Using Chemometric Method to Adsorption Fast Green Dye by Nano Charcoal Activated

Mohanad Hazim Halboos* and Noorhan Farhan Awad AL janabi
Department of Ecology, Faculty of Science, University of Kufa, Najaf, Iraq

*Corresponding author e-mail: muhaned_halbus@uokufa.edu.iq

Abstract. In this paper; a modern method was used to remove the Fast Green dye (FGD) from its aqueous solutions by chemometric separation. The Nano charcoal activated (NCA) was used to remove the (FGD), and the factors affecting the adsorption process were studied simultaneously to reduce a number of experiments that were followed and to rely on Box-Behnken design and the method of response surface by applying STATISTICA 12 program. That gives the relationship between all the variables simultaneously. It was found that, the optimum removal efficiency reached 97.604% and it was obtained under the following conditions; The initial concentration of (FGD) 17.392 mg/L, Amount of Nano charcoal activated 0.341 g, pH 3.419, Shaking time 22.678 min, and Temperature 311.075 K.

Keyword. Chemometric Method, Fast Green 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 are among most critical diseases [3]. These dyes are used in many vital industries, such as paper, fabric, tanning, and painting [4]. Fast Green dye (FGD), 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 \((C_{37}H_{34}N_{2}O_{10}S_{3}Na_{2})\) [6]. Despite the benefits of its use in the medical field and the food field, 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 painless preparation [10]. (NCA) had stimulated research society to solve the problems of the environment [11]. This nano is 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].

The present work involves used the Nano charcoal activated (NCA) to remove Fast Green dye (FGD) from its aqueous solutions by chemometric separation method, making the process less expensive, more productive, and environmentally friendly after determining the optimum adsorption conditions.

![Figure 1. Chemical Structure of Fast Green Dye (FGD)](image)

2. The experimental part

2.1. Chemicals and instruments

Throughout this study, the highly pure and analytical grade was used for all chemical substances and reagents, including Nano charcoal activated (NCA) from (BDH), Fast Green dye (FGD), 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 (FGD) 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 (FGD) was prepared by dissolving 0.01000 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 (50-0.05) mg/L solutions to create a calibration curve. The dye concentration in the aqueous solution was measured via the absorbance (Abs.) at $\lambda_{max}$ equal to 632 nm by the Least-squares method.

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

2.2. The methodology of experiments

In this study, all experiments were performed after adding amount of (FGD) 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 (FGD) 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 (FGD), the amount of Nano charcoal activated, pH, shaking time, and the temperature depended on Box-Behnken design [19] and the method of response surface [20] by used 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  | X1     | 5  | 25 | 45 | 20              |
| (FGD), mg/L                   |        |    |    |    |                 |
| Amount of Nano charcoal       | X2     | 0.25 | 0.5 | 0.75 | 0.25          |
| activated, g                  |        |    |    |    |                 |
| pH                            | X3     | 1  | 5  | 9  | 4               |
| Shaking time, min             | X4     | 15 | 60 | 105 | 45             |
| Temperature, K                | X5     | 288 | 303 | 328 | 15             |

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

\[X1 = \frac{(\text{[FGD]} \text{mg/L} - 25)}{20}; \quad X2 = \frac{(\text{NCA} - 0.5/0.25); \quad X3 = (\text{pH} - 5)/4; \quad X4 = (\text{Time} - 60/45)}{X5 = (\text{Temperature} - 303)/15}.\]

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

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

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 (FGD) adsorbed onto Nano charcoal activated \(q_e\) (mg/g) and the removal efficiency \(R\%\), which were determined by the following equations:

\[q_e = \frac{V L}{m_g} (C_0 - C_e)\]

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

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

3. Result and Discussion

3.1. Calibration curve for (FGD)

Concentrations of (FGD) ranged between (50-0.05) mg/L in their aqueous solutions and the absorbances were measured at \(\lambda_{\text{max}} = 632\) 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 Fast Green dye (FGD) from its aqueous solutions by chemometric separation in different conditions [22]; The obtained results are presented Figures (3-12).

Figure 2. Calibration Curve for Fast Green Dye (FGD)

Figure 3. The Relationship between Fast Green Dye (FGD) and Nano Charcoal Activated
Figure 4. The Relationship between Fast Green Dye (FGD) and pH

Figure 5. The Relationship between Fast Green Dye (FGD) and Time

Figure 6. The Relationship between Fast Green Dye (FGD) 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
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 (FGD), mg/L | X1     | 17.392             |
| Amount of Nano charcoal activated, g   | X2     | 0.341              |
| pH                             | X3     | 3.419              |
| Shaking time, min              | X4     | 22.678             |
| Temperature, K                 | X5     | 311.075            |

When applying this model to the (FGD) dye, it was found that the removal efficiency R% reached 97.604%, as shown in Figure (13).

Figure 13. The Removal Efficiency of Fast Green Dye (FGD)

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 thus reducing pollution inside the laboratory. Our method relied on the use of Nano charcoal activated to remove the Fast Green Dye (FGD) from its aqueous solutions based on five factors which are the initial concentration of (FGD), the amount of Nano charcoal activated, pH, shaking time, and the temperature depended on Box-Behnken 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.

