Effective adsorption of crystal violet from aqueous solutions with effective adsorbent: equilibrium, mechanism studies and modeling analysis

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ABSTRACT
In this work, NaOH-activated Aerva javanica leaf (NAJL) powder was successfully developed as a cost-effective adsorbent for removal of crystal violet (CV) from an aqueous environment. The prepared adsorbent was characterized using FTIR, SEM, and their surface area was determined by BET technique. Different parameters affecting the adsorption of CV dye such as pH solution, adsorbent dose, equilibrium time, initial CV concentration, and temperature were investigated. The results revealed that the best-optimized values were found as pH–9, dose–20 mg, time–30 min, temperature–25 °C. The adsorption experimental data exhibited excellently fitted well to the nonlinear Langmuir isotherm and Pseudo-first-order kinetic models. The maximum monolayer adsorption capacity of CV dye was 315.2 mg/g. The experimental parameters of thermodynamic analysis exhibited that the CV dye adsorption onto NAJL powder was exothermic and spontaneous. Electrostatic attraction, π-π interactions, and Hydrogen bonding were the mechanism behind the adsorption of CV dye.

1. Introduction
Nowadays, organic dyes are one of the main sources of water pollution due to their wide application in industry such as for dyeing papers, textile fibers, plastics, leathers and pharmaceuticals [1]. According to a recent report, about 10 thousand various types are produced with a rate of more than 700 thousand tons/year, and most of the dyes available in the market [2]. Dyes such as malachite green (MG), methylene blue (MB) and crystal violet (CV) have a negative effect on water quality, and it is carcinogenic dyes that can potentially affect human as well as animal life [3–5]. Hence, the removal of toxic dyes poses challenges to the researchers in finding excellent methods for the elimination of dyes before their release into the aqueous environment. Numerous techniques of treating dye effluents including electrochemical [6] ion exchange [7] membranes [8], ozonation [9], degeneration [10,11] and adsorption [12–14]. Among them, adsorption is a simple method widely used in water treatment due to its low cost, effectiveness and easy regeneration [15,16]. Elimination of dyes from wastewater can be accomplished by various adsorbents that were used in adsorption techniques like TLAC/Chitosan [17], bentonite-alginate composite [18], cellulose-based adsorbent (CGS) [19], coffee husks [20], polypropylene-based KOH-activated carbon [21], acid-modified eucalyptus leaves [22]. Commercially activated carbon is applied for dye adsorption from wastewater, but these adsorbents are highly expensive, limiting its commercial application [23–25]. The suitable adsorbent can be described by low cost, high removal capacity and high renewability [26].

Recently, the adsorbents based on agricultural material or biosorption (biomass) have been a special interest due to its offer several benefits; they are cost-effective, non-toxic, biodegradable, and it has in its structure many functional groups that can form bonds with dyes. Some of the bio adsorbents that have been applied to eliminate pollutants include Moringa oleifera [27], Senna alata [28], Gmelina leaves [29], Imperata cylindrica [30], Walnut shell [31], Antocarpus camansi Blanco core [32], Casuarina equisetifolia needle [33], Pine leaves [34], Pinus nigra [35], etc. Therefore, the utilization of abundantly available biomass from plants is a feedstock for the production of excellent adsorbents having a wide range of energy and environmental applications.

Aerva javanica is a herb and widely dispersed in countries of the world. It is found in some Asian countries like Saudi-Arabia (Western-Southern parts) and the native of Aerva javanica is Africa [36]. Aerva javanica is a herb medicinal plant and has various medicinal benefits. Almost all parts of Aerva javanica exhibit antioxidant, antiviral and antidiabetic activities [37]. Anand et al. conducted a study to examine the components of Aerva javanica and the results revealed that the presence of flavonoids, alkaloids, phenols,
glycosides, tannins, saponins and a minute amount of terpenoids [38].

