

Article

Copper Oxide-Doped Bismuth Oxychloride Heterostructures for Heterogeneous Photocatalysis: Design, Kinetics, and Photocatalytic Degradation Mechanism for Water Decontamination

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Abstract

Bismuth oxychloride (BiOCl)–copper oxide (CuO) heterostructures were synthesized via a solvothermal route and assessed as visible-light-driven photocatalysts for methyl orange (MO) degradation. Different CuO loadings deposited on BiOCl microspheres were investigated to identify the optimal composition. Structural and physicochemical characterization revealed that low CuO content (0.6 wt. %) promoted uniform dispersion and enhanced surface area, whereas higher loadings led to nonuniform coverage and reduced photocatalytic efficiency. Operating conditions were optimized using response surface methodology based on a central composite design, considering catalyst dosage (0.1–0.8 g L^{−1}) and pH (4–9). The highest degradation efficiency (~50% after 60 min irradiation) was achieved at pH = 4 and a catalyst dosage of 0.8 g L^{−1} using the BiOCl surface modified with 0.6% CuO. Kinetic analysis followed a pseudo-first-order model. Mass spectrometry identified transient intermediates associated with demethylation and desulfonation pathways, while radical scavenger experiments confirmed hydroxyl radicals (•OH) as the dominant oxidizing species, with a secondary contribution from superoxide radicals (•O₂[−]). These results highlight the critical role of CuO dispersion and interfacial quality in enhancing charge separation and photocatalytic performance, providing practical guidelines for the rational design of BiOX–CuO heterostructures for water remediation applications.

Keywords: bismuth oxychloride; CuO nanoparticles; heterostructure; photocatalysis; water remediation



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1. Introduction

Recently, water contamination has emerged as a major global concern. This issue has been widely pointed out by the scientific community because of its impact on ecosystems and human health. Among the main contributors, industrial dyes represent one of the largest groups of organic pollutants [1]. These synthetic colorants, commonly discharged by textile, paper, plastic, and leather industries, are often toxic, mutagenic, and carcinogenic. As a result, serious risks to aquatic ecosystems and human health are generated [2]. Moreover, the low biodegradability of these compounds further amplifies their environmental persistence and ecological impact [3].

Among these dyes, methyl orange (MO), an anionic mono-azo dye, has attracted particular attention due to its extensive industrial use and high toxicity. During degradation or metabolic transformation, MO can produce aromatic amines, which exhibit carcinogenic potential when ingested and may affect organs, such as the liver and intestines [4]. Conventional wastewater treatment technologies show limited efficiency for MO removal [5]. In contrast, advanced oxidation processes (AOPs) have been developed as effective alternatives for the complete degradation and mineralization of organic contaminants. These processes are able to transform pollutants into less harmful products, such as CO₂ and water, through radical-driven oxidation routes. In addition, AOPs require low chemical consumption, operate at mild temperatures, and remain economically competitive [6,7]. Among the available AOPs, heterogeneous photocatalysis (HP) has been increasingly focused on as a sustainable approach for addressing water pollution and energy-related challenges. In this process, semiconductor materials are used to convert solar energy into chemical energy [8]. Upon light irradiation, photogenerated charge carriers are produced within the crystalline semiconductor and subsequently participate in redox reactions with water and dissolved oxygen. As a result, reactive radical species are formed, which drive the degradation and mineralization of adsorbed contaminants at the catalyst surface [9,10].

Recently, bismuth-based photocatalysts, particularly bismuth oxyhalides [BiOX (X = Cl, Br, I)], have been widely investigated due to their chemical stability, promising photocatalytic activity, and low toxicity [11,12]. Even when TiO₂ remains one of the most studied photocatalysts, several reports have shown that Bi-based materials can outperform TiO₂ under ultraviolet irradiation for the degradation of organic pollutants. For example, bismuth oxychloride (BiOCl) exhibited higher degradation efficiency than P-25 TiO₂ during three consecutive photocatalytic cycles for MO degradation [13].

To achieve high photocatalytic performance, precise control of the BiOCl nanostructure is required. This property can be tuned by adjusting synthesis conditions [14]. Among the available preparation methods, solvothermal synthesis has been carried out as an effective strategy to obtain hierarchical nanostructures with enhanced surface area and improved photocatalytic activity [15]. However, pristine BiOCl exhibits a wide band gap ($E_g = 3.4$ eV), mainly absorbing ultraviolet irradiation. Therefore, its activity under visible light remains limited. To overcome this drawback, chemical and structural modifications have been built on to construct visible-light-responsive heterostructures [8].

Recent research on BiOCl-based photocatalysts has primarily focused on heterojunction engineering, including type-II and Z-/S-scheme architectures, as well as defect modulation and facet/interface regulation. These strategies have been applied to mitigate rapid charge-carrier recombination and broaden the photo-response of pristine BiOCl under visible light irradiation [11,13,16]. Within this framework, coupling *n*-type BiOCl with *p*-type CuO has emerged as a promising approach. CuO is a narrow-band-gap semiconductor that enables the formation of *p*-*n* heterojunctions with internal electric fields. This configuration promotes interfacial charge separation and extends visible-light absorption compared with monophase BiOCl [17–19]. So far, most studies have mainly reported performance improve-

ments, while systematic correlations between CuO loading, interfacial dispersion, surface coverage, textural properties, and photocatalytic kinetics remain scarce. One effective strategy could involve decorating BiOCl with narrow-band-gap materials to enhance light absorption and charge transport. CuO, a *p*-type semiconductor with a band gap energy of 1.43 eV, has been widely applied to improve the activity of *n*-type semiconductors, such as BiOCl, under visible irradiation [17,18]. The formation of BiOCl-CuO *p-n* heterojunctions has enabled the efficient degradation of various organic contaminants. In addition to material properties, operating conditions also play a critical role. Parameters such as catalyst dosage and solution pH strongly influence photocatalytic degradation rates in HP systems [20]. Building on this context, the present study moves beyond the conventional performance-reporting approach commonly used in the BiOCl-CuO literature. Rather than focusing solely on degradation efficiency, it aims to establish quantitative relationships between CuO loading, interfacial dispersion, surface properties, and photocatalytic kinetic behavior. To address these aspects, BiOCl-CuO heterostructures were synthesized via a solvothermal route with systematically controlled CuO loadings (0.6–10 wt. %). The goal was to elucidate how CuO content and interfacial quality shape photocatalytic performance toward MO degradation under visible-light irradiation. An integrated experimental strategy was set, combining physicochemical and surface characterization, kinetic analysis, response surface methodology (RSM) optimization of solution pH and catalyst dosage, radical scavenging experiments, and identification of degradation intermediates by LC-MS/MS. This approach enables the establishment of quantitative correlations among CuO loading, interfacial dispersion, textural properties, and photocatalytic kinetics within a unified framework.

