



# Development of Mesoporous Cu-doped ZnO/rGO Nanocomposites with High Surface Area for Efficient Ethyl Violet Removal: Kinetics, Isotherms and AI-driven Predictive Modeling

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## ABSTRACT

A mesoporous Cu-doped ZnO/rGO nanocomposite was made by a one-step co-precipitation process and employed effective adsorbent for the elimination of ethyl violet (EV) from aqueous solutions. Structural, morphological, and surface properties of the synthesized material were examined using X-ray diffraction (XRD), Brunauer-Emmett-Teller (BET), and scanning electron microscopy (SEM) analyses. The findings revealed mesoporous structural characteristics exhibiting a substantial surface area of 115.8 m<sup>2</sup>/g, an average pore diameter of 29.6 nm, and a distinctive small-angle X-ray diffraction (SAXRD) peak at 0.83°, offering several active sites for adsorption. Batch adsorption investigations revealed that the removal effectiveness varied from 72.4% to 93.3%, contingent upon operational parameters including starting concentration, pH, sonication duration, and adsorbent dosage. The process was statistically analyzed by response surface methodology (RSM), demonstrating non-significant lack of fit ( $p = 0.321$ ) and high significance ( $F = 82.44$ ,  $p < 0.0001$ ), confirming acceptable model adequacy. To improve predictive accuracy, an artificial neural network-based model. The BP-ANN model showed comparatively better predictive performance, while the RBF model indicated worse predictive capability ( $R^2 = 0.83812$ ). Optimization by ANN-GA determined the ideal parameters as a concentration of 348.92 mg/L, pH 4.91, a sonication duration of 9.82 minutes, and a dosage of 17.03 mg, resulting in a predicted removal efficiency of 93.33%, which closely aligned with the experimental value of 92.10%, exhibiting a negligible error of 1.23%. Kinetic investigation revealed that adsorption adhered to the pseudo-second-order model ( $R^2 = 0.997$ ), suggesting possible chemisorption involvement, whereas equilibrium tests demonstrated that the Langmuir isotherm ( $R^2 = 0.9502$ ) most accurately characterized the process, with a maximum adsorption capacity of 965 mg/g. The amalgamation of statistical modeling and hybrid AI optimization provides an effective approach for process optimization, indicating that Cu-doped ZnO/rGO nanocomposites possess potential for wastewater treatment applications.

**Keywords:** Mesoporous Cu-doped ZnO/rGO; Batch adsorption; Adsorption kinetics; Dye wastewater treatment; Artificial intelligence; Ethyl violet.

## 1. INTRODUCTION

The decolorization of organic dyes from industrial effluents is an important step toward environmental sustainability. ZnO-based materials have attracted considerable attention in wastewater treatment due to their high catalytic efficiency, stability, and cost-effectiveness. Recent studies have focused on improving ZnO performance through doping, heterostructure formation, and surface modification to enhance adsorption and photocatalytic efficiency. For example, Ag-decorated ZnO nanoparticles synthesized using green

reducing agents exhibited enhanced visible-light absorption and efficient dye degradation performance (Simović *et al.* 2025). Similarly, green-synthesized ZnO nanostructures prepared using plant extracts demonstrated high surface area and improved photocatalytic degradation efficiency under sunlight irradiation (Vinayagam *et al.* 2022). In addition, doped ZnO systems such as Ag/N co-doped ZnO, Sr-doped ZnO, Mo-doped ZnO, Zr-doped ZnO, and Cd-incorporated ZnO have shown improved charge separation, enhanced reactive oxygen species generation, and superior degradation efficiency toward various

organic pollutants (Naik *et al.* 2021; Mariyappillai *et al.* 2025; Sargunavathi *et al.* 2025; Thendral *et al.* 2026).

Heterostructure-based ZnO composites have also demonstrated enhanced pollutant removal performance due to improved electron transfer and suppression of electron-hole recombination. CuWO<sub>4</sub>/ZnO nanocomposites exhibited effective methylene blue degradation through enhanced charge separation (Koedsiri *et al.* 2024), while graphene-supported ZnO systems showed improved visible-light absorption and catalytic activity (Dai *et al.* 2021). Furthermore, Ni-doped ZnO supported on reduced graphene oxide nanosheets demonstrated enhanced degradation of pharmaceutical contaminants due to improved interfacial electron transport (Abdi *et al.* 2025). Structural modifications such as porous and nanofibrous ZnO architectures have also been reported to improve surface activity and adsorption efficiency (Chen *et al.* 2025). Optimization approaches such as response surface methodology have also been employed to improve wastewater treatment efficiency in ZnO- and rGO-based systems (Preethy *et al.* 2024; Seloglu *et al.* 2024).

Despite these advancements, several limitations still exist in ZnO/rGO-based systems, including insufficient adsorption capacity, limited active surface sites, and inadequate integration of adsorption studies with predictive optimization approaches. In particular, studies combining mesoporous Cu-doped ZnO/rGO nanocomposites with systematic statistical and machine learning-based optimization for dye removal remain limited.

Therefore, the present study focuses on the synthesis of mesoporous Cu-doped ZnO/rGO nanocomposites through a one-step co-precipitation method for the removal of ethyl violet dye from aqueous solutions. The adsorption process was optimized using response surface methodology and artificial neural network-based models to evaluate the relationship between operational parameters and adsorption performance. The study aims to provide an improved understanding of the adsorption behavior and optimization capability of Cu-doped ZnO/rGO nanocomposites for wastewater treatment applications.

## 2. MATERIALS AND METHODOLOGY

### 2.1 Materials

Copper (Cu) precursor, typically copper nitrate (Cu(NO<sub>3</sub>)<sub>2</sub>·3H<sub>2</sub>O, ≥99% purity), and Zinc precursor, typically zinc nitrate hexahydrate (Zn(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O, ≥98% purity), were procured from Star Scientific

Enterprises, Erode, Tamil Nadu, India. Reduced graphene oxide (rGO) (purity ≥99%, particle size <100 nm) nanopowder, characterized by high surface area and amorphous structure, was used as the supporting matrix. Sodium hydroxide (NaOH, analytical reagent grade, ≥98% purity) and ethanol (analytical grade, ≥99.5% purity) were employed during the synthesis process. For the preparation of the Cu-ZnO/rGO nanocomposite, copper precursor was introduced at 5 mol% relative to the zinc precursor concentration, while rGO was incorporated at 2 wt% of the total metal oxide content. Deionized (DI) water was used throughout the experimental procedures for solution preparation, washing, and dilution. Ethyl violet (EV) dye was also purchased from Star Scientific Enterprises, Erode, Tamil Nadu, India.

### 2.2 Synthesis of Cu-doped ZnO/rGO Nanocomposite

The Cu-doped ZnO/rGO nanocomposite was synthesized by a one-step co-precipitation technique to achieve uniform deposition of ZnO and Cu species onto the graphene support (Shewale and Yun, 2020). The synthesis was carried out using 0.1 M zinc nitrate hexahydrate and 0.005 M copper nitrate solutions, corresponding to a Cu doping concentration of 5 mol% relative to the Zn precursor. Reduced graphene oxide (rGO) was incorporated at 2 wt% of the total metal oxide content. The rGO was dispersed in an ethanol-deionized water mixture (1:1 v/v) using ultrasonication at 40 kHz and 200 W for 30 min to obtain a homogeneous suspension. Subsequently, the precursor solution was stirred at 800 rpm for 4 h under ambient conditions. Initially, reduced graphene oxide (rGO) was dispersed at mixture of ethanol and deionized water using ultrasonication for 30 min to obtain homogeneous suspension. An appropriate amount of zinc and copper precursors was dissolved in deionized water and directly introduced into the rGO suspension with continuous magnetic stirring. The pH of the reaction mixture was adjusted to 9–10 with NaOH solution, initiating the simultaneous co-precipitation of Zn<sup>2+</sup> and Cu<sup>2+</sup> ions in the form of their respective hydroxides onto the rGO surface. The reaction mixture was continuously stirred at 800 rpm for 4 h to ensure uniform nucleation and growth of Cu-doped ZnO particles on the rGO surface. The precipitate was collected via filtration, washed with DI water and ethanol to eliminate residual impurities, and then dried at 80 °C overnight. The dried product was calcined at 500 °C for 4 h in an ambient air atmosphere using a heating rate of 5 °C min<sup>-1</sup> to obtain highly crystalline Cu-doped ZnO/rGO nanocomposites.

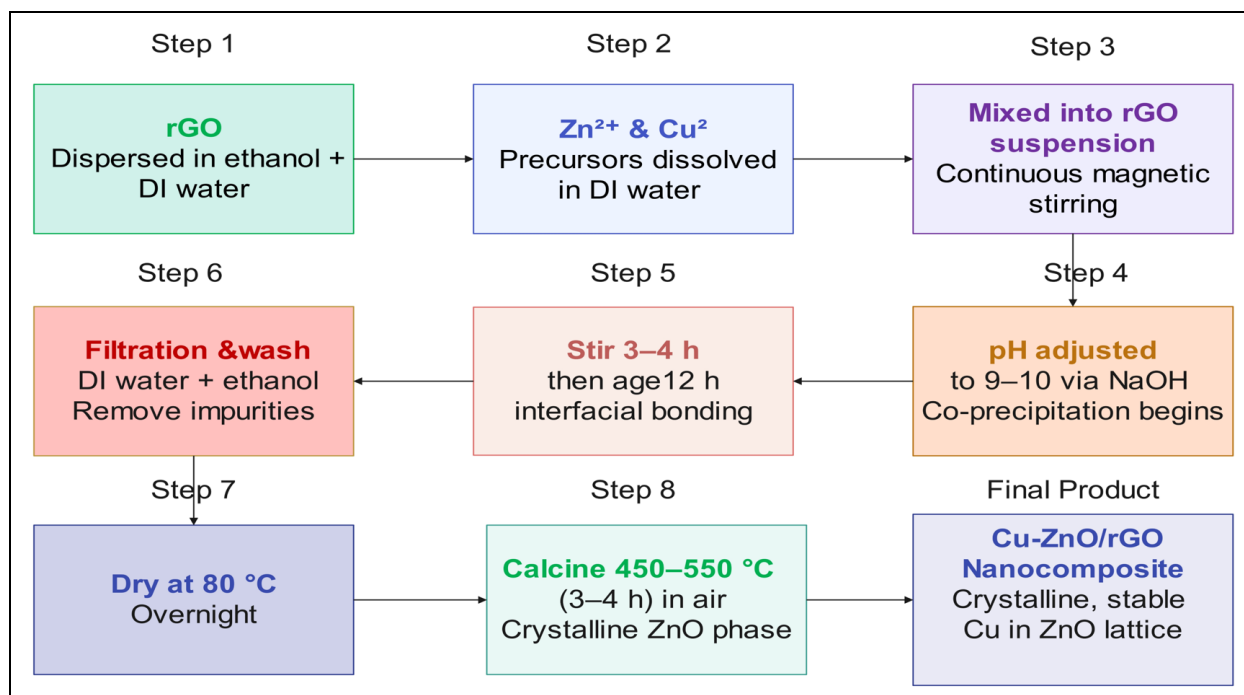


**Fig. 1: Schematic representation of the synthesis of Cu-doped ZnO/rGO nanocomposite via the co-precipitation method**

### 2.3 Characterization

The structural properties and crystalline phases of ZnO – Cu and Cu -doped ZnO/rGO nanocomposites were analyzed by X-ray diffraction (XRD) at Bruker D8 Advance X-ray Diffractometer, with Cu-K $\alpha$  radiation, within a scanning range of  $2\theta = 5^\circ - 90^\circ$  (Wang and Gao, 2009). Oxidation states and surface elemental composition were analysed by X-ray photoelectron spectroscopy with PHI 5000 VersaProbe II XPS. Raman analysis was performed using a WITEC alpha 300R Microscope equipped with a 532 nm excitation laser to study structural defects and vibrational modes. The microstructural and morphological characteristics were analysed by FESEM on a Gemini ZEISS SEM. Elemental composition and mapping were carried at integrated energy-dispersive X-ray spectroscopy detector.

Textural properties such as pore volume and specific surface area were determined via nitrogen adsorption-desorption evaluation by Micromeritics ASAP 2020 Surface Area at 77 K. A Brunauer-Emmett-Teller were used for surface area calculation, and the Anton Paar Autorb model was applied for pore size evaluation. Small-angle X-ray diffraction (SA-XRD) was conducted using a Rigaku SmartLab X-ray Diffractometer to evaluate mesostructural ordering.

Magnetic measurements were performed solely to evaluate the influence of Cu incorporation on the magnetic response of the nanocomposite and to assess its potential applicability in adsorbent recovery processes.

