Removal of Congo red using Vernonia amygdalina leaf powder: optimization, isotherms, kinetics, and thermodynamics studies

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ABSTRACT
Dye effluents generated from industries are the main source of water pollution. The elimination of dyes from water bodies is essential for environmental protection. From an ecological and financial standpoint, the adsorption strategy using low-cost adsorbents is a sensible solution to remove dye pollutants from wastewater. In this study, Vernonia amygdalina leaf powder (VALP) adsorbent was prepared and used to eliminate Congo red dye (CRD) from aqueous solutions. Scanning Electron Microscopy (SEM) and Fourier Transmission Infrared (FT-IR) spectroscopy techniques were used to study VALP morphology as well as the nature of the interaction between VALP and CRD. Batch adsorption experiments were conducted to examine the influence of adsorbent dose, CRD concentration, contact time, and pH on CRD adsorption using VALP. As a result, 0.5 g of adsorbent dose, 100 mg/L CRD solution, 70 minute contact time, and a solution pH of 8 were determined as optimum values. Temkin adsorption isotherm models were used to test the experimental data, and the result is fitted well to the Langmuir model with a maximum adsorption capacity of 57.47 mg/g. Adsorption kinetics models such as pseudo-first-order, pseudo-second-order, and intraparticle diffusion were used to determine adsorption parameters. As a result, pseudo-second-order was fitted well to the experimental data. Thermodynamic parameters such as $\Delta H^\circ$ (5.702 kJ/mol) and $\Delta G^\circ$ (−1674.6566 to −994.6388 J/mol) show endothermic and spontaneous adsorption. The current study confirmed that VALP is one of the most effective, eco-friendly, and sustainable dye adsorbents from solution compared to other low-cost adsorbents.

1. Introduction
Nowadays, water usage has been increasing because of industrialization and rapid population growth. This growth leads to heavy metals, dyes, and other hazardous chemicals generated in enormous quantities [1]. Many toxic substances generated from different sources discharge into the water reservoir without proper pollutant removal or reduction measures [2]. Dye effluents from different industries like textiles, plastics, paint, and printing discharge into bodies of water without effective treatment, causing pollution [3]. Many dyes have been linked to allergic dermatitis, skin irritation, reproductive, and central nervous system problems [4]. Congo red is an anionic diazo dye having colour-assisted functional groups [5]. It is commonly used as a colouring material in many industries such as textiles, cosmetics, paper, etc. [6,7]. On the other hand, CRD has long been banned owing to its carcinogenic qualities [7,8]. Therefore, it is essential to eliminate CRD from industrial waste and other sources before being discharged into the environment.

Currently, there are many methods used to remove dye from wastewater, for example, adsorption [9], ion exchange [10], coagulation [11], reverse osmosis [12], etc. However, except for adsorption method, alternative removal strategies have certain disadvantages, like high operating prices, the formation of hazardous by-products, and extremely high energy requirements [9]. Even if the adsorption method is better than the above-mentioned dye removal methods, selecting a good adsorbent for the adsorption process is a very difficult job. For example, activated carbon is a better adsorbent material for dye adsorption from wastewater, but its application is limited due to its high cost and difficulty to regenerate after the adsorption process is completed. Due to this, there has been an increase in an investigation into cheap, effective, and eco-friendly adsorbents [13].

Dye effluents from different sources can be treated by low-cost adsorbents prepared using the agricultural by-product, industry residues, and natural materials. For example, adsorbents such as wheat husk [14], coconut shell [15], magnesium oxide-coated kaolinite [16], sumac leaves [17], jackfruit leaf [18], tree and sea plant leaves [19], Jamun leaf powder [20], syringa Vulgaris leaves [21], and ginkgo leaves [22], etc., were used to remove dye from wastewater. CRD pollutants also can be removed using low-cost adsorbents such as tea waste [23], orange peel [24], cabbage waste powder [25], Raphanus sativus peels [26], Pisum
Plant leaves are packed with various functional groups such as alcohols, carboxylic acids, ethers, phenols, etc., which are useful in the adsorption of dye molecules [18]. Some adsorbents prepared from plant leaves that have been used for CRD removal from solution include Spathodea campanulata leaves [27], Typha australis leaves [28], Teucrium polium L [29]. However, there is no scientific report on the removal of CRD from solution using VA plant leaves adsorbent.