This work represents a comprehensive evaluation of BiOCl-CuO heterostructures, integrating kinetic modeling, mechanistic analysis, statistical optimization, and catalyst stability assessment. The results provide mechanistic insight and practical design guidelines for the rational development of efficient BiOCl-CuO photocatalysts for UV-visible environmental remediation.

2. Results and Discussion

2.1. Determination of the Active Heterostructure

To identify the optimal CuO loading that maximizes the MO photocatalytic removal, BiOCl-based heterostructures containing CuO loadings ranging from 0.6 to 10 wt. % were systematically tested. The overall removal efficiency after 60 min, considering both adsorption in the dark and photocatalytic degradation under irradiation, was determined from UV-Vis spectrophotometric measurements. As shown in Table 1, pristine BiOCl exhibited limited removal performance, reaching 22.1% adsorption and 29.7% photocatalytic degradation. The incorporation of a modest CuO loading significantly enhanced the BiOCl photoactivity, with the BiOCl-CuO_{0.6%} sample achieving the highest photocatalytic removal efficiency ($49.3 \pm 2.1\%$) after 60 min of irradiation. This corresponds to an improvement of approximately 1.7 times compared to pristine BiOCl, which may be attributed to the beneficial role of CuO in promoting charge separation and interfacial charge transfer within the heterostructure.

In contrast, increasing the CuO content beyond 3.4 wt. % resulted in a progressive decrease in photocatalytic performance. Samples containing ≥ 6 wt. % CuO displayed markedly lower degradation efficiencies ($\leq 25.0\%$), which can be attributed to excessive CuO coverage on the BiOCl surface. The darker appearance of these samples suggests enhanced light shielding and reduced photon penetration, leading to suppressed photoactivation of the semiconductor matrix. Similar behavior has been predicted by theoretical and experimental studies, where excessive co-catalyst loading promotes recombination centers and optical

losses [21]. Based on these results, BiOCl–CuO_{0.6%} was selected as the optimal heterostructure composition and used for subsequent structural, optical, and photocatalytic analyses.

Table 1. Time-dependent removal by preliminary BiOCl–CuO material in tests at different CuO concentrations, measured via UV-Vis spectrophotometry.

Sample	MO Remotion by Adsorption After 60 min (%)	MO Remotion by Photocatalysis After 60 min (%)
BiOCl	22.1	29.7
BiOCl–CuO _{0.6%}	39.1	49.3
BiOCl–CuO _{3.4%}	20.5	29.7
BiOCl–CuO _{6%}	23.0	25.0
BiOCl–CuO _{10%}	10.5	10.6

2.2. Physicochemical and Surface Characterization of the Synthesized Heterostructures

To elucidate the structure-property relationships impacting on the photocatalytic performance of the synthesized materials, comprehensive physicochemical and surface characterizations were conducted. The surface morphology and microstructural features were examined by SEM, as shown in Figure 1. Pristine BiOCl exhibited a porous micro-spherical architecture composed of interconnected nanosheets (Figure 1a), consistent with previously reported morphologies obtained using similar solvothermal synthesis conditions [15]. In contrast, pure CuO exhibited a fusiform morphology consisting of agglomerated nanostructures with irregular shapes (Figure 1b), in agreement with earlier reports [22].

The characteristic micro-spherical morphology of BiOCl is preserved after CuO incorporation, although notable morphological modifications were observed depending on the CuO loading. At a low CuO content (0.6 wt. %, Figure 1c), the heterostructure maintained the overall spherical architecture of pristine BiOCl, while a higher degree of micro-sphere agglomeration was detected, which can be attributed to the anchoring of CuO species on the BiOCl surface. Increasing CuO loading to 3.4 wt. % (Figure 1d) led to the formation of lamellar, plate-like structures associated with CuO domains deposited on the external surface of BiOCl microspheres, as previously reported for similar heterostructured systems [17]. The heterogeneous spatial distribution of these lamellae suggests partial segregation and the formation of isolated CuO clusters, which may weaken the interfacial contact between both materials. This phenomenon became more pronounced at high CuO loading (10 wt. %, Figure 1e), where irregular and partially amorphous CuO agglomerates with nonuniform surface coverage were observed. Such morphological deterioration is expected to negatively impact light harvesting and charge transfer processes, in agreement with the significant decrease in photocatalytic activity observed for this sample.

Elemental mapping and compositional analysis were performed by EDS analysis to evaluate the spatial distribution of Cu within the heterostructures (Figure 2). Reference spectra for pristine BiOCl and CuO are shown in Figure 2a and 2b, respectively. For the BiOCl–CuO_{0.6%} sample (Figure 2c), no distinct Cu signal was detected by EDS. This observation was attributed to the intrinsic detection limit of the technique, which typically ranges between 0.5 and 1 wt. %, depending on the instrumental configuration and matrix composition. Therefore, the absence of a detectable Cu peak does not imply the absence of CuO in the heterostructure.

At a CuO loading of 3.4 wt. % (Figure 2d), weak but spatially distributed Cu signals became visible, indicating successful incorporation of CuO species onto the BiOCl surface. When the CuO content was increased to 10 wt. % (Figure 2e), the Cu signal intensity markedly increased displaying a heterogeneous distribution, which confirmed the formation of CuO-rich agglomerates along with the loss of uniform heterostructure coverage.

