Ecofriendly Green Synthesis of the ZnO-Doped CuO@Alg Bionanocomposite for Efficient Oxidative Degradation of p-Nitrophenol

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ABSTRACT: In the present study, ecofriendly green synthesized ZnO/CuO nanorods were prepared by using the stabilizing and reducing characteristics of the alginate biopolymer. The bionanocomposite (BNC) material was characterized by various sophisticated analytical tools such as Fourier transform infrared spectroscopy, X-ray diffraction, scanning electron microscopy—energy dispersive X-ray spectroscopy, transmission electron microscopy, UV—visible spectroscopy, differential scanning calorimetry, and the Brunauer—Emmett—Teller (BET) method. The composition of ZnO/CuO@Alg BNC was found to be C (16.16 ± 0.42%), O (42.26 ± 1.87%), Cu (31.96 ± 1.05%), and Zn (9.62 ± 0.48%), which also supports the approximate 3:1 ratio of Cu²⁺ and Zn²⁺ taken as the precursor. The nanocrystalline spinel ferrite was found to have a BET specific surface area of 19.24 m² g⁻¹ with a total pore volume of 0.075 cm³ g⁻¹ and 1.45 eV as the band gap energy (Eg). Further, the material was applied for the photodegradation of p-nitrophenol (PNP) under the advanced oxidative process (AOP) under visible sunlight irradiation. The visible light radiation was used for the degradation of PNP under pH 2 conditions and resulted in 98.38% of the photocatalytic efficiency, which suggests that the degradation of PNP was accomplished by the *OH oxidative radical.

1. INTRODUCTION

The introduction of nitroaromatics in aquatic systems pertains to the release of waste effluents from pharmaceutical, pesticide, and explosive industries.¹,² The agriculture sector introduces p-nitrophenols (PNPs) to the soil and drinkable water system through extensive use of organophosphorus pesticides which on hydrolysis convert into PNP.³,⁴ Additionally, these PNPs owing to their persistent toxic and mutagenic nature are generally too secure to be separate from soil and water by self-decomposition and hence possess a great threat to aquatic and human life.¹,⁵,⁶ The U.S. Environmental Protection Agency (EPA) has catalogued the PNP as the major pollutant with maximum permissible limits in the commercial sewerage as 1–20 mg L⁻¹.⁷ Human exposure to these PNPs may lead to numerous complications and diseases such as an increased metabolism, an increase of heart beats, hyperthermia, skin allergies, cataracts, cardiovascular disease, and premature death.⁸,⁹ Significantly, it is a matter of serious concern to handle these phenolic compounds for the environmental protection. To date, assorted treatment methodologies have been adopted for the removal of PNP from wastewater such as adsorption, biological degradation, and electrochemical degradation. However, in the adsorption degradation process, there is only the transfer of the pollutant from one phase to another phase, and the biological degradation processes are inefficient because the toxic nature of PNP on microorganisms results in a slow degradation rate.¹⁰,¹¹ On the other hand, the electrochemical degradation process has elevated operatory costs which exceptionally restraint its wide application.¹² Recently, the most sturdy and promising technique for the treatment of wastewater is the advanced oxidation process through photocatalytic degradation, which functions by the bombarding of light (photons) on the organic molecule using a catalyst
involving the transition of electrons from the valence band (VB) to the conduction band (CB). The transition triggers the formation of reactive oxidants (RO) such as superoxide (*O₂⁻*) and hydroxyl radicals (*OH) that attack on the toxic organic molecule to mineralize it into small nontoxic entities.13–15

In the current scenario, scientists and researchers examined the metal oxide nanoparticles and metal matrix-based nanocomposite materials for multidisciplinary applications. The best role of these nanoparticles was found in the field of catalysis because of their large surface area, chemical stability, low cost, less resistance to diffusion, faster rate of equilibrium, and capacity to detect hazardous pollutants.16 In the literature, several metal oxide-based nanoparticles have been utilized for the efficient oxidative degradation of PNP, such as ZnO.17 SnO₂,18 NiO,19 CeO₂,20 CuO,21 and WO₃.22 In the present study, we have tried to enhance the photocatalytic activity of CuO nanoparticles through fusion of the ZnO nanostructure using the chemical coprecipitation method. Generally, ZnO and CuO are referred to as the most prevalent nanoparticles because of their eminent chemical, physical, and mechanical properties such as a low melting temperature, a larger surface area, structural stability, high diffusion, and high surface energy.23 ZnO is an n-type semiconductor having its wide direct energy band gap of 3.37 eV, while CuO is a p-type semiconductor which manifests a narrow band gap (2.5 eV).24,25 CuO is regarded as a prevailing heterogeneous catalyst despite its use in solar energy conservation, chemical corrosion resistance, and low hardness and antimicrobial activities.26,27 Therefore, the fusion of ZnO nanoparticles into the CuO matrix was taken into consideration through green synthesis, which resulted in a reduced band gap of 1.45 eV as compared to the precursors. The reduction in band gap of ZnO/CuO@Alg reflected the enhanced photocatalytic activity as compared to the materials synthesized by green synthesis such as ZnO/CuO-Theobroma cacao, ZnO/CuO-Mentha longifolia, ZnO/CuO-Vaccinium arctostaphylos L, CuO/ZnO-Melissa officinalis L, and guar gum–ZnO.28–31 Sodium alginate (SA) performs both as a reducing agent and as a capping agent because agglomeration in the case of nanoparticles poses a big hurdle to their efficiency. Alginate polyionic polysaccharides extracted from brown algae species are nonpoisonous, inexpensive, biodegradable, and easily accessible natural polymers.32 The structure is composed of two residues, gulurionate, named D-block, and mannuronate, named M-block, attached to each other through 1–4 glycosidic linkage.33 Therefore, the functionalization of ZnO/CuO nanoparticles with alginate biopolymer chains not only provides the stabilization but also increases their photocatalytic properties by decreasing the band gap energy value (1.45 eV). The reduction in E₆ value reflects the reduction in particle size through reducing characteristics of alginate.34 Response surface methodology (RSM) can be recognized as an efficient mathematical and statistical tool for optimizing the reaction parameters. It develops a quadratic regression equation with high desirability and good precision, which can be frequently used in numerous fields such as bacterial growth, biological hydrogen production, enzyme synthesis, and azo dye decolorization.35 The biggest benefit of taking RSM is that it decreases the replication of experiments which are needed to determine different parameters and interactions between them.36 The aim of the present study was to synthesize ZnO/CuO@Alg bionanocomposite (BNC) with efficiency toward the degradation of toxic PNP in the presence of visible light. The consequences of numerous variables were improved by using central composite design (CCD) of RSM.