### 2.4 Dye Removal Procedure

Batch adsorption experiments for the removal of ethyl violet (EV) were conducted by altering critical operating parameters, such as solution pH, sonication duration (minutes), beginning, adsorbent dosage (mg) and dye concentration (mg/L), in 100 mL Erlenmeyer flasks (Abdessemed *et al.* 2019). All studies was conducted at ambient temperature under ultrasonic irradiation to improve mass transfer and adsorption efficacy. The pH of EV solutions was meticulously calibrated to specified values utilizing 0.1 M hydrochloric acid (HCl) and 0.1 M sodium hydroxide (NaOH) before the adsorption procedure. Upon completion of the adsorption process, the adsorbent was separated from the solution by centrifugation at 5000 rpm for 10 min, followed by filtration prior to UV–Vis analysis. Residual concentration of EV at solution was measured by UV–Visible spectrophotometer at the peak absorption wavelength ( $\lambda_{\text{max}}$ ) of 595 nm. Dye clearance percentage was calculated by assessing the variation in initial and final concentrations using the usual formula.

$$Y(\%) = (C_0 - C_t)/C_0 \times 100\% \quad \dots (1)$$

In this expression,  $Y$  denotes the percentage removal of ethyl violet (EV),  $C_0$  shows the starting concentration of dye in the solution (mg/L), and  $C_t$  shows the remaining dye concentration after a specified period post-adsorption (mg/L).

$$q_e = (C_0 - C_t) \times V/m_s \quad \dots (2)$$

Here  $m_s$  indicates adsorbent dosage (g),  $V$  shows the volume of EV solution, and  $q_e$  denotes the removal equilibrium of EV (mg/g).

Ultrasonic-assisted adsorption experiments were conducted using an ultrasonic bath operating at a frequency of 40 kHz and a power output of 200 W. The adsorption experiments were performed at room temperature ( $25 \pm 2$  °C) with an equilibrium contact time of 60 min. Each experiment was conducted in triplicate, and the average value was reported.

## 2.5 Design and Optimization Using Response Surface Methodology (RSM) in Minitab

**Table 1. Experimental factors and their coded levels**

| Factors                                     | Coded Variable Levels |      |     |     |          |
|---------------------------------------------|-----------------------|------|-----|-----|----------|
|                                             | $-\alpha$             | $-1$ | $0$ | $1$ | $\alpha$ |
| Initial concentration (mg L <sup>-1</sup> ) | 200                   | 275  | 350 | 425 | 500      |
| Initial pH                                  | 2                     | 3    | 4   | 5   | 6        |
| Sonication time (min)                       | 5                     | 8    | 11  | 14  | 17       |
| Dosage (mg)                                 | 8                     | 12   | 16  | 20  | 24       |

In this study, RSM was implemented using Minitab to evaluate and optimize the removal efficiency of ethyl violet using Cu-doped ZnO/rGO nanocomposites. Response Surface Methodology (RSM) based on a Central Composite Design (CCD) was employed using Minitab software to evaluate the effects of four independent variables, namely initial dye concentration (200–500 mg L<sup>-1</sup>), solution pH (2–6), sonication time (5–17 min), and adsorbent dosage (8–24 mg), on ethyl violet removal efficiency. A total of 30 experimental runs were generated by the CCD matrix, and the obtained results were analyzed using ANOVA to identify statistically significant model terms and interaction effects. A central composite design (CCD) was adopted to systematically investigate the influence of key process variables (Najari *et al.* 2023). The

relationship between coded variables and actual process parameters is presented in Table 1, which forms the basis for model development and subsequent optimization.

The statistical analysis method employed was analysis of variance (ANOVA) to elucidate the intricate link among four independent variables and two dependent variables within the entire dataset.

## 2.6 Artificial Neural Network

The backpropagation ANN were prevalent ML method for modeling intricate nonlinear systems. Neural networks demonstrate enhanced adaptability, noise resilience, and generalization capabilities compared to traditional rule-based or knowledge-driven methodologies. All neural network simulations in this study were conducted using MATLAB R2016a. A nonlinear predictive model was constructed utilizing the experimental dataset derived from response surface methodology (RSM) through a three-layer feedforward architecture, which uses a hidden layer, input layer, and output layer. The network architecture had four input parameters: solution pH, adsorbent dosage, beginning ethyl violet (EV) concentration, and sonication duration, with a single output node indicating elimination effectiveness of EV utilizing Cu-doped ZnO/rGO nanocomposites. Fig. 2 depicts a schematic form of the created BP-ANN model.

The ANN model was developed in MATLAB R2016a using a feed-forward backpropagation architecture consisting of four input neurons, one hidden layer with 10 neurons, and one output neuron. The tangent sigmoid (tansig) activation function was employed in the hidden layer, while a linear (purelin) activation function was used in the output layer. The network was trained using the Levenberg–Marquardt backpropagation (trainlm) algorithm. The dataset comprising 30 CCD experiments was randomly divided into training (70%), validation (15%), and testing (15%) subsets. Model performance was evaluated using the coefficient of determination ( $R^2$ ), root mean square error (RMSE), and mean absolute error (MAE).

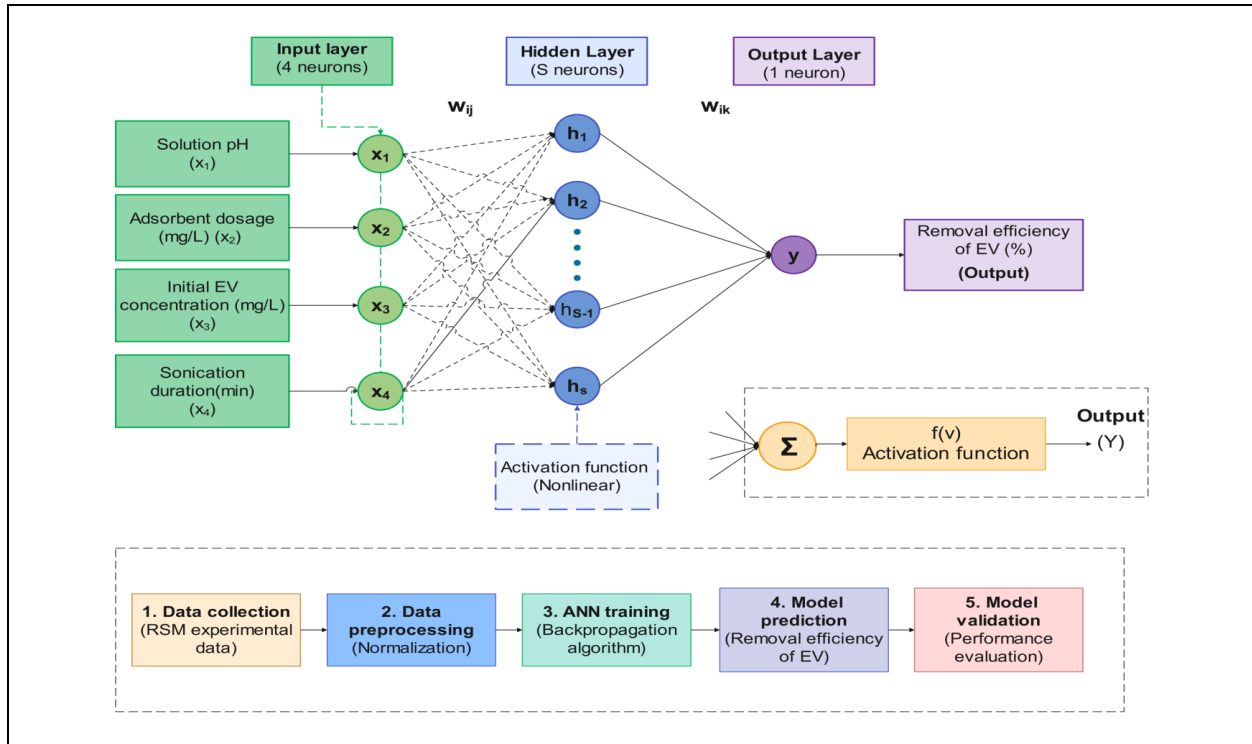


**Fig. 2: Architecture of the BP-ANN model used for prediction of ethyl violet removal efficiency**

Out of the 30 experimental datasets produced using RSM, 24 samples were employed for training, while the remaining 6 datasets were allocated for testing and validating network performance. Before model creation, all output and input variables were normalized to a range of 0.1–0.9 to ensure numerical stability and enhance the convergence behavior of the neural network. Subsequent to the training phase, the predictive efficacy of the BP-ANN model was evaluated utilizing standard statistical metrics. The model's accuracy was assessed by computing mean squared error (MSE), and concordance among predicted and experimental results was measured by the coefficient of determination. The equations for calculating MSE and  $R^2$  are presented in the following expressions.

$$y = 2 \times \left( \frac{x - x_{\min}}{x_{\max} - x_{\min}} \right) - 1 \quad \dots (3)$$

$$MSE = \frac{1}{N} \sum_{i=1}^N (|y_{pred,i} - y_{exp,i}|)^2 \quad \dots (4)$$

$$R^2 = 1 - \frac{\sum_{i=1}^N (y_{pred,i} - y_{exp,i})}{\sum_{i=1}^N (y_{pred,i} - y_m)} \quad \dots (5)$$

In the normalization process,  $x$  signifies an individual input parameter chosen from the dataset, whereas  $y$  denotes the corresponding scaled value acquired post-normalization. The phrases  $x_{\max}$  and  $x_{\min}$  indicate the upper and lower bounds of the corresponding input variable

In model evaluation,  $y_{pred,i}$  denotes the output predicted by the ANN model for the  $i^{\text{th}}$  observation, while  $y_{exp,i}$  refers to the experimentally measured value. The parameter  $N$  signifies the total count of data samples included in the analysis, while  $\bar{y}$  specifies the mean of the experimentally observed values.

## 2.7 Optimization Using ANN-GA

Genetic Algorithm optimization was implemented in MATLAB using a population size of 100, a crossover probability of 0.8, a mutation probability of 0.01, and a maximum of 200 generations. The trained ANN model served as the fitness function to identify the optimum operating conditions for maximum ethyl violet removal efficiency. An appropriate set of operational circumstances was determined to assess the dependability and prediction efficacy of the proposed models. Validation studies were conducted under optimum conditions to verify the accuracy of the ANN–GA-based predictions for ethyl violet (EV) elimination utilizing Cu-doped ZnO/rGO nanocomposites. The genetic algorithm (GA), a stochastic optimization method based on population dynamics and inspired by evolutionary concepts, was utilized to identify the global optimum. The process commences with the creation of an initial population of candidate solutions, which were progressively enhanced by evolutionary mechanisms including selection, crossover, and mutation. The algorithm systematically investigates the search space across successive generations, converging on the ideal

combination of process variables to maximize EV removal efficiency.

## 2.8 Random Forest

The Random Forest model was developed using 500 decision trees with bootstrap aggregation. The number of predictor variables considered at each split was optimized through cross-validation. Model performance was assessed using  $R^2$ , RMSE, and MAE values obtained from the testing dataset. Random forest were ensemble ML technique generates set of decision trees and adds their outputs to enhance forecast accuracy. It combines classification and regression tree techniques using a bootstrap aggregating (bagging) approach. Within this architecture, each decision tree is constructed independently utilizing randomly chosen sections of the training data, yielding varied models that jointly improve robustness and accuracy. A decision tree illustrates a hierarchical framework where the dataset is recursively partitioned into smaller subsets according to feature-based splitting criteria. This method, referred to as recursive partitioning, allocates input variables to internal nodes, whereas the terminal nodes (leaves) yield the ultimate prediction results. Each division is ascertained by assessing the most effective characteristic and threshold that most effectively segregates the data. The efficacy of Random Forest (RF) stems from two principal mechanisms: (i) random feature selection, which diminishes correlation among individual trees and enhances generalization ability, and (ii) bootstrap sampling, wherein multiple sub-datasets are derived from the original data to train each tree, thus mitigating overfitting and ensuring consistent model performance.

## 3. RESULTS AND DISCUSSION

### 3.1 Surface Analysis of ZnO–Cu Nanoparticles and Cu-ZnO/rGO Composites

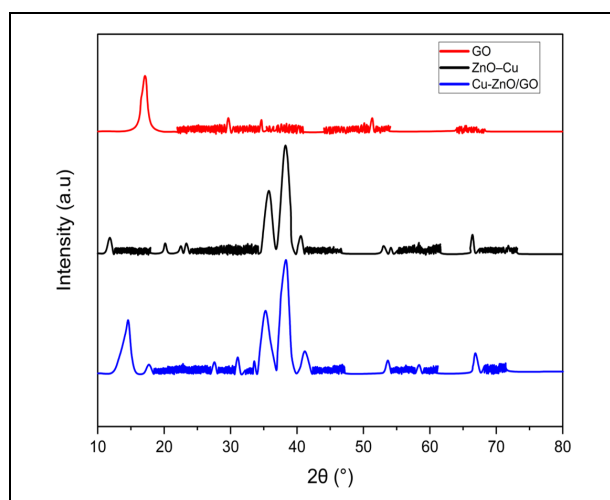


**Fig. 3: XRD patterns of rGO, ZnO–Cu nanoparticles, and Cu-doped ZnO/rGO nanocomposite**

The X-ray diffraction patterns of ZnO–Cu and Cu-doped ZnO/rGO are depicted in Fig. 3.