2. Material and methods

2.1. Chemicals

CRD (C_{28}H_{32}N_{4}Na_{2}O_{6}S_{3}), NaOH (AR grade), and HCl (AR grade) were purchased from Merck, Mumbai, India and used without further purification process. 1000 mg/L CRD stock solution prepared using 1 g of CRD into a 1 L volumetric flask with an appropriate amount of distilled water. Then, the required concentrations were prepared from 1000 mg/L via a dilution mechanism using distilled water.

2.2. Plant material preparation

VA plants, which grow near Debremakos University, were used to prepare an adsorbent (VALP). VA leaves were collected, washed with distilled water, and dehydrated at a temperature of 80°C for 24 h, respectively. Then, using pestle and mortar, dried leaves were crushed and then sieved through a 355 μm sieve.

2.3. Characterization

The FT-IR spectrum of VALP before and after CRD adsorption was recorded using an FT/IR-6600type A spectrometer, over a 400–4000 cm⁻¹ range, using the KBr disk method, and at 4 cm⁻¹ resolution operating parameters. The morphology of VALP was analyzed using JCM-6000Plus Benchtop SEM at a 15 kV accelerated voltage operating condition.

2.4. Batch adsorption experiments

A batch adsorption experiment was conducted with 0.25 L conical flasks holding 0.150 L of CRD with measured VALP weight. The mixture was then shaken on a digital shaker for 120 minutes (except for the effect of contact time) at 25°C at 150 rpm. Finally, the concentrations of CRD that remained in the supernatant solution was measured by a UV/Vis spectrophotometer (Shimadzu UV-1700 Spectrophotometer) with λmax = 498 nm. The VALP dose influence on CRD removal percentage was evaluated by adding 80 mg/L of CRD solution in a separate conical flask with 0.1, 0.2, 0.3, 0.4, 0.5, 0.6, and 0.7 g of VALP. To examine the initial concentration effect on the adsorption process, 20, 40, 60, 80, 100, and 120 mg/L of CRD solutions with 0.5 g of VALP were employed. The influence of contact time on adsorption was studied by adding 0.5 g VALP and 100 mg/L CRD to a separate conical flask, followed by adsorption measurements at 10, 20, 30, 40, 50, 60, 70, 80, and 90 minutes. The solution pH effect was evaluated using pH values of 3, 4, 5, 6, 7, 8, 9, and 10 in a separate conical flask containing 100 mg/L CRD and 0.5 g VALP. 0.1 M HCl or 0.1 M NaOH solutions were used for working solutions pH modification purposes.

The adsorption capacity of VALP was determined by equation 1 [18]:

\[ q_e = \frac{(C_i - C_f)}{W} x V \]  

Where \( q_e \) (mg/g) – the adsorbed amount of CRD at equilibrium, \( C_i \) – the initial CRD concentration (mg/L), \( C_f \) – CRD concentration at equilibrium (mg/L), \( V \) – working solution volume (L), and \( W \) – VALP weight (g).

The CRD removal percentage was determined by equation 2 [18]:

\[ \% \text{removal} = \left( \frac{C_i - C_f}{C_i} \right) \times 100 \]  

Note: This text is a part of the original document and has been formatted for better readability and comprehension.
2.5. Mathematical modeling

2.5.1. Adsorption isotherm studies

Adsorption isotherm study was conducted using 0.250 L conical flasks with 0.150 L of 20, 40, 60, 80, 100, and 120 mg/L of CRD solutions having a pH of 8, and 0.5 g of VALP. Using a digital shaker, the mixture was shaken at 150 rpm at 25°C for 70 min. The residual concentration of CRD was measured using UV/Vis spectrophotometer (Shimadzu UV-1700 Spectrophotometer) at λmax = 498 nm.

The Langmuir isotherm model assumes that the monolayer adsorption process happens on a uniform surface [31]. The Langmuir isotherm was calculated by using equation 3 [32]:

\[
\frac{Ce}{qe} = \frac{Ce}{qm} + \frac{1}{KLqm}
\]

Where \( qe \) – the adsorbed amount of CRD at equilibrium (mg/g), \( qm \) – monolayer adsorption capacity (mg/g), \( Ce \) – CRD concentration at equilibrium (mg/L), and \( KL \) – Langmuir constant (L/mg).\( \frac{Ce}{qe} \) vs. \( Ce \) plot slope and intercept values were applied for \( qm \) and \( KL \) value determination, respectively.