2. MATERIALS AND METHODS

2.1. Chemicals. Low-molecular-weight sodium alginate (SLR, Fischer Chemical, and PNP (C₆H₅NO₃, yellow crystals/peptide synthesis), Fisher Bioreagents, were purchased from Sigma-Aldrich, India. Zinc nitrate [Zn(NO₃)₂·6H₂O white crystals] and copper nitrate [(Cu(NO₃)₂·5H₂O hemic pentahydrate 98%)] were purchased form Merck, India. All the chemical materials were used without any purification or refinement. All the aqueous solutions were prepared using deionized water.

2.2. One-Pot Green Synthesis of CuO–ZnO@Alg BNC. The BNC material was consolidated by using the chemical coprecipitation scheme using ecological green routes.37 In a three-necked round-bottom flask, a mixture of 100 mL of 0.3 M Cu(NO₃)₂·5H₂O (2.326 g) and 100 mL of 0.1 M Zn(NO₃)₂·6H₂O was taken and placed under magnetic stirring (900 rpm) for 30 min to obtain homogeneity. A solution of 2% alginate was prepared by dissolving 2 g of the biopolymer powder in 100 mL of deionized water under vigorous stirring at 40 °C for 2 h to obtain a complete bubble-free homogeneous solution. Then, the blended solution of alginate was added drop by drop to the aqueous metal nitrate mixture of Cu²⁺/Zn²⁺ in order to expand the reducing character of alginate to the bulk. The mixture remained under vigorous stirring under observation at 40 °C, and the progress of the reaction was checked by observing the change in color (blue) and taking small aliquots of the reaction mixture at different time intervals for UV–visible (UV–vis) testing (Figure 6). Finally, after 6 h, a complete light-blue-colored colloid was obtained, from which the product was extracted using a centrifuge (REMI rpm 8500). The product was squeezed using deionized water seven to eight times for the efficient removal of nonreactive species and dried in a hot air oven for 3 h at 60 °C.

2.3. Analytical Techniques Used for Material Characterization. The prepared material and its crystal structure were characterized by several analytical techniques. The type of bonding and functional groups present in the synthesized material were investigated by using Fourier transform infrared (FTIR) spectroscopy, PerkinElmer (PE1600, USA), in the frequency range of 400–4000 cm⁻¹ with the transmission mode. The crystal phases of the synthesized material were collected on an X-ray diffractometer (A Rigaku Ultima 1V). The morphologies of the sample were analyzed by using scanning electron microscopy (SEM; JEOL GEM 6510LV, Japan). The elemental size and dispersion of the sample were examined using a JEM 2100 (Japan) transmission electron microscope. The heat capacity, enthalpy of fusion, and enthalpy of crystallization were observed by differential scanning calorimetry ([DSC, Mettler Toledo, DSC (822e)]) for the analysis of aliquots of the PNP sample for quantitative analysis, a Shimadzu UV-1900 UV–vis double-beam spectrophotometer was taken into consideration. The specific surface areas of the synthesized material were tested on a Micromeretics Tristar II and calculated using the Brunauer–Emmet–Teller (BET) method.

2.4. Experiment Design and Photocatalytic Activity. Minitab17 software was utilized for conducting the experimental design that was subsequently executed via the RSM-coupled CCD to establish the synergistic or antagonistic effects...
of two or more variables on the response of the nano-composite. The variable parameter table given in Table S1 mainly consists of three reaction variables including (i) irradiation time A (20–220 min), (ii) pH of PNP solution B (1.98–7.02), and (iii) catalyst dose C (11.59–28.41 mg) for a 50 mg L⁻¹ PNP concentration (fixed based on EPA guidelines) at 25 °C. For the efficient degradation of PNP using the ZnO/CuO@Alg BNC, the above-mentioned variables can be articulated using quadratic regression eqs 1 and 2

\[
y = b_0 + \sum_{i=1}^{n} b_i x_i + \sum_{i=1}^{n} b_{ij} x_i x_j + \varepsilon
\]

where \(x_i\) and \(x_j\) represent the linear functions that transform the original actual values, \(X_i = -\alpha C_i X_i - C_i X_i + C_i x_i + \alpha C_i\) to the coded values \(-\alpha, -1, 0, +1,\) and \(\alpha\)

\[
x = \frac{(X - x_i)}{C_i}
\]

