

Interfacial Engineering and Photon-Activated Photocatalysis of SCG-Derived Carbon/g-C₃N₄/Fe₃O₄ Ternary Hetero structures for Methylene Blue Degradation

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Abstract

The pollution of natural water bodies by persistent industrial chemicals and organic dyes represents a critical environmental and public health threat. This study investigates the development of a highly efficient, recyclable magnetic heterojunction photocatalyst derived from spent coffee grounds (SCG), graphitic carbon nitride (g-C₃N₄), and magnetite Fe₃O₄ nanoparticles for the targeted photo degradation of Methylene Blue (MB) under visible light irradiation. The bio waste-derived SCG carbon was prepared via controlled carbonization at 500°C, while the g-C₃N₄ matrix was synthesized via thermal polymerization of melamine at 550°C. Magnetic Fe₃O₄ nanoparticles were synthesized using an alkaline chemical co-precipitation method.

The structural, optical, and morphological characteristics of the synthesized ternary nanocomposite were thoroughly evaluated using Dynamic Light Scattering (DLS), Fourier Transform Infrared Spectroscopy (FTIR), X-ray Diffraction (XRD), Scanning Electron Microscopy with Energy Dispersive Spectroscopy (SEM-EDS), Zeta Potential analysis, and UV-Visible spectroscopy. Central Composite Design (CCD) under Response Surface Methodology (RSM) was employed to systematically evaluate and optimize the individual and interactive operational parameters, including solution pH, initial dye concentration, catalyst dosage, and reaction time. The quadratic regression analysis identified the quadratic model as being statistically significant for predicting degradation pathways ($R^2 = 0.8941$; $p < 0.0001$). Under optimised conditions (pH 7.4, initial MB concentration of 2.29 ppm, a nanocomposite dosage of 3.06 mg and a reaction time of 45.4 min) the maximum degradation efficiency was attained. The engineered ternary composite has demonstrated excellent magnetic recovery characteristics which may provide a sustainable, cost-effective, closed-loop treatment methodology for the remediation of dye-containing wastewater.

Keywords: Graphitic carbon nitride g-C₃N₄, Magnetite (Fe₃O₄), Spent coffee grounds, Response Surface Methodology (RSM), Central Composite Design (CCD), Methylene Blue.

1. Introduction

Due to the rapid growth of global industrial manufacturing, there has been an increase in the release of many different types of organic contaminants from manufacturing facilities, dyes, and pigments into aquatic ecosystems [4,27]. These pollutants have created a serious global threat to the environment/ecology [4]. The traditional methods used to treat water are usually based on coagulation, sedimentation, and simple filtration; however, most of these systems have very high operating costs, very low operational efficiencies, and create secondary sludge pollution, which causes additional harm to our environment. The use of advanced oxidation processes (AOPs), specifically visible-light-driven heterogeneous photo catalysis, provides a sustainable and environmentally-friendly approach to remediating contaminated waters by mineralizing recalcitrant compounds (organic pollutants) into inorganic end-products[4]. Graphitic carbon nitride g-C₃N₄ has attracted considerable scientific attention as a metal-free polymeric photo catalyst due to its narrow bandgap (~2.7 eV), robust chemical stability, low synthesis costs, and non-toxic nature. However, the practical application of pristine g-C₃N₄ is severely restricted by its rapid photo-excited electron-hole (e⁻/h⁺) recombination rates and low specific surface area [32].

To address these fundamental challenges, this research investigates a new structural integration approach:

- Spent Coffee Grounds (SCG): Used as an inexpensive, value-added, carbon source to increase the overall surface area, provide active surface functional groups, and assist with rapid movement of charge carriers [31].
- Magnetite Fe₃O₄ Nanoparticles: Co-assembled within the SCG matrix forming a substantial magnetic field, allowing for rapid separation and excellent recyclability from treated waste streams using an external magnetic field [44].

This research also designs, synthesizes, and characterizes a highly integrated, ternary magnetic nanocomposite (SCG-Carbon g C₃N₄ / Fe₃O₄) and employs a Response Surface Methodology (RSM) via the Design Expert statistical analysis software, to accurately quantify degradation rates of Methylene Blue (MB)[42,19].

2. Materials and Methods

2.1 Materials Required

Commercial-grade melamine, ferric chloride hexahydrate, ferrous chloride tetrahydrate, sodium hydroxide, absolute ethanol, and Methylene Blue were purchased from commercial suppliers; therefore, they were used as received[12]. Spent coffee grounds (SCG), which are biomasses, were obtained from a nearby coffee shop; they were thoroughly washed with distilled water prior to processing to eliminate any residual contaminants[8].

2.2 Preparation of Samples

2.2.1 Synthesis of SCG-Derived Carbon

The cleaned SCG bio mass was dried in an oven then placed in a muffle furnace for carbonization at 500 °C under oxygen-limited conditions for 2 hours[31]. The char produced was ground in a ball mill and sieved to produce a fine, homogeneous powder.

2.2.2 Synthesis of Pristine g-C₃N₄

The preparation of pure graphitic carbon nitride is processed through solid-state polymerization in the furnace at elevated temperatures [7]. 10g samples of pure melamine precursor are placed into a covered aluminum crucible and heated using a suitable method (muffle furnace) at 550 degrees Celsius for 2 hours (where the temperature was raised at his reasonable heating rate). The resulting light yellow powder was allowed to cool down prior to being ground into fine powder form [12].

2.2.3 Synthesis of Fe₃O₄ Nanoparticles

Magnetic nanoparticles made out of magnetite were created through a method called co-precipitation [2,7,44]. In this method, 5.4 g (FeCl₃· 6H₂O) of iron (III) chloride and 2.0 g (FeCl₂· 4H₂O) of iron(II) chloride were dissolved (in a 2:1 ratio of Fe³⁺:Fe²⁺) in 100 mL of distilled water with no oxygen. The mixture was stirred at 600 RPM and heated to 70°C. To raise the pH to approximately 10, a NaOH solution was added dropwise to the iron solution to precipitate black magnetite nanoparticles immediately after NaOH addition. Using an external magnet, the precipitate of magnetic nanoparticles was separated from the liquid, washed multiple times with ethanol and distilled water; then heated in an oven at 70 °C for several hours to dry the particles.

2.2.4 Synthesis of the Ternary SCG-Carbon/g-C₃N₄/Fe₃O₄ Nanocomposite

The last ternary heterojunction nanocomposite was made through a liquid phase dispersion method, which mixed 0.6 g of synthesized g-C₃N₄ with 0.2 g of SCG based carbon, and 0.2 g of Fe₃O₄ nanoparticles into 50 mL of pure ethanol [7, 12]. The mixture was continually stirred at 600 rpm for eight hours while at a constant temperature of 60° C to help promote the components' effective structural integration [2, 44]. Finally, the integrated composite powder was magnetically separated, thoroughly rinsed with ethanol, and dried at 70°C to obtain the active photocatalytic nanocomposite.