A Langmuir model character is also determined using \( R_L \) (separation factor) [32]. A separation factor can be calculated using equation 4:

\[
R_L = \frac{1}{1 + KLx}
\]

Where \( Ci \) (mg/L) – CRD starting concentration.

The adsorption process and isotherm shape can be determined using \( R_L \). If \( R_L \) is between 0 and 1, greater than 1, equal to 1, equal to 0, means favorable, unfavorable, linear, and irreversible, respectively [33].

The Freundlich model posits that adsorption occurs on the surface of a heterogeneous medium, and there is a proportionality between adsorption capacity and adsorbate concentration [34]. The Freundlich isotherm was calculated using equation 5 [35]:

\[
\log qe = \log K_F + \frac{1}{n} \log Ce
\]

Where \( K_F \) (mg/g)/(mg/L)\(^{1/n} \) and \( n \) – Freundlich constant are related to adsorption capacity and intensity, respectively. \( \log qe \) vs. \( \log Ce \) plot intercept and slope values were used to determine \( K_F \) and \( n \) values, respectively.

A Temkin isotherm was used to calculate the adsorption enthalpy and interaction between an adsorbent and an adsorbate. The Temkin model was expressed using equation 6 [33]:

\[
qe = \frac{RT}{bT} \ln K_T + \frac{RT}{bT} \ln Ce
\]

Where \( T \) – temperature (K), \( R \) – universal gas constant, \( bT \) – adsorption enthalpy (J/mol), and \( K_T \) – equilibrium binding constant (L/g). \( qe \) vs. \( Ce \) plot slope and intercept values were used to compute the \( bT \) and \( K_T \) values, respectively.

2.5.2. Adsorption kinetics studies

In a separate 0.250 L conical flask, 0.5 g VALP and 0.150 L of 100 mg/L CRD solution having a pH of 8 were added. Using a digital shaker, the mixture was shaken at 150 rpm at 25°C. Then, a sample was withdrawn at a 10-min interval from 10 to 90 min. Finally, the residual concentration of CRD was measured by a UV/Vis spectrophotometer (Shimadzu UV-1700 Spectrophotometer) at λmax = 498 nm.

By applying different kinetics models, the adsorption process parameter was investigated. Pseudo-first-order kinetics was calculated by using equation 7 [36]:

\[
\log (qe - qt) = \log qe - \frac{k_1}{2.303} t
\]

Where; \( qt \) (mg/g) – the adsorbed amount of CRD at time \( t \) (min), \( qe \) (mg/g) – the adsorbed amount of CRD at equilibrium, and \( k_1 \) – pseudo-first-order rate constant (min\(^{-1} \)). \( (qe - qt) \) vs. \( t \) plot were used to calculate \( k_1 \) and \( qe \) values, respectively.

Pseudo-second-order kinetics calculated using equation 8 [36]:

\[
\frac{t}{qt} = \frac{1}{k_2qe^2} + \frac{1}{qe} t
\]

Where \( k_2 \) – pseudo-second-order rate constant (g/mg min). The \( k_2 \) and \( qe \) values were determined using intercept and slope values from the \( \frac{t}{qt} \) vs. \( t \) plot.

An intraparticle diffusion model was used to study the possibility of intraparticle diffusion [37]. The intraparticle diffusion model was calculated using equation 9 [37]:

\[
qt = k_{id}t^{1/2} + C
\]

Where \( C \) – boundary layer effect constant, and \( k_{id} \) – intraparticle diffusion rate constant (mg/g min\(^{1/2} \)). \( qt \) vs. \( t^{1/2} \) plot intercept and slope values were used to calculate \( C \) and \( k_{id} \) values, respectively.

2.5.3. Adsorption thermodynamics studies

Thermodynamic studies were conducted by adding 0.150 L of 100 mg/L CRD solution and 0.5 g of VALP into a separate 0.250 L conical flask, and then the temperature of the flask was adjusted to 298, 313, and 328 K with agitation speed 150 rpm for 70 minutes. Finally, the residual CRD was determined using UV/Vis spectrophotometer (Shimadzu UV-1700 Spectrophotometer) at λmax = 498 nm.