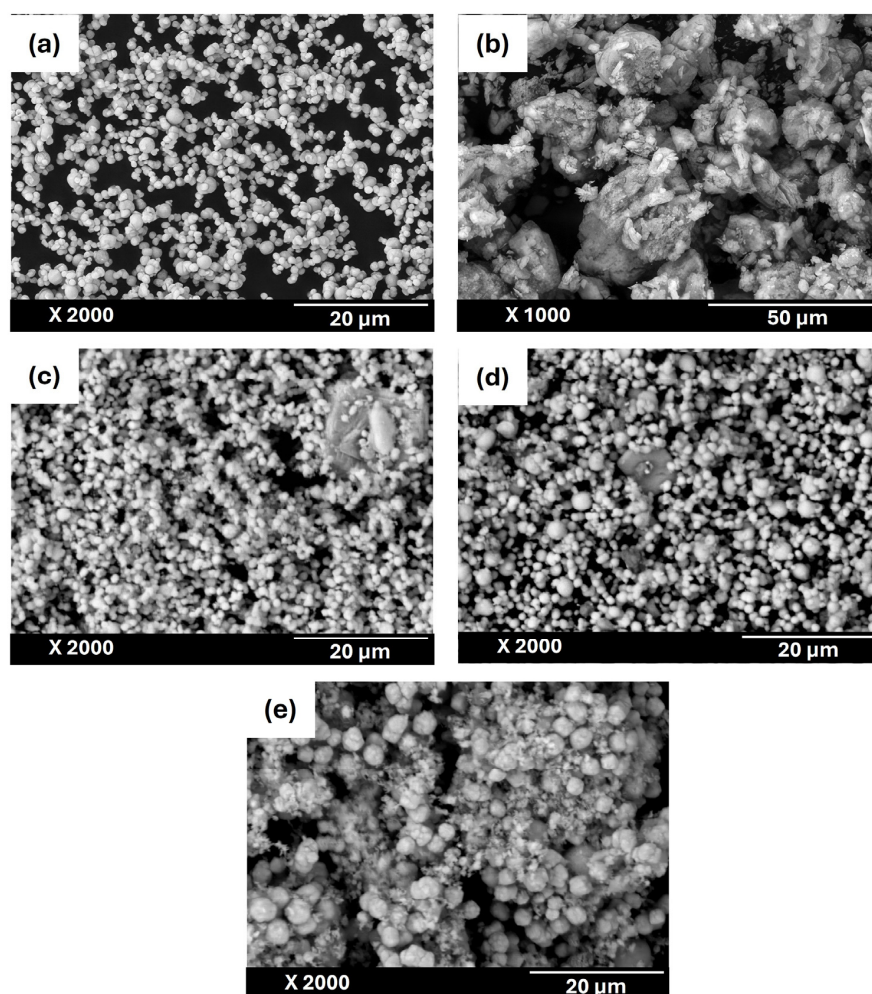


Figure 1. SEM images of (a) BiOCl, (b) CuO, (c) BiOCl-CuO_{0.6%}, (d) BiOCl-CuO_{3.4%}, and (e) BiOCl-CuO_{10%}.

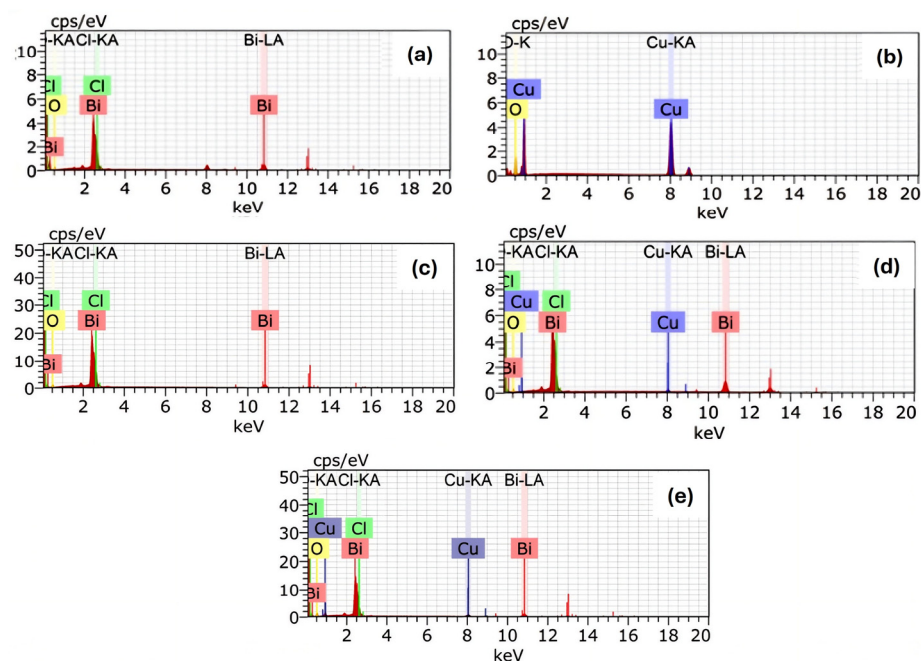


Figure 2. EDS spectra of (a) BiOCl, (b) CuO, (c) BiOCl-CuO_{0.6%}, (d) BiOCl-CuO_{3.4%}, and (e) BiOCl-CuO_{10%}.

Quantitative elemental analysis by total-reflection X-ray fluorescence (TXRF, Table 2) confirmed the presence of Cu in all synthesized heterostructures, including BiOCl–CuO_{0.6%}, thereby validating the EDS observations and supporting the successful incorporation of CuO even at low loading levels. It should be noted that the EDS provides reliable detection primarily for elements with atomic numbers $Z \geq 17$; consequently, lighter elements are below the effective detection range and are not considered in this analysis.

Table 2. Elemental composition and textural properties of parent materials and BiOCl–CuO heterostructures synthesized at different CuO loadings.

Material	Elemental Composition			Surface Area S_{BET} (m ² /g)	Pore Diameter D_p (nm)	Pore Volume V_p (cm ³ /g)
	%Bi	%Cl	%Cu			
BiOCl	97.69	30	3.8	30	3.8	0.034
CuO	N/D	N/D	56	56	3.3	0.061
BiOCl–CuO _{0.6%}	97.54	39	3.3	39	3.3	0.055
BiOCl–CuO _{3.4%}	95.83	26	6.4	26	6.4	0.040
BiOCl–CuO _{10%}	93.85	20	6.5	20	6.5	0.038

The surface textural parameters of the synthesized materials are summarized in Table 2. Compared to pristine BiOCl, the BiOCl–CuO_{0.6%} heterostructure exhibited an increased specific surface area (S_{BET}), although remaining lower than that of pure CuO. This result indicates that low CuO incorporation moderately enhanced surface exposure without substantially altering the intrinsic porous framework of BiOCl.