The photocatalytic experiments were performed by taking 20 mL of 50 mg L⁻¹ PNP in a 100 mL conical flask and placing under magnetic stirring under visible light radiation by disbursing a prescribed amount of catalyst/time/pH combination suggested by the RSM—CCD model. The final concentration of PNP after completion of the degradation process was quantified using a UV-vis spectrophotometer and was expressed by eq 3

\[
\%\text{ PNP degradation} = \frac{C_0 - C_i}{C_0} \times 100
\]

where \(C_0\) and \(C_i\) are the concentrations of PNP before and after photodegradation, respectively.

3. RESULTS AND DISCUSSION

3.1. Characterization of the Cu–Zn@Alg BNC. The FTIR spectra of alginate, CuO, ZnO, and ZnO/CuO@Alg BNC are displayed in Figure 1. The FTIR spectra of alginate are shown in Figure 1a, which shows the peaks at 3404 cm⁻¹ (OH stretching), 2929 cm⁻¹ (aliphatic –CH stretching), 1738 cm⁻¹ (C=O stretching), 1605 cm⁻¹, and 1418 cm⁻¹ (COO⁻ symmetric and asymmetric stretching) and the peaks between 828 and 1158 cm⁻¹ (pyranoid C–O–C ring stretching). The FTIR spectra of CuO nanoparticles (Figure 1b) showed characteristic peaks at 450 and 602 cm⁻¹ (due to the Au and Bu modes of CuO) and 1085 and 3387 cm⁻¹ surface-adsorbed H₂O molecules (–OH bending and stretching vibrations).21 The FTIR spectra of ZnO nanoparticles shown in Figure 1c constitute peaks at 478, 600, and 770 cm⁻¹ (Zn–O bond stretching) and 1085 and 3385 cm⁻¹ surface-adsorbed H₂O molecules (–OH bending and stretching vibrations).17 The FTIR spectra of the ZnO/CuO@Alg BNC in Figure 1d show all the characteristic peaks from CuO, ZnO, and alginate with a shifted vibrational frequency, for example, 508 cm⁻¹ (Cu–O stretching), 616 cm⁻¹ (Zn–O stretching), 828–1144 (C–O–C alginate pyranoid ring), 1505 cm⁻¹, 1497 cm⁻¹ (COO⁻ symmetric and asymmetric stretching), 2923 cm⁻¹ (C–H aliphatic stretching of alginate), and 3238 cm⁻¹ (–OH stretching). The shift in the carboxylic acid vibrational frequency suggests that the reduction as well as stabilization of Zn²⁺ and Cu²⁺ into oxides was done through donation of electrons (lone pairs) from oxygen form a Cu–O–Zn-type lattice.38

Figure 2 shows the X-ray diffraction (XRD) spectra of ZnO, CuO, and the ZnO/CuO@Alg BNC, which provide information about how the fusion of ZnO into the CuO matrix affects the lattice structure. The XRD spectra of ZnO nanoparticles are positioned at 2θ values of 31.68, 32.82, 36.16, 47.48, 56.49, 58.64, 62.71, and 67.81°, which correspond to miller index values of the (100), (002), (101), (102), (110), (103), (112), and (200) crystalline planes of ZnO (JCPDS 89-0510), respectively.39 The XRD spectra of CuO nanoparticles consist of 2θ peaks at 28.02, 40.16, 49.81, 58.29, 66.07, and 73.30°, which are associated with miller index values of (110), (210), (111), (220), (211), and (003), respectively (JCPDS 80-1268).40 While looking at the spectra of the ZnO/CuO@Alg BNC, the characteristics peaks from both CuO and ZnO nanoparticles appeared at 2θ values of 22.33°, 28.25° (CuO), 30.75° (ZnO), 33.63° (ZnO), 35.96° (ZnO), 48.41° (CuO), and 52.77° with corresponding miller index values of (001), (100), (101), (002), (110), (200), and (202), respectively. The spectrum reveals the peaks with a shifted diffraction angle (2θ values) from the precursor values with reduced intensity due to fusion of ZnO into the CuO matrix and functionalization with alginate biopolymer chains, which imparted a small amorphous character to the BNC material.

Further information about the lattice structure, deformations on fusion, and crystallite size was obtained using Scherer’s formula from eqs 4–7

\[
D = \frac{0.94}{\beta \cos \theta}
\]

\[
\text{Dislocation density} = \frac{1}{D^2}
\]

\[
\text{Interlayer spacing} = \frac{n\lambda}{2 \sin \theta}
\]

\[
\%\text{ Crystallinity} = \frac{\text{area under the crystalline peaks}}{\text{total area}} \times 100
\]

