Used central composite chemometric method to adsorption gentian violet dye by nano activated charcoal

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Abstract. In this paper; a modern method was used to remove the Gentian violet dye (GV) from its aqueous solutions by chemometric separation. The Nano charcoal activated (NCA) was used to remove the GV, and the factors affecting the adsorption process were studied simultaneously to reduce the number of experiments followed and to rely on a central composite design which type CCD and the method of response surface by used STATISTICA 12 program. That gives the relationship between all the variables simultaneously. It was found that, the optimum removal efficiency reached 98.042% and it was obtained under the following conditions; The initial concentration of (GV) 12.086 mg/L, Amount of Nano charcoal activated 0.371 g, pH 7.567, Shaking time 22.934 min, and Temperature 312.092 K.

Keyword: Central Composite Chemometric Method, Gentian Violet Dye, Nano Charcoal Activated, Adsorption, and Simultaneously.

1. Introduction

Environmental pollution in general and water pollution, in particular, is a problem of significant importance in many countries [1]. Water pollution hurts human health [2], as liquid pollutants such as heavy metal ions and dyes can cause critical diseases [3]. These dyes are used in many vital industries, such as paper, fabric, tanning, and painting [4]. (GV), Figure (1), is one of the known industrial dyes, and it is one of the oldest dyes used [5]. The molecular formula for this dye is (C₂₅H₃₀ClN₃) [6]. Despite the benefits of its use in the medical field and the food field such as oral histology, but when discharged into water, it causes pollution [7]. There are many techniques for removing dyes from water, and adsorption is one of the most crucial methods [8]. Adsorption is used to remove dyes from water because it is simple to operate, cheap, and highly efficient [9]. Nano charcoal activated (NCA) is widely used as an adsorbent in separation processes due to its large surface area, low price, and harmless preparation [10]. (NCA) had stimulated research society to solve the problems of the environment [11]. Nano materials are highly useful for removing by adsorption of various water, air, and soil contaminants [12]. Moreover, the decline in water quality has led researchers to use new adsorbents to treat water with charcoal activated [13]. (NCA) it is an excellent adsorbent as its surface can be adjusted with the addition of other materials, and has a high ratio of the volume to the surface area, in addition to the
high biocompatibility, its relatively low cost of production, and its ability to reuse [14]. Using coating, stabilizing, and functionalization (NCA) can be modified surface [15]. In the (NCA) surface coating process, clusters are not formed due to the particle dispersion when water molecules containing contaminants (hydrophilicity) are attracted [16]. Therefore, the surface modification of (NCA) will improve its ability to adsorb many pollutants, such as dyes and ions of heavy metals [17]. The coating of surface phenomenon helps convert the geometry of closely-packed cubic to nanoparticles in compacts and robust [18].

In this study, we used the Nano charcoal activated (NCA) to remove Gentian violet dye (GV) from its aqueous solutions by chemometric separation, making the process less expensive, more productive, and environmentally friendly after determining the optimum adsorption conditions.

![Chemical Structure of Gentian Violet Dye (GV).](image)

**Figure 1.** Chemical Structure of Gentian Violet Dye (GV).

### 2. The experimental part

#### 2.1. Chemicals and instruments

Throughout this study, all chemicals were used for all chemical substances and reagents, including Nano charcoal activated (NCA) from (BDH), Gentian violet dye (GV), HCl, and NaOH from (Sigma-Aldrich). During the experiments, ultra-pure water was used. Shimadzu UV-Vis Spectrophotometer 1650Pc was used for specifying the residual (GV) in the experiments. Adjusted pH by adding 0.01 M NaOH or 0.01 M HCl and measured by WTW pH meter InoLab 730. A shaker water bath from Amerexa has been used to maintain a steady mixing temperature, and it was set to 150 rpm throughout the experiments. The stock solution of 100 mg/L of (GV) was prepared by dissolving 0.0100 g in a small volume of ultra-pure water and transferred to a 100 mL volumetric flask, diluted with water to a mark. Every day freshly prepares in range (20-0.05) mg/L solutions to create a calibration curve. The dye concentration in the aqueous solution was measured via the absorbance (Abs.) at \( \lambda_{\text{max}} \) equal to 512 nm by the Least-squares method.

\[
[GV]_{\text{mg/L}} = \frac{\text{Abs.} - \text{Intercept}}{\text{Slope}}
\]

#### 2.2. The methodology of experiments

In this study, all experiments were performed after an added amount of (GV) with Nano charcoal activated in the Erlenmeyer flask, placed in the shaker water bath. In order to obtain the optimum conditions for the process of removing (GV) from its aqueous solutions, the effect of five different factors was studied simultaneously and at three levels as shown in table (1); the initial concentration of (GV), the amount of Nano charcoal activated, pH, shaking time, and the temperature depended on central composite design [19] and the method of response surface [20] by using STATISTICA 12 program.
Table 1. Factors, Symbol and Coded level to Natural Level by Chemometric Separation.