This trend is further supported by the BJH pore-size distribution and pore volume analysis, which revealed a mesopore-centered distribution at low CuO loading (0.6 wt. %). Such behavior suggests a homogeneous interfacial dispersion of CuO nanoparticles, improving surface accessibility while preserving the hierarchical porous architecture of BiOCl microspheres. Similar trends have been reported for metal-oxide-modified BiOX heterostructures with low secondary-phase content [23,24].

In contrast, increasing the CuO loading above 0.6 wt. % resulted in a progressive reduction in the S_{BET} , reaching values lower than those of the individual components. This decrease correlates with pronounced modifications in the BJH pore-size distribution, including a reduction in accessible mesopores and broadening toward larger pore diameters, which are characteristic of partial pore blockage and nonuniform surface coverage induced by excessive accumulation of the CuO phase [23,25,26]. A similar tendency was observed for the total pore volume (V_p). While BiOCl–CuO_{0.6%} exhibited a pore volume comparable to that of pristine BiOCl, higher CuO loadings led to increased V_p values accompanied by reduced S_{BET} . This inverse correlation was attributed to structural disruption and interparticle void formation caused by CuO agglomeration, which generated larger but less accessible pores and ultimately limited the effective catalytic surface area. These structural changes are consistent with the morphological observations obtained by SEM.

Nitrogen adsorption–desorption isotherms of BiOCl, CuO, and BiOCl–CuO heterostructures presented a type-IV behavior with H3 hysteresis loops (Figure S1), which are characteristic of mesoporous materials with slit-like pores formed by aggregated plate-like structures [24]. The morphological, elemental, structural, and surface analyses confirmed the successful synthesis of the BiOCl–CuO heterostructures. CuO nanoparticles were effectively incorporated onto the BiOCl surface while preserving the crystalline framework, with optimal dispersion achieved at intermediate loadings. However, excessive CuO content promoted agglomeration, structural heterogeneity, and partial pore blockage, which might adversely affect photocatalytic performance.

The FTIR spectroscopy bands (Figure 3; Table S1) provided further structural insights. The band at 1080 cm^{-1} was attributed to the Bi-Cl stretching vibrations [27], while the band at 1384 cm^{-1} was ascribed to symmetric and asymmetric Bi-Cl modes [28], confirming the Bi-Cl bond formation within the crystal lattice. It should be noted that the absence of major spectral shifts in the FTIR profiles after CuO incorporation is consistent with the formation of a physical heterojunction rather than a new chemically bonded phase. In this system, CuO is mainly deposited on the BiOCl surface and interacts through interfacial contact and electronic coupling instead of forming new Bi-O-Cu covalent bonds. Therefore, the dominant Bi-Cl vibrational framework remains preserved, while subtle surface-related features reflect CuO incorporation and residual surface species. Additional vibrational features associated with organic functional groups were observed at higher CuO loadings. The band at 870 cm^{-1} was attributed to C-H bending vibrations, being particularly pronounced in the BiOCl-CuO_{10%} sample, weak in BiOCl-CuO_{3.4%}, and absent in BiOCl-CuO_{0.6%}. A weak absorption band at approximately 2925 cm^{-1} , corresponding to C-H stretching vibrations, was also detected exclusively for BiOCl-CuO_{10%}. Furthermore, the band near 1280 cm^{-1} was assigned to C-O stretching vibrations, indicating the presence of residual alkyl or ester-type species, likely originating from ethylene glycol used during the solvothermal synthesis process [29]. The presence of these organic-related bands at higher CuO loadings suggested partial retention or surface entrapment of organic residues, which has been previously reported for BiOX-based heterostructures synthesized under similar conditions [15,29]. Such residual species may negatively influence photocatalytic performance by blocking active sites, modifying surface wettability, and hindering interfacial charge transfer processes [30]. It is important to note that the washing procedure, based on alternating cycles of DIW and ethanol, was identical for all samples. The absence of organic-related vibrational bands in BiOCl-CuO_{0.6%} indicated that the washing protocol was effective at low CuO loading. Therefore, the higher organic retention observed at elevated CuO contents was mainly attributed to morphological heterogeneity and nonuniform CuO surface coverage rather than insufficient post-synthesis purification [27].

The band located at approximately 1633 cm^{-1} was associated with O-H bending vibrations of physically adsorbed water molecules, while the broad absorption centered near 3400 cm^{-1} was ascribed to O-H stretching modes, indicating atmospheric moisture adsorption on the material surface. Lastly, the appearance of a Cu-O stretching vibration at approximately 609 cm^{-1} in the BiOCl-CuO composites, which is absent in pristine BiOCl, provided additional confirmation of successful CuO incorporation into the heterostructures [31].

The photocatalytic performance of the BiOCl-CuO heterostructures is in strong agreement with the trends observed in physicochemical and surface characterizations. At low CuO loading, the incorporation of CuO promoted improved dispersion of BiOCl microspheres and moderated enhancement of the accessible surface area, which are both favorable for photocatalytic reactions. An increased effective surface area provides a higher density of active sites, thereby facilitating reactant adsorption and accelerating photodegradation kinetics [26,32,33]. In contrast, excessive CuO incorporation leads to heterogeneous catalyst distribution, partial surface coverage, agglomeration of isolated CuO domains, and retention of residual synthesis solvent, all of which indicate incomplete heterostructure formation. These structural and surface irregularities limit photon absorption, reduce interfacial charge transfer efficiency, and block catalytically active sites, ultimately resulting in inferior photocatalytic performance.

Based on these observations, subsequent experiments were designed to focus exclusively on photocatalytic degradation under irradiation, excluding the contribution of dark adsorption, in order to accurately evaluate the intrinsic photocatalytic activity of the optimized heterostructures.

