e values, were utilized to compute the error functions using the aforementioned equations. The outcomes are presented in Table 1. According to the data presented in Table 2, there is a direct relationship between the size of the error functions and the applicability and reproducibility of the isothermal models. Specifically, as the error functions decrease, the applicability and repeatability of the models increase. Based on observations, the Temkin and Langmuir isotherm models are the most appropriate for the adsorption process. This is owing to their low error values in comparison to other isotherm models. The order of isotherms applicable for the adsorption of MB and CV dyes on *Prunus spinosa* L. can be ranked as follows: Temkin > Langmuir > Freundlich > D-R.

3.4 Adsorption kinetic studies and possible adsorption mechanism

Adsorption kinetic models are crucial for assessing the efficiency of the adsorbent and studying the mechanisms of adsorption mass transfer. This work employed *pseudo-first-order* and *pseudo-second-order* kinetic models to examine the kinetic parameters and mechanism of the adsorption of cationic dyes onto the surface of the adsorbent. The non-linear equations corresponding to these kinetic models are displayed below [59].

$$q_t = q_e \times (1 - e^{-k_1 \times t}) \quad (14)$$

$$q_t = \frac{q_e^2 \times k_2 \times t}{1 + q_e \times k_2 \times t} \quad (15)$$

In these equations, k_1 and k_2 are the *pseudo-first-order* (min^{-1}) and *pseudo-second-order* ($\text{g/mg} \cdot \text{min}$) rate constants.

Figure 6 displays the linear graphs corresponding to Eqs. (14) and (15). The kinetic parameters were determined from non-linear curves shown in Fig. 6. These values are shown in Table 3.

The *pseudo-first-order* kinetic model characterizes the adsorption reactions occurring at the interface between particles and liquid. This model often demonstrates a two-stage kinetic behavior, with an early phase of rapid reaction rates followed by a subsequent phase of slower rates. This scenario can be understood as a two-step reaction process of the first order, taking place in regions that are initially readily accessible and in less accessible interior regions. The second-degree kinetic model of adsorption is predicated on the premise that the decisive stage could involve chemical adsorption facilitated by valence forces, wherein electrons are shared or exchanged between the adsorbent and the adsorbate [84, 85]. Table 3 reveals that while examining the correlation coefficients, it was determined that the *pseudo-second-order* kinetic model is appropriate for the adsorption of MB and CV dyes onto *Prunus spinosa* L. Moreover, while analyzing the computed and experimental q_e values, the proximity between them suggested that the *pseudo-second-order* kinetic model was a more appropriate choice.

Numerous investigations have revealed significant interactions, including electrostatic interactions, pore-filling mechanisms, and hydrogen bonding, that facilitate the removal of organic dyes by adsorbents [86–88]. The binding mechanism of CV and MB dyes to the surface of *Prunus spinosa* L. was elucidated by FTIR-ATR spectra. The investigation indicates that the adsorption of MB and CV dyes onto the surface of *Prunus spinosa* L. was influenced by alterations in the vibrations of $-\text{COOH}$ and $-\text{OH}$ groups, as well as $\text{C}=\text{O}$ carbonyl groups. Consequently, these polar functional groups contributed to the binding of MB and CV dyes. Figure 7 illustrates the diverse contributions to the adsorption mechanism of MB and CV dyes on the surface of *Prunus spinosa* L. The adsorption process for MB and CV dyes may involve the following mechanisms: pore-filling, hydrogen bonding, and electrostatic interactions. An elevation in pH levels may induce the formation of negative charges on the surface of *Prunus spinosa* L., perhaps facilitating electrostatic interactions with the positively charged MB and CV dye molecules. Furthermore, the carboxy groups and $-\text{COOH}$ on the surface of *Prunus spinosa* L. may potentially establish hydrogen bonds with the nitrogen atoms of MB and CV dyes.