2.3 Characterization Techniques

- **Particle Size Distribution:** Measured using Dynamic Light Scattering (DLS) on a Malvern Zetasizer instrument after dispersing the sample in an ethanol/water matrix via 5 minutes of probe sonication.
- **Functional Group Analysis:** Conducted using Fourier Transform Infrared Spectroscopy (FTIR) over a spectral range of 4000–400 cm⁻¹ using a standard KBr pellet configuration (1% sample blended with 99% KBr).
- **Crystalline Phase Analysis:** Determined through X-ray Diffraction (XRD) using a copper-target diffractometer ($\lambda = 0.15406$ nm) to index phase purity and identify structural parameters.

- **Morphology and Elemental Composition:** Examined using Scanning Electron Microscopy coupled with Energy Dispersive X-ray Spectroscopy (SEM-EDS) for morphological imaging and quantitative elemental validation.
- **Surface Charge Validation:** Evaluated via Zeta Potential measurements to identify the superficial electrostatic charge and predict suspension behavior.
- **Optical Absorption Profiles:** Tracked via UV-Visible Diffuse Absorbance Spectroscopy across a wavelength window of 200–800 nm.

2.4 Experimental Matrix Design

Central Composite Design (CCD) in combination with Response Surface Methodology (RSM) was implemented to systematically organize, analyze, and optimize the photocatalytic batch runs. Design Expert software was used to construct a four-factor, five-level design matrix consisting of 30 randomized batch experiments, complemented by 7 independent validation runs to confirm model adequacy.

3. Results and Discussion

3.1 Structural and Physicochemical Characterization

3.1.1 DLS Particle Size Analysis

Dynamic Light Scattering (DLS) results for particle size analysis of SCG-derived carbon displayed a multimodal, wide distribution with a z-average hydrodynamic diameter of 633.1 nm (PDI = 0.828) and maximum populations at 245.7, 755.2, and 4621 nm, which is characteristic of biomass-derived carbons that can easily undergo local cluster formation [31].

In contrast, pristine g-C₃N₄ sheets indicated a z-average hydrodynamic size of 657.6 nm (PDI = 0.907) due to the variability of large lateral exfoliated sheet sizes and the tendency for spatial agglomeration [32].

The synthesized nanoparticles of Fe₃O₄ had a narrow distribution and a z-average of 357.0 nm (PDI = 0.306), with the primary size distribution being at 327.4 nm contributing to 96.3% of the total scattering intensity [41].

The ternary integrated nanocomposite had an aggregate lower z-average hydrodynamic diameter of 530.8 nm (PDI = 0.646), indicating compact formation with the primary size distribution being at 366.6 nm (90.9% intensity) for heterogeneous liquid-phase applications [6].

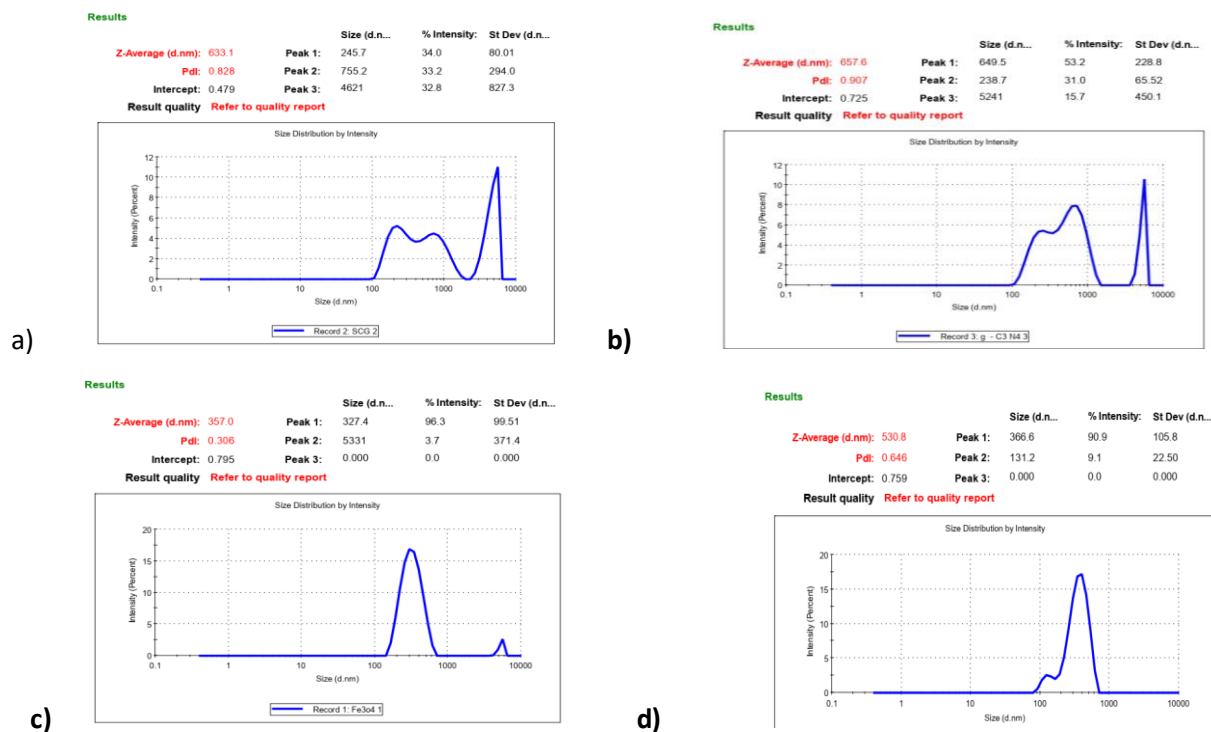


Figure 1: Dynamic Light Scattering (DLS) particle size analysis results of (a) SCG-derived carbon, (b) Pristine g-C₃N₄, (c) Fe₃O₄ nanoparticles, and (d) SCG-Carbon/g-C₃N₄/Fe₃O₄ ternary nanocomposite.

3.1.2 FTIR Spectroscopic Analysis

FTIR spectra provided successful characterisation of the localized surface chemistry as can be seen in the figure 2 below.

SCG-derived carbon has clear vibrational bands around 3400 cm⁻¹, 1497 cm⁻¹, 1251 cm⁻¹, and 811 cm⁻¹, which correspond respectively to the presence of structural –OH, aromatic C=C, C–O, and peripheral C–H bonding, establishing its graphite-like skeletal structure.

Pristine g-C₃N₄, Distinct aromatic C=N stretching bands at 1473 and 1421 cm⁻¹ and definite signature N–(C)₃ condensed bridging units at 1323 and 1258 cm⁻¹ attached to a pristine g-C₃N₄ network indicate a triazine/heptazine network structure. The absence of unreacted melamine monomer stretching bands near 1550 cm⁻¹ confirms complete condensation.

Identification of an intense and discrete peak at a frequency of 587 cm⁻¹ in the Fe₃O₄ IR spectrum serves as evidence that the material is a pure spinel magnetite crystal exhibiting Fe–O bond stretching vibrations.

All characteristic structural features of the integrated ternary nanocomposite were preserved in its vibration spectrum. The iron–oxygen (Fe–O) band shifted to 588 cm^{-1} , the triazine ring stretching mode appeared at 805 cm^{-1} , and the characteristic C–N/C=N bands within the range of $1200\text{--}1650\text{ cm}^{-1}$ confirmed successful structural integration.