where \(D\) is the crystal’s size, \(\lambda\) is the wavelength used (i.e., 1.54 Å), \(\beta\) is the half-width of the most intense peak, and \(\theta\) is the angle of diffraction. Using eq 4, the average particle sizes of ZnO nanoparticles, CuO nanoparticles, and the ZnO/CuO@
Alg BNC were found to be 33.57, 5.52, and 15.51 nm, respectively. The particle size of the BNC was also found to be in close agreement with the particle size (15.73 nm) obtained by TEM analysis. Therefore, the increase in particle size of CuO nanoparticles from 5.52 to 15.51 nm suggested the successful inclusion of ZnO nanoparticles in the metal oxide matrix, which is also supported by the increase in interlayer spacing value from 0.18 Å in CuO nanoparticles to 0.23 Å in the ZnO/CuO@Alg BNC given in Table 1. These interactions of ZnO nanoparticles and alginate biopolymer chains with CuO nanoparticles resulted in an increased value of dislocation density from $0.54 \times 10^{15}$ to $3.12 \times 10^{15}$ m$^{-2}$ and a decreased % crystallinity from 61 to 44% in the ZnO/CuO@Alg BNC. The XRD data analysis clearly suggested that there is successful inclusion of ZnO nanoparticles in the CuO matrix, followed by surface functionalization by alginate biopolymer chains.

TEM was used for the elucidation of the optimized diameter and the variation in the alginate biopolymer matrix. Figure S1a,b shows the TEM image of the green synthesized ZnO/CuO@Alg BNC at 50 and 5 nm magnification ranges with the mapping images of C, O, Zn, and Cu. Figure S1a,b shows the loose agglomeration of tiny rod-shaped particles completely distributed along the alginate matrix. The average size of nanorods was found to be 16.05 nm, which is in close concurrence with XRD (15.51 nm) and TEM results (16.05 nm).

DSC is all about obtaining information about the type of process (fusion or crystallization) while dealing with solid-state reactions. Figure 4 shows the DSC curve for the ZnO/CuO@Alg BNC in a temperature range of 50 to 350 °C, and the two insets show the fusion and crystallization processes occurring.
in the ZnO and CuO solid-state matrixes with temperature. The first endothermic trough appearing at 85 °C belongs to the glass-transition temperature \(T_g\) of the alginate biopolymer matrix functionalized with ZnO/CuO nanoparticles. There was a continuous weight loss of the material until the temperature of 267 °C (crystallization of ZnO nanoparticles), which constituted a total enthalpy of crystallization \(\Delta H_c\) of 2.42 J g\(^{-1}\). After 267 °C, there was further weight loss of the material until another exothermic peak appeared at 314 °C, which belongs to the crystallization of CuO nanoparticles with an amount of enthalpy of crystallization \(\Delta H_c\) of 30.77 J g\(^{-1}\). No further peaks appeared after 338 °C, which suggest that decomposition of all the carbonaceous content of the precursor occurred up to about 338 °C. Table 2 constitutes the important solid-phase information that can be extracted from the DSC curve, such as an initial melting/fusion temperature \(T_i\) of 249 °C, a final melting/fusion temperature \(T_f\) of 265 °C, an enthalpy of fusion \(\Delta H_f\) of 23.56 J g\(^{-1}\), and the heat capacity at the initial temperature \(T_i\) of 26.75 J g\(^{-1}\) °C.

### Table 2. DSC Results for the ZnO/CuO@Alg BNC

| nanoparticle matrix | initial melting temperature \(^\circ\)C | final melting temperature \(^\circ\)C | enthalpy of fusion \(\Delta H_f\) J g\(^{-1}\) | heat capacity at \(T_i\) J g\(^{-1}\) °C | enthalpy of crystallization \(\Delta H_c\) J g\(^{-1}\) |
|---------------------|------------------------|------------------------|--------------------------|-------------------------------|--------------------------|
| ZnO                 | 249                    | 265                    | 23.56                    | 26.75                         | 2.42                     |
| CuO                 | 284                    | 302                    | 15.01                    | 12.66                         | 30.77                    |

Figure 3. SEM image of the ZnO/CuO@Alg BNC at (a) 3000x, 5 \(\mu\)m and (b) 15000x, 1 \(\mu\)m and (c) EDX spectra.

Figure 4. DSC curve for the ZnO/CuO@Alg BNC obtained between 30 and 350 °C (with inset 1 and inset 2 showing the enthalpy of fusion and crystallization for ZnO and CuO nanoparticles).
°C⁻¹ for ZnO nanoparticles, while for CuO nanoparticles, the value of initial melting/fusion temperature \((T_i)\) is 284 °C, the final melting/fusion temperature \((T_f)\) is 302 °C, the enthalpy of fusion \((\Delta H_f)\) is 15.01 J g⁻¹, and the heat capacity at the initial temperature \((C_p)\) is 12.66 J g⁻¹ °C⁻¹.

The BET isotherm for the ZnO/CuO@Alg BNC was obtained by the nitrogen adsorption–desorption method. The BET plot for the ZnO/CuO@Alg BNC shown in Figure 5 shows a type IV pattern, which suggested that the synthesized BNC has nearly a mesoporous structure. The value of BET specific surface area for the ZnO/CuO@Alg BNC was found to be 19.24 m² g⁻¹ with a total pore volume of 0.075 cm³ g⁻¹. The reported values of BET specific surface area of bulk ZnO/CuO nanoparticles synthesized by different routes are given as 75.50, 32.50, and 22.48 m² g⁻¹. Therefore, the reduction in specific surface area for the current BNC material suggests the incorporation of organic moieties of alginate, which lead to block some pores because of surface functionalization.