Thermodynamic parameters (\( \Delta G^\circ \), \( \Delta H^\circ \), and \( \Delta S^\circ \)) can be calculated by using equations 10, 11, and 12 [38].
\[ \Delta G^\circ = -RT \ln K_c \]  \hspace{1cm} (10) 
\[ \ln K_c = -\frac{\Delta H^\circ}{RT} + \frac{\Delta S^\circ}{R} \] \hspace{1cm} (11) 
\[ K_c = \frac{q_e}{C_e} \] \hspace{1cm} (12)

Where \( \Delta G^\circ \) (J/mol) – the standard-free energy change, \( \Delta H^\circ \) (kJ/mol) – the standard enthalpy change, \( \Delta S^\circ \) (J/(mol K)) – the standard entropy change, \( T \) – the temperature (K) and \( R \) – the universal gas constant (J/(mol K)), \( K_c \) – the equilibrium constant, \( q_e \) (mg/g) – the adsorption capacity at equilibrium, and \( C_e \) (mg/L) – the concentration of dye at equilibrium. The \( \Delta H^\circ \) and \( \Delta S^\circ \) values can be determined using the intercept and slope of \( \ln K_c \) versus \( T^{-1} \) plot.

### 2.6. Desorption studies

The desorption experiment was carried out by pouring 0.150 L of 0.01 M NaOH, 0.01 M HCl, and deionized water into a separate 0.250 L conical flask holding 0.5 g of CRD-loaded VALP. The mixture was then agitated for 70 minutes at 150 rpm at 25 C. After filtration, the amount of CRD in the solution was measured using UV/Vis spectrophotometer (Shimadzu UV-1700 Spectrophotometer) at \( \lambda_{\text{max}} = 498 \) nm. The percentage of desorption was determined using equation 13 [39].

\[ \% \text{desorption} = \left( \frac{C_{\text{des}}}{C_{\text{ad}}} \right) \times 100 \] \hspace{1cm} (13)

Where \( C_{\text{des}} \) – the desorbed concentration of dye (mg/L) and \( C_{\text{ad}} \) – the adsorbed amounts of dye (mg/L)

### 2.7. Statistical methods and data analysis

All experimental measurements were carried out in triplicate and recorded the mean values. Triplicate measurements also were used to determine tests repeatability and standard deviation. Error bars were added for the graphs in the result and discussion part by using standard deviations values. To plot graphs and draw reaction mechanisms MS Excel, Chem3D Ultra 8.0, and Origin 8.5 were used to plot graphs.

### 3. Result and discussion

#### 3.1. Adsorbent characterization

The FTIR analysis of before and after the adsorption of CRD using VALP is described in Figure 1. As seen in Figure 1a, before dye adsorption, the peaks are shown at 3416.27 cm\(^{-1}\), and 2924.48 cm\(^{-1}\) were assigned to be the O-H and C-H stretching, respectively [40,41]. The absorption peaks at 2374.9 and 2329.58 cm\(^{-1}\) showed O-H in carboxylic acid stretching molecules [42]. At the time, the broad peak observed at 1634.37 and 1417.42 cm\(^{-1}\) were C=C stretching and O-H bending of carboxylic acid, respectively. The band at 1256.39 cm\(^{-1}\) corresponds to the C-O stretching of an aromatic ester. The peak at 1041.37 cm\(^{-1}\) is due to the C-N stretching vibration of amines. While the peak observed at 717.38, 576.6–536.11 cm\(^{-1}\) due to the C = C bending and C-I stretching vibration, respectively. In general, an absorption peaks between 400 and 500 cm\(^{-1}\) corresponds to C-halogen stretching. However, absorption peak below 1000 cm\(^{-1}\) is a difficult task to assign a specific functional group for each peak due to peak overlapping a result of complex interacting vibration [43]. As seen in Figure 1b, after dye adsorption some peak positions were shifted, some peaks disappeared, and new peaks were found. The absorption peak was shifted from 2329.58 to 2355.62, 1634.37 to 1644.01, 1417.42 to 1440.56, 1041.37 to 1108.86, and 717.38 to 618.07 cm\(^{-1}\). This shift indicates the active participation of VALP functional groups in CRD adsorption. Similarly, other studies have also been reported [18,44].