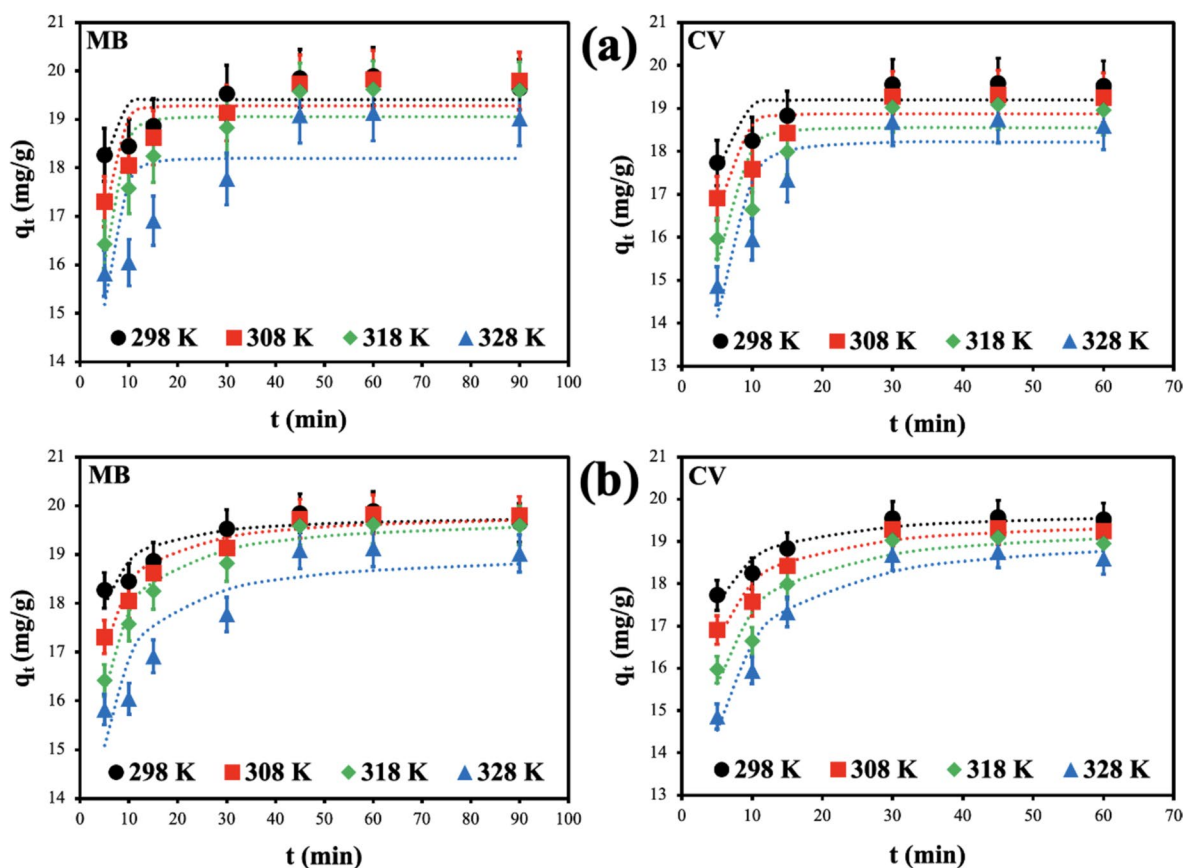


Fig. 6 The non-linear kinetic curves (initial concentration 20 mg/L; agitation rate 120 rpm; adsorbent dosage 0.05 g/50 mL; initial pH 7): **a** pseudo-first-order and **b** pseudo-second-order

3.5 Adsorption thermodynamic studies

Thermodynamic parameters were calculated to analyze the characteristics and spontaneity of adsorption. To achieve this objective, the thermodynamic parameters, including standard Gibbs free energy (ΔG°), standard enthalpy (ΔH°), and entropy (ΔS°), were calculated utilizing the following equations [89, 90]:

$$K_e^\circ = \frac{1000 \times K_L \times M_{MBorCV} \times [Adsorbate]^\circ}{\gamma} \quad (16)$$

$$\ln K_e^\circ = -\frac{\Delta G^\circ}{R \times T} = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{R} \times \frac{1}{T} \quad (17)$$

$$\Delta G^\circ = \Delta H^\circ - T \times \Delta S^\circ \quad (18)$$

In these equations, K_e° is the thermodynamic equilibrium constant, K_L is the Langmuir constant (L/mg), M_{MBorCV} is the molecular weight of MB or CV dye (g/mol), $[Adsorbate]^\circ$ is the standard concentration, and γ is the dimensionless factor.