Optical absorption and the energy band gap profile of the synthesized ZnO/CuO@Alg BNC were assessed via UV–vis spectroscopy in the wavelength range of 200–600 nm and are shown in Figure 6, in which the absorption maxima \((\lambda_{max})\) of the ZnO/CuO@Alg BNC are observed around 364 nm. From the literature, it was found that the absorption maxima for bulk ZnO nanoparticles and CuO nanoparticles were found in the range of 301–290 nm. Therefore, a red shift from 290 to 403 nm clearly suggests that incorporation of ZnO into the CuO matrix was successful with surface functionalization by alginate biopolymer chains. The surface functionalization resulted in contraction of the band gap by providing the lone pairs from the oxygen atom of the polymer blend to the empty d orbital of the Cu²⁺ matrix involving an nπ* transition with a weak R band. The inset in Figure 6 is Tauc’s plot, which is used for the determination of band gap energy \((E_g)\) of the semiconductor by using eq 8:

\[
(ah\nu) = A(h\nu - E_g)^n
\]

where \(h = \) absorption coefficient, \(h = \) Planck’s constant, \(\nu = \) frequency of radiations, \(A = \) constant, and \(n = \) constant of transition variations, that is, \(n = 1/2\) for direct transitions and \(n = 2\) for the indirect transitions. When we plotted a graph between \((ah\nu)^2\) and \(E [\text{energy (eV)}]\), the intercept gave rise to the value of energy band gap. Tauc’s plot specified the value of \(E_g = 1.45 \text{ eV}\) for the synthesized ZnO/CuO@Alg BNC. In the literature, \(E_g\) values for bulk ZnO and CuO nanoparticles were found to be 3.37 and 2.45 eV, respectively. Therefore, reduction in the value of energy band gap of CuO nanoparticles from 2.45 to 1.45 eV owes to the fusion of ZnO nanoparticles in the CuO matrix and thereby contraction in size of the particle through reduction power of alginate functionalized on the surface.

### 3.2. RSM-Coupled Approach and Statistical Exploration

RSM is considered to be the most colossal source of statistical and mathematical procedures. Among the various models constituted with RSM, CCD has been regarded as the influential and experimental design because of its ability to adjudge the parameters of the quadratic regression model, recognition of lack of fit of the model, and building of sequential designs. The experimental design was constructed for the optimization of three operational variables, namely, radiation time \(A (20–220 \text{ min})\), pH of PNP solution \(B (1.98–4.6)\), and temperature \(C (90–110 \degree C)\).
7.02), and catalyst dose C (11.59–28.41 mg) given in Table S1. A quadratic regression modeling was employed between the responses of respective coded values of three variables, which is based upon the experimental and predicted outcomes termed in the design table given in Table S2, and the obtained quadratic equation can be expressed by eq 9

\[
\% D = 101.1 + 0.104A - 18.41B - 2.70C - 0.00382A^2 \\
+ 1.622B^2 + 0.0274C^2 - 0.0045AB + 0.00078AC \\
+ 0.076BC
\]  

(9)

In the above equation, the positive sign indicates the synergistic effect, whereas the negative sign indicates the antagonistic effect. As exposed in the equation, the radiation time is positive. This suggests that photodegradation of PNP by ZnO/CuO@Alg can be recovered with the increment in this parameter.

3.2.1. Analysis of Variance. The statistical implication and interaction results of each term obtained from the quadratic model are manifested via analysis of variance (ANOVA), as shown in Table 3. The respective coefficient terms and the significance of the regression model are evaluated by the P and F values using Fisher’s null hypothesis method. Here, increased applicability is associated with the quadratic relevance model, and each coefficient term is imposed by the small P and large F values. The large F and small P values confirm the model’s appropriateness, as evidenced by the RSM-coupled CCD. The condition proposed by Fisher P > F < 0.05 can be seen in Table 3. Here, the reasonable P > F value of 0.032 noted in the proposed quadratic regression model is statistically significant and relevant for the photocatalytic degradation of PNP on the ZnO/CuO@Alg BNC. Linear variable terms such as the irradiation time (A, P > F = 0.755) are not significant, while the PNP solution’s pH (B, P > F = 0.018) and the catalyst dose (C, P > F = 0.003) are statistically significant. When only the statistically significant terms in eq 9 are taken into consideration, we obtain eq 10

\[
\% D = 101.1 - 18.41B - 2.70C + 1.622B^2 - 0.0045AB \\
+ 0.076BC
\]  

(10)

Figure S2a shows the normal probability plot for obtaining the approximation of the real system by the regression model. As can be seen in Figure S2a, the points dispersed across the straight line without response portray an appropriation curve of residuals. A scheme was imposed between the predicted values and actual values obtained by the experimental designs and is portrayed in Figure S2b. The standard deviation of the model was found to be 5.5 with correlation values of $R^2$ and $R^2_{adj}$ as 0.92 and 0.85, respectively, individually indicating that there is a correlation between the theoretical and experimental values of the photocatalyst’s response.