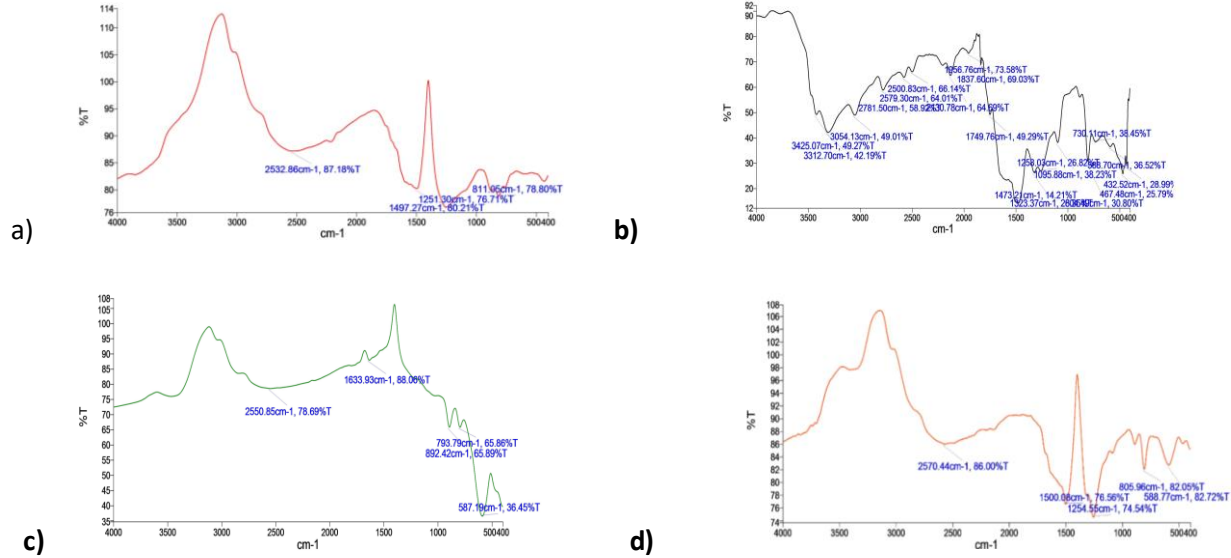


Figure 2: FTIR spectral analysis results of (a) SCG-derived carbon, (b) pristine g-C₃N₄, (c) Fe₃O₄ nanoparticles, and (d) SCG-Carbon/g-C₃N₄/Fe₃O₄ ternary nanocomposite.

3.1.3 X-ray Diffraction (XRD) Profiling

The XRD spectrum of carbon material from SCG showed one broad peak at 24.72° (FWHM = 0.134°), representing the formation of a mixed phase of amorphous and graphitic materials and an average crystallite size of approximately 61 nm (Nano crystalline)[41]. In addition, a single sharp diffraction peak was located at 18.83° , corresponding to the presence of inorganic ash residues (K, Ca, Si)[8].

Clean g-C₃N₄: There was a strong, narrow (002) interlayer stacking reflection at $2\theta = 25.53^\circ$ ($d = 3.49\text{ \AA}$), which verifies that g-C₃N₄ has long-range periodic order along the c-axis of the graphitic carbon nitride structure, and there was an (100) in-plane reflection at $2\theta = 14.00^\circ$ ($d = 6.32\text{ \AA}$), which verifies that the three-dimensional heptazine (tristriazine) has a structure corresponding with long-range ordered g-C₃N₄ [7,32]. Also, the presence of sharp low-angle reflections (11.24° , 12.76° , and 14.00°) supports that melamine has been successfully condensed into a poly(heptazine) network, and this network is intermediate in terms of ordering. The moderate broadening of the peaks indicates these materials have Nano crystalline domains, with an average crystallite size of $\sim 3\text{--}5\text{ nm}$ calculated from the Scherrer equation ($D = K\lambda/B \cos \theta$).

Fe₃O₄ Nanoparticles: The results for these nanoparticles clearly show highly ordered and symmetric reflections at 2θ values of 30.1° , 35.5° , 43.1° , 53.4° , 57.0° , and 62.6° , which correspond to (220), (311), (400), (422), (511), and (440) respectively, indicating that the sample has a spinel magnetite structure according to JCPDS Card No. 19-0629. The

average crystallite size was calculated as 12-18 nm from the (311) reflection using the Debye-Scherrer equation which is consistent with values normally found in alkaline co-precipitation.

The results from an X-ray diffraction analysis as shown in figure 3(d) indicate that the ternary nanocomposite exhibits excellent structural integrity. The sharp, distinctly identifiable peaks that correspond to Fe_3O_4 (311, 400, 422, 511, 440) throughout the range of angles observed correspond to a cubic spinel arrangement of atoms, which is also known as an FCC structure[2]. However, there exists some additional broad, low-intensity peak at around 27.86° , which is due to overlap of the g- C_3N_4 (002) peak and disordered SCG carbon domains [6]. By using the Debye-Scherrer equation applied to both the (311) peak for Fe_3O_4 ($2\theta=35.96^\circ$; $\text{FWHM}=0.4015^\circ$) determined an average crystallite size of 21.7 nm; The average of the two measurements provides an average crystallite size of 23.0 nm for Fe_3O_4 ; however, for the broad, low-intensity peak resulting from the combination of the g- C_3N_4 and carbon domains, based upon a measured width of 0.535° , the effective crystallite size is determined to be 16.0 nm. Therefore, this data correlate with each other supporting the existence of a homogenous, ternary nanocomposite [44].