The objective of this study was for activation of the Aerva javanica leaves and inflorescence using H₂O₂ and NaOH reagent. Then, the untreated Aerva javanica leaves & inflorescence and NaOH-activated Aerva javanica leaves and inflorescence adsorbents were used for the elimination of CV dye ions from the aqueous solution. The NAJL powder were characterized using SEM, FTIR and BET techniques. The effect of pH, contact time, initial CV concentration, adsorbent dose and temperature on the adsorption process was achieved. The nonlinear three isotherms and kinetic adsorption were studied to quantify the adsorption equilibrium and mechanism adsorption. Further, the spontaneity and nature of the adsorption process were described via thermodynamic study.

2. Experiment

2.1. Chemicals and instrumentation

The chemicals used in this study were analytical reagents (AR). Rhodamine B (RB), crystal violet (CV) and methylene blue (MB) dyes were procured from Sigma Aldrich. HNO₃, HCl and NaOH were obtained from BDH, England. Deionized water was used in this work. The adsorbent material was characterized by different techniques such as scanning electron microscopy (Model JEM-2100 F, JEOL, Japan), Fourier transform infrared spectroscopy (Nicolet i550 FTIR, Thermo Scientific), BET surface area and pore diameter analyzer Micromeritics (Gemini VII, 2390, USA). The CV, MB and RB dye concentrations in the solution were determined using UV–Vis spectrophotometer (Shimadzu UV-1800, 900 T).

2.2. Chemical treatment

For the present study, Aerva javanica leaves (AJL) and Aerva javanica inflorescence (AJF) were collected from Albahe City in Saudi Arabia. AJL and inflorescence materials were washed several times with deionized water to eliminate any dirt and other contaminants followed by dried at 100°C on the oven for 24 h. Then, the dried AJL and AJF were crushed separately in a grinder to get a fine powder. After that, 50 g of leaf powder was taken in a beaker containing 200 mL of 10% H₂O₂ under stirring for 24 h at room temperature [39] [40]. The powder was washed with deionized water followed by separation using centrifuge. The AJL powder was immersed in a 200 mL 1 M NaOH solution. The mixture solution was stirred at room temperature for 24 h and washed off with deionized water and dried at room temperature for 72 h to get NaOH-activated Aerva javanica leaf (NAJL) powder adsorbent. The same procedure was applied for activation of the Aerva javanica inflorescence (AJF) to produce NaOH-activated Aerva javanica inflorescence (NAJF) powder adsorbent. The preparation of NALJ powder adsorbent is shown in Figure 1.

2.3. Adsorption studies

To test the adsorption efficiencies of CV, MB and RB dyes onto four adsorbents: untreated AJL and untreated AJF, NAJL and NAJF powder adsorbent, the batch adsorption was applied. CV dye adsorption experiment was executed under different temperature (25, 35 and 45°C), pH solution (3–11), adsorbent dose (1–100 mg), contact time (5–120 min), initial CV dye concentration (50–250 mg/L). In general, a definite amount of adsorbents was added to the conical flask containing 50 mL of CV dye solution with a certain initial concentration at the preferred pH value and temperature. The initial pH solution was adjusted by 0.1 M NaOH and 0.1 M HCl solution. The mixture was shaken by a shaker at 200 rpm. The residual CV, MB and RB dye ions concentrations were determined by UV/Visible spectrometer at λ max (590 nm), (663 nm) and (556 nm), respectively. The adsorption efficiency (%) of CV, MB and RB dye ions onto adsorbents and adsorption capacities (mg/g) of adsorbents are calculated according to Equation (1) and Equation (2), respectively.

\[
\% \text{adsorption} = \frac{C_0 - C_e}{C_0} \times 100 \tag{1}
\]

\[
q_e = \frac{(C_0 - C_e)V}{m} \tag{2}
\]

where C₀ (mg/L) is the initial CV dye concentration; Cₑ (mg/L) is the CV dye concentration at equilibrium; m (g) is the amount of adsorbent and V (L) is the solution volume of the CV, MB and RB dyes.