The SEM micrographs of VALP before and after CRD adsorption are shown in Figure 2. The rough and irregular structure of VALP before adsorption of CRD is

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**Figure 1.** FT-IR spectrum of VALP: (a) before CRD adsorption and (b) after CRD adsorption.
shown in Figure 2 (a) and (b), which provides an appropriate adsorption place to adsorb the CRD molecule. However, after CRD adsorption, the surface of VALP was shielded as shown in Figure 2 (c) and (d). This is realized by CRD removal using Moringa oleifera seeds [45].

3.2. Optimization parameters

3.2.1. Influence of VALP dose
In Figure 3, the influence of VALP dose on removal percentage is shown. As seen in the graph, the percentage of removal was enhanced from 22.70 to 85.38 after the VALP dose was enlarged from 0.1 to 0.5 g.

Figure 2. VALP SEM photographs: a, b before CRD adsorption, and c, d after CRD adsorption.

Figure 3. The influence of adsorbent dose on CRD removal from aqueous solution using VALP.
Adsorption capacity improved when the number of adsorption sites increased as the dose increased [46]. Figure 3 also shows that after the optimum dosage, the removal percentage did not change significantly. After the optimum adsorbent dose, overlapping adsorption sites limit the accessible surface for removal and extend the diffusion channel, resulting in a loss of adsorption capacity [47]. A related approach was described for CRD removal using *Spathodea campanulata* leaves [27].

Figure 4. The influence of initial concentration on CRD removal from aqueous solution using VALP.

Figure 5. The influence of contact time on CRD removal from aqueous solution using VALP.

Figure 6. The influence of solution pH on CRD removal from aqueous solution using VALP.
3.2.2. Influence of initial concentration
The influence of the starting CRD amount on the removal percentage is shown in Figure 4. As seen in the graph, when the initial concentration increased from 20 mg/L to 100 mg/L, the removal percentage reduced from 89.20% to 83.28%. A high starting dye concentration causes an overload of the available adsorbent sites, resulting in a large amount of dye in the solution [48]. However, after 100 mg/L CRD, the removal percentage did not change meaningfully. At

![Graph a](image1)

![Graph b](image2)

![Graph c](image3)

Figure 7. Adsorption isotherm plot for CRD removal from aqueous solution using VALP: a) Langmuir, b) Freundlich, and c) Temkin.
optimum dye concentration, there was a limited number of places available to adsorb dye molecules, and no further dye removal was attempted [48]. A 100 mg/L concentration is the optimum value for CRD elimination using VALP. A related report for CRD removal using Eichhornia crassipes root yielded similar results [49].

3.2.3. Influence of contact time
The CRD removal percentage using VALP was measured at different contact times, and the outcomes are presented in Figure 5. As a result, indicated that the percentage of removal was increased from 59.6 to 80.16 when reaction time rose from 10 to 70 minutes. Due to vacant spaces at the adsorbent site at the start and the high solute concentration gradient, dye adsorption was rapid for the first 70 minutes. However, after 70 minutes of contact time, there was no significant change in removal percentage. After the optimum reaction time, the rate of removal decreased near the end of an experiment due to a lack of unoccupied adsorbent places [33]. The adsorption of CRD using Eichhornia crassipes root yielded similar results [49].

3.2.4. Influence of solution pH
Figure 6 shows that the CRD solution pH influences the adsorption process. As a result, when solution pH rose from 3 to 8, the removal percentage improved from 48.72% to 86.80%. As the pH of the solution rises due to OH− ion adsorption on the adsorbent surface, positive charge site reductions and negative charge adsorbent site rises can happen. However, after an optimum pH value was reached, the percent of dye removed decreased again. Electrostatic repulsions are established between positive-charge dye ions and negative-charge adsorbent surfaces. Similar results were reported for CRD removal using Spathoda campanulata leaves [27].

3.3. Adsorption isotherms
The adsorption process parameters were determined using models appropriate for adsorption experiments. Figure 7 depicts the plot of the Langmuir, Freundlich, and Temkin isotherms.