The X-ray diffraction pattern of graphene precursor had a prominent reflection at around  $2\theta = 11.5^\circ$ , commonly linked to its ordered structural configuration. Nonetheless, this distinctive peak was absent in the diffraction pattern of Cu-doped ZnO/rGO, indicating substantial structural alteration of the graphene framework during the synthesis process. The diffraction peaks observed in the ZnO-containing samples were compared with the standard JCPDS card data for hexagonal wurtzite ZnO. The characteristic reflections corresponding to the (100), (002), (101), (102), (110), (103), and (112) crystallographic planes were expected according to JCPDS Card No. 36-1451. However, these peaks were either significantly broadened or absent in the Cu-doped ZnO/rGO nanocomposite. This behavior can be attributed to the extremely small crystallite size, low crystallinity, and high dispersion of ZnO nanoparticles on the rGO surface. Furthermore, the incorporation of Cu species and strong interfacial interactions with the graphene matrix may suppress crystal growth and reduce diffraction intensity. Similar observations have been reported for highly dispersed metal oxide–graphene nanocomposites, where the active phases remain poorly crystalline or partially amorphous while still exhibiting excellent surface activity and adsorption performance (Alam *et al.* 2020). Furthermore, in both ZnO–Cu and Cu-doped ZnO/rGO systems, the absence of distinct diffraction peaks corresponding to ZnO and Cu phases indicates that these phases were not clearly detectable under the present XRD conditions. Based solely on XRD analysis, definitive conclusions regarding the crystallinity or dispersion state of these phases cannot be established. Therefore, the interpretation was limited to the observed diffraction behavior and supported by complementary SEM, EDS, Raman, and XPS analyses.

The surface properties of ZnO–Cu nanoparticles and Cu-doped ZnO/rGO were evaluated via SEM, as shown in Figure 4(a–d). The micrograph associated with Figure 4(a) demonstrates that the ZnO–Cu particles generally possess a spherical morphology and are uniformly dispersed across the supporting surface. In contrast, the Cu-doped ZnO/rGO nanocomposite (Figure 4c) exhibits a comparatively finer and more uniform particle distribution, signifying enhanced integration within the graphene matrix. The mean particle size of the Cu-doped ZnO/rGO nanocomposite was around 78.9 nm, while the ZnO–Cu nanoparticles displayed a greater average size of about 125.6 nm, thereby validating the size reduction attained by integration into the rGO matrix. Particle size analysis was performed using ImageJ software by measuring randomly selected nanoparticles from multiple SEM micrographs acquired at different locations of the sample. The average particle size was estimated from representative SEM micrographs using image-based measurements. The particle size

distribution was determined from the measured particle diameters, and the average particle size was reported as the arithmetic mean value. The obtained size reduction in the Cu-doped ZnO/rGO nanocomposite indicates that the

rGO matrix effectively restricted nanoparticle agglomeration and promoted more uniform particle dispersion.

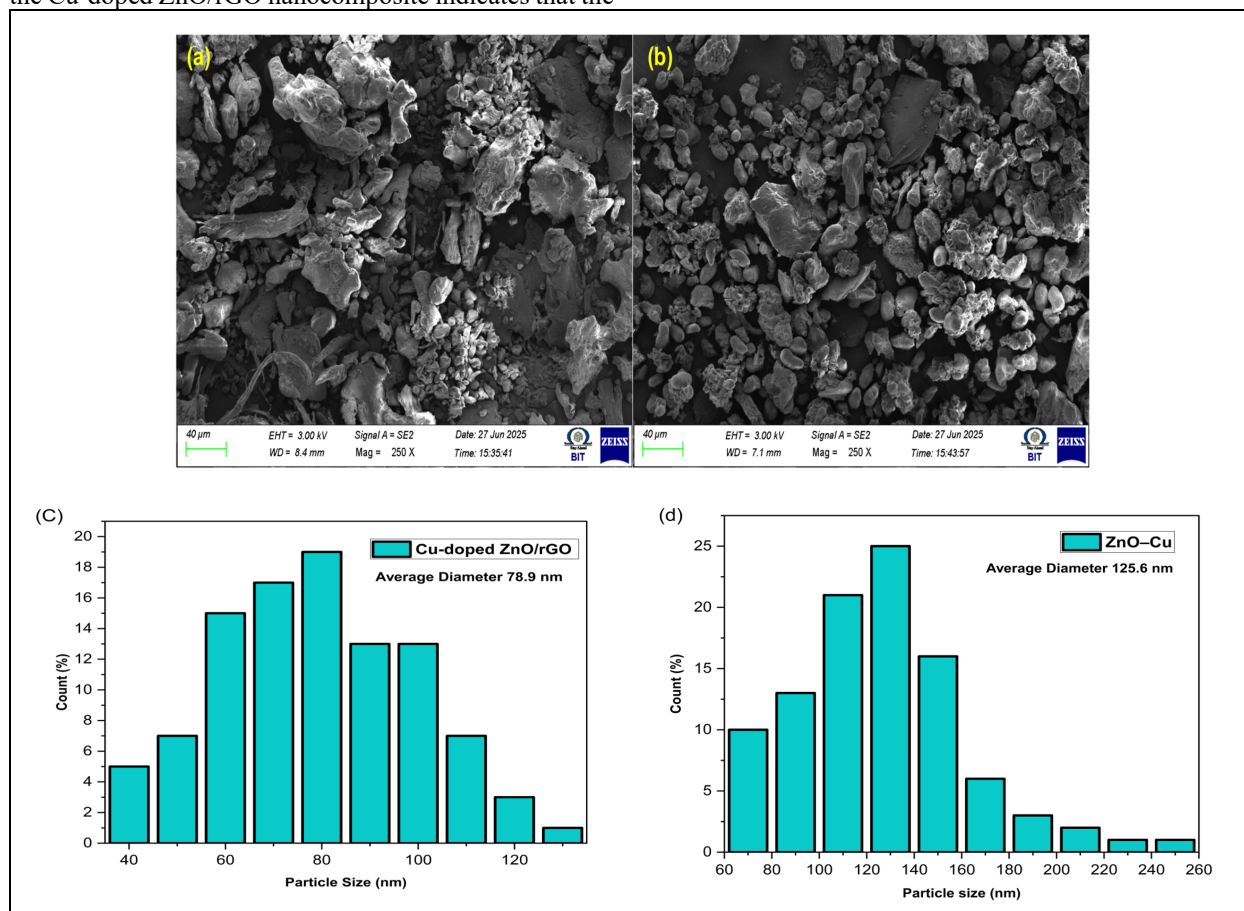


**Fig. 4: SEM micrographs of (a,b) ZnO–Cu nanoparticles and (c,d) Cu-doped ZnO/rGO nanocomposite**

An EDS analysis validated the composition of ZnO–Cu and Cu-doped ZnO/rGO, as shown in Figure 5.

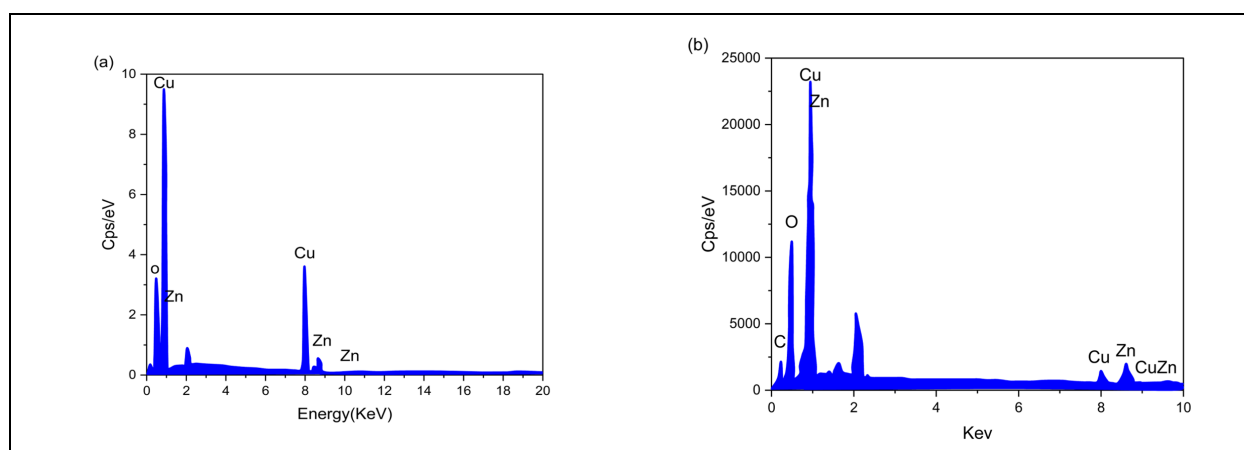


**Fig. 5: EDS spectra of (a) ZnO–Cu nanoparticles and (b) Cu-doped ZnO/rGO nanocomposite**

Elemental composition of materials was evaluated by energy-dispersive X-ray spectroscopy. The ZnO–Cu sample exhibited elemental weight percentages

of C, O, Cu, and Zn at approximately 6.5, 16.8, 63.4, and 13.3 wt%, respectively. The Cu-doped ZnO/rGO nanocomposite exhibited elemental compositions of 15.8

wt% C, 10.6 wt% O, 2.4 wt% Cu, and 71.2 wt% Zn, signifying the inclusion of graphene and enhanced carbon-related contributions. It is essential to recognize that EDS offers localized qualitative and semi-quantitative data, as the examination is conducted over a restricted surface area rather than the full specimen. The experimentally determined Cu-to-ZnO ratio (~1:50) at the Cu-doped ZnO/rGO nanocomposite is markedly inferior to the anticipated theoretical ratio. This divergence is due to the uneven spatial distribution of Cu species and the propensity of ZnO nanoparticles to cluster at the nanoscale on the rGO support, resulting in localized compositional changes.

Fig. 6 shows Raman spectra of the rGO matrix and Cu- ZnO/rGO nanocomposite. Two distinct bands are noted at roughly  $1570\text{ cm}^{-1}$  and  $1315\text{ cm}^{-1}$ , representing the G-band and D-band. The D-band correlates with structural disorder and defect sites, whereas G-band signifies in-plane vibrational modes of  $\text{sp}^2$ -bonded carbon species.

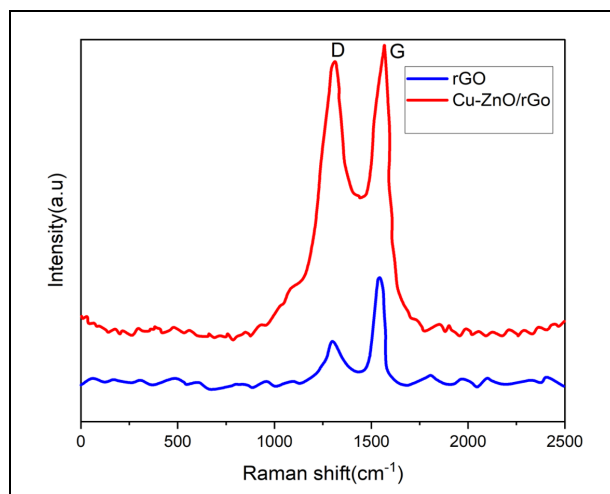


**Fig. 6: Raman spectra of rGO and Cu-doped ZnO/rGO nanocomposite**

The Raman D-band is typically linked to defect sites and structural flaws in carbon-based materials, while G-band at in-plane vibrational modes of  $\text{sp}^2$ -hybridized carbon atoms, corresponding to double degenerate phonon mode at the center of the Brillouin zone. The intensity ratio for Cu-doped ZnO/rGO was 1.5, above the value recorded for the rGO sample (1.2). The rise in the ID/IG ratio shows a heightened degree of structural disorder and a decrease in the dimensions of organized  $\text{sp}^2$  carbon domains, possibly introduced during synthesis or modification. Surface chemical states and elemental composition of ZnO–Cu and Cu-doped ZnO/rGO nanocomposites were analyzed by X-ray photoelectron spectroscopy (XPS). Figure 7 shows high-resolution spectra for core levels, offering extensive insights into the bonding environment and oxidation states of constituent elements.