The values of enthalpy change (ΔH°) and entropy change (ΔS°) were derived from the graph of the natural logarithm of the equilibrium constant ($\ln K_e^\circ$) plotted against the reciprocal of temperature ($1/T$) in Fig. 8. The slope of the graph corresponds to the ΔH° value, while the intercept corresponds to the ΔS° value. Table 4 provides the thermodynamic parameters for the adsorption of MB and CV dyes by *Prunus spinosa* L. The negative values of ΔG° signify that the adsorption of MB and CV dyes is a spontaneous process. Conversely, the negative values for ΔS° signify a reduction in the randomness of the adsorption system as the adsorption of MB dye onto *Prunus spinosa* L. nears equilibrium. This results from the reduction in the degrees of freedom of the adsorbate molecules in solution [91]. The positive ΔS° value of the CV dye indicates that the randomness increases in the adsorbent active sites. The presence of negative ΔH° values indicates that the adsorption processes of MB and CV dyes are exothermic.

Table 3 Kinetic parameters and error functions for the adsorption of MB and CV dyes on *Prunus spinosa* L. (initial concentration 20 mg/L; agitation rate 120 rpm; adsorbent dosage 0.05 g/50 mL; initial pH 7)

Temperature (K)	Methylene blue					Crystal violet		
	298	308	318	328	298	308	318	328
Pseudo-first-order								
k_1 (min ⁻¹)	0.5474	0.4324	0.3694	0.3598	0.4947	0.4269	0.3585	0.3007
q_e (cal) (mg/g)	19.85	19.73	19.58	19.09	19.55	19.28	19.02	18.69
q_e (exp) (mg/g)	19.41	19.28	19.06	18.19	19.20	18.88	18.55	18.21
r^2	0.9999	0.9999	0.9999	0.9999	0.9999	0.9999	0.9999	0.9999
SSE	1.575	2.199	2.627	7.115	1.183	1.813	3.099	3.471
ARE	1921	1892	1854	1767	1890	1845	1793	1735
RMSE	0.7246	0.8563	0.9357	1.541	0.6279	0.7773	1.017	1.076
SD	0.4743	0.5606	0.6126	1.008	0.4439	0.5497	0.7188	0.7606
χ^2	0.0814	0.1152	0.1407	0.4002	0.0619	0.0973	0.1729	0.2039
EABS	2.827	3.513	3.973	6.575	2.361	2.933	3.782	4.149
MPSD	0.0044	0.0063	0.0079	0.0243	0.0034	0.0056	0.0106	0.0129
Pseudo-second-order								
k_2 (g/mg.min)	0.0981	0.0603	0.0454	0.0395	0.0806	0.0587	0.0419	0.0317
q_e (cal) (mg/g)	19.85	19.73	19.58	19.09	19.55	19.28	19.02	18.69
q_e (exp) (mg/g)	19.83	19.89	19.79	19.09	19.75	19.58	19.46	19.29
r^2	0.9999	0.9999	0.9999	0.9999	0.9999	0.9999	0.9999	0.9999
SSE	0.4654	0.3546	0.3154	2.395	0.2159	0.3281	0.7376	0.7135
ARE	1921	1892	1855	1768	1891	1846	1795	1736
RMSE	0.3939	0.3438	0.3243	0.8934	0.2683	0.3307	0.4958	0.4877
SD	0.2579	0.2251	0.2123	0.5849	0.1897	0.2338	0.3506	0.3
								448
χ^2	0.0246	0.0191	0.0172	0.1407	0.0116	0.0182	0.0426	0.0427
EABS	1.585	1.511	1.398	3.891	0.9796	1.161	1.624	1.729
MPSD	0.0013	0.0011	0.0009	0.0084	0.0006	0.0011	0.0026	0.0026