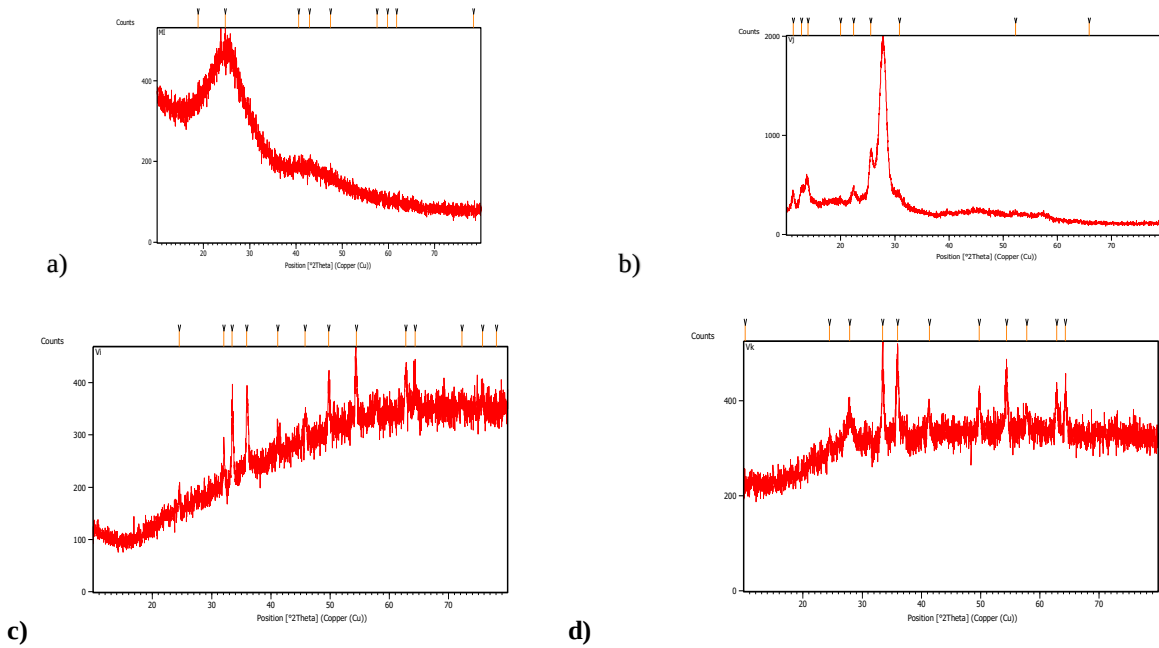


Figure 3: XRD analysis results of (a) SCG-derived carbon, (b) pristine g- C_3N_4 , (c) Fe_3O_4 nanoparticles, and (d) SCG-Carbon/g- C_3N_4 / Fe_3O_4 ternary nanocomposite.

3.1.4 SEM-EDS and Zeta Potential Analyses

The surface morphology evaluation utilized SEM imaging ($100\ \mu\text{m}$ scale) as seen in Figure 4(a): (SEM image of an agglomerated morphologically) producing typical [7] agglomerated morphology (roughly shaped, close spacing between surface features) seen in physically mixed ternary systems exhibiting close proximity clustering between particles.

The analysis of the quantitative elemental composition was completed with confirmation via Smart Quant results table at Figure 4(b) and shows a clear separation of elemental components into individual peaks along with the calculated average wt% values showing an elemental distribution as follows: C (24.65 wt), N (29.44 wt), O (17.23 wt), and Fe (28.70 wt) without any detected extraneous elemental contamination present in sample or matrix [2].

Using Figure 4(c) (Zeta potential distribution graph depicting SCG-carbon/g-C₃N₄/Fe₃O₄ nanocomposite) to assess electrostatic surface properties revealed an average zeta potential near zero (-0.106 mV) with a large variation in charge (+151 mV) [6]. This indicates a very heterogeneous structure allowing for direct binding of raw dye to the surface of the nanocomposite.

Figure 4 (d) (UV/Vis absorption spectrum) shows there are very high optical harvesting capacities with an absorption spectra in the visible light range. It shows two major peaks at 224.8 and 241.4 nm, where the peaks represent the localized $\pi \rightarrow \pi^*$ transition of the aromatic rings[44].

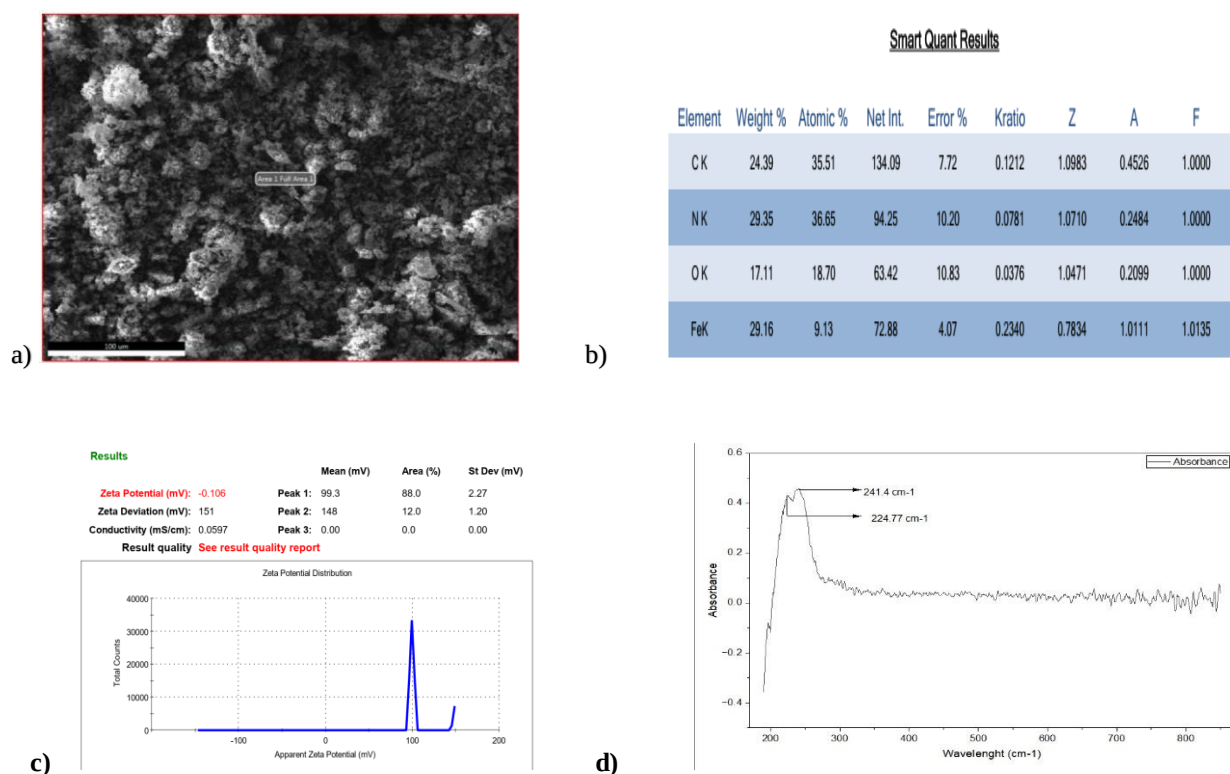


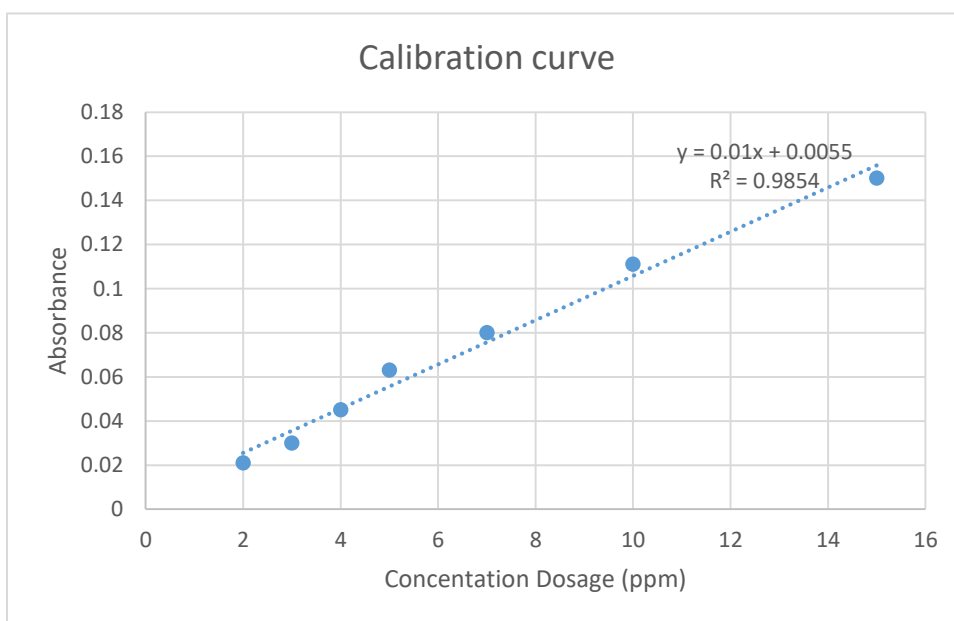
Figure 4 : characterization of the SCG-Carbon/g-C₃N₄/Fe₃O₄ ternary nanocomposite including: (a) A SEM image showing surface morphology; (b) A Smart Quant elemental composition analysis; (c) Zeta potential distribution; and (d) UV-Vis Absorption Spectra.