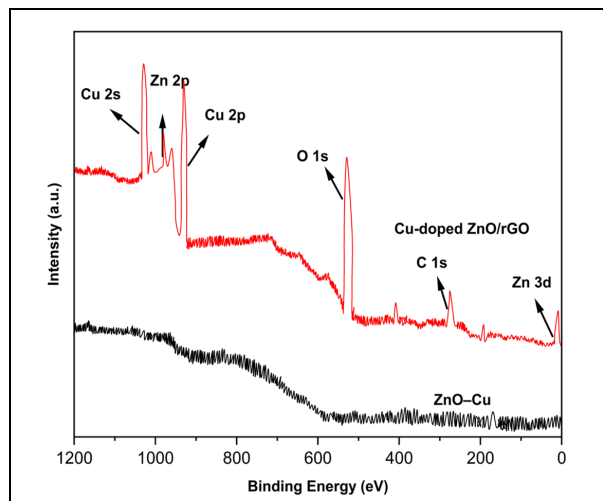


**Fig. 7: XPS spectra of Cu-doped ZnO/rGO and ZnO–Cu nanocomposites**

The XPS survey spectrum revealed the presence of C, O, Cu, and Zn elements in the Cu-doped ZnO/rGO nanocomposite. The characteristic peaks observed at approximately 284.6 eV, 530.2 eV, 933.4–953.5 eV, and 1021.8–1044.9 eV were assigned to C 1s, O 1s, Cu 2p, and Zn 2p core levels, respectively. The Cu-to-Zn atomic ratio derived from XPS examination was roughly 1:2.6, which is less than the anticipated theoretical ratio. This mismatch is due to the surface-sensitive characteristics of XPS, which examines only a limited depth (often within a few nanometers). Consequently, a substantial portion of ZnO and Cu species embedded within the mesoporous rGO matrix may remain undetected, with just the elements on the outer surface contributing to the measured signal.

Figure 8(a) presents the high-resolution Zn 2p spectrum of the Cu-doped ZnO/rGO nanocomposite. The characteristic peaks observed at binding energies of approximately 1021.8 eV and 1044.9 eV correspond to Zn  $2\text{p}_{3/2}$  and Zn  $2\text{p}_{1/2}$ , respectively, confirming the presence of  $\text{Zn}^{2+}$  species within the composite structure. Figure 8(d) shows the high-resolution Cu 2p spectrum, where the peaks located at approximately 933.4 eV and 953.5 eV are assigned to Cu  $2\text{p}_{3/2}$  and Cu  $2\text{p}_{1/2}$ , respectively, indicating the presence of oxidized copper species. The O 1s peak observed at approximately 530.2 eV in the survey spectrum is attributed to lattice oxygen associated with the metal oxide framework. These results confirm the successful incorporation of Zn and Cu species into the rGO-supported composite. The Cu 2p spectrum exhibited two characteristic peaks at app

Approximately 933.4 eV and 953.5 eV, corresponding to Cu  $2\text{p}_{3/2}$  and Cu  $2\text{p}_{1/2}$ , respectively. The O 1s peak observed at approximately 530.2 eV is associated with lattice oxygen species in the metal oxide structure. The lack of supplementary peaks indicative of metallic phases implies that both Zn and Cu species are

effectively integrated into the oxide matrix. The XPS outcomes validate effective synthesis of a Cu-doped ZnO/rGO nanocomposite, exhibiting stable oxidation states of constituent elements, with no indication of

extraneous phases or core-shell structures. Figures 8c and 8d illustrate the Cu<sub>2p</sub> peak of ZnO–Cu and the Cu-doped ZnO/rGO.

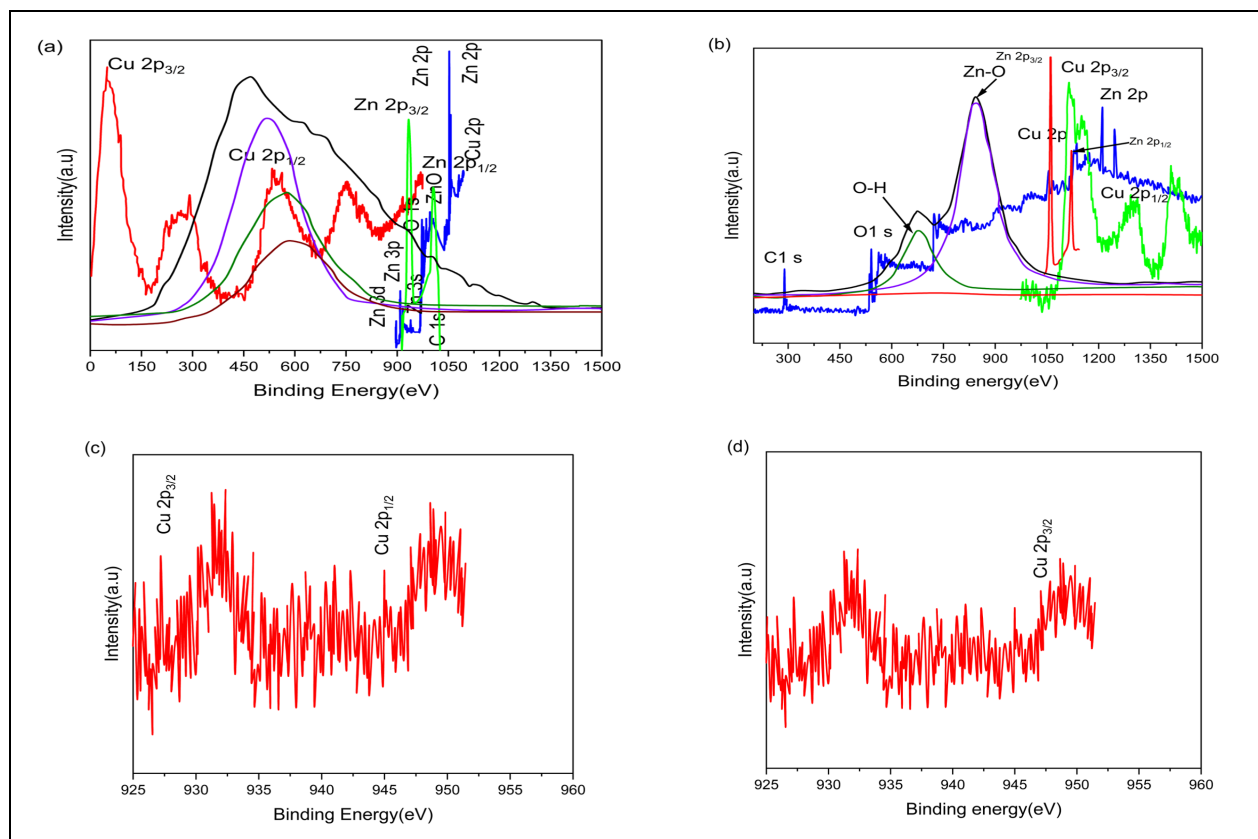


**Fig. 8.** XPS analyses of (a) Zn<sub>2p</sub> XPS spectra of ZnO–Cu nanoparticles, (b) Zn<sub>2p</sub> XPS spectra of Cu–ZnO/rGO composite, (c) Cu<sub>2p</sub> XPS spectra of ZnO–Cu nanoparticles and (d) Cu<sub>2p</sub> XPS spectra of Cu–ZnO/rGO composite

Fig. 9 illustrates the adsorption–desorption of ZnO–Cu and Cu–ZnO/rGO nanocomposites.

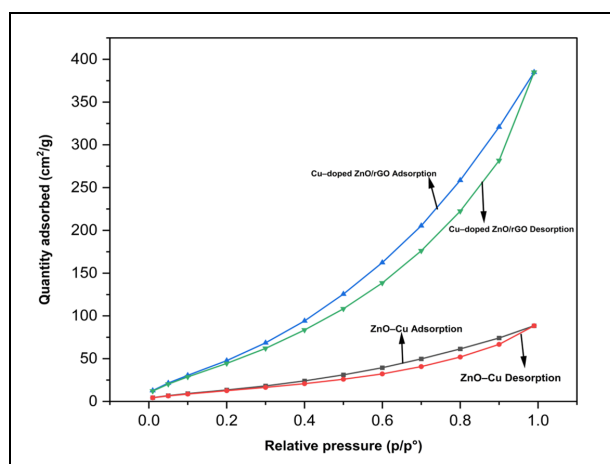


**Fig. 9:** Nitrogen isotherms of ZnO–Cu and Cu–ZnO/rGO.

The textural characteristics of the produced materials were assessed by nitrogen adsorption–desorption analysis. The Brunauer–Emmett–Teller

surface area of the ZnO–Cu sample was measured at 22.5 m<sup>2</sup>/g, while the Cu-doped ZnO/rGO nanocomposite has a greater surface area of 115.8 m<sup>2</sup>/g. This improvement is due to the mesoporous graphene framework, which offers a greater quantity of accessible active sites for adsorption. Fig. 10 depicts size distribution patterns of both ZnO–Cu and Cu–ZnO/rGO. The findings reveal a very uniform pore structure, with predominant pore sizes of approximately 29.6 nm for ZnO–Cu and 32.4 nm for Cu-doped ZnO/rGO, thereby affirming the establishment of a mesoporous architecture in the composite material.

The nitrogen adsorption–desorption profile of the Cu-doped ZnO/rGO nanocomposite displays a Type IV isotherm with an H<sub>3</sub> hysteresis loop, indicative of mesoporous materials with pore diameters generally between 2 and 50 nm. The Type IV isotherm accompanied by an H<sub>3</sub> hysteresis loop confirms the mesoporous nature of the Cu-doped ZnO/rGO nanocomposite and suggests the presence of slit-shaped pores generated by the aggregation of graphene sheets. The average pore diameter of 32.4 nm falls within the mesoporous range (2–50 nm), facilitating efficient

diffusion of ethyl violet molecules into the adsorbent framework. The enhanced Brunauer–Emmett–Teller surface area of  $115.8 \text{ m}^2 \text{ g}^{-1}$  compared to  $22.5 \text{ m}^2 \text{ g}^{-1}$  for ZnO–Cu indicates that incorporation of rGO significantly improves the accessibility of adsorption sites. These textural characteristics are comparable to those reported for graphene-supported metal oxide adsorbents used in dye removal applications, where high surface area and mesoporous structures are recognized as key factors contributing to enhanced adsorption performance (Hussein *et al.* 2025a). This action signifies the existence of slit-like pores and a cohesive porous network within the graphene-supported framework. The elevated specific surface area of the nanocomposite increases the accessibility of active adsorption sites, hence enhancing interaction between the adsorbent and ethyl violet (EV) molecules. The mesoporous design substantially enhances the effectiveness of dye removal from aqueous solutions.

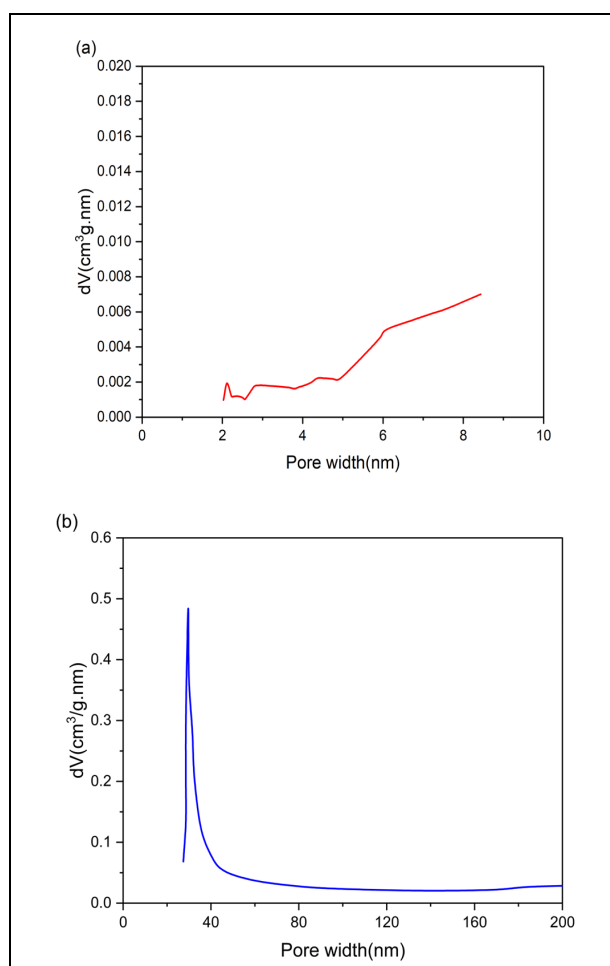


**Fig. 10: Pore size distribution of (a) ZnO/Cu and (b) Cu-ZnO/rGO**

Figure 11(a) presents the magnetization behavior of the Cu-doped ZnO/rGO nanocomposite under an applied magnetic field. The magnetization increases progressively with increasing field strength and

approaches a saturation tendency at higher magnetic fields, indicating the presence of magnetic interactions within the composite system. The observed magnetic response is attributed to defect-induced magnetism, oxygen vacancies, and the incorporation of Cu ions into the ZnO lattice, which can introduce localized magnetic moments. Following the adsorption process, the Cu-doped ZnO/rGO nanocomposite was recovered from the solution by conventional separation methods prior to further analysis. Furthermore, the interaction between Cu-doped ZnO nanoparticles and the rGO framework contributes to the overall magnetic behavior through charge transfer and interfacial effects. The low hysteresis characteristics suggest a magnetically responsive material with minimal remanence and coercivity, which is advantageous for potential recovery and reuse of the adsorbent after the adsorption process. Structural characteristics of the Cu-doped ZnO/rGO nanocomposites were analyzed by small-angle X-ray diffraction (SAXRD), as illustrated in Figure 11(b). The low-angle diffraction peak observed at  $2\theta = 0.83^\circ$  confirms the presence of an ordered mesostructured framework within the Cu-doped ZnO/rGO nanocomposite. According to Bragg's law ( $n\lambda = 2d \sin\theta$ ), the corresponding interplanar spacing ( $d$ -spacing) was calculated to be approximately 10.6 nm, indicating a well-developed porous structure with long-range ordering. Such ordered mesostructural characteristics facilitate efficient diffusion of dye molecules and improve accessibility to active adsorption sites. The SAXRD results are consistent with the BET analysis, which revealed a mesoporous architecture and enhanced surface area, further supporting the suitability of the Cu-doped ZnO/rGO nanocomposite for adsorption applications.