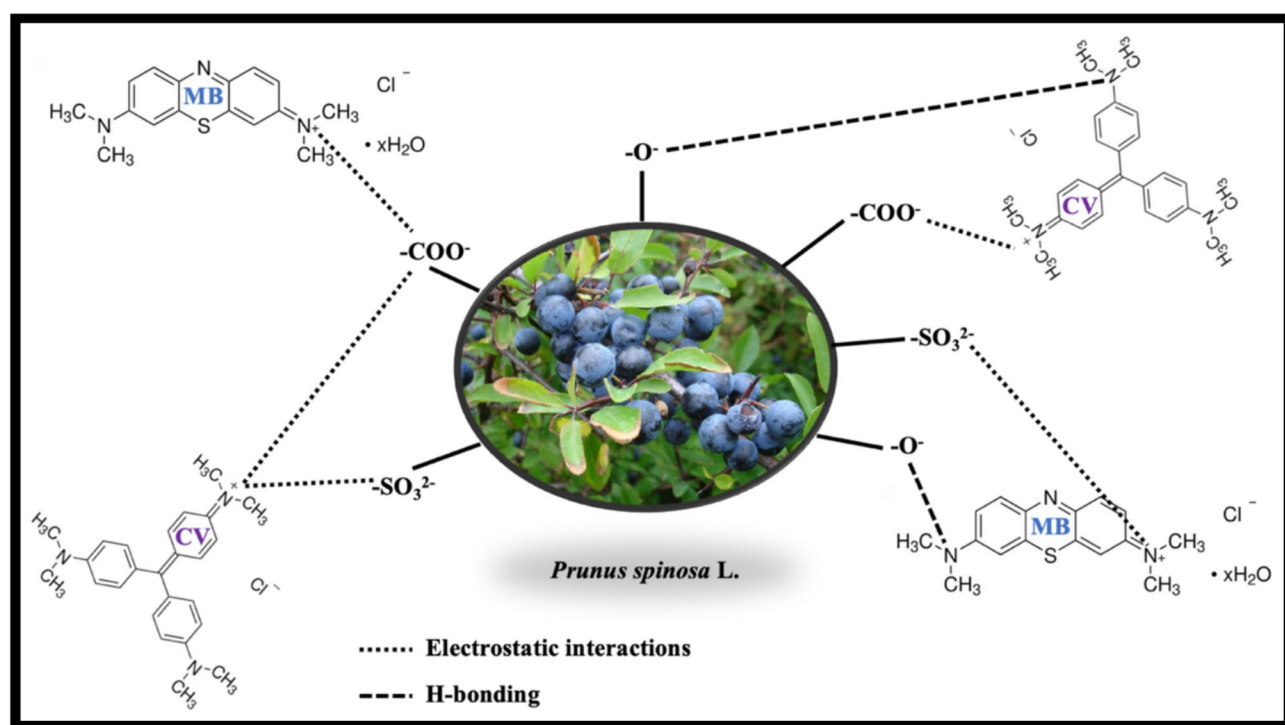


Fig. 7 The possible adsorption mechanism of MB and CV dye onto *Prunus spinosa* L.