3. Results and discussion

3.1. Characterization of adsorbents

Figure 2(a,b) shows the FTIR spectrum for AJL and NAJL, and CV dye loaded on NAJL. The complex nature of AJL powder results in the existence of some absorption peaks. In the spectrum of untreated AJL powder (Figure 2(a)), the broad peak at 3325 cm⁻¹ assigned to the stretching vibration of O-H groups suggesting the presence of carboxylic and hydroxyl groups on the surface of AJL powder [41]. The peaks at 2922 and 2855 cm⁻¹ were attributed to asymmetric and symmetric vibration of aliphatic C–H, respectively. The peak at 1731 cm⁻¹ was assigned to carbonyl stretching in AJL structure [42,43]. The strong peak at 1620 cm⁻¹ was described as C = O stretching from the carboxylic group and also for aromatic bending of the alkene
The peaks at 1310–1370 cm$^{-1}$ and 1237 cm$^{-1}$ were assigned to the symmetric stretching vibration of deprotonated carboxyl group (-COO$^-$) and (C-O-C) respectively. All these functional groups present in the structure of AJL powder are attributed to some compounds, such as lignin, phenol, alkaloids, flavonoids, glycosides and tannins [44,45]. After chemical activation of AJL powder with H$_2$O$_2$ and NaOH (Figure 2(a)), the intensities of –OH, -COO$^-$ /C = C and C-O-C peaks were increased. As we are known that the peak area commonly reflects mole percentage of the corresponding functional group and FTIR can be used for such qualitative analysis with acceptable accuracy when a known unaffected
peak was used as an internal standard. Therefore, the peak areas of the carboxylate bands from both AJL and NAJL powder were calculated. In this regard, it is assumed that the peak corresponding to CH, CH₂, and CH₃ (sp³ C-hybridization) in the range 3000–2800 cm⁻¹ were unaffected during the application of H₂O₂ and thus can be used as an internal standard. By comparing the peak areas of –COO⁻ with respect to CH₃ in both, we found that COO/CH₃ is 11.7 and 9.5 in both NAJL and AJL, respectively indicating –COO⁻ mole fraction increase after treatment. The disappearance of the COOH peak at 1731 cm⁻¹ is possibly due to transformation into carboxylate which causes a slight shift into lower frequency and thus overlapped with other carbonyl, carboxyl derivatives, etc., of the peak centered at 1620 cm⁻¹ [47].

A new peak at 1422 cm⁻¹ attributed to stretching of –OH bonds in carboxyl groups may be due to increasing the carboxylic groups in the NAJL surface [48]. These results confirmed the activation of AJL powder with H₂O₂ and NaOH. After the CV dye adsorption (Figure 2(a)), some bands disappeared, decreased in intensity and shifted to lower frequency. The bands at 3325 cm⁻¹ and 1620 cm⁻¹ were reduced intensity and moved to 3312 cm⁻¹ and 1598 cm⁻¹, respectively which confirmed the binding of these bands with CV dye ions over the NAJL surface. Therefore, the results indicated that a large number of –OH, –COOH, C = O groups were available on the surface NAJL powder [49].

The morphology of AJL, NAJL powder, and CV dye loaded on NAJL powder are shown in Figure 3(a,c)). The AJL powder exhibits an irregular rough surface with fewer pores with some impurities (Figure 3(a)). After being activated with NaOH reagent, the surface of AJL powder was smooth, pores, visible cavities with different shapes and sizes due to the removal of impurities from the surface of the AJL powder adsorbents by activation agent (NaOH) (Figure 3(b)). Thus, the NAJL powder adsorbent with these characteristics generally has a good surface, which provides them a good removal efficiency. After CV dye adsorption onto the NAJL powder, the surface of adsorbents appeared to be fewer pores and covered with CV dye ions (Figure 3(c)), indicating successful loading of CV dye on the NAJL powder surface.