3.2.2. Interpretation of the 3D Surface Data and Interaction Curves. Figure 7a–c depicts the 3D surface plots for two variable interactions between the radiation time pH and catalyst dose while keeping the other variable constant for the 50 mg L⁻¹ PNP concentration under visible light irradiation. It was observed from surface plots that a higher irradiation time, low pH values, and a low catalyst dose favored the higher degradation of PNP. The reason behind the trend may be attributed to surface charge density of the ZnO/CuO@Alg BNC. At low pH values (pH < 3), the surface of the catalyst is positive, which facilitates the accumulation of the phenolate anions to the surface and thereby photodegradation of the PNP molecule by the electronically generated $\text{OH}^\cdot$ radical from $\text{HOH}_2$ groups present on the surface in the presence of visible light. Therefore, pH 2 favored higher degradation of PNP, while with the increase in pH from 3 to 6, the positive charge density of the surface decreases, which resulted in lesser degradation of PNP at higher pH values (Figure 7a). The photocatalytic efficiency moving from pH 2 to pH 6 varies as 98.38–39.38%.

The reason behind the higher irradiation time may be attributed to the large number of active pore sites on the surface that facilitate extensive host–guest interactions. As the reaction proceeds, more amount of radiation was absorbed by the catalyst, which resulted in excitation of electrons from the VB to the CB, resulting in more generation of the $\text{OH}$ radical and resulting in a higher percent degradation of PNP under longer irradiation times. Therefore, moving from 20 to 220 min of irradiation time, the degradation efficiency increases until 140 min, and beyond this, no further change in efficiency was observed, indicating that maximum active sites present in the catalyst are utilized in the photodegradation process. Figure 7b shows the effect of radiation time and catalyst dose on the photocatalytic degradation of PNP while keeping the pH of the medium as constant. As can be seen from the 3D-surface plot, a high irradiation time and a low catalyst dose favored the higher degradation of PNP. The catalyst dose in photocatalytic reactions always plays a key role by providing an effective surface for the host–guest inclusion process. It can be inferred that a low catalyst amount leads to better distribution and diffusion of substrate molecules to the surface and hence resulted in higher photodegradation capacity.

With the increase in catalyst amount from 11.59 to 25 mg, the process of agglomeration of nanoparticles hinders the substrate molecule to reach at the bulk of the surface, which resulted in photocatalytic degradation. Figure 7c also supported the discussion of the effect of low values of PNP solution pH and catalyst dose on the photocatalytic efficiency of the catalyst. Figure 7d shows the optimization plot consisting of optimized values for all the photocatalytic reaction variables, that is, irradiation time, pH of the medium, and catalyst dose with the desirability limit. The optimum values are found as 137 min for irradiation time, 1.98 for pH of the medium, and 11.59 mg for catalyst dose with a desirability of $D = 1.00$. 

Table 3. ANOVA for the Regression Model

| source | $D_i$ | sum of squares (SS) | mean square (MS) | F-value | P > F value |
|--------|------|-------------------|----------------|----------|-------------|
| model  | 9    | 958.81            | 106.534        | 3.48     | 0.032       |
| time   | 1    | 3.15              | 3.149          | 0.10     | 0.755       |
| pH     | 1    | 246.21            | 246.206        | 8.05     | 0.018       |
| dose   | 1    | 465.67            | 465.674        | 15.23    | 0.003       |
| $A^2$  | 1    | 27.31             | 27.307         | 0.89     | 0.367       |
| $B^2$  | 1    | 192.05            | 192.052        | 6.28     | 0.031       |
| $C^2$  | 1    | 6.74              | 6.742          | 0.22     | 0.649       |
| $AB$   | 1    | 1.32              | 1.320          | 0.04     | 0.28        |
| $AC$   | 1    | 0.44              | 0.443          | 0.01     | 0.907       |
| $BC$   | 1    | 2.59              | 2.588          | 0.08     | 0.007       |
| error  | 10   | 305.77            | 30.577         |          |             |
| pure error | 5 | 26.25 | 5.249 |          |             |
| total  | 19   | 1264.58           |                |          |             |
3.3. Kinetics of Photocatalysis. The data obtained by the irradiation time experiment were utilized to find out the type of kinetic model, followed by the degradation process. Figure S3a,b shows the time-dependent UV−vis spectra for the 10−50 mg L−1 PNP degradation within the range of 10−137 min at λmax = 359 nm. From Figure S3a, the percent degradations of 50 mg L−1 PNP with respect to time were found to be 68.09% at 10 min, 83.68% at 30 min, 86.87% at 60 min, 89.32% at 90 min, 90.79% at 120 min, and 91.90% at 137 min, while from Figure S3b, the photodegradation efficiencies were found to be 68.09% for 10 mg L−1, 86.50% for 20 mg L−1, 92.31% for 30 mg L−1, 94.95 for 40 mg L−1, and 96.42% for 50 mg L−1 PNP. The data obtained for 10−50 mg L−1 PNP degradation at pH 1.98 for a time irradiation range of 10−137 min were applied to pseudo-first-order and pseudo-second-order kinetic models.54 The mathematical equations and the corresponding half-life period of the individual model are given by eqs 11−14

$$\ln \left( \frac{C_t}{C_0} \right) = kt$$

(11)

$$t_{1/2} = \frac{0.693}{k_1}$$

(12)

$$\frac{1}{C_t} = \frac{k_1}{C_0} - \frac{1}{C_0}$$

(13)

$$t_{1/2} = \frac{1}{k_2 C_0}$$

(14)

where k1 (min−1) and k2 (L mg−1 min−1) are the pseudo-first-order and pseudo-second-order rate constants, respectively, while C0 and Ct (mg L−1) are the substrate concentrations at equilibrium and after time t (min), respectively. t1/2 is the half-life period of the reaction.