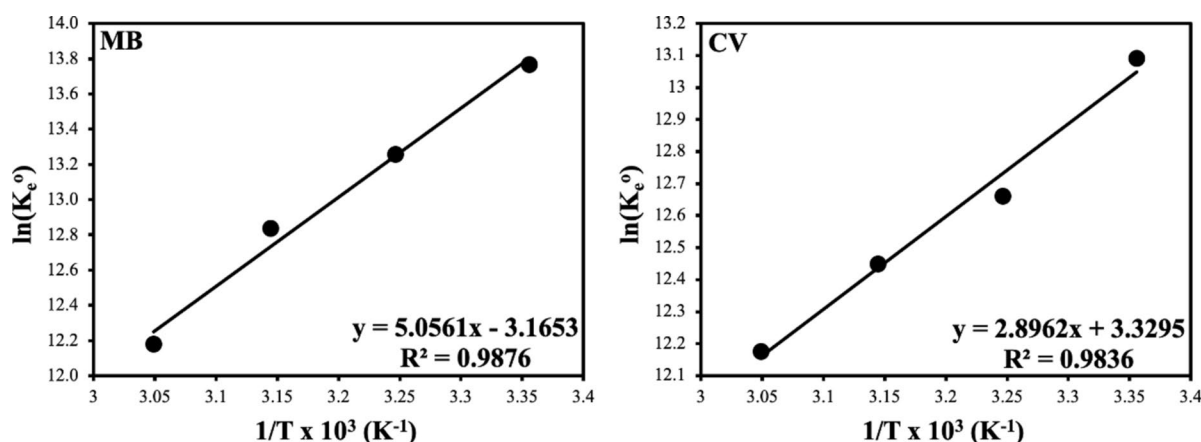


Fig. 8 The linear Van't Hoff plot of MB and CV dye adsorption on *Prunus spinosa* L. (contact time 45 min for MB dye and 30 min for CV dye; agitation rate 120 rpm; adsorbent dosage 0.05 g/50 mL; initial pH 7)

Table 4 Thermodynamic parameters for the adsorption of MB and CV dyes on *Prunus spinosa* L. (contact time 45 min for MB dye and 30 min for CV dye; agitation rate 120 rpm; adsorbent dosage 0.05 g/50 mL; initial pH 7)

Thermodynamic parameters	ΔH_A° (kJ/mol)	ΔS_A° (J/mol.K)	ΔG_A° (kJ/mol)			
			298 K	308 K	318 K	328 K
Methylene blue	−42.04	−26.32	−34.20	−33.93	−33.67	−33.41
Crystal violet	−24.08	27.68	−32.33	−32.61	−32.88	−33.16

3.6 Influence of salt concentration on the adsorption process

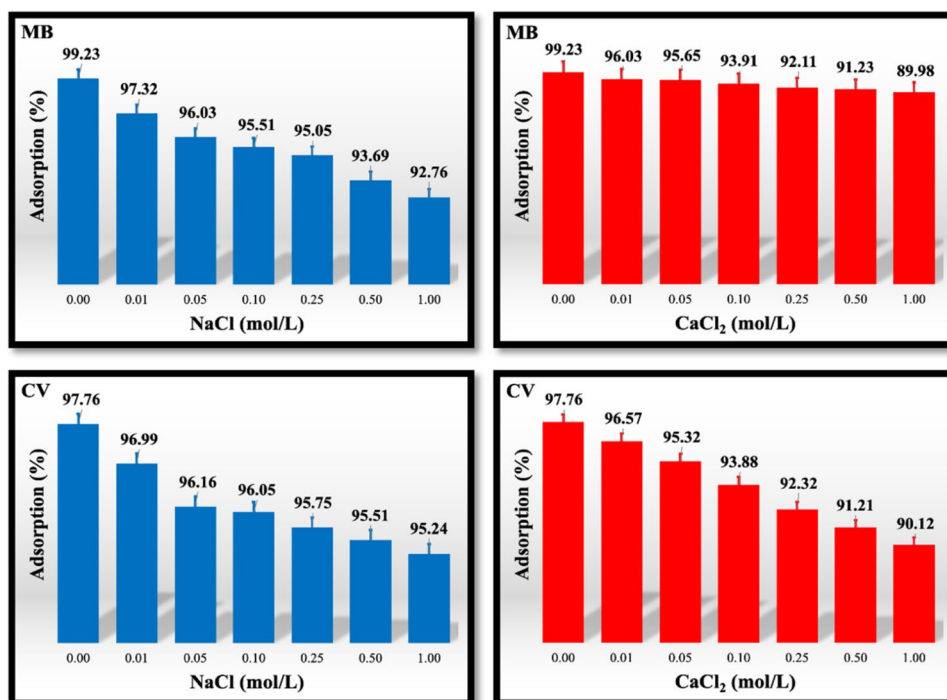
The adsorption studies were carried out at a temperature of 298 K using various concentrations ranging from 0.01 to 1.00 mol/L of NaCl and CaCl₂ for 50 mL solutions of MB and CV dyes. Figure 9 displays the results. As the ionic strength increases, the removal efficiency of *Prunus spinosa* L. decreases due to the higher salt content. According to Fig. 9, the adsorption percentage of *Prunus spinosa* L. falls gradually when NaCl and CaCl₂ are used. The adsorption efficiency of MB dye reduced from 99.23% to 92.76% when NaCl salt was added, and from 99.23 to 89.98% when CaCl₂ salt was added. Conversely, the adsorption percentage of CV dye reduced from 97.76 to 95.24% when NaCl salt was added, and from 97.76 to 90.12% when CaCl₂ salt was added. This scenario suggests that the electrostatic interactions between the dye molecules and the adsorbent surface are significantly influential.