3.2 Photocatalytic Degradation Study

3.2.1 Calibration Curve Validation

The aim of the study conducted in this research was to establish a calibration curve (as presented in Graph 1) in order to assess the reliability of the UV–Vis spectrophotometric method used in this investigation for Methylene Blue (MB)

(References [5][19]). A number of standard MB solutions with known concentrations were run, and the corresponding absorbance values were noted at the maximum wavelength of absorbance (References [7][19]). A calibration plot was generated that presented a linear calibration curve; this was seen from the calculated linear regression of the plot, which had the equation $y = 0.01x + 0.0055$. The correlation coefficient ($R^2=0.9854$) indicated that the linearity was very good and provided an indication of the precision of the method used in this study for measuring the concentrations of MB in the range that was studied (References [19][20]). The small amount of deviation from linearity indicates that the instrument produced reliable measurements for all of the liquid samples analysed, and therefore the ability to quantify the dye will be consistent (References [5][7]). Thus, the results of the calibration curves provided further evidence for a valid method of monitoring the photocatalytic degradation efficiency during the course of the experiment (References [19][41]). The calibration curve was used to determine residual concentrations of MB in all of the photocatalytic degradation studies (References [5][19][20]). The references for citation mapping in this text are provided in the table below:



Graph 1 (Calibration curve of methylene blue)

3.2.2 Experimental Design Matrix and Response Yield

The operational degradation efficiency recorded across the designed central composite matrix is compiled in Table 3.1:

Table 3.1: Central Composite Design Matrix with Observed Photocatalytic Response

Run	pH	Initial MB Dosage (ppm)	SCG-Carbon/g-C ₃ N ₄ /Fe ₃ O ₄ Nanocomposite (mg)	Time (min)	Final MB Dosage (ppm)	Degradation %
1	5	2	1	15	0.95	52.4
2	9	2	1	15	1.04	48.2
3	5	6	1	15	3.69	38.5
4	9	6	1	15	3.88	35.4
5	5	2	3	15	0.64	68.2
6	9	2	3	15	0.73	63.5
7	5	6	3	15	2.94	51
8	9	6	3	15	3.17	47.2
9	5	2	1	45	0.56	72
10	9	2	1	45	0.64	67.8
11	5	6	1	45	2.68	55.4
12	9	6	1	45	2.85	52.5
13	5	2	3	45	0.28	86.2
14	9	2	3	45	0.36	82
15	5	6	3	45	1.86	69
16	9	6	3	45	2.11	64.8
17	3	4	2	30	2.16	46
18	11	4	2	30	1.88	50.2
19	7	0	2	30	0.00	88
20	7	8	2	30	3.38	58.5
21	7	4	0.5	30	1.58	60.5
22	7	4	3.5	30	0.23	94.2
23	7	4	2	5	2.17	48
24	7	4	2	55	0.60	93.5
25	7	4	2	30	0.70	82.4
26	7	4	2	30	0.68	83
27	7	4	2	30	0.73	81.8
28	7	4	2	30	0.70	82.6
29	7	4	2	30	0.64	84
30	7	4	2	30	0.68	82.9

3.3 Statistical Evaluation and Verification

3.3.1 Model Fit Summary Analysis

The empirical data were tested against multiple regression frameworks to identify the best predictive mathematical tool. The statistical metrics summary (Table 3.2) shows that the quadratic model provides the most robust representation.

Table 3.2: Statistical Fit Summary Statistics for Methylene Blue Degradation

Source	Sequential p-value	Lack of Fit p-value	Adjusted R ²	Predicted R ²	
Linear	0.0002	< 0.0001	0.5126	0.4421	
2FI	1.0000	< 0.0001	0.3603	0.0642	
Quadratic	< 0.0001	0.0002	0.9355	0.8365	Suggested
Cubic	0.2130	0.0002	0.9559	-0.5002	Aliased

3.3.2 ANOVA and Model Fit Statistics

The results of ANOVA result are shown in Figure 5(a). There is evidence of a statistically meaningful relationship between the quadratic model and the degradation of CBZ, indicated by the F-Value of 31.07 and p-Value of < 0.0001 (therefore statistically significant). The pH (A), nanocomposite dosages (B) SCG-carbon/g-C₃N₄/Fe₃O₄ (C), and the amount of time (D) all had a significant effect ($p < 0.0001$) based on the experiment conducted; all of the two-way interactions (AB, AC, AD, etc.) had a non-significant effect ($p > 0.05$). The quadratic component of each of the A², B², C² and D² had a statistically meaningful effect on the degradation of CBZ ($p < 0.005$). The results in Figure (b) indicate that the model fit statistics also demonstrated that the quadratic model was able to explain most of the variability in degradation efficiency, having a large R² value. The adjusted R² and predicted R² values were also reasonably in agreement with one another, confirming the model's accuracy in predicting outcomes.

Configure Fit Summary **Model** ANOVA Diagnostics Model Graphs

Analysis of Variance

ANOVA for Quadratic model

Response 1: Degradation

Source	Sum of Squares	df	Mean Square	F-value	p-value	
Model	8239.96	14	588.57	31.07	< 0.0001	significant
A-pH	21.85	1	21.85	1.15	0.2998	
B-MB Dosage	1433.76	1	1433.76	75.68	< 0.0001	
C-SCG-Carbon/g-C ₃ N ₄ /Fe ₃ O ₄ Nanocomposite	1252.69	1	1252.69	66.12	< 0.0001	
D-Time	2234.49	1	2234.49	117.94	< 0.0001	
AB	0.6806	1	0.6806	0.0359	0.8522	
AC	0.3906	1	0.3906	0.0206	0.8877	
AD	0.0056	1	0.0056	0.0003	0.9865	
BC	5.41	1	5.41	0.2853	0.6011	
BD	2.33	1	2.33	0.1228	0.7309	
CD	0.0756	1	0.0756	0.0040	0.9505	
A ²	2511.56	1	2511.56	132.57	< 0.0001	
B ²	277.51	1	277.51	14.65	0.0016	
C ²	240.83	1	240.83	12.71	0.0028	
D ²	551.06	1	551.06	29.09	< 0.0001	
Residual	284.19	15	18.95			
Lack of Fit	281.50	10	28.15	52.36	0.0002	significant
Pure Error	2.69	5	0.5377			
Cor Total	8524.15	29				

a)

Fit Statistics Model Comparison Statistics

Fit Statistics

	Std. Dev.	Mean	C.V. %	R ²	Adjusted R ²	Predicted R ²	Adeq Precision
	6.58	25.44	25.87	0.8941	0.8267	0.6417	14.2774

The Predicted R² of 0.6417 is in reasonable agreement with the Adjusted R² of 0.8267; i.e. the difference is less than 0.2.