Figure 4(a,b) displays the N₂ adsorption-desorption isotherms and pore diameter distribution of the AJL and NAJL powder. The pore-volume, pore diameter and surface area of the AJL and NAJL powder are shown in Table 1. The results revealed that the BET surface area of NAJL powder was 10.65 m²/g which is greater than untreated AJL powder 6.20 m²/g (Figure 4(a)) due to the pore structure being formed after

Figure 3. SEM image of AJL powder (a), NAJL powder (b) and CV dye adsorption onto NAJL powder (c).
activating with NaOH agent which led to the increased surface area of NAJL powder. The pore diameter of AJL and NAJL powder was 10.2 nm and 18.6 nm (Figure 4 (b)), respectively indicating the mesoporous structure of adsorbents.

### 3.2. Adsorption studies

#### 3.2.1. Selectivity studies of adsorbent

The selective adsorption of cationic dyes MB, RB and CV dyes from aqueous environments was tested on four different adsorbents: untreated AJL, AJF, NAJL and NAJF powder (Table 2). The results showed that the NAJL powder exhibited selective and higher removal efficiencies towards CV dye ions than that is untreated AJL, AJF and NAJF powder. The highest CV dye removal efficiency of 97.49% was achieved by NAJL powder at the conditions of the parameters (dose – 50 mg, T – 25°C, C_0 – 50 mg/g). The removal efficiencies of MB and RB were 71.26% and 3.0% by NAJL powder at the same conditions, respectively. The decrease in adsorption efficiency of MB and RB dyes onto NAJL adsorbent may be due to the MB dye has a positive charge on its S atom due to its resonance form. This positive charge of S atom binds to the negative carboxyl and hydroxyl groups on the NAJL surface. Therefore, MB molecules occupy larger areas on the NAJL surface, hindering the binding of additional MB molecules, leading to a decrease in adsorption efficiency [50]. RB has a carboxylic group in its structure which has an electrostatic effect with carboxyl groups on NAJL surface, and also it has a larger steric hindrance that affects its ability to be absorbed on the NAJL surface, leading to a decrease in adsorption efficiency. The high removal efficiency of CV dye on NAJL powder may be due to the use of H_2O_2 and NaOH as an activation agent. The NaOH reacts with silica in AJL powder adsorbent to produce a soluble sodium silicate in water and is eliminated by the washing process. Thus, the pore structure is formed which led to the increased surface area of the adsorbent [51,52]. The NAJL powder adsorbent was selected for CV dye removal from an aqueous solution.

#### 3.2.2. Effect of pH

As we know, the adsorption process is strongly dependent on pH value because the pH is the effect on the

**Table 1.** Pore structure parameter for AJL and NAJL powder adsorbent.

| Adsorbents                        | BET surface area (m²/g) | Pore volume (cm³/g) | Pore diameter (nm) |
|-----------------------------------|-------------------------|---------------------|-------------------|
| Aerva javanica leaf (AJL)         | 6.20                    | 0.0119              | 10.2              |
| NaOH-activated Aerva javanica leaf (NAJL) | 10.66                  | 0.0496              | 18.6              |

**Table 2.** Selectivity studies of cationic dyes onto the adsorbents.

| Adsorbents                        | CV Adsorption capacity (mg/g) | Removal efficiency (%) | MB Adsorption capacity (mg/g) | Removal efficiency (%) |
|-----------------------------------|------------------------------|------------------------|------------------------------|------------------------|
| Aerva javanica leaf (AJL)         | 35.60                        | 71.19                  | 33.71                        | 67.42                  |
| Aerva javanica flower (AJF)       | 40.16                        | 80.31                  | 35.99                        | 71.98                  |
| NaOH-activated Aerva javanica leaf (NAJL) | 48.75                    | 97.49                  | 35.63                        | 71.26                  |
| NaOH-activated Aerva javanica flower (NAJF) | 41.48                    | 82.96                  | 41.01                        | 82.01                  |
The surface charge of adsorbent and ionic state of adsorbent. Therefore, the effect of pH solution on CV dye adsorption on NAJL powder was tested in the range (3 – 11) as shown in Figure 5(a). It was observed that the CV dye removal efficiency and adsorption capacity were increased from (39.2% to 79.8%) and (49 to 99.71 mg/g) with rising pH values from 3 to 9 due to increasing the negative charge of NAJL powder adsorbent with rising pH value. With a further increase in pH from 8 to 9, no change in CV dye removal efficiency was noticed. A similar tendency of pH effect was noticed for the CV adsorption on NaOH-modified rice husk [53]. In an acidic medium, the adsorption capacity of CV dye was low due to the protonation of adsorbent’s active sites [54]. With rising pH of the solution, the adsorption process was increased significantly to 99.71 mg/g at pH 9 due to deprotonation of active sites of NAJL powder adsorbent, and the electrostatic attraction CV dye was attracted to these negatively charged groups on the surface of NAJL powder adsorbent [55]. Thus, pH 9 was selected for further experiments.