The kinetic plots belonging to the pseudo-first-order and pseudo-second-order models are shown in Figure S3c,d. The calculated reaction rate constants from the slope of a straight

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Table 4. Pseudo-First- and Second-Order Kinetic Parameters for Photodegradation of PNP by the ZnO/CuO@Alg BNC

| s.no. | PNP concentration (mg L−1) | rate constant (K1) (min−1) | half-life t1/2 (min) | R2 | RMSE | rate constant (K2) (L mg−1 min−1) | half-life t1/2 (min) | R2 | RMSE |
|-------|--------------------------|----------------------------|---------------------|----|------|-------------------------------|---------------------|----|------|
| 1     | 10                       | 0.013                      | 53.31               | 0.99 | 0.018 | 0.004                         | 25.00               | 0.95 | 0.042 |
| 2     | 20                       | 0.016                      | 43.31               | 0.99 | 0.021 | 0.003                         | 16.67               | 0.90 | 0.047 |
| 3     | 30                       | 0.019                      | 36.47               | 0.99 | 0.016 | 0.003                         | 11.12               | 0.88 | 0.054 |
| 4     | 40                       | 0.021                      | 33.00               | 0.99 | 0.019 | 0.003                         | 8.34                | 0.88 | 0.056 |
| 5     | 50                       | 0.023                      | 30.13               | 0.99 | 0.040 | 0.003                         | 6.67                | 0.87 | 0.063 |

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Figure 7. 3D-surface interactive plots for (a) irradiation time vs pH of the medium, (b) irradiation time vs catalyst dose, (c) pH of the medium vs catalyst dose, and (d) optimization plot with desirability for a 50 mg L−1 PNP concentration.
line for a plot of $-\ln \left( C_t / C_0 \right)$ versus $t$ and $1 / C_t$ versus $t$ with their half-life time values are summarized in Table 4. The values of rate constant for the pseudo-first-order model ($k_f$) were calculated as 0.013, 0.016, 0.019, 0.021, and 0.023 min$^{-1}$, while those for the pseudo-second-order model were 0.004, 0.003, 0.003, and 0.003 L mg$^{-1}$ min$^{-1}$ for 10–50 mg L$^{-1}$ PNP concentrations. The combination of the statistical error analysis tool with the obtained data was employed to find out the more precise kinetic model that plays a critical role during the photodegradation reaction. Therefore, the root-mean-square error (RMSE) was taken into consideration with the regression coefficient to optimize the data values for the most preferential model. The equation for RMSE is given by eq 15

$$\text{RMSE} = \sqrt{\frac{1}{n} \sum_{i=1}^{n} \left( q_{i,\text{cal}} - q_{i,\text{exp}} \right)^2}$$  (15)

Therefore, with a high value of coefficient of determination $R^2$ and a low value of RMSE at 10–50 mg L$^{-1}$ PNP concentrations, the photocatalysis degradation reaction of PNP on the ZnO/CuO@Alg BNC surface was best defined by the pseudo-first-order kinetic model. The mechanism first involves the adsorption of PNP on the catalyst surface and thereby degradation of the substrate by the generated hydroxyl radicals under the influence of visible radiation. The radiation on interacting with the surface of the catalyst results in transition of electrons from the VB to the CB. Because the energy of the photon is dependent on the light intensity and also as more radiations fall on the catalyst surface, more hydroxyl radicals ($^{*}\text{OH}$) are produced, which result in a higher degradation rate of PNP.13 Again, to check the significance of data obtained for each of the concentration terms, that is, 10–50 mg L$^{-1}$, pertaining to both pseudo-first-order and second-order models, ANOVA tables given in Table S3 and S4 were taken into consideration. For a term to be more significant, the $P > F$ value should be less than or equal to 0.05. From Tables S3 and S4, it was observed that the values of the $P > F$ term for each concentration term for both pseudo-first-order and second-order models were less than 0.05. The lower values of $P > F$ terms for the pseudo first order as compared to the pseudo second order suggested the higher reliability of the model to define the kinetics of photodegradation reaction. The values of half-life time ($t_{1/2}$) for the pseudo-first- and second-order models are reported in Table 4 for 10–50 mg L$^{-1}$ PNP concentrations. The kinetic data also suggested that the photocatalysis of PNP is more efficient at a higher concentration (50 mg L$^{-1}$) as compared to a low concentration (10 mg L$^{-1}$) because of the masking effect which results in more hydroxyl radical generation in the presence of a higher number of PNP molecules at the solid/liquid interface.

3.4. Effect of Scavengers and the Mechanism of Photocatalysis. ROs are the typical active species which are responsible for the degradation of toxic organic molecules into small nontoxic entities. For this purpose, experiments were performed by taking a 20 mL aliquot of 50 mg L$^{-1}$ PNP at pH 1.98 with 11.59 mg of the ZnO/CuO@Alg BNC under 137 min of visible light irradiation. The individual aliquot sample was mixed with a 3 mM solution of different scavengers such as $t$-butyl alcohol (TBA, for the $^{*}\text{OH}$ radical), EDTA (for $e^{-}$), triphenyl phosphene (TPP, for the $^{*}\text{O}_2^{-}$ radical), and acrylamide (AA, for the $h_{\text{VB}}^{+}$ scavenger).5–57 The results are given in Figure 8, which suggests that the rate of photodegradation was affected to a high extent with an antagonistic trend from 98.12 to 54.16% in the presence of TBA. Because TBA is known as a scavenger for trapping of bulk $^{*}\text{OH}$ radicals from the reaction medium, a decreased photocatalytic efficiency has been received. Therefore, it was concluded that the $^{*}\text{OH}$ radicals are the key ROs during the whole course of photocatalysis reaction of PNP with the ZnO/CuO@Alg BNC. A hypothesis for the reaction mechanism based on the results obtained by scavenging tests is proposed by eqs 16–22.58