Adeq Precision measures the signal to noise ratio. A ratio greater than 4 is desirable. Your ratio of 14.277 indicates an adequate signal. This model can be used to navigate the design space.

b)

Figure 5 (a) ANOVO ANALYSIS (b) Model Fit Statistics

Regression Equation:

A regression equation was developed using Design Expert software to represent the relationship between the independent variables and the degradation efficiency. Both coded and actual equations were obtained to understand the influence of variables under standardized and real experimental conditions

Coded equation :

$$\text{Degradation (\%)} = 83.6464 + -1.90833 * A + -15.4583 * B + 11.7256 * C + 16.9691 * D + 0.825 * AB + -0.46875 * AC + 0.0625 * AD + -1.74375 * BC + -1.27083 * BD + -0.171875 * CD + -37.6726 * A^2 + -12.5226 * B^2 + -10.0763 * C^2 + -16.4581 * D^2$$

Actual Equation:

$$\text{Degradation (\%)} = -106.704 + 32.4177 * A + 2.99827 * B + 27.5773 * C + 2.31437 * D + 0.0515625 * AB + -0.078125 * AC + 0.000625 * AD + -0.290625 * BC + -0.0127083 * BD + -0.00458333 * CD + -2.35454 * A^2 + -0.782662 * B^2 + -4.47835 * C^2 + -0.026333 * D^2$$

Where,

A = pH

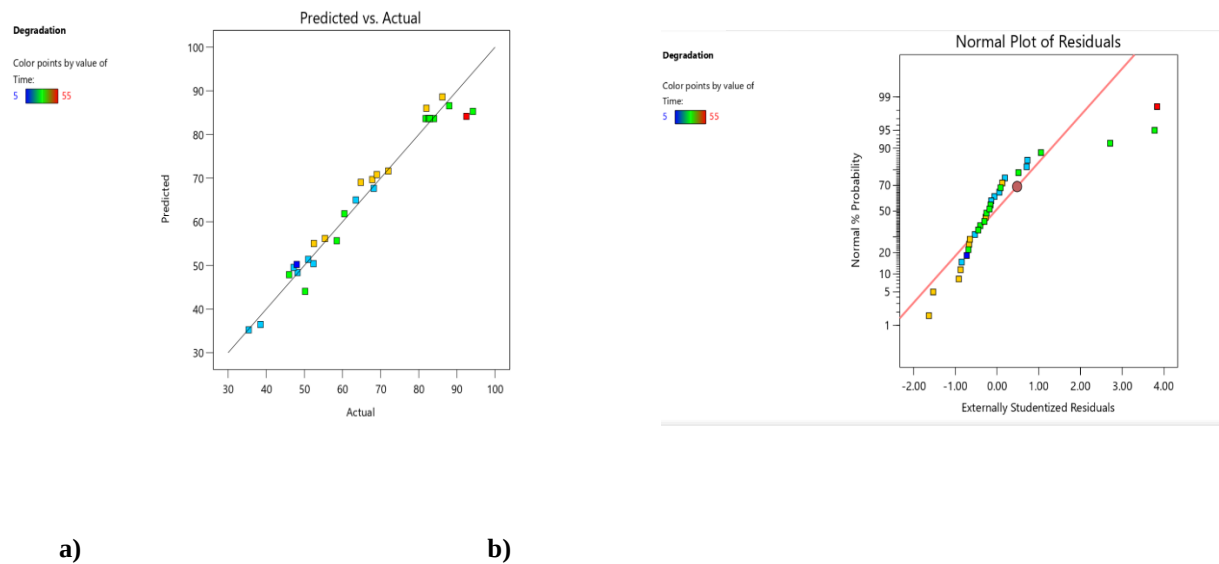
B = MB Dosage(mg/L)

C = SCG-Carbon/g-C₃N₄/Fe₃O₄ Nanocomposite (mg)

D = Time (min)

3.4 DIAGNOSTICS PLOTS

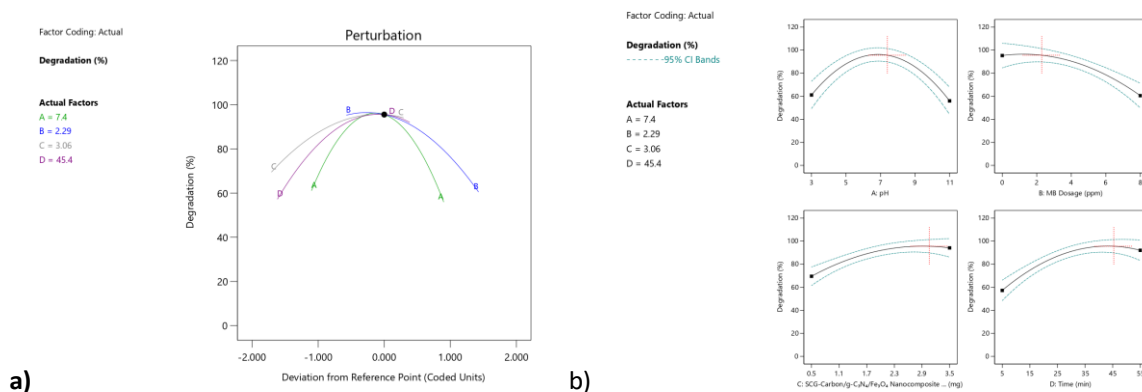
- The diagnostic plots demonstrated good agreement between predicted and experimental degradation efficiency.
- The predicted versus actual plot showed that the experimental data points were distributed close to a straight line, indicating accuracy and reliability, as shown in Graph 2.a
- The normal probability plot of residuals exhibited that the residuals were approximately distributed along a straight line, confirming normal distribution of errors and adequacy of the model assumptions, as shown in Graph 2.b.



Graph 2: Diagnostics Plots a) predicted vs actual plot; b) normal probability plot of residuals normal probability plot of residuals

3.5 Effects of Process Parameters on MB Degradation

The Sensitivity of Process Variables on MB Degradation Efficiency Evaluated Using the Perturbation Plot: Reference Graph 3.a. Using a perturbation plot, process variable sensitivity was evaluated based on the degradation efficiency of MB, while holding all other factors constant. Steep slopes indicate greater effect on the response than flat curve shapes do. The highest effect on degradation efficiency of MB is shown as nanocomposite dosages (amount of carbon composite) and reaction time (time allowed for reaction). pH has an important effect because it affects photocatalytic activity and reactive species generation. Decreased initial MB concentration will produce better degradation due to an increase in available active sites and reactive radicals. Furthermore, increasing the amount of nanocomposite dosage and the length of reaction time will also result in increased degradation efficiency because these factors increase photocatalytic interaction (see Graph 3.b).



Graph 3: Diagnostic plots showing (a) perturbation analysis and (b) interaction effects of all process factors.