3.2.3. Effect of adsorbent dose

The influence of NAJL powder adsorbent dose on CV dye elimination was studied under various adsorbent doses from 1 to 100 mg to obtain the best appropriate amount of adsorbents at condition parameters (C<sub>0</sub>–50 mg/L; time – 30 min; T – 25°C), as shown in Figure 5(b). The result displayed that as the amount of NAJL powder adsorbent increased from 1 to 20 mg the removal efficiency of CV dye improved from 54.1% to 98.9% due to an increase in the active site number adsorbent. On the other hand, the adsorption capacity of NAJL powder adsorbent decreased from 195.35 to 3.57 mg/g with an increase of the amount of adsorbent from 1 to 100 mg. At lower adsorbent amount, the CV dye is more easily accessible to NAJL surface; thus, the removal of CV dye per unit weight of adsorbent is higher. With the rise in the mass of NAJL adsorbent, some of the adsorption sites present on the surface of NAJL remaining unoccupied during the adsorption process due to the fact that, at higher adsorbent mass, there is a very fast superficial adsorption onto the NAJL surface that produces a lower CV dye.

Figure 5. Effects of pH (a), adsorbent dose (C<sub>0</sub>–50 mg/L; time–30 min; T – 25°C) (b), contact time (dose–20 mg; pH–9; T–25°C) (c) and initial CV dye concentration (dose – 20 mg; pH–9; time – 30 min) (d) on adsorption capacity of NAJL powder.
concentration in the solution than when the adsorbent dose is lower [56]. Therefore, with rising adsorbent amounts from 1 to 100 mg, the quantity of CV dye adsorbed per unit mass of adsorbent is decreased [57]. Also, the reduction in adsorption capacity may be due to a decline in the total surface area and a rise in diffusion path length resulting from aggregation or overlapping of adsorption active sites of adsorbent, leading to a reduction in adsorption. These results are in agreement with the findings of literature reported in [58,59]. Thus, the optimum adsorbent dose for removal of CV dye onto NAJL powder adsorbent was 20 mg.

3.2.4. Effect of contact time at various concentrations

The influence of contact time on the elimination of CV dye at various initial concentrations 75 and 100 mg/L onto NAJL powder adsorbent at condition parameters (T–25°C; dose–20 mg; pH–9) are presented in Figure 5 (c). The results revealed that, at all initial CV dye concentrations, the adsorption capacity of NAJL powder adsorbent for CV dye was rapidly increased from 99.39 to 132.09 mg/g at 75 mg/L and from 120.54 to 177.83 mg/g at 100 mg/L with increasing time from 5 to 30 min. Hence, 30 min was chosen as the best equilibrium time for further work. A similar tendency of contact time effect was noticed for the CV adsorption on grapefruit peel (GFP) [60].

3.2.5. Effect of initial concentration at various temperatures

Figure 5(d) displays the influence of initial CV dye concentration on the adsorption process at different concentrations (50 to 250 mg/L) and different temperatures (25, 35 and 45°C) under condition (dose – 20 mg; pH – 9; time – 30 min). The results exhibited that the adsorption capacity of NAJL powder adsorbent increased from 101.57 to 268.70 mg/g when the CV dye concentrations increased from 50 to 250 mg/L at 25°C. The high rise in adsorption capacity at higher initial concentrations, due to the increase of the driving force for mass transfer from the solution to the NAJL powder adsorbent surface [61, 62].