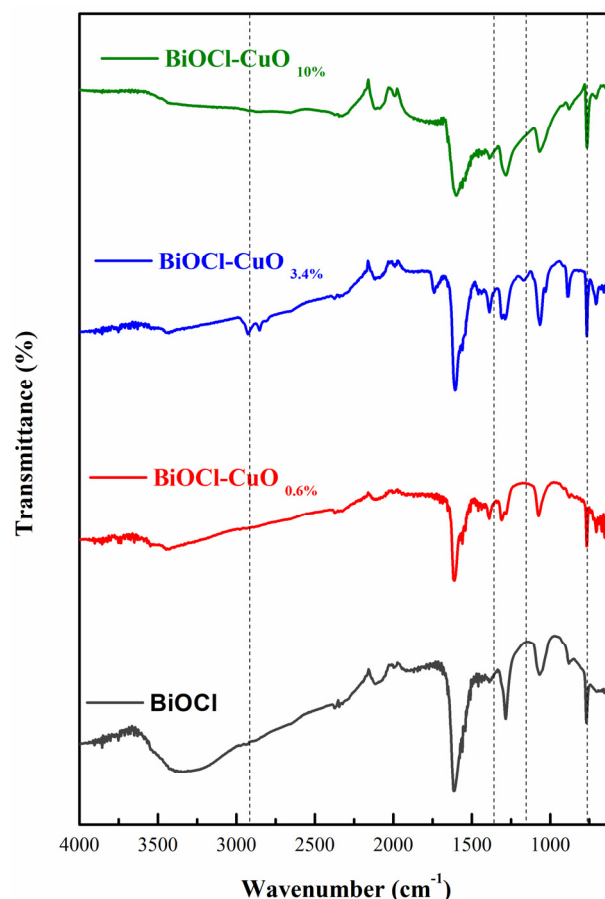


Figure 3. FTIR spectra of BiOCl and CuO-modified BiOCl heterostructures with varying CuO contents.

2.3. Characterization of the Active Photocatalyst

High-magnification SEM images of the BiOCl-CuO_{0.6%} heterostructure (Figure 4) revealed that the microspheres were composed of regularly arranged BiOCl nanosheets that were interconnected to form a hierarchical spherical architecture. XRD patterns of BiOCl (JCPDS No. 01-083-7690), CuO (JCPDS No. 01-076-7800), and BiOCl-CuO_{0.6%} (Figure 5) confirmed the coexistence of both crystalline phases. For pristine BiOCl, characteristic diffraction peaks were observed at 2θ values of 11.8° , 25.8° , 32.6° , and 46.8° , whereas CuO exhibited a prominent reflection at $2\theta = 38.7^\circ$. The BiOCl-CuO_{0.6%} sample displayed sharper and more intense BiOCl diffraction peaks compared with pristine BiOCl, indicating the successful incorporation of CuO nanoparticles without inducing significant structural distortion of the BiOCl lattice. These results confirmed the formation of the BiOCl-CuO heterostructure while preserving the intrinsic crystallinity of BiOCl.

XPS analysis was carried out to further verify the elemental composition and oxidation states of the BiOCl-CuO_{0.6%} material (Figure 6). Survey spectra confirmed the presence of Bi, O, Cl, and Cu, with corresponding signals observed in the Bi 4f, O 1s, Cl 2p, and Cu 2p regions. High-resolution spectra showed a well-defined Bi 4f doublet at approximately 159 eV ($4f_{7/2}$) and 164 eV ($4f_{5/2}$), which is characteristic of Bi³⁺ species in BiOCl (Figure 6a). The Cl 2p_{3/2} (~198 eV) and Cl 2p_{1/2} (~200 eV) peaks were consistent with Cl[−] ions in the BiOCl lattice (Figure 6b). In the O 1s spectrum, the signal at ~530.1 eV was assigned to lattice oxygen in BiOCl, whereas the peak at ~529 eV corresponded to oxygen species associated with the CuO phase (Figure 6c). The Cu 2p_{3/2} peak located at ~933 eV, together with the characteristic satellite features in the 940–945 eV range, confirmed the occurrence of Cu²⁺ species (Figure 6d). Slight shifts in binding energies, particularly in the Cu 2p region, suggested electronic interactions and possible charge transfer between BiOCl and CuO,

supporting the formation of a heterojunction interface between the two semiconductors [34–36]. Similar binding energy shifts observed in the Bi 4f, Cu 2p, and O 1s spectra have been commonly associated with interfacial electronic redistribution in semiconductor heterostructures [34–36]. In the BiOCl–CuO system, these shifts were consistent with the formation of a *p–n* heterojunction, where intimate interfacial contact promoted energy-level alignment, generating an internal electric field that enhanced spatial separation of photogenerated charge carriers.

To assess the optical properties, diffuse reflectance spectra were recorded for BiOCl, CuO, and BiOCl–CuO_{0.6%} over the wavelength range of 200–750 nm. The optical band gap energy (E_g) was estimated from the Tauc plots derived from the absorbance data using Equation (1).

$$(\propto h\nu)^{\frac{1}{2}} = A(h\nu - E_g) \quad (1)$$

where α represents the absorption coefficient, h is Planck's constant, ν is the light frequency, E_g is the band gap energy, and n corresponds to the semiconductor transition type [37].