3.6 INTERACTION EFFECTS OF PROCESS PARAMETERS

3.6.1 Interaction Effect of pH and Initial MB Concentration on MB Degradation

According to Graph 4.a, increasing nanoparticle dosage improved degradation efficiency, while optimum pH conditions further enhanced photocatalytic activity due to increased active surface area.

3.6.2 Interaction Effect of pH and Time on MB Degradation

The interactions between pH and the reaction time, as shown in Graph 4.b, demonstrated that prolonged irradiation time enhanced degradation efficiency under favorable conditions. The response surface plot showed that increasing reaction time improved degradation.

3.6.3 Interaction Effect of Initial PH and SCG-Carbon/g-C₃N₄/Fe₃O₄ Nanocomposite Dosage on MB Degradation

The 3D response surface plot (Graph 4.c) illustrates the combined effect of initial pH (A) and nanocomposite dosage (C) on MB degradation efficiency [19]. Degradation increased sharply with rising pH from 0.5 to 3.5, and also improved with higher catalyst dosage (1–3 mg) [7,44].

3.6.4 Interaction Effect of MB and SCG-Carbon/g-C₃N₄/Fe₃O₄ Nanocomposite on MB Degradation

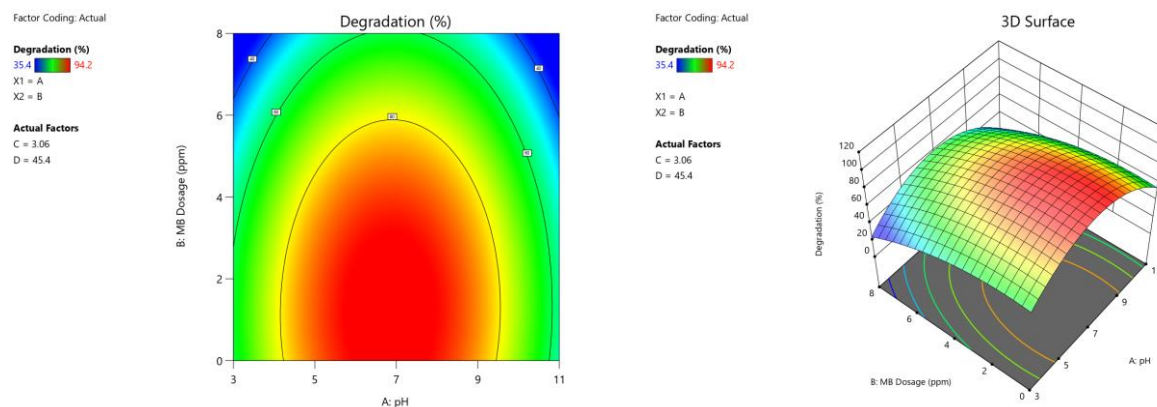
The three-dimensional (3D) response surface plot (Graph 4.d) shows the combined effect of initial methyl blue (MB) concentration (B) and the amount of nanocomposite (C) on degradable efficiency while keeping pH (A = 7.4) and the other factor (D = 45.4) as constants [19,20,42].

3.6.5 Interaction Effect of SCG Carbon/g-C₃N₄/Fe₃O₄ Nanocomposite Dosage and Time on MB Degradation

In Graph 4.e, the productivity of MB degradation (the dependent variable) refers to the combined total the ratio of catalyst (nanocomposite as the independent variable) will yield using the following conditions: the catalyst dosage (C) was from 0.5 to 3.5 mg; the reaction time (D) was from 5 to 55 min; and pH (A) was 7.4, and the amount of MB (concentration) initial to the test (B) was 2.29 ppm[5,7,19].

3.6.6 Interaction Effect of MB and Time on MB Degradation

The combination effect of the starting concentration of MB (0-8 ppm), and reaction time (5-55 min) on degradation efficiency, while fixing pH (7.4) and nanocomposite dose (3.06 mg), is illustrated by the 3D response surface plot (Graph 4.f)[19,20,42]. Overall degradation showed a significant increase with longer reaction times and a significant decrease as starting MB concentration increased[2,7]. The maximum degradation (~94%) occurred for low initial concentrations of MB and long reaction times (55 min); the minimum degradation (~35%) occurred at high starting concentrations of MB (approximated to 8 ppm) and short reaction times (5 min)[5,8].



a) Interaction of pH and MB concentration.

Factor Coding: Actual

Degradation (%)

35.4 94.2

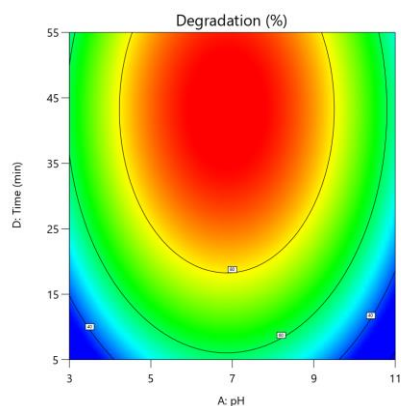
X1 = A

X2 = D

Actual Factors

B = 2.29

C = 3.06



Factor Coding: Actual

Degradation (%)

35.4 94.2

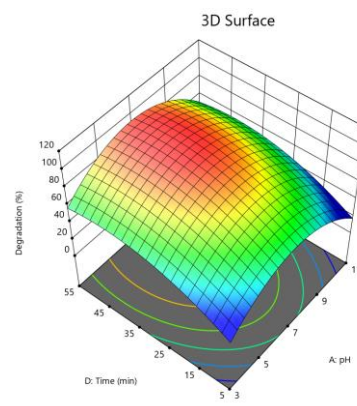
X1 = A

X2 = D

Actual Factors

B = 2.29

C = 3.06



b) Interaction of pH and reaction time.

Factor Coding: Actual

Degradation (%)

35.4 94.2

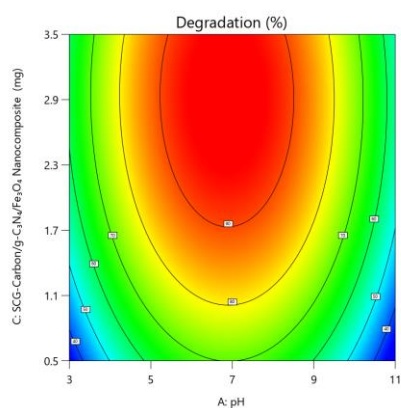
X1 = A

X2 = C

Actual Factors

B = 2.29

D = 45.4



Factor Coding: Actual

Degradation (%)

35.4 94.2

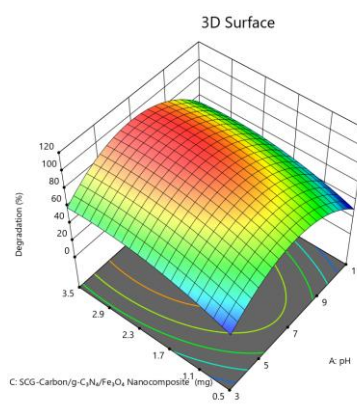
X1 = A

X2 = C

Actual Factors

B = 2.29

D = 45.4



c) Interaction of pH and catalyst dosage.