3.2.6. Effect of temperatures

The influence temperature on CV dye adsorption onto NAJL powder adsorbent was performed at various temperatures (25, 35 and 45°C) and at different concentrations (50 to 250 mg/L) under condition (dose – 20 mg; pH–9; time–30 min). The obtained results are presented in Figure 6(a). It was noticed that the adsorption capacity slightly reduced with rising temperature, indicating that the adsorption of CV dye was an exothermic process. This is due to the destruction of binding forces on the surface of NAJL powder adsorbent at higher temperatures [40]. This result is in agreement with the study done by Shoukat et al. [63].

3.2.7. Adsorption isotherm

CV dye adsorption onto NAJL powder adsorbent with different initial concentrations (50- 250 mg/L) and different temperature was studied with keeping other the other parameters constants (pH–9; dose– 20 mg; time–30 min; 200 rpm). The adsorption experimental data are investigated by Langmuir (Equation (3)) [64], Freundlich (Equation (4)) [65] and Dubinin Radushkevich nonlinear isotherm models (Equations (5–7)) [66]. Isotherm experimental data for isotherm modeling is presented in Table 3.

\[ q_e = \frac{q_m K_c C_e}{1 + K_c C_e} \]  
(3)

\[ q_e = K_c C_e^{1/n} \]  
(4)
where \( q_e \) (mg/g) is the amount of CV dye adsorbed at equilibrium, \( q_m \) (mg/g) is maximum adsorption capacity; \( C_e \) (mg/L) is the CV dye concentration at equilibrium; \( K_L \) (L/mg) is Langmuir constant represents the adsorption affinity. \( K_f \) and \( K_D \) are Freundlich constant and constant related to the adsorption energy, respectively; \( n \) is the parameter that characterizes the system heterogeneity; \( E \) (kJ/mol) refers to mean free energy; \( \varepsilon \) is the Polanyi potential.

The results suggested that the adsorption of CV on NAJL powder adsorbent was a monolayer adsorption process. The maximum adsorption of CV on NAJL powder adsorbent was 315.2 mg/g at 25°C. The \( R_L \) values at different temperatures (25, 35 and 45°C) are shown in Figure 7(a–c). Based on the high correlation coefficients (\( R^2 \)) of nonlinear isotherm models, the Langmuir model (\( R^2 > 0.9843 \)) is the best fit of experimental data than that’s Dubinin Radushkevich and Freundlich model. These results indicated that the adsorption of CV on NAJL powder adsorbent was a monolayer adsorption process. The maximum adsorption of CV on NAJL powder adsorbent was 315.2 mg/g at 25°C. The \( R_L \) values at different temperatures (25, 35 and 45°C) are shown in Figure 7(a–c).
temperatures (25–45°C) were in the range (0.044–0.026), indicating favorable adsorption. The comparison of parameter condition and adsorption capacities of NAJL powder adsorbent for CV dye removal with different adsorbents such as NaOH-modified rice husk (NMRH) [53], grapefruit peel [60], Eichhornia crassipes live roots [67], jackfruit leaf powder (JLP) [68], banyan leaf powder [69], treated ginger waste (TGW) [70] are shown in Table 4. Based on the results of the Dubinin–Radushkevich isotherm model, the free energy value ($E$) was less than 8 kJ mol$^{-1}$ which suggests that the CV adsorption on NAJL powder adsorbent is physisorption.

### 3.2.8. Kinetics adsorption

Applicability of different nonlinear kinetic models such as Elovich (Equation (8)) models [71], pseudo-first-order (Equation (9)) [72] and pseudo-second-order (Equation (10)) models was used to analyze the kinetic experimental data.

\[
q_t = q_e(1 - e^{-kt})
\]  
(8)

\[
q_t = \frac{q_e^2k_t}{1 + q_ek_t t}
\]  
(9)

\[
q_t = \frac{1}{\beta} \ln(1 + \alpha t)
\]  
(10)

where, $k_1$ and $k_2$ are the equilibrium rate constant of pseudo-first-order adsorption and pseudo-first-order, respectively. $q_t$ is the adsorption capacity at t time (mg/g); $\alpha$ and $\beta$ are the desorption capacity and the initial adsorption rate, respectively.