5. References
[1] Wang X, Zhang C and Zhang Z 2019 Pollution haven or porter? The impact of environmental regulation on location choices of pollution-intensive firms in China J. Environ. Manage. 248 109248

[2] Sayhood A A and Mohammed H J 2015 Synthesis of novel azo reagents derived from 4-aminoantipyrine and their applications of enhancement of silver nano particles Der Pharma Chem. 7 50–8

[3] Aljafery A M A, Sayhood A, Abdulridha W M and Yousif A M 2018 Evaluation the tensile strength of cold-cured acrylic resin denture base material by adding silver nanoparticles Indian J. Public Heal. Res. Dev. 9 917–22
[4] Vankar P S and Shukla D 2019 Newer Natural Dyes for Various Textiles New Trends in Natural Dyes for Textiles (Elsevier) pp 1–69

[5] Guler U A, Ersan M, Tuncel E and Dügenci F 2016 Mono and simultaneous removal of crystal violet and safranin dyes from aqueous solutions by HDTMA-modified Spirulina sp. Process Saf. Environ. Prot. 99 194–206

[6] Kaur S, Rani S, Mahajan R K, Asif M and Gupta V K 2015 Synthesis and adsorption properties of mesoporous material for the removal of dye safranin: Kinetics, equilibrium, and thermodynamics J. Ind. Eng. Chem. 22 19–27

[7] Mohamed F, Abukhadra M R and Shaban M 2018 Removal of safranin dye from water using polypyrrole nanofiber/Zn-Fe layered double hydroxide nanocomposite (Ppy NF/Zn-Fe LDH) of enhanced adsorption and photocatalytic properties Sci. Total Environ. 640–641 352–63

[8] Sahoo T R and Prelot B 2020 Adsorption processes for the removal of contaminants from wastewater Nanomaterials for the Detection and Removal of Wastewater Pollutants (Elsevier) pp 161–222

[9] Hokkanen S and Sillanpää M 2020 Nano- and microcellulose-based adsorption materials in water treatment Advanced Water Treatment (Elsevier) pp 1–83

[10] Cukierman A L, Nunell G V. and Bonelli P R 2019 Removal of emerging pollutants from water through adsorption onto carbon-based materials Emerging and Nanomaterial Contaminants in Wastewater: Advanced Treatment Technologies (Elsevier) pp 159–213

[11] Ciambelli P, La Guardia G and Vitale L 2019 Nanotechnology for green materials and processes Studies in Surface Science and Catalysis vol 179 (Elsevier Inc.) pp 97–116

[12] Bhateria R and Singh R 2019 A review on nanotechnological application of magnetic iron oxides for heavy metal removal J. Water Process Eng. 31 100845

[13] Halboos M H, Ammar Sayhood A and Ala'a Hussein T 2019 Determination celiprolol hydrochloride drug by used zero, first, second and third order derivative and peak area spectrophotometry method in its pure form and in pharmaceutical tablets J. Phys. Conf. Ser. 1294 052035

[14] Sayhood A A and Mohammed H J 2015 Synthesis of new azo reagent for determination of Pd(II), Ag(I) and applied to enhance the properties of silver nano particles Int. J. Chem. Sci. 13 1123–36

[15] Dutta B, Rawoot Y A, Checker S, Shelar S B, Barick K C, Kumar S, Somani R R and Hassan P A 2020 Micellar assisted aqueous stabilization of iron oxide nanoparticles for curcumin encapsulation and hyperthermia application Nano-Structures and Nano-Objects 22 100466

[16] Al-Shirifi A N M, Dikran S B and Halboos M H N 2018 Application of central composite design method to oxidative coupling spectrophotometric determination of metoclopramide hydrochloride in pure form and pharmaceutical preparations J. Glob. Pharma Technol. 10 143–52

[17] Sayhood A A, Hussein B J and Halboos M H 2020 Analytical determination for chlorprothixene.hcl drug in pure form and medicinal tablets by spectrophotometric derivatives Syst. Rev. Pharm. 11 1478–82
[18] Jain M, Yadav M, Kohout T, Lahtinen M, Garg V K and Sillanpää M 2018 Development of iron oxide/activated carbon nanoparticle composite for the removal of Cr(VI), Cu(II) and Cd(II) ions from aqueous solution *Water Resour. Ind.* **20** 54–74

[19] Salman M, Shahid M, Sahar T, Naheed S, Mahmood-ur-Rahman, Arif M, Iqbal M and Nazir A 2020 Development of regression model for bacteriocin production from local isolate of Lactobacillus acidophilus MS1 using Box-Behnken design *Biocatal. Agric. Biotechnol.* **24** 101542

[20] Vakili-Azghandi M, Fattah-alhosseini A and Keshavarz M K 2018 Optimizing the electrolyte chemistry parameters of PEO coating on 6061 Al alloy by corrosion rate measurement: Response surface methodology *Meas. J. Int. Meas. Confed.* **124** 252–9

[21] McNamee J M and Pan V Y 2013 Nearly Optimal Universal Polynomial Factorization and Root-Finding *Studies in Computational Mathematics* vol 16 (Elsevier B.V.) pp 633–717

[22] Halboos M H, Hussein B J and Sayhood A A 2020 Preparation of a new azo compound (HAZM) used for analytical spectrophotometric determination of glucose in blood and saliva *Period. Tche Quim.* **17** 569–78

[23] Faris A, Hussain A and Halboos M H 2020 Adsorption of safranin dye from their aqueous solutions by using CA and Nano FeO/CA *J. Phys. Conf. Ser.* **1660** 12080