| Factors                                      | Symbol | -1  | 0   | +1  | Coded level to natural level |
|----------------------------------------------|--------|-----|-----|-----|------------------------------|
| The initial concentration of (GV), mg/L      | X1     | 10  | 15  | 20  | 5                            |
| Amount of Nano charcoal activated, g         | X2     | 0.15| 0.3 | 0.45| 0.15                         |
| pH                                           | X3     | 2   | 7   | 11  | 5                            |
| Shaking time, min                            | X4     | 10  | 20  | 30  | 10                           |
| Temperature, K                               | X5     | 290 | 310 | 330 | 20                           |

For the passage from coded variable level to natural variable level, the following equations were used: 

\[ X1 = \frac{(GV\_mg/L - 25)}{5}; X2 = \frac{(NCA - 0.3)}{0.15}; X3 = \frac{(pH - 7)}{5}; X4 = \frac{(Time - 20)}{10} \text{ and } X5 = \frac{(Temperature - 310)}{20}. \]

The adsorption process behaviour can be explained based on the empirical second-order polynomial model below [21]:

\[ \text{Response} = \beta_0 + \sum_{i=1}^{n} \beta_i X_i + \sum_{i=1}^{n} \beta_{ii} X_i^2 + \sum_{i=1}^{n-1} \sum_{j=i+1}^{n} \beta_{ij} X_i X_j \]

Where \( \beta_0 \) is a constant, \( \beta_i \) is the linear coefficient, \( \beta_{ii} \) is the quadratic coefficient, and \( \beta_{ij} \) is the interaction effect coefficient. \( X_i \) and \( X_j \) are the symbolic values of the factors. The amount of residual dye was measured at \( \lambda_{\text{max}} \). The quantity of (GV) adsorbed onto nano charcoal activated \( q_e \) (mg/g) and the removal efficiency \( R\% \), which were determined by the following equations:

\[ q_e = (C_0 - C_e) * \frac{V_L}{m_g} \]

\[ R\% = \frac{C_0 - C_e}{C_0} * 100 \]

Where the initial concentration of (GV) is \( C_0 \) (mg/L), the equilibrium concentration \( C_e \) (mg/L) of (GV), the Nano charcoal activated mass is \( m \) (g), and the solution volume is \( V(L) \).

3. Result and Discussion

3.1. Calibration curve for (GV)

Concentrations of (GV) ranged between (20.0-0.05) mg/L in their aqueous solutions were measured at \( \lambda_{\text{max}} = 512 \text{ nm} \) for creating the calibration curve, as in Figure (2) by the Least-squares method.
3.2. The optimum conditions:
After studying simultaneously for Nano charcoal activated (NCA) to remove Gentian violet dye (GV) from its aqueous solutions by chemometric separation in different conditions [22]; The following results were obtained in Figures (3-12).

![Graph showing calibration curve for Gentian Violet Dye (GV).](image)

**Figure 2.** Calibration Curve for Gentian Violet Dye (GV).

![Graph showing relationship between Gentian Violet Dye (GV) and Nano Charcoal Activated.](image)

**Figure 3.** The Relationship between Gentian Violet Dye (GV) and Nano Charcoal Activated.
Figure 4. The Relationship between Gentian Violet Dye (GV) and pH.

Figure 5. The Relationship between Gentian Violet Dye (GV) and Time.

Figure 6. The Relationship between Gentian Violet Dye (GV) and Temperature.
Figure 7. The Relationship between Nano Charcoal Activated and pH.

Figure 8. The Relationship between Nano Charcoal Activated and Time.

Figure 9. The Relationship between Nano Charcoal Activated and Temperature.
Figure 10. The Relationship between pH and Time.

Figure 11. The Relationship between pH and Temperature.

Figure 12. The Relationship between Time and Temperature.
By studying the relationship between the five variables with each other and using the STATISTICA 12 program, optimal conditions were found for each factor [23], as shown in Table (2).

| Factors                                      | Symbol | Optimal Conditions |
|----------------------------------------------|--------|--------------------|
| The initial concentration of (GV), mg/L      | X1     | 12.086             |
| Amount of Nano charcoal activated, g         | X2     | 0.371              |
| pH                                           | X3     | 7.567              |
| Shaking time, min                            | X4     | 22.934             |
| Temperature, K                               | X5     | 312.092            |

When applying the optimal conditions established by this model to the (GV) dye, it was found that the removal efficiency R% reached 98.042%, as shown in figure (13).

Figure 13. The Removal Efficiency of Gentian Violet Dye (GV).

4. Conclusions
The chemometric separation method is one of the modern, easy, and inexpensive methods, as it depends on reducing the number of experiments and reducing pollution inside the laboratory. Our method relied on the use of Nano charcoal activated to remove the Gentian violet dye (GV) from its aqueous solutions based on five factors which are the initial concentration of (GV), the amount of Nano charcoal activated, pH, shaking time, and the temperature depended on central composite design and the method of response surface by used STATISTICA 12 program, and to study the effect of these factors on each other at the same time. The results obtained are satisfactory compared to the classic methods used in the process of removing dyes.

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