In this study, different adsorption isotherm factors were calculated and summarized in Table 1. The R² value for the Langmuir isotherm was 0.9915, which is greater than that of the Freundlich and Temkin isotherms, that is, 0.9896 and 0.9777, respectively. Therefore, the Langmuir model fitted well for CRD removal using VALP. There is a big difference observed between Langmuir and experimental adsorption capacity. This is due to no attraction or repulsion between adsorbent and adsorbate in case Langmuir assumption causing a high adsorption capacity (57.47 mg/g), in contrast, experimental adsorption capacity is highly affected by electrostatic interaction and repulsions among adsorbate-adsorbate and adsorbent-adsorbent, which limit the VALP-CRD interaction, causing a less adsorption capacity (24.98 mg/g). The value of R² = 0.171 is in the range of 0 and 1, which indicates a favorable adsorption process. Furthermore, n = 1.357, which is greater than 1 indicate the chemisorption adsorption process. The value of bT (236.50 J/mol), which is greater than zero indicates an endothermic adsorption process. CRD removal using other low-cost adsorbents such as Eichhornia Crassipes [50], Spathoda campanulata leaves [27], Typha australis leaves [28], Cabbage waste powder [25], etc., have also been seen to follow the Langmuir isotherm. Table 2 lists the Langmuir isotherm constants for CRD removal using various low-cost adsorbents. From this table, VALP has much higher maximum adsorption capacities than numerous other adsorbents, indicating that it could be a promising adsorbent for dye removal from solution.

3.4. Adsorption kinetics
Adsorption parameters were evaluated by the slope and intercept values of kinetic model plots as shown in Figure 8.

Table 3 summarizes the calculated adsorption kinetics data. The correlation coefficient (R²) value obtained for pseudo-second-order was 0.9968, which is greater than that obtained from pseudo-first-order and intraparticle diffusion. Additionally, a calculated value (qe, 2 cal) was close to the experimental value.
Figure 8. The adsorption kinetics plot for CRD removal from aqueous solution using VALP: a) pseudo-first-order, b) pseudo-second-order, and c) Intraparticle diffusion.

Table 3. The kinetic parameters for CRD removal from aqueous solution using VALP.

| experiment | pseudo-first-order | pseudo-second-order | intraparticle diffusion |
|------------|--------------------|---------------------|--------------------------|
|            | q_e, exp (mg g\(^{-1}\)) | k_1 (min\(^{-1}\)) | R^2 | q_e,1cal (mg g\(^{-1}\)) | k_2 (g/mg min) | R^2 | q_e,2cal (mg g\(^{-1}\)) | R^2 | k_{id} (mg/g min\(^{1/2}\)) | C | R^2 |
|            | 24.98              | 0.0329              | 11.63 | 0.9702 | 0.00512 | 26.25 | 0.9968 | 0.00512 | 26.25 | 0.9968 | 1.116 | 14.29 | 0.9769 |
Table 4. Pseudo-second-order kinetics for CRD removal using different low-cost adsorbents.

| Adsorbent          | \(k_2\) (g/min mg) | \(q_{e, 2cal}\) (mg/g) | \(R^2\) | Reference   |
|--------------------|---------------------|-------------------------|---------|-------------|
| Cabbage waste powder | 0.01276             | 1.7337                  | 0.975   | [52]        |
| Typha australis leaves | 2.21                | 0.267                   | 0.9663  | [28]        |
| Teucrium polium L. | 0.00167             | 45.87                   | 0.999   | [29]        |
| Eichhornia Crassipes | 0.533               | 15.760                  | 1       | [50]        |
| VALP               | 0.00154             | 46.95                   | 0.9887  | Present study |

Figure 9. In \(K_c\) versus \(T^{-1}\) plot for CRD adsorption using VALP.

Table 5. Thermodynamic parameters for CRD adsorption using VALP.

| Temperature (K) | \(K_c\) (J/mol) | \(\Delta G^\circ\) (J/mol) | \(\Delta S^\circ\) (J/(mol K)) | \(\Delta H^\circ\) (kJ/mol) |
|-----------------|-----------------|-----------------------------|-------------------------------|-----------------------------|
| 298             | 1.494           | −994.6388372                | 22.293                        | 5.702                       |
| 313             | 1.561           | −1158.865503                |                               |                             |
| 328             | 1.848           | −1674.656622                |                               |                             |

Figure 10. Mechanism for CRD adsorption using VALP.
(qe, exp). CRD removal from aqueous using VALP fitted well to pseudo-second-order. Similar results were stated for CRD using Teucrium polium L [29]. The adsorption of CRD using other low-cost adsorbents such as Cabbage waste powder [52], Typha australis leaves [28], Eichhornia Crassipes [50], Teucrium polium L [29], etc., have also been stated to follow the pseudo-second-order model. Table 4 compares the kinetic parameters acquired by other researchers with the current investigation. This table shows that our pseudo-second-order rate constant value k2 = 0.00512 g/min mg, which is within the comparable interval of literature values (0.00154–2.21 g/min mg).