The experiment examined four principal operational variables: feed concentration (200–500 mg/L), solution pH (2–6), ultrasonic treatment duration (5–17 min), and nanocomposite loading (8–24 mg). The dye removal percentage, serving as the performance indicator, ranged from 72.4% to 93.3% across the studies conducted. A total of 30 experimental runs were prepared and conducted utilizing a Central Composite Design (CCD) methodology to evaluate the impacts of the chosen parameters:  $X_1$  (concentration),  $X_2$  (pH),  $X_3$  (ultrasonication duration), and  $X_4$  (adsorbent dosage). The experimental observations were analyzed using a quadratic response surface model to elucidate the relationship among the input elements and the response output. A strong alignment between the anticipated outcomes from the model and the actual experimental values validates the dependability and robustness of the created regression model. Furthermore, the collective interactions and individual effects of each variable on dye removal efficiency were accurately encapsulated and depicted by the established second-order polynomial equation.

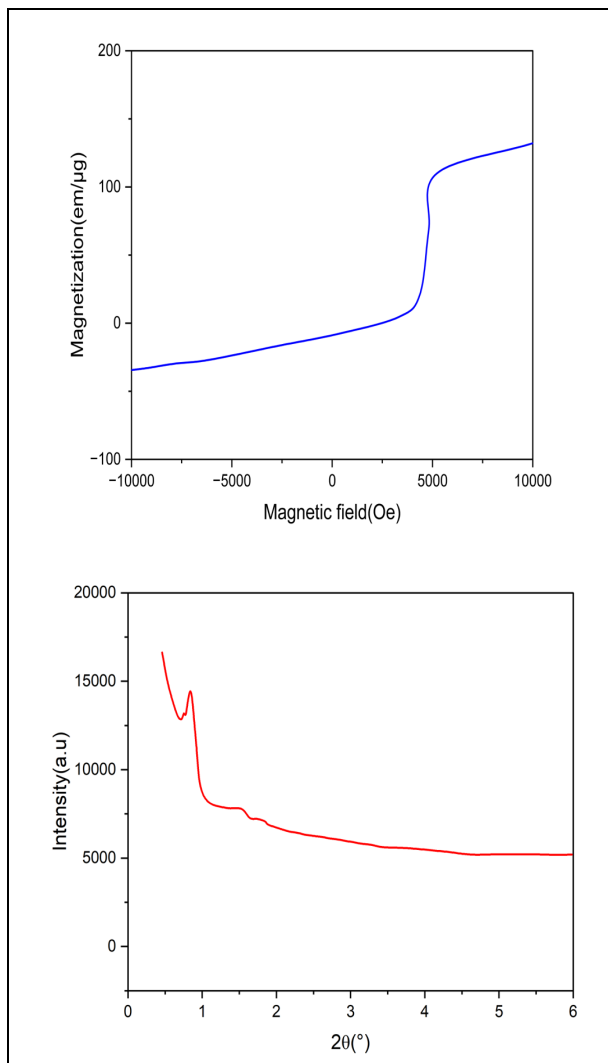


**Fig. 11: Magnetization and SAXRD patterns of Cu-ZnO/rGO**

### 3.2 Central Composite Design (CCD)

$$Y = \beta_0 + \beta_1 X_1 + \beta_2 X_2 + \beta_3 X_3 + \beta_4 X_4 + \beta_{12} X_1 X_2 + \beta_{13} X_1 X_3 + \beta_{14} X_1 X_4 + \beta_{23} X_2 X_3 + \beta_{24} X_2 X_4 + \beta_{34} X_3 X_4 + \beta_{11} X_1^2 + \beta_{22} X_2^2 + \beta_{33} X_3^2 + \beta_{44} X_4^2$$

where  $Y$  represents the predicted dye removal efficiency (%),  $X_1, X_2, X_3$ , and  $X_4$  denote feed concentration, solution pH, ultrasonication time, and

adsorbent dosage, respectively, while  $\beta_0, \beta_i, \beta_{ii}$ , and  $\beta_{ij}$  represent the intercept, linear, quadratic, and interaction coefficients.

The close agreement between experimental and predicted values confirms the adequacy of the developed quadratic model. Model reliability was further evaluated through ANOVA and validation statistics. The sufficiency and statistical validity of the constructed quadratic model were assessed by analysis of variance (ANOVA), with findings displayed in Table 3. The model demonstrated a highly significant F-value of 82.44 with a p-value  $< 0.0001$ , affirming the statistical robustness of the regression model in accurately depicting the removal process. The importance of individual model terms was evaluated by the p-value criterion ( $p < 0.05$ ). Among the linear parameters, initial concentration (A), sonication time (C), and dosage (D) significantly influenced removal efficiency, whereas pH (B) exhibited a minor effect within the examined range. Concerning interaction terms, all were statistically insignificant ( $p > 0.05$ ), signifying that the combined impacts of process factors do not substantially influence the response. Conversely, all quadratic terms had substantial statistical significance ( $p < 0.05$ ), underscoring the nonlinear characteristics of the process and the significance of curvature effects within the system. The lack-of-fit test produced an F-value of 1.70 and a p-value of 0.321, suggesting that lack of fit is not statistically significant compared to pure error. This verifies that the produced model accurately aligns with experimental data and may be dependably utilized for predictions within the examined parameter range. The ANOVA findings show that the suggested quadratic regression model was significant, well-fitted, and appropriate for forecasting removal efficiency under different operational situations. Several studies reported that, machine learning models (SVR, ANN, RF) accurately predicted performance, with SVR achieving the highest accuracy ( $R^2 = 0.9854$ ), while ANOVA confirmed Zn loading, catalyst dosage, and reaction time as key influencing factors (Yoney and Aras, 2025).

Fig. 12 illustrates the correlation between observed and model-predicted removal efficiencies of Cu-doped ZnO/rGO nanocomposites. The data points are well matched along a linear trend line, indicating robust concordance and great consistency between the experimental results and anticipated values.

**Table 2. CCD experimental matrix showing actual and predicted ethyl violet removal efficiencies**

| Run No. | Initial Concentration (mg L <sup>-1</sup> ) | Initial pH | Sonication Time (min) | Adsorbent Dosage (mg) | Removal Efficiency (%) | Prediction Efficiency (%) |
|---------|---------------------------------------------|------------|-----------------------|-----------------------|------------------------|---------------------------|
| 1       | 200                                         | 2          | 5                     | 8                     | 75.6                   | 75                        |
| 2       | 350                                         | 4          | 11                    | 16                    | 92.1                   | 92                        |
| 3       | 500                                         | 6          | 5                     | 24                    | 74                     | 73                        |
| 4       | 350                                         | 4          | 11                    | 16                    | 93.3                   | 92                        |
| 5       | 500                                         | 6          | 5                     | 8                     | 72.4                   | 72                        |
| 6       | 200                                         | 6          | 5                     | 8                     | 74.8                   | 75                        |
| 7       | 200                                         | 6          | 17                    | 8                     | 77.2                   | 76                        |
| 8       | 350                                         | 4          | 11                    | 16                    | 91.2                   | 92                        |
| 9       | 500                                         | 6          | 17                    | 8                     | 75.6                   | 75                        |
| 10      | 200                                         | 6          | 5                     | 24                    | 76                     | 76                        |
| 11      | 500                                         | 2          | 17                    | 24                    | 76.8                   | 77                        |
| 12      | 200                                         | 2          | 17                    | 8                     | 78.4                   | 78                        |
| 13      | 200                                         | 2          | 5                     | 24                    | 76.8                   | 76                        |
| 14      | 500                                         | 6          | 17                    | 24                    | 77.2                   | 77                        |
| 15      | 500                                         | 2          | 5                     | 24                    | 75.2                   | 75                        |
| 16      | 500                                         | 2          | 17                    | 8                     | 77.6                   | 77                        |
| 17      | 200                                         | 2          | 17                    | 24                    | 80                     | 79                        |
| 18      | 500                                         | 2          | 5                     | 8                     | 73.6                   | 73                        |
| 19      | 350                                         | 4          | 11                    | 16                    | 92.6                   | 92                        |
| 20      | 200                                         | 6          | 17                    | 24                    | 79.6                   | 80                        |
| 21      | 350                                         | 4          | 11                    | 8                     | 88.8                   | 89                        |
| 22      | 200                                         | 4          | 11                    | 16                    | 84.4                   | 84                        |
| 23      | 500                                         | 4          | 11                    | 16                    | 84.4                   | 83                        |
| 24      | 350                                         | 4          | 11                    | 16                    | 91.8                   | 92                        |
| 25      | 350                                         | 4          | 5                     | 16                    | 88.2                   | 87                        |
| 26      | 350                                         | 4          | 11                    | 24                    | 89.6                   | 90                        |
| 27      | 350                                         | 6          | 11                    | 16                    | 84.8                   | 85                        |
| 28      | 350                                         | 4          | 11                    | 16                    | 93                     | 92                        |
| 29      | 350                                         | 2          | 11                    | 16                    | 84.8                   | 85                        |
| 30      | 350                                         | 4          | 17                    | 16                    | 88.2                   | 88                        |

**Table 3. ANOVA outcomes for quadratic response surface model**

| Source                   | Sum of Squares | df | Mean Square | F Value | p-Value | Remark          |
|--------------------------|----------------|----|-------------|---------|---------|-----------------|
| Model                    | 1418.59        | 15 | 94.57       | 82.44   | <0.0001 | Significant     |
| A(Initial concentration) | 168.06         | 1  | 168.06      | 12.40   | 0.003   |                 |
| B (pH)                   | 2.88           | 1  | 2.88        | 2.51    | 0.135   |                 |
| C(Sonication time)       | 32.00          | 1  | 32.00       | 27.89   | <0.0001 |                 |
| D (Dosage)               | 6.97           | 1  | 6.97        | 6.07    | 0.027   |                 |
| AB                       | 0.04           | 1  | 0.04        | 0.03    | 0.855   |                 |
| AC                       | 0.00           | 1  | 0.00        | 0.00    | 1.000   |                 |
| AD                       | 0.36           | 1  | 0.36        | 0.31    | 0.584   |                 |
| BC                       | 0.04           | 1  | 0.04        | 0.03    | 0.855   |                 |
| BD                       | 0.64           | 1  | 0.64        | 0.56    | 0.467   |                 |
| CD                       | 0.04           | 1  | 0.04        | 0.03    | 0.855   |                 |
| A <sup>2</sup>           | 700.83         | 1  | 700.83      | 87.91   | <0.0001 |                 |
| B <sup>2</sup>           | 172.42         | 1  | 172.42      | 77.11   | <0.0001 |                 |
| C <sup>2</sup>           | 23.14          | 1  | 23.14       | 13.86   | 0.002   |                 |
| D <sup>2</sup>           | 5.73           | 1  | 5.73        | 5.00    | 0.042   |                 |
| Residual                 | 16.06          | 14 | 1.147       |         |         |                 |
| Lack of Fit              | 13.00          | 10 | 1.30        | 1.70    | 0.321   | Not Significant |
| Pure Error               | 3.06           | 4  | 0.765       |         |         |                 |
| Total                    | 1434.65        | 29 |             |         |         |                 |