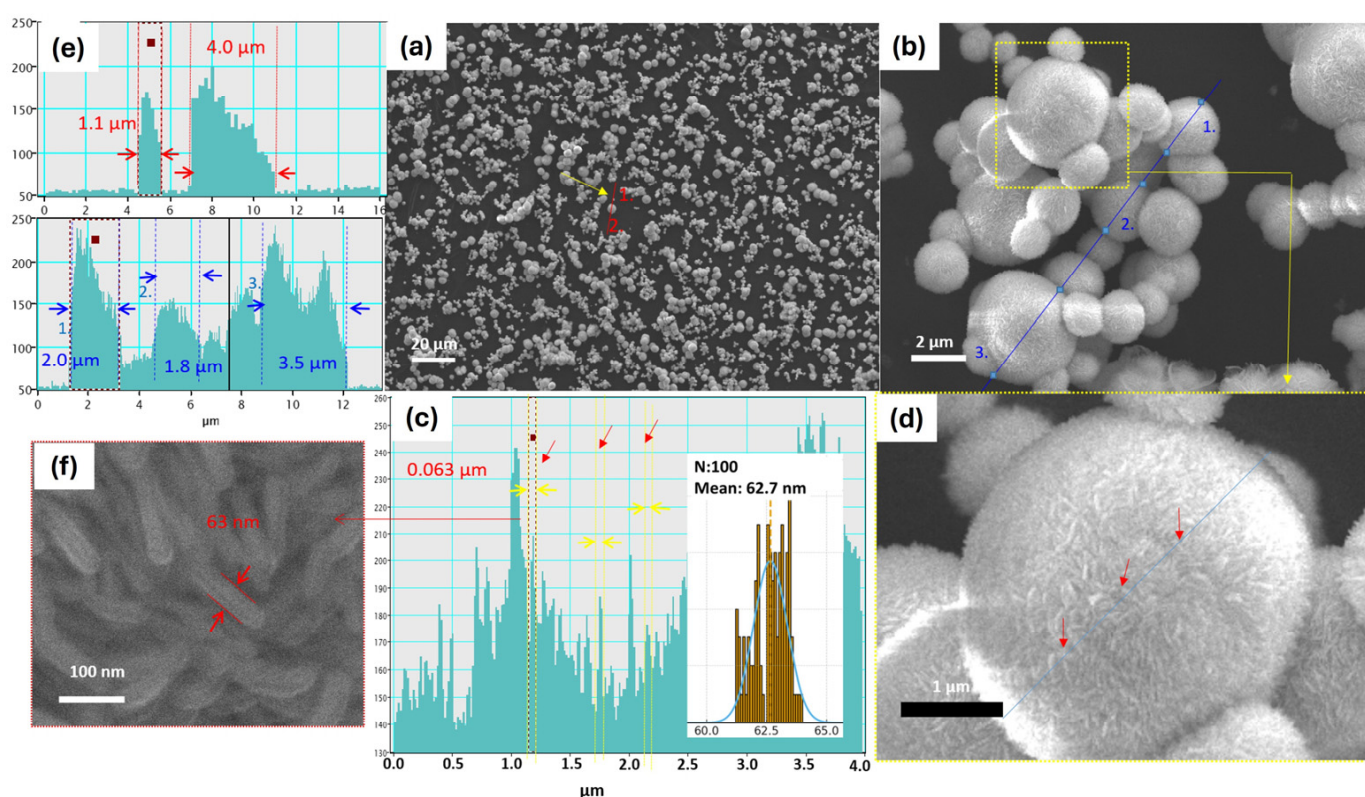


Figure 4. Enlarged SEM images of BiOCl–CuO (0.6%). (a) Low-magnification SEM image showing the overall morphology and homogeneous distribution of the microspheres. (b) Higher-magnification image displaying the hierarchical assembly of quasi-spherical particles composed of aggregated submicron units. (c) Particle size distribution histogram obtained from SEM measurements, indicating an average diameter of ~62.7 nm ($N = 100$). (d) Magnified view of a single microsphere highlighting the rough surface texture and radially arranged nanosheets. (e) Size distribution analysis at different magnifications, showing particle populations centered at approximately 1.1–4.0 μm and 1.8–3.5 μm , respectively. (f) High-resolution SEM image revealing the nanosheet substructure with an average thickness of ~63 nm.

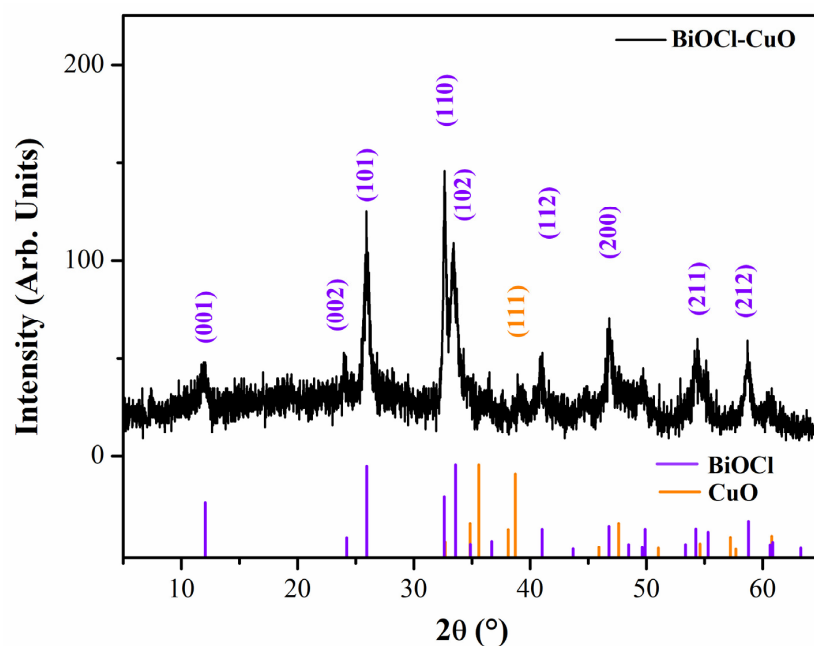


Figure 5. Diffraction patterns of BiOCl, CuO, and BiOCl-CuO_{0.6%}.