### Table 4. Comparison of the maximum adsorption capacities ($q_m$) for CV adsorption with different plant adsorbents.

| Adsorbent                        | Conditions | $q_m$ (mg/g) | Ref.   |
|----------------------------------|------------|--------------|--------|
| NaOH-modified rice husk (NMRH)   | C$_p$ 50 mg/L; pH-8; T-22°C; dose-1000 mg; time-90 min | 44.87 | [53]   |
| Grapefruit peel                  | C$_p$ 25-100 mg/L; pH-6; T-25°C; dose-1000 mg; time-60 min | 249.68 | [60]   |
| Eichhornia crassipes live roots  | C$_p$ 250–1000 mg/L; pH-7; T-27°C; time-180 min | 20.84 | [67]   |
| Jackfruit leaf powder (JLP)      | C$_p$ 20-100 mg/L; pH-7; T-22°C; dose-1000 mg; time-120 min | 43.39 | [68]   |
| Banyan leaf powder               | C$_p$ 50-150 mg/L; pH-8; T-25°C; time-120 min; dose-250 mg | 81 | [69]   |
| Treated ginger waste (TGW)       | C$_p$ 5-20 mg/L; pH-8; T-50°C; dose-50 mg; time-150 min | 277.7 | [70]   |
| NaOH-activated Aerva javanica leaf (NAJL) study | C$_p$ 50-250 mg/L; pH-9; T-25°C; dose-20 mg; time-60 min | 315.2 | This  |

Nonlinear curves of kinetic models at condition parameters (dose – 20 mg; pH-9; time – 30 min, $C_p$ – 75 mg/L) are presented in Figure 7(d). The results of the models employed are listed in Table 5. It was observed that the pseudo-first-order model shows better $R^2$ ($R^2 = 0.997$) values compared to that’s pseudo-second-order ($R^2 = 0.976$) and Elovich ($R^2 = 0.974$), suggesting the involvement of the physical adsorption process. The experimental adsorption capacity ($q_{e,exp}$ = 132 mg/g) was very close to $q_{e,cal}$ 132.5 mg/g in pseudo-first-order model.

### 3.2.9. Adsorption thermodynamics

To understand the nature of the adsorption process for CV dye adsorption onto NAJL powder adsorbent, the experiments were achieved at various temperatures (25, 35 and 45°C) and concentration (50,100 and 150 mg/L). Thermodynamic factors including change in free energy ($\Delta G^\circ$) (Equation (11)), enthalpy ($\Delta H^\circ$) and entropy ($\Delta S^\circ$) (Equation (12)) were calculated using the following equations:

\[
\Delta G^\circ = -RT \ln K_c
\]  
(11)

\[
\ln K_c = \frac{\Delta H^\circ}{RT} + \frac{\Delta S^\circ}{R}
\]  
(12)

where $T$ (K) is the temperature in Kelvin, $R$ is the gas constant (8.314 J mol$^{-1}$ K$^{-1}$). $K_c$ is the equilibrium constant. The values of $\Delta H^\circ$ and $\Delta S^\circ$ were calculated from the slope and intercept of the plot of $\ln K_c$ versus (1/T) as presented in Figure 6(b). Table 6 presents the thermodynamic factors for CV dye adsorption onto NAJL powder adsorbent. The results revealed that the negative values of $\Delta H^\circ$ and $\Delta S^\circ$ verifies the exothermic nature of CV dye adsorption onto NAJL powder adsorbent and reduced in randomness. The negative values of $\Delta G^\circ$ indicating the spontaneous of the adsorption process [73,74]. The value of $\Delta H^\circ$ was 29.8 kJ/mol that means the CV dye adsorption onto NAJL powder adsorbent was physisorption [75].