3.5. Adsorption thermodynamic
The efficiency of dye removal can be determined using thermodynamic parameters [53]. The plot shown in Figure 9 is to determine $\Delta S^\circ$ and $\Delta H^\circ$. Additional thermodynamic parameters were determined using equations 10, 11, 12 and results are summarized in Table 5. The positive value of $\Delta H^\circ$ and the negative value of $\Delta G^\circ$ indicate endothermic and spontaneous adsorption. In addition, positive $\Delta S^\circ$ values reflect increased randomness at the VALP/CRD solution interface [38].

3.6. Adsorption mechanism
The existence of – OH and – COOH in VALP was discovered by FT-IR investigation. The – OH and – COO\(^-\) groups are the most responsible functional groups for dye adsorption [54]. The functional group present in VALP can interact with the hydroxyl group on the surface of VALP through the H-bond. The surface functional groups are protonated, thus the change would be formed on the surface. In an acidic medium – OH and – COOH functional groups available at VALP surface C-OH\(_2\)^+ occur [55]. The electrostatic interaction was formed among SO\(_4\)^− and carboxylic groups of O = C-OH\(_2\)^+. Figure 10 shows the proposed mechanism of CRD adsorption using VALP.

3.7. Desorption studies
The desorption studies help researchers to understand how depleted adsorbents recovered [56]. Figure 11 shows the CRD desorption efficiency from CRD-adsorbed VALP during the first desorption cycle. A significant desorption percentage (77.58%) of CRD from CRD-adsorbed VALP observed during 0.01 M NaOH eluent was utilized. 0.01 M HCl and pure water, on the other hand, showed lower desorption percentages. The dye was firmly bound to the adsorbent by chemisorption, as evidenced by the low desorption efficiency in an acidic solution [57].

4. Conclusion
This research aims to produce eco-friendly dye adsorbent materials for energy-efficient, cost-effective, and cleaner water production to achieve sustainable and cleaner water production. The findings of this study show that VALP is a good material for removing CRD from aqueous solutions. In VALP, there are numerous functional groups and a porous surface. The strength of absorption peaks was reduced after dye adsorption, revealing the interaction of these functional groups with dye cations. The adsorption process is influenced by the adsorbent dosage, contact time, solution pH, and starting concentration. The working parameters for optimum removal are a 0.5 g dose of VALP, a starting 100 mg/L CRD solution, 70 minutes of contact time, and a solution pH of 8. According to the isotherm study, the Langmuir model fit the experimental data well. Kinetic investigation showed the adsorption process well expressed by a pseudo-second-order model. Thermodynamic analysis indicated
that the removal of CRD using VALP adsorbent is a spontaneous and endothermic adsorption process. The most effective VALP desorption percentage is with 0.01 M HCl. Based on this study findings and comparisons to other adsorbents previously published, it is possible to conclude VALP is an eco-friendly, effective, and sustainable adsorbent to remove CRD from wastewater because of its high adsorption capacity and reusability. The application of VALP for real wastewater treatment will be the focus of future research.

**List of abbreviations**

| Abbreviation | Description                          |
|--------------|--------------------------------------|
| VALP         | Vernonia amygdalina leaf powder       |
| VA           | Vernonia amygdalina                  |
| CRD          | Congo red dye                        |
| SEM          | Scanning Electron Microscopy         |
| FT-IR        | Fourier Transform Infrared Spectroscopy |
| UV/Vis       | Ultraviolet/Visible Spectroscopy     |

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**Data availability of statement**

The datasets used and/or analyzed during the current study are available from the corresponding author on reasonable request.

**Authors’ contributions**

Belete Geremew and Dagme Zewde created the original concept and main idea, as well as designed and carried out the experiments. Dagme Zewde managed the research. Belete Geremew and Dagme Zewde analyzed data, wrote the paper and revised the final manuscript. All authors read and approved the final manuscript.

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