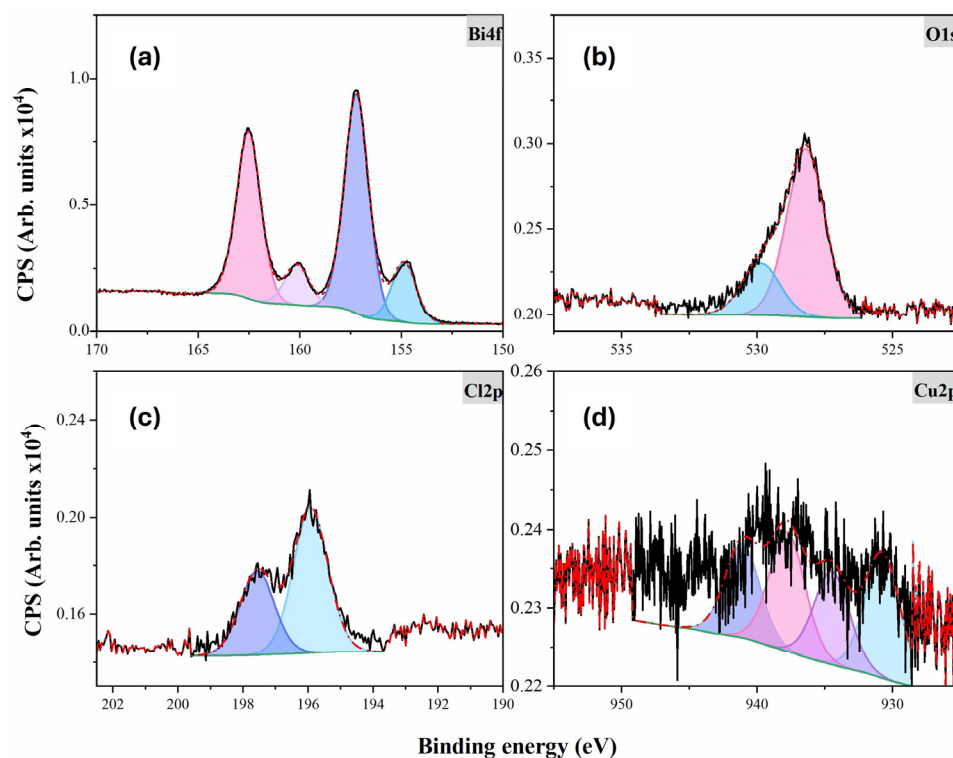


Figure 6. High-resolution XPS spectra of BiOCl-CuO_{0.6%}: (a) Bi 4f, (b) Cl 2p, (c) Cu 2p, and (d) O 1s.

As shown in Figure 7, pristine BiOCl exhibited an E_g value of 3.35 ± 0.01 eV, which is consistent with the typical behavior of wide-bandgap semiconductors [38]. After CuO incorporation, the BiOCl-CuO heterostructure displayed a slightly reduced E_g of 3.28 ± 0.01 eV, indicating enhanced visible-light absorption as a result of the formation of interfacial electronic states. In contrast, pristine CuO exhibited a significantly narrower E_g value of approximately 2.70 ± 0.01 eV, thereby extending the absorption edge of the heterostructure into the visible region [39]. This band alignment promotes efficient charge separation, suppresses electron-hole recombination, and thus improves photocatalytic activity under solar irradiation.

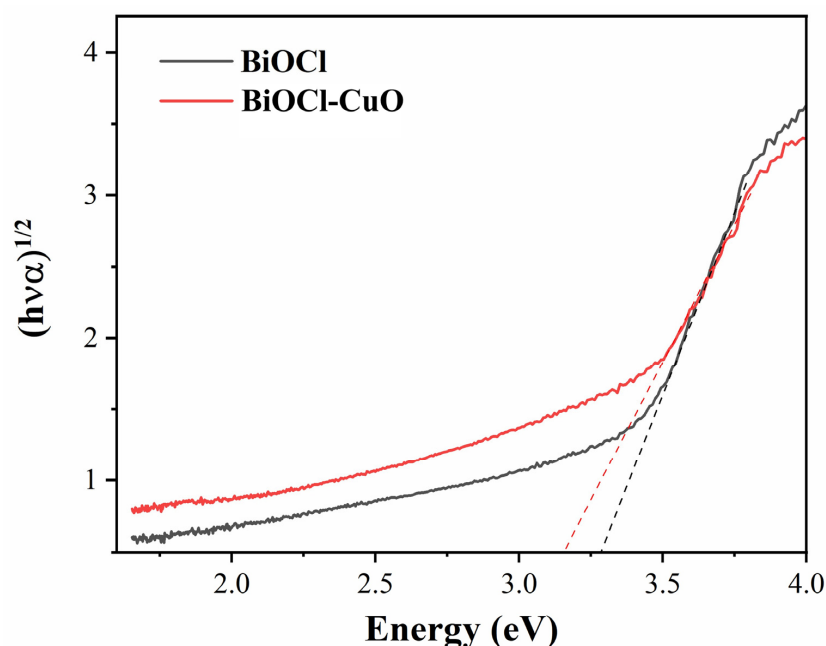


Figure 7. Determination of bandgap energy of BiOCl and BiOCl–CuO_{0.6%} using the Tauc approach.

To further clarify the electronic structure, the valence band (E_{VB}) and conduction band (E_{CB}) edge potentials of BiOCl and CuO were estimated by using the absolute electronegativity values (X), a free-electron energy (E_e) of 4.5 eV, and the experimentally determined E_g values. As summarized in Table 3, BiOCl exhibited E_{VB} and E_{CB} values of 3.54 eV and 0.19 eV, respectively, whereas CuO showed corresponding values of 2.66 eV and -0.04 eV, referenced to the normal hydrogen electrode [40].

Table 3. E_{VB} and E_{CB} values of BiOCl and CuO.

Semiconductor	E_g (eV)	X (eV)	E_{VB} Value (eV)	E_{CB} Value (eV)
BiOCl	3.35	6.36	3.54	0.19
CuO	2.70	5.81	2.66	-0.04

The estimated band alignment suggests the formation of a type-II heterojunction between BiOCl and CuO. In this configuration, photogenerated electrons in the conduction band of CuO (-0.04 eV vs. NHE) are transferred to the conduction band of BiOCl (0.19 eV vs. NHE), while photogenerated holes migrate from the valence band of BiOCl (3.54 eV vs. NHE) to the valence band of CuO (2.66 eV vs. NHE), as illustrated in Figure 8. This directional charge migration is driven by the internal electric field formed at the p – n junction interface and promotes spatial separation of photogenerated carriers, thereby suppressing recombination and enhancing photocatalytic performance.

The band edge positions further indicate that oxidative pathways are thermodynamically favored in the BiOCl–CuO system. Specifically, the highly positive valence band potentials of both semiconductors are adequate to promote the oxidation of surface hydroxyl groups or water molecules to generate hydroxyl radicals. This prediction is consistent with scavenger experiments, which identified $\bullet\text{OH}$ as the dominant reactive species. Conversely, the relatively weak reduction potential of the conduction bands limits the one-electron reduction in O_2 to $\bullet\text{O}_2^-$ radicals, explaining their secondary contribution under the studied conditions.