4 Conclusions

Prunus spinosa L. fruit pomace, which is inexpensive, natural, readily available, and falls under the category of zero waste, has been effectively and quickly utilized to remove

MB and CV dyes from water-based solutions. FTIR-ATR analysis demonstrated that hydroxyl, carboxyl, and sulfate groups significantly contribute to the adsorption process on the surface of *Prunus spinosa* L. Furthermore, the scanning electron microscope (SEM) images reveal that the surface of the adsorbent exhibits a dispersed, uneven, and fractured texture. The pH_{pzc} value of *Prunus spinosa* L. was determined as 4.96. The adsorption trials yielded the following optimal physicochemical parameters: an initial pH of roughly 7, a contact time of 45 min for MB dye and 30 min for CV dye, and an adsorbent quantity of 0.05 g/50 mL. The maximum adsorption capacity values were determined as 59.59 mg/g for MB and 53.19 mg/g for CV dyes. The ranking of the acceptable isotherm models for the adsorption process of MB and CV dyes on *Prunus spinosa* L. was determined as Temkin > Langmuir > Freundlich > D-R, based on the correlation coefficient and error functions. The pseudo-second-order kinetic model has yielded the most accurate fit for the kinetic profiles. The thermodynamic characteristics indicate that the adsorption process for both dyes is exothermic ($\Delta H^\circ = -42.04$ kJ/mol MB dye and $\Delta H^\circ = -24.08$ kJ/mol for CV dye) and spontaneous ($\Delta G^\circ = -34.20$ kJ/mol for MB dye and $\Delta G^\circ = -32.33$ kJ/mol for CV dye at 298 K. Furthermore, it was noted that varying salt concentrations have a detrimental impact on the adsorption process, and

Fig. 9 The influence of NaCl and CaCl₂ salt on MB and CV dye adsorption onto *Prunus spinosa* L. (contact time 45 min for MB dye and 30 min for CV dye; agitation rate 120 rpm; adsorbent dosage 0.05 g/50 mL; initial pH 7; initial concentration 20 mg/L)



electrostatic interactions significantly contribute to the effectiveness of the adsorption process. The adsorption efficiency of MB dye decreased from 99.23 to 92.76% with the addition of NaCl and from 99.23 to 89.98% with the addition of CaCl₂. The adsorption percentage of CV dye decreased from 97.76 to 95.24% with the addition of NaCl, and from 97.76 to 90.12% with the addition of CaCl₂. To summarize, the findings of this study suggest that *Prunus spinosa* L. can serve as a highly efficient and fast-acting adsorbent for treating water contaminated with dyes such as MB and CV.

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Author contribution All authors contributed to the study's conception and design. Material preparation, data collection, and analysis were performed by Elif Burcu Onuk and Birol Isik. The first draft of the manuscript was written by Birol Isik, and all authors commented on previous versions of the manuscript. All authors read and approved the final manuscript.

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Data availability The data that support the findings of this study are available from the corresponding author upon reasonable request.

Declarations

Ethical approval Not applicable.

Consent to participate Not applicable.

Consent for publication Not applicable.

Competing interests The authors declare no competing interests.

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