$$\text{ZnO/CuO@Alg} + \text{hv} \rightarrow \text{ZnO/CuO@Alg}(h_{\text{VB}}^{+} + e_{\text{CB}}^{-})$$  (16)
$$\text{ZnO/CuO@Alg}(e_{\text{CB}}^{-}) + \text{O}_2 \rightarrow \text{ZnO/CuO@Alg} + ^{*}\text{O}_2^{-}$$  (17)
$$h_{\text{VB}}^{+} + \text{OH}^{-} \rightarrow ^{*}\text{OH}$$  (18)
$$^{*}\text{O}_2^{-} + \text{H}^{+} \rightarrow ^{*}\text{HO}_2$$  (19)
$$\text{ZnO/CuO@Alg}(e_{\text{CB}}^{-}) + \text{HO}_2 + \text{H}^{+} \rightarrow \text{H}_2\text{O}_2$$  (20)
$$\text{H}_2\text{O}_2 + \text{ZnO/CuO@Alg}(e_{\text{CB}}^{-}) \rightarrow ^{*}\text{OH} + \text{OH}^{-}$$  (21)

On mixing ZnO/CuO@Alg with PNP under solar light radiations ($\text{hv}$), an electron $e_{\text{CB}}^{-}$ gets excited from the VB to the CB, which leads to the creation of a hole in the VB, $h_{\text{VB}}^{+}$, concurrently. The electrons present on the surface of the catalyst inhibit the molecular oxygen, and therefore, generation of the first superoxide radical anion ($^{*}\text{O}_2^{-}$) takes place and holes ($h_{\text{VB}}^{+}$) combine with H$_2$O to form hydroxyl radicals ($^{*}\text{OH}$). Now, there is a recombination of hydrogen ions ($\text{H}^{+}$) and ($^{*}\text{O}_2^{-}$) radicals existing in the solution to form ($^{*}\text{OH}$) radicals. Furthermore, there is a generation of ($^{*}\text{OH}$) radicals by the attack of trapped electrons on ($^{*}\text{HO}_2^{-}$) radicals, which is accountable for the effective photocatalytic degradation of PNP through eqs 16–22. It may be inferred that during the mineralization process of PNP, the attack of ($^{*}\text{OH}$) resulted in ring opening of the PNP resulting in aliphatic compounds,

![Figure 8](image_url)
which further converts into CO$_2$, H$_2$O, and other inorganic compounds. The proposed mechanism is schematically shown in Figure 9. In support of the mechanism proposed in Figure 9, total organic carbon (TOC) and chemical oxygen demand (COD) studies were performed, which are given in Figure S5a,b.

4. CONCLUSIONS

Herein, we report the synthesis of ZnO/CuO@Alg BNC via the green route chemical coprecipitation method using the alginate biopolymer as a reducing as well as stabilizing agent. Various analytical techniques, including FTIR, XRD, SEM−EDX, TEM, UV−vis, DSC, and BET, were employed to determine bonding interactions and chemical characteristics of the BNC material. The optimized RSM-coupled reaction conditions were a 137 min irradiation time in a 50 mg L$^{-1}$ PNP solution at a pH value of 2. Here, the PNP degradation was 98.32% at a desirability of 1.00. The values of rate constant for the pseudo-first-order model ($k_1$) were calculated as 0.013, 0.016, 0.019, 0.021, and 0.023 min$^{-1}$ with half-life periods of 53.31, 43.31, 36.47, 33.00, and 30.13 min for 10−50 mg L$^{-1}$ PNP concentrations in the presence of ZnO/CuO@Alg (11.59 mg). The results indicated that the reaction followed the pseudo-first-order kinetic model with an $R^2$ value of 0.99. TBA suppressed the degradation reaction, indicating the involvement of $^\cdot$OH radicals in PNP degradation via the conversion of PNP to aliphatic compounds and, eventually, to CO$_2$, H$_2$O, and other inorganic compounds. The small band gap between the valence and conduction bands in ZnO/CuO@Alg (1.45 eV) facilitated charge-transfer processes and improved photocatalytic efficiency. The authors are further exploring the properties of nanocrystalline ZnO/CuO nanorods such as different synthesis routes, annealing temperature, doping with other photocatalytic metals/semiconductors such as Zn$^{2+}$, Co$^{2+}$, Ag$^+$, Mg$^{2+}$, and so forth, and their photocatalytic efficiencies under UV and visible light radiations.

ASSOCIATED CONTENT

Supporting Information
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Notes
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ABBREVIATIONS

BNC, biocomposite
FTIR, Fourier transform infrared
SEM, scanning electron microscopy
TEM, transmission electron microscopy
XRD, X-ray diffraction
EDX, energy-dispersive X-ray
dSC, differential scanning calorimetry
UV−vis, UV−visible
BET, Brunauer−Emmett−Teller

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