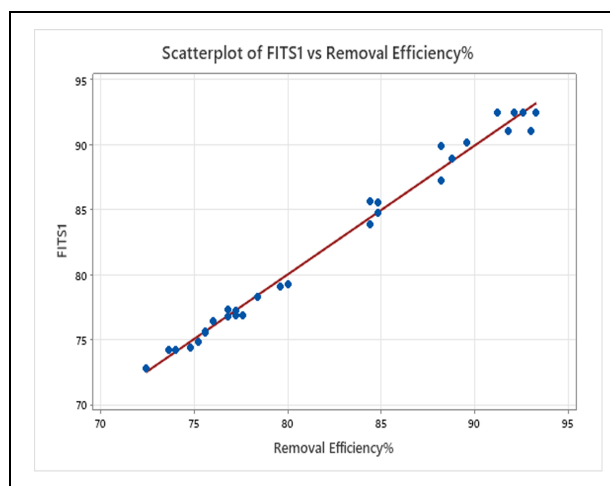
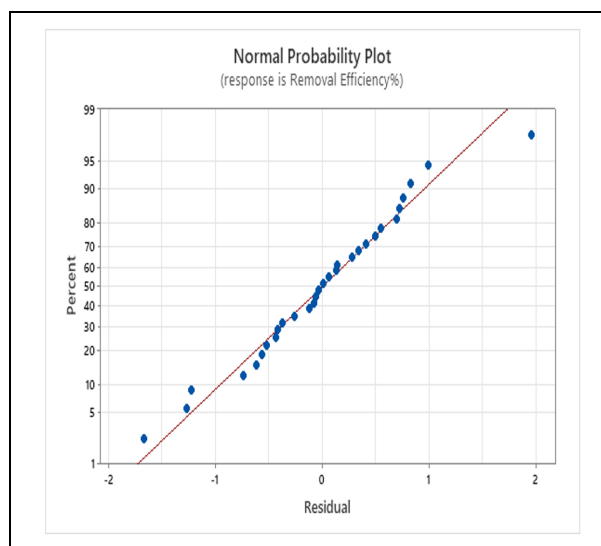
**Fig. 12: Comparison of predicted and experimental EV removal**

Fig. 13 illustrates the normal probability distribution of residuals for the Cu-doped ZnO/rGO system. The majority of data points align along a linear trajectory, validating the normal distribution of errors and suggesting that the RSM model yields dependable predictions.

**Fig. 13: Normal probability plot of residuals**

The addition of initial concentration and pH on removal efficiency of EV using Cu-doped ZnO/rGO nanocomposites was evaluated through a contour plot (Figure 14), while sonication time and dosage were maintained at constant levels.

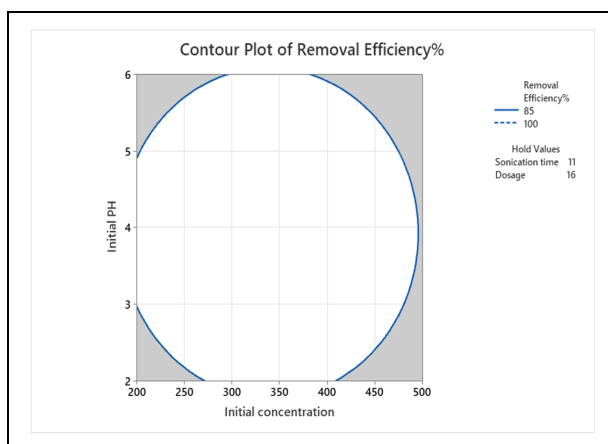
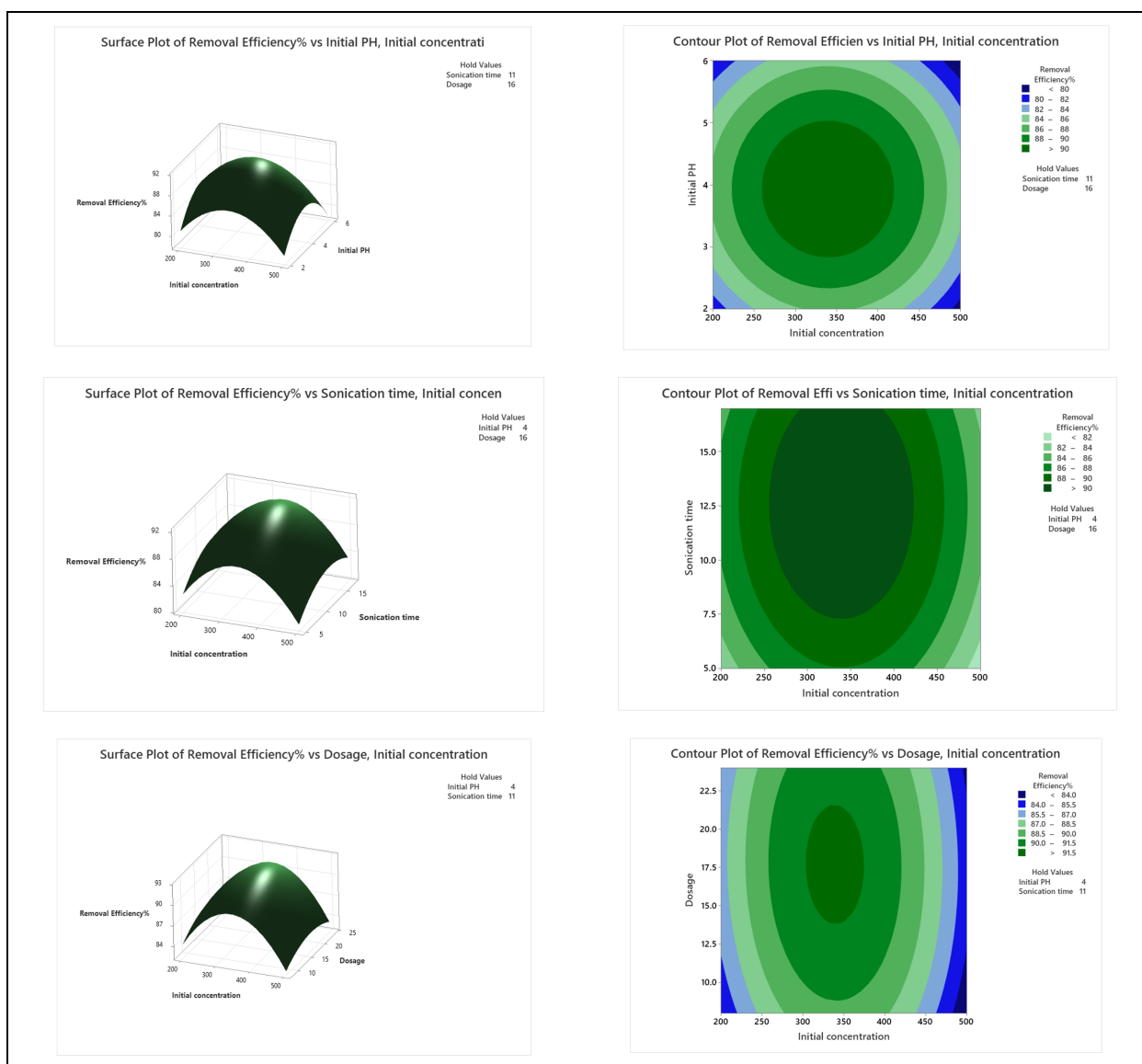


**Fig. 14: Contour plot of removal efficiency versus concentration and pH**

The results demonstrate that the removal of EVs utilizing Cu-doped ZnO/rGO nanocomposites is predominantly affected by starting concentration and adsorbent dosage, rather than by pH levels and sonication duration. The interaction of variables is depicted using three-dimensional contour and response surface plots. Figure 15(a) indicates that dye removal efficiency remained relatively stable within the investigated pH range (4–6). Although slightly higher removal efficiencies were observed at pH 4–6, ANOVA results confirmed that the effect of pH was statistically less significant than those of initial concentration, sonication time, and adsorbent dosage. Moreover, the efficacy of dye removal enhances with a raised dosage of adsorbent, whereas it diminishes with a rise in initial EV concentration (Figure 15(c)).



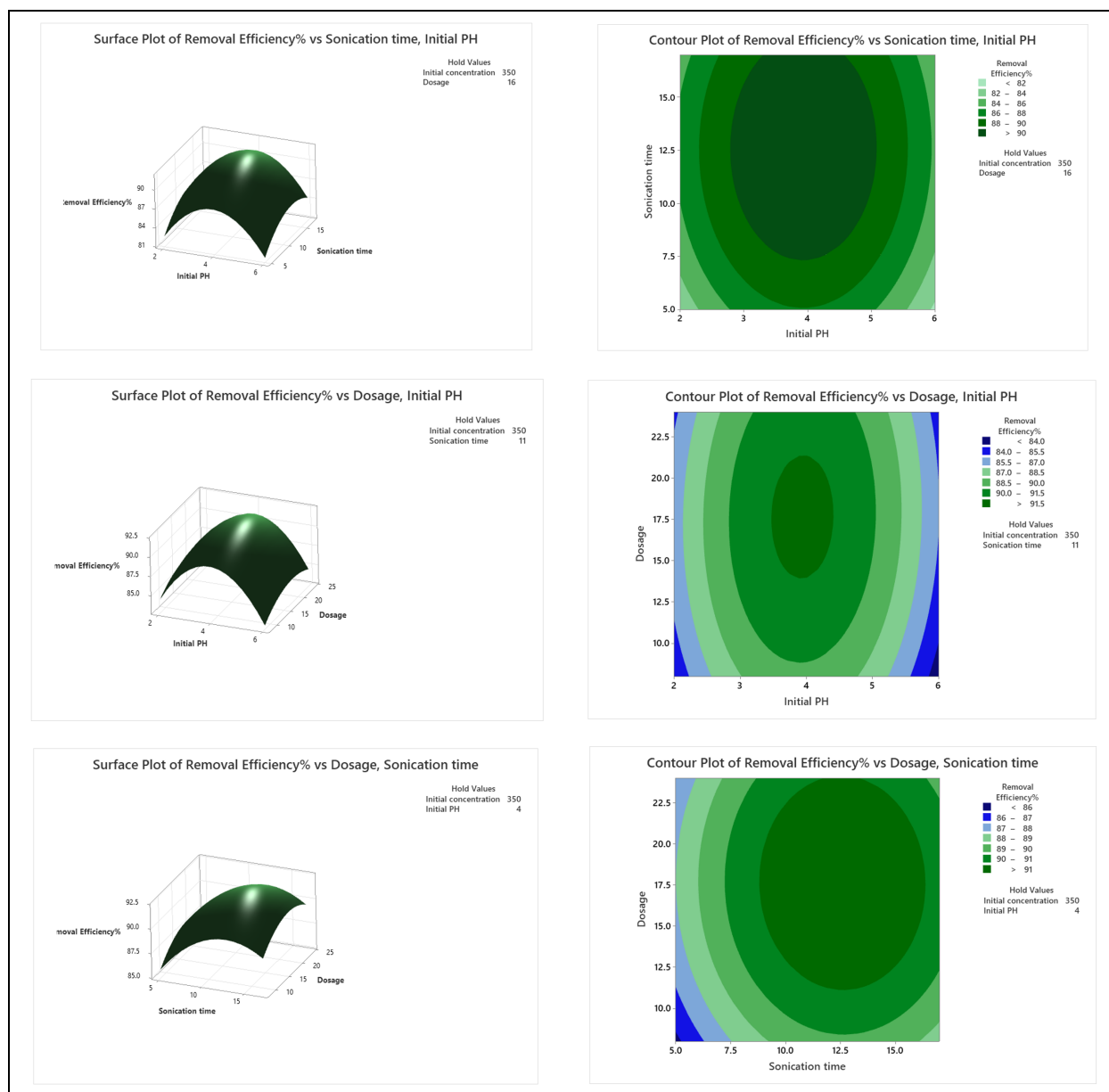


**Fig. 15: Response surface and contour plots showing variable interactions**

The response surface plots revealed that the interaction effects among the investigated variables were relatively weak, which is consistent with the ANOVA results showing that all interaction terms were statistically insignificant ( $p > 0.05$ ). Nevertheless, the contour and three-dimensional surface plots provided useful insights into the combined influence of process parameters. The removal efficiency increased with increasing adsorbent dosage and decreased with increasing initial dye concentration, whereas the effects of pH and sonication time were comparatively less pronounced within the studied range. The nearly elliptical contour patterns and absence of steep curvature further indicate limited interaction among the process variables, suggesting that the adsorption performance

was primarily governed by the individual effects of concentration and adsorbent dosage.