### 3.3. Adsorption mechanism

The FTIR analysis results in Figure 1 result shown that the existence of negatively charged binding sites such as carboxylic (COOH), and hydroxyl (–OH) and (– C = O) groups onto the NAJL powder adsorbent

### Table 5. Nonlinear kinetic models parameters for CV adsorption on NAJL powder adsorbent.

|          | Pseudo-first-order | Pseudo-second-order | Elovich |
|----------|--------------------|---------------------|---------|
| $C_p$ (mg/L) | $q_{e,exp}$ (mg/g) | $q_{e,cal}$ (mg/g) | $K_1$ (1/min) | $R^2$ | $q_{e,exp}$ (mg/g) | $q_{e,cal}$ (mg/g) | $K_2$ (g/mg-min) | $R^2$ | $A$ (mg/g min)$^{-1}$ | $B$ (mg/g) | $R^2$ |
| 75       | 132                | 132.5               | 0.2391   | 0.997 | 136.20              | 0.0038             | 0.976               | 70,006.4 | 0.099             | 0.974 |
Table 6. Thermodynamic parameters for the adsorption of CV on NAJL powder adsorbent.

| Concentration CV dye (mg/L) | (-ΔH°) (kJ/mol) | (-ΔS°) (J/mol.K) | (-ΔG°) (kJ/mol) |
|-----------------------------|------------------|------------------|------------------|
| 50                          | 29.8             | 88.2             | 3.63 2.62 1.87   |
| 100                         | 15.3             | 44.9             | 1.93 1.667 1.02  |
| 150                         | 13.2             | 40.9             | 1.10 0.653 0.286 |

surface that can be strongly adsorbed CV dye from aqueous solutions by different mechanisms included π-π interactions between the aromatic ring molecule in the NAJL powder adsorbent surface and the aromatic ring in the CV dye molecule, electrostatic interactions between −COO− and −OH groups in the surface of NAJL powder and +N(CH$_3$)$_2$ in the CV dye molecule, hydrogen bonding between dimethylamino (−N(CH$_3$)$_2$) group of CV dye and -OH group of the NAJL powder adsorbent surface.

3.4. Desorption study

Two eluents (0.1 M HNO$_3$ and 0.1 M HCl) were used for desorption of CV dye from NAJL powder adsorbent surface. The CV dye-loaded NAJL powder was washed with deionized water and then added into 50 mL of 0.1 M HNO$_3$ as eluent. The mixture was shaken at 200 rpm for 30 min. After that, the mixture was separated, and the residual CV dye concentration was determined by UV/Visible spectrometer. The percentage desorption was calculated by the following Equation (13):

$$\%\text{desorption} = \frac{\text{Concentration of CV dye desorbed by the eluent}}{\text{Initial concentration of CV dye adsorbed on NAJL}} \times 100$$  

(13)

The results show that the best eluent for recovery of CV dye from NAJL powder adsorbent surface was 0.1 M HNO$_3$ (39%) compared to 0.1 M HCl (14%) (Figure 8).

4. Conclusion

The present study shows that NAJL powder is an effective adsorbent for the elimination of CV dye from aqueous solution. The adsorbent performance of NAJL powder was strongly affected by different parameters, such as pH initial CV dye ion concentration, temperature, contact time and adsorbent dose. Langmuir isotherm model is well fitted for the equilibrium data adsorption of CV dye compared with Freundlich and Dubinin–Radushkevich models, indicating monolayer adsorption with maximum adsorption capacity of 315.2 mg/g of the NAJL powder at 25°C and pH 9. The CV dye adsorption onto NAJL powder was fitted well to pseudo-first-order model indicating physisorption. The calculated thermodynamic parameters exhibited that the adsorption process was exothermic and spontaneous. Generally, the results obtained suggest that NAJL powder can be applied as an efficient adsorbent and environmentally friendly for the elimination of CV dye from aqueous solutions.

![Figure 8. Adsorption/desorption study (C$_0$–50 mg/L; dose–20 mg; desorption time – 30 min; pH–9; T–25°C).](image-url)
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Disclosure statement

The author declares no competing financial interest.

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