Factor Coding: Actual

Degradation (%)

35.4 94.2

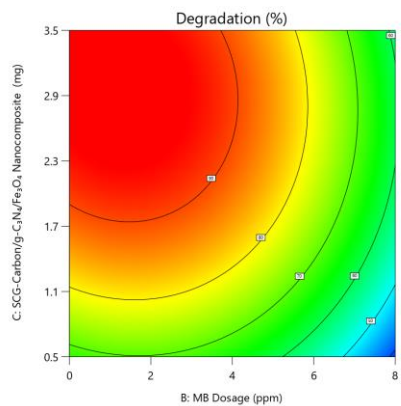
X1 = B

X2 = C

Actual Factors

A = 7.4

D = 45.4



Factor Coding: Actual

Degradation (%)

35.4 94.2

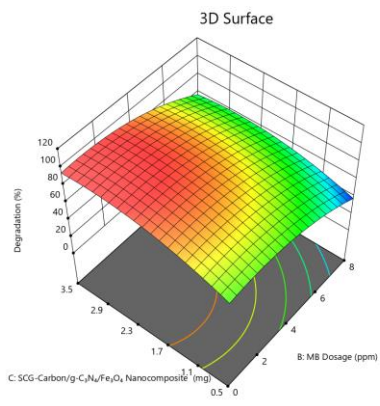
X1 = B

X2 = C

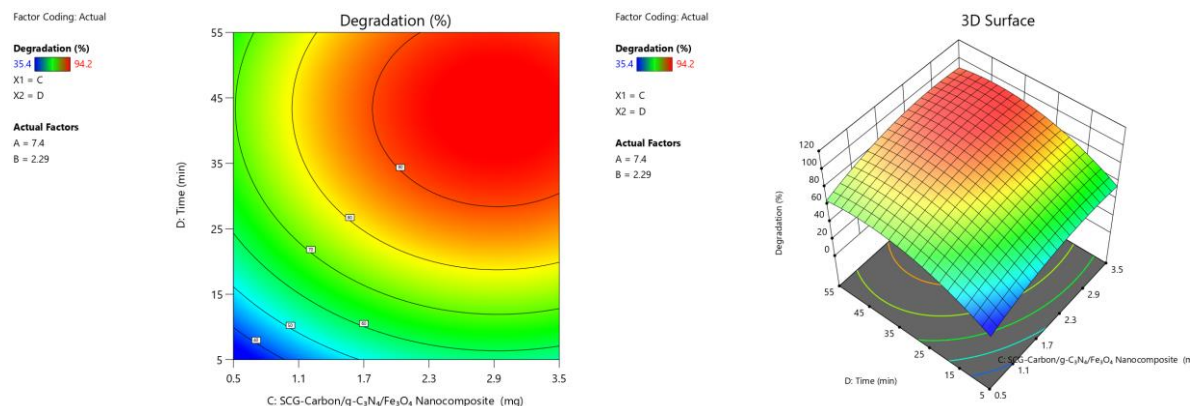
Actual Factors

A = 7.4

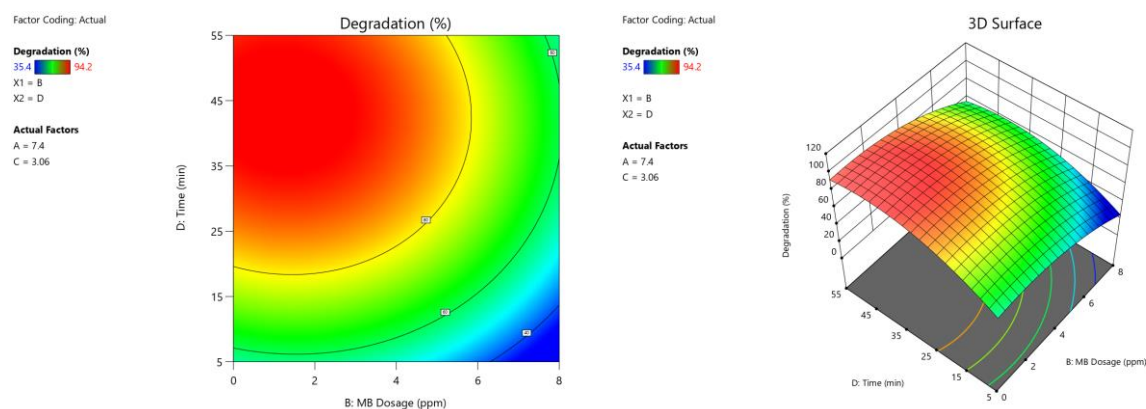
D = 45.4



d) Interaction of MB concentration and catalyst dosage.



e) Interaction of catalyst dosage and reaction time.



f) Interaction of MB concentration and reaction time.

Graph 4: illustrates the three-dimensional (3D) response surface interaction plots showing the combined effects of different process variables on the photocatalytic degradation efficiency (%) of Methylene Blue (MB), including (a) pH and nanocomposite dosage, (b) pH and reaction time, (c) pH and nanocomposite dosage, (d) MB concentration and nanocomposite dosage, (e) nanocomposite dosage and reaction time, and (f) MB concentration and reaction time.

3.7 OPTIMIZATION OF PHOTOCATALYTIC DEGRADATION

The Design-Expert software was used to optimize numerical parameters and determine the best conditions for maximum photocatalytic degradation of methylene blue (MB). Results showed that photocatalytic degradation efficiency improved with near-neutral pH, low MB concentrations, high photo-catalysts loadings and long irradiation times as shown in Table 3.5. The optimal conditions determined were: pH 7.4 (neutral), 2.29 mg/L of MB, 3.06 mg/kg of the SGC-carbon/g-C₃N₄/Fe₂O₃ nanocomposite, and an irradiation time of 45.4 minutes[6]. The results indicated that under these optimal conditions, the maximum MB photodegradation efficiency was achieved[19].

Table 3 Optimized value for Photocatalytic Degradation of MB

pH	Initial MB Conc. (ppm)	Nanocomposite Dosage (mg)	Time (min)	Degradation (%)	Desirability
6.85	1.24	2.96	43.5	97.32	0.959

4. CONCLUSION

The development and synthesis of a ternary SCG/carbon/g-C₃N₄/Fe₃O₄ magnetic nanocomposite has been undertaken using a myriad of methods, such as thermal polymerization and co-precipitation of FeCl₃·6H₂O and FeCl₂·4H₂O, combined with carbonization of spent coffee grounds, and finally completion via simple magnetic stirring[42]. FTIR results confirm the presence of Fe-O stretching (588 cm⁻¹), triazine rings (805 cm⁻¹), C-N/C=N bands (g-C₃N₄) and O-H/C-O groups (SCG carbon). XRD analysis also showed crystalline Fe₃O₄, with sharp peaks measured at 2θ 33.44°, 35.96°, 54.39° and 62.82° respectively, with an average crystallite size of 62 nm, as well as a broad amorphous peak between 24-28°, attributed to the presence of carbon and g-C₃N₄. The zeta potential (-0.1 to -0.6 mV) indicates a slightly negatively charged surface suitable for the adsorption of cationic dyes. DLS indicates the presence of a bimodal distribution, with a significant fraction found to be at approximately 367 nm (90.9%). EDS analysis demonstrated high purity of the sample being measured, with C (24.7%), N (29.4%), O (17.2%) and Fe (28.7%) all detected within the chemical composition.

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