### 3.3 Back Propagation ANN

In ANN methodology, determining the optimal number of neurons at hidden layer is essential for ensuring model precision and preventing overfitting. The ideal architecture was determined by examining the fluctuation of mean squared error (MSE) in relation to the quantity of hidden neurons. Figure 16 demonstrates that the MSE initially declines, attains a minimum, and thereafter rises with the further incorporation of neurons. The minimum MSE of 0.0201 was achieved with 7 hidden neurons, signifying that this arrangement yields

the optimal predictive efficacy for the constructed ANN model.

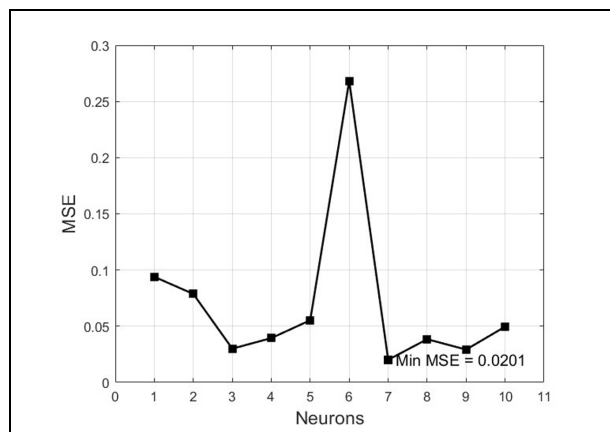


Fig. 16: MSE versus hidden neuron count relationship

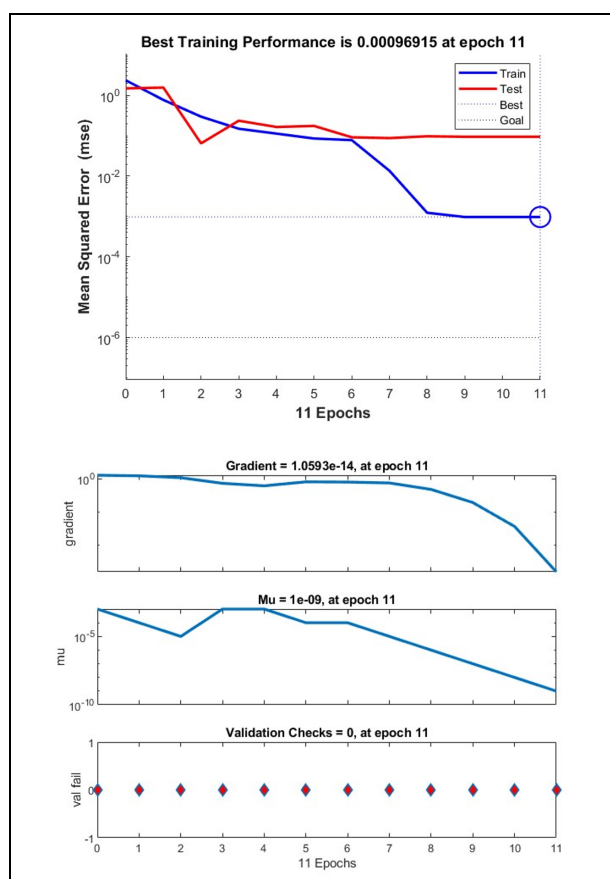


Fig. 17: BP-ANN model training performance evolution

Figures 17 and 18 depict the training behavior and convergence features of the BP-ANN model. The training procedure achieved its peak at epoch 11, with the optimal validation performance (MSE) of 0.00096915, signifying swift convergence and effective learning. At this juncture, the gradient value diminished to  $1.0593 \times 10^{-14}$ , indicating that the network attained a stable minimum with minimal error fluctuation. The validation

checks remained at zero during the training procedure, indicating no overfitting and confirming model generalization. The regression analysis produced a strong correlation coefficient ( $R = 0.99888$ ) between anticipated and experimental values, with data points closely matched along the optimal fit line. The conjunction of exceptionally low MSE and a correlation coefficient approaching unity substantiates the outstanding predictive capacity, precision, and dependability of the established BP-ANN model.

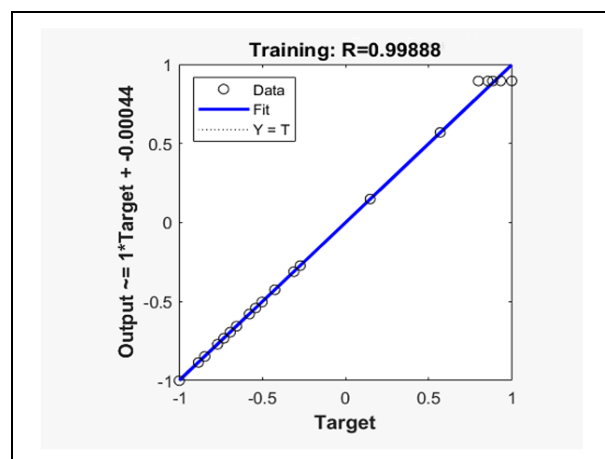


Fig. 18: BP-ANN predicted versus experimental EV removal

### 3.4. RSM and ANN-GA Optimization for Ethyl Violet Removal

The optimal circumstances for the four parameters were determined as follows: dose (GA 17.03 mg), sonication time (GA 9.82 min), initial pH (GA 4.91), and initial concentration (GA 348.92mg/L). The models created using ANN-GA and RSM were evaluated and validated against projected optimal circumstances (Table 4).

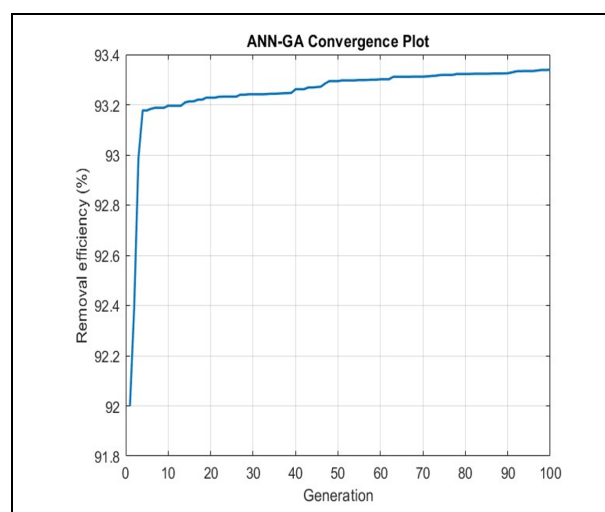


Fig 19: Genetic algorithm (GA) optimum value of ethyl violet removal efficiency

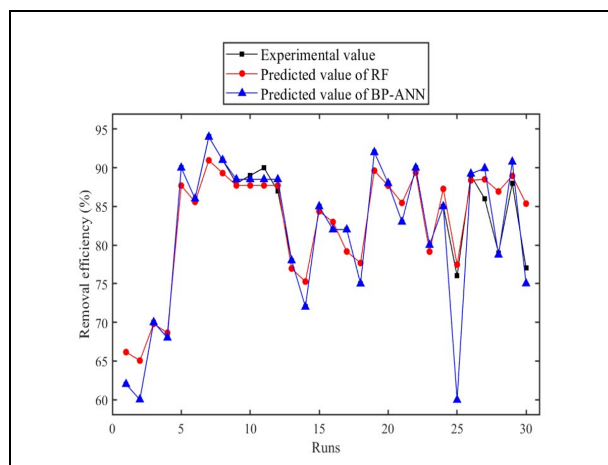
**Table 4. Comparison of predicted and validated results**

| Process Parameters                     | Optimization |        |
|----------------------------------------|--------------|--------|
|                                        | ANN-GA       | RSM    |
| Initial concentration (mg/L)           | 348.92       | 339.39 |
| Initial pH                             | 4.91         | 3.9    |
| Sonication time (min)                  | 9.82         | 12.63  |
| Dosage (mg)                            | 17.03        | 17.69  |
| Decolorization efficiency of model (%) | 93.33%       | 92.03% |
| Average values of absolute errors (%)  | 1.23%        | 0.267% |
| R <sup>2</sup>                         | 0.99888      | 0.9379 |
| MSE                                    | 0.00096915   |        |

The findings indicate that mean absolute errors for RSM and ANN-GA models were 1.23%, and 0.267%. In comparison to the RSM model, ANN models have a superior R<sup>2</sup> value. An ANN-GA model was deemed most effective for forecasting the elimination of Ethyl violet by Cu-doped ZnO/rGO. According to previous investigations, ZnO nanoparticle-catalyzed ozonation was optimized using CCD–RSM for lignin degradation, achieving ~99.99% removal under optimal conditions. The developed quadratic model showed strong statistical significance (R<sup>2</sup> = 0.9480), confirming the efficiency of ZnO-assisted advanced oxidation (Amnath and Aiyathiti, 2026).

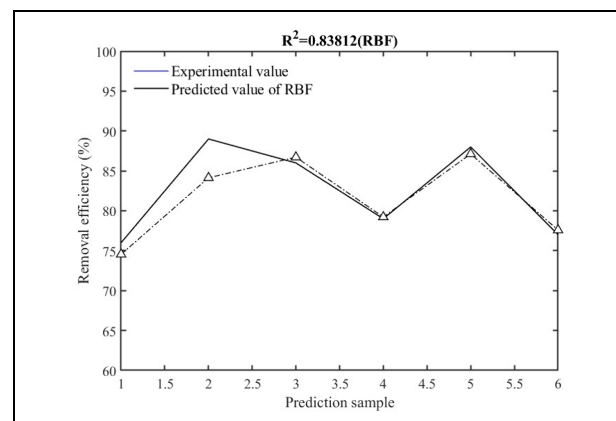
### 3.5. Comparative evaluation of RBF, RF, and BP-ANN techniques

In conjunction with RSM, 30 sets were forecasted by BP-ANN and RF (Fig. 20).

**Fig. 20: RF and BP-ANN prediction comparison**

The prediction efficacy of various ML models was assessed by contrasting their statistical accuracy

metrics. The mean absolute error (MAE) values indicated that the BP-ANN model had greater accuracy than other models, whereas comparatively larger deviations were noted for alternative methods such as RF. Figure 21 demonstrates that the RBF model yielded a moderate correlation coefficient (R<sup>2</sup> = 0.83812), signifying a satisfactory albeit imprecise alignment between anticipated and experimental results. Conversely, the BP-ANN model exhibited markedly superior prediction accuracy, with its regression coefficient nearing unity, thus affirming its robust generalization and learning proficiency. The graphical comparison indicates that the projected values derived from the RBF model align with the experimental trend, albeit with significant variations at specific data points. The comparative analysis demonstrates that BP-ANN surpasses RBF and RF models in elucidating the nonlinear correlations between process factors and removal efficiency. Both RBF and BP-ANN models may forecast removal performance; however, BP-ANN demonstrates superior reliability, enhanced fitting accuracy, and greater predictive efficiency in modeling the elimination process.

**Fig. 21: RBF experimental versus predicted values comparison**

### 3.6. Adsorption Isotherms

Adsorption characteristics of EV into Cu-doped ZnO/rGO nanocomposites were assessed at various dye concentrations, maintaining a constant sonication duration of 23 minutes and pH of 5. Equilibrium data were evaluated using Freundlich, Temkin, and Langmuir isotherm models to identify the best suitable mechanism characterizing the adsorption process (Castro *et al.* 2025).

$$\frac{C_e}{q_e} = \frac{1}{k_L q_m} + \frac{C_e}{q_m} \quad \dots (6)$$

$$q_e = \frac{q_m k_L C_e}{1 + k_L C_e} \quad \dots (7)$$

Where,  $q_m$  reflects maximum adsorption capacity;  $K_L$  represents Langmuir constant to adsorption affinity;  $q_e$  shows quantity of EV adsorbed per unit mass

of Cu-doped ZnO/rGO at equilibrium and  $C_e$  signifies equilibrium concentration of EV in solution. Additionally, the Langmuir model was assessed utilizing the dimensionless separation factor,  $R_L$ , derived from Equation (8):

$$R_L = \frac{1}{1 + K_L C_0} \quad \dots (8)$$

Here  $C_0$ (mg/L) represents initial concentration of EV. The value of  $R_L$  reflects interaction behavior between EV and Cu-doped ZnO/rGO nanocomposites. An  $R_L$  value of 0 shows irreversible adsorption, while a value of 1 shows linear adsorption;  $R_L > 1$  denotes an unfavorable process, whereas  $0 < R_L < 1$  confirms favorable adsorption.

where  $C_0$ (mg/L) were starting concentration of EV. A value of  $R_L$  indicates interaction behavior between EV and Cu-doped ZnO/rGO nanocomposites. An  $R_L$  value of 0 signifies irreversible adsorption, whereas a value of 1 indicates linear adsorption;  $R_L > 1$  signals an unfavorable process, but  $0 < R_L < 1$  verifies favorable adsorption.

The Freundlich isotherm model delineates an empirical framework that characterizes the heterogeneous and multilayer adsorption behavior of EV onto Cu-doped ZnO/rGO nanocomposites. The linear and nonlinear formulations of the Freundlich model are presented in Equation (9) and Equation (10), respectively.

$$\ln q_e = \ln k_F + \frac{1}{n} \ln C_e \quad \dots (9)$$

$$q_e = k_F C_e^{1/n} \quad \dots (10)$$

where,  $K_F$ (mg/g) denotes the Freundlich constant associated with adsorption capacity, and  $1/n$  signifies adsorption intensity for EV onto Cu-doped ZnO/rGO nanocomposites. The Temkin isotherm is articulated in its linear form

$$q_e = B_T \ln K_T + B_T \ln C_e \quad \dots (11)$$

where  $B_T$  and  $K_T$  are the Temkin constants.

Figure 22 illustrates adsorption isotherm characteristics at EV on Cu-doped ZnO/rGO nanocomposites, whereas Table 5 consolidates the relevant Langmuir, Freundlich, and Temkin parameters together with their correlation coefficients ( $R^2$ ).

The adsorption of EV onto the Cu-doped ZnO/rGO nanocomposite is governed by a combination of electrostatic attraction,  $\pi$ - $\pi$  interactions, pore-filling effects, and surface complexation mechanisms. The mesoporous structure and high surface area of the nanocomposite provide abundant active sites for dye adsorption and facilitate rapid diffusion of EV molecules

into the porous network. Furthermore, the aromatic rings of EV can interact with the  $sp^2$ -hybridized carbon domains of rGO through  $\pi$ - $\pi$  stacking interactions, while oxygen-containing functional groups on the composite surface contribute to additional adsorption through hydrogen bonding and electrostatic interactions. The incorporation of Cu-doped ZnO nanoparticles further enhances the surface reactivity and availability of adsorption sites, resulting in improved adsorption performance. These synergistic interactions collectively contribute to the efficient removal of EV from aqueous solutions.

**Table 5. Isotherm parameters for EV removal on Cu-ZnO/rGO**

| Adsorption Equilibrium Models | Isotherm Constants | Parameters from Linear Regression | Parameters from Nonlinear Regression |
|-------------------------------|--------------------|-----------------------------------|--------------------------------------|
| Freundlich                    | $1/n$              | 0.0755                            | 0.0738                               |
|                               | $K_f$ (mg/g)       | 591.53                            | 598.42                               |
|                               | $R^2$              | 0.9554                            | 0.9486                               |
| Langmuir                      | $R^2$              | 0.9502                            | 0.9415                               |
|                               | $q_m$ (mg/g)       | 942.31                            | 965.40                               |
|                               | $K_L$ (L/mg)       | 0.1295                            | 0.1182                               |
|                               | $R_L$              | 0.0127–0.0372                     |                                      |
|                               | $K_T$ (L/g)        | $3.74 \times 10^3$                |                                      |
| Temkin                        | $R^2$              | 0.9659                            |                                      |
|                               | $B_T$              | 65.45                             |                                      |

The Langmuir separation factor ( $RL$ ) varied from 0.0127 to 0.0372, showing good adsorption onto Cu-doped ZnO/rGO nanocomposites with the highest adsorption capacity of 965 mg/g. In the Freundlich model, a value of  $1/n$  ( $0.062 < 0.5$ ) signifies strong adsorption intensity and surface heterogeneity. Linear and nonlinear fits were conducted utilizing the Langmuir and Freundlich models. Similarly, NiFe<sub>2</sub>O<sub>4</sub>/rGO nanocomposites were optimized by CCD-RSM for efficient adsorption of both anionic and cationic dyes, achieving removal efficiencies of ~96–98%. The adsorption followed Langmuir/Freundlich isotherms with high model accuracy ( $R^2 > 0.99$ ), confirming strong predictive capability and adsorption performance (Bazgir *et al.* 2019). The  $R^2$  values in Table 5 indicate that the linear approach exhibited superior concordance, with the Langmuir model ( $R^2 = 0.9502$ ) most accurately depicting the adsorption behavior among all models.

The maximum adsorption capacity of 965 mg g<sup>-1</sup> obtained for the Cu-doped ZnO/rGO nanocomposite

is comparatively higher than many graphene- and metal oxide-based adsorbents reported for dye removal. This enhanced performance can be attributed to the synergistic combination of the high surface area ( $115.8 \text{ m}^2 \text{ g}^{-1}$ ), mesoporous architecture, abundant active adsorption sites, and strong  $\pi$ - $\pi$  interactions between EV molecules and the rGO framework. In addition, Cu doping introduces surface defects and additional adsorption centers that facilitate dye uptake. To provide a comprehensive assessment of the adsorption performance, a comparison with previously reported adsorbents has been included in Table 6, demonstrating the competitive adsorption capability of the developed Cu-doped ZnO/rGO nanocomposite.

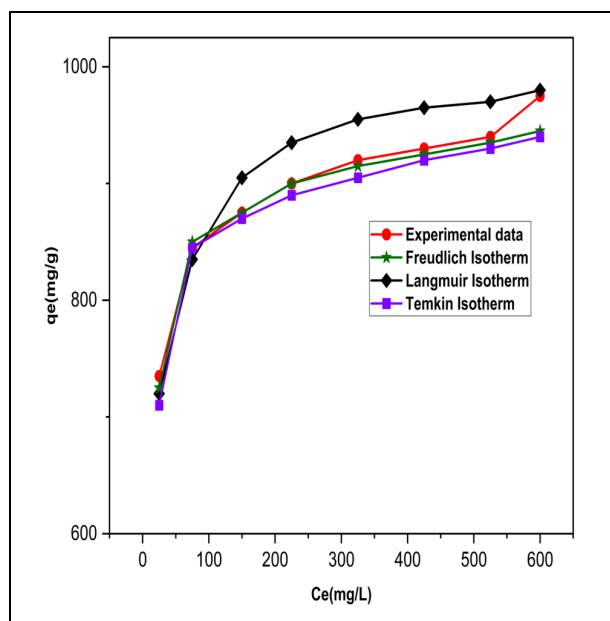


Fig. 22: EV adsorption isotherm on Cu-ZnO/rGO

Table 6. Comparison of adsorption capacities of various adsorbents reported for dye removal

| Adsorbent                                | Dye            | Adsorption Capacity (mg/g) | Reference              |
|------------------------------------------|----------------|----------------------------|------------------------|
| Graphene Oxide/Chitosan Composite        | Methylene Blue | 476                        | (Khiam et al. 2022)    |
| Reduced Graphene Oxide/ZnO Nanocomposite | Methylene Blue | 625                        | (Hussein et al. 2025b) |
| Magnetic Graphene Oxide Nanocomposite    | Crystal Violet | 714                        | (Adel et al. 2022)     |
| ZnO/Graphene-Based Adsorbent             | Organic Dyes   | 580–850                    | (Mohammed et al. 2024) |
| Cu-doped ZnO/rGO Nanocomposite           | Ethyl Violet   | 965                        | Present Work           |

Table 7. Kinetic parameters of EV removal by Cu-ZnO/rGO

| Adsorption Models       | Kinetic Expressions                                              | Kinetic Constants                | Calculated Constants   |
|-------------------------|------------------------------------------------------------------|----------------------------------|------------------------|
| Elovich                 | $q_t = \frac{1}{\beta} \ln(\alpha\beta) + \frac{1}{\beta} \ln t$ | $\alpha$ (mg/g/min)              | 824.41                 |
|                         |                                                                  | $\beta$ (g/mg)                   | $5.342 \times 10^{-3}$ |
|                         |                                                                  | $R^2$                            | 0.9634                 |
| Pseudo-second-order     | $\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e}$            | $k_2$ (g/mg/min)                 | $0.316 \times 10^{-3}$ |
|                         |                                                                  | $q_e$ (mg/g)                     | 971.77                 |
|                         |                                                                  | $R^2$                            | 0.9978                 |
| Pseudo-first-order      | $\log(q_e - q_t) = \log q_e - \frac{k_1 t}{2.303}$               | $k_1$ (1/min)                    | 0.2369                 |
|                         |                                                                  | $q_e$ (mg/g)                     | 839.63                 |
|                         |                                                                  | $R^2$                            | 0.9787                 |
| Intraparticle diffusion | $q_t = k_d t^{0.5} + C$                                          | $k_d$ (mg/g/min <sup>1/2</sup> ) | 114.39                 |
|                         |                                                                  | $C$ (mg/g)                       | 320.24                 |
|                         |                                                                  | $R^2$                            | 0.8488                 |

### 3.7. Kinetics Studies

Four kinetic models (pseudo-first-order, second-order, Elovich, and intraparticle diffusion) were utilized to assess adsorption of EV onto Cu-doped ZnO/rGO. Nanocomposites. Relevant model parameters and computed  $q_t$  values as a function of time were shown in Table 7 and depicted in Fig. 23.

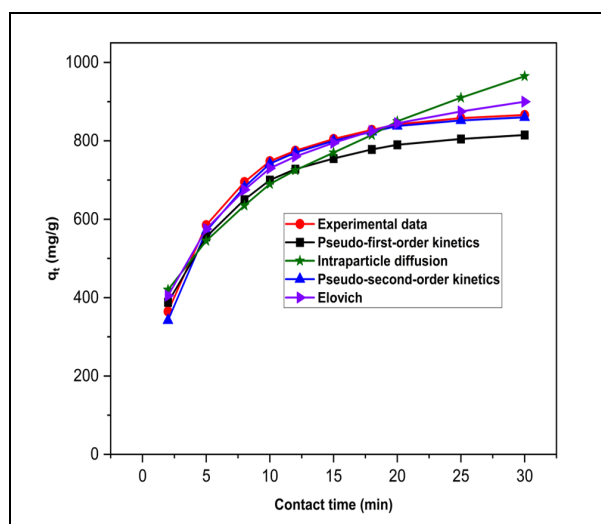


Fig. 23: Time-dependent EV removal using Cu-ZnO/rGO system

According to Fig. 23, the uptake of EV by Cu-ZnO/rGO nanocomposites escalates with prolonged

sonication time, attaining equilibrium at 25 minutes. A fast adsorption phase transpires within the initial 5 minutes, resulting from the migration of EV molecules from bulk solution to the adsorbent's external surface, followed by the progressive filling of active sites until equilibrium is attained. The correlation coefficients for pseudo-first-order, intraparticle diffusion, Elovich models, and second-order were 0.941, 0.932, 0.957, and 0.992, respectively. Elevated  $R^2$  value indicates that pseudo-second-order model ( $R^2 = 0.997$ ) most accurately represents adsorption kinetics. In previous studies demonstrated that, the polyaniline-modified chitosan/ZnO-Fe<sub>3</sub>O<sub>4</sub> nanocomposite achieved 94.51% Cu(II) removal (328.4 mg/g) following Langmuir isotherm and pseudo-second-order kinetics with ~95% recyclability (Kavosi *et al.* 2019).

#### 4. CONCLUSION

Mesoporous Cu-doped ZnO/rGO nanocomposites were successfully synthesized via a one-step co-precipitation method and exhibited a high specific surface area (115.8 m<sup>2</sup> g<sup>-1</sup>) with an average pore size of 29.6 nm. The adsorption performance for ethyl violet (EV) removal was effectively evaluated using both RSM and ANN-GA approaches. The removal efficiency ranged from 72.4% to 93.3%, while ANOVA confirmed the significance of the developed quadratic model ( $F = 82.44$ ,  $p < 0.0001$ ) with a non-significant lack of fit ( $p = 0.321$ ). The optimum operating conditions predicted by ANN-GA were a concentration of 348.92 mg L<sup>-1</sup>, pH 4.91, sonication time of 9.82 min, and adsorbent dosage of 17.03 mg, resulting in a maximum removal efficiency of 93.33%. Adsorption behavior followed the pseudo-second-order kinetic model ( $R^2 = 0.9978$ ) and was best described by the Langmuir isotherm model ( $R^2 = 0.9502$ ), indicating favorable monolayer adsorption with a maximum adsorption capacity of 965 mg g<sup>-1</sup>. The study demonstrates the potential of Cu-doped ZnO/rGO nanocomposites as an effective adsorbent for dye-contaminated wastewater treatment. Nevertheless, the predictive models were developed using a limited experimental dataset, and further studies involving larger datasets, cross-validation, external validation, and real wastewater systems are recommended to enhance model robustness and practical applicability.

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#### CONFLICTS OF INTEREST

The authors declare that there is no conflict of interest.

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