Although the observed photocatalytic behavior and band alignment are consistent with a type-II charge-transfer mechanism, alternative Z-scheme or S-scheme pathways cannot be completely excluded without direct spectroscopic evidence. However, in the absence of experimental signatures, such as preserved strong reduction ability or enhanced superoxide generation, the present results support a type-II-dominated charge separation mechanism for the BiOCl-CuO heterostructure under visible-light irradiation. Further in situ photoelectrochemical and spectroscopic (EPR) studies would be required to conclusively distinguish between these mechanisms [41,42].

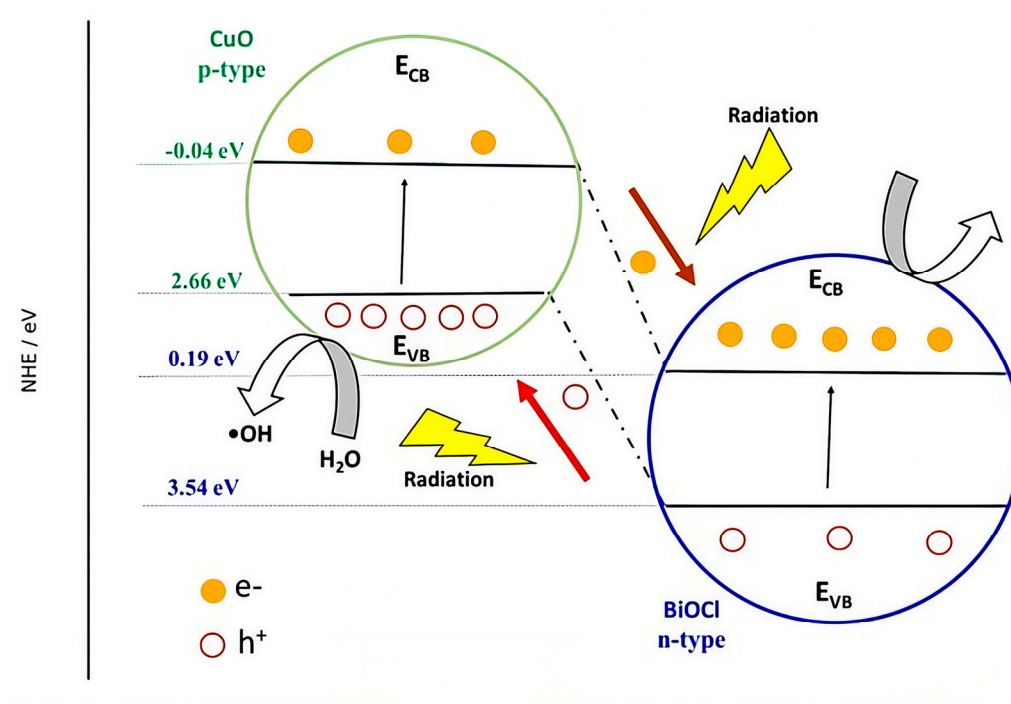


Figure 8. Proposed charge transfer mechanism using BiOCl-CuO.

2.4. Optimization of Experimental Conditions Using the Active Heterostructure

BiOCl-CuO_{0.6%} was selected for further optimization of MO degradation using a central composite design (CCD) generated with MODDE 13. Experimental conditions for each run are summarized in Table 4. This statistical approach has been widely applied to identify optimal operational parameters, such as solution pH and catalyst dosage, in HP systems [43–46]. The degradation kinetics were modeled using a pseudo-first order rate equation, applying multiple linear regression for parameter estimation [47,48].

The CCD results (Table 4) indicated that the highest degradation efficiencies were obtained under mildly acidic conditions. This behavior is attributed to the increased H⁺ concentration, which alters the surface charge of the photocatalyst and enhances electrostatic interactions with negatively charged dye molecules. In addition, an acidic environment promotes the generation of •OH radicals [49] via the reaction of photogenerated h⁺ with water molecules on the catalyst surface [50].

Catalyst dosage was also identified as a key parameter influencing MO degradation. Increasing the photocatalyst concentration up to 0.8 g L^{−1} improved degradation efficiency due to the higher availability of active sites for light absorption. This effect enhances charge-carrier generation and subsequent radical formation [30]. However, beyond an optimal dosage, excess catalyst diminished light penetration through shielding effects, ultimately reducing performance.

Table 4. Comparative data of theoretical and experimental MO photocatalytic degradation (%) measured via HPLC after 60 min of visible-light irradiation.

Experiment	pH	Catalyst Loading g/L	MO Degradation % Experimental Values	MO Degradation % Predicted Values
1	4	0.2	15.4	13.4
2	8	0.2	12.6	15.6
3	4	0.8	46.9	48.6
4	8	0.8	15.5	20.1
5	3.2	0.5	20.4	20.2
6	8.8	0.5	17.9	13.4
7	6	0.08	6.2	4.9
8	6	0.9	48.2	44.3
9	6	0.5	39.5	36.3
10	6	0.5	32.9	36.3
11	6	0.5	36.2	36.3

Analysis of variance results obtained from the CCD confirmed the robustness of the developed statistical model. A high correlation coefficient (R^2) value of approximately 0.954 and an adjusted R^2 of approximately 0.894 indicated a strong agreement between experimental and predicted values. In addition, the predictive relevance (Q^2) value of 0.641 exceeded the commonly accepted threshold ($Q^2 \geq 0.5$), confirming satisfactory predictive capability of the model. Based on these statistical results, a second-order polynomial equation (Equation (2)) was derived to describe the relationship between MO degradation efficiency and the independent variables, namely pH and catalyst concentration. According to the optimization output, the maximum degradation efficiency was achieved at pH 4 and a catalyst dosage of 0.8 g L⁻¹ within the evaluated experimental domain.

$$Y_{(pH,Con)} = 36.21(\pm 7.98) - 2.49(\pm 5.64) \times pH + 13.95(\pm 5.64) \times C - 9.77(\pm 5.99) \times pH^2 - 5.77(\pm 5.99) \times C^2 - 11.62(\pm 8.93) \times pH \times C \quad (2)$$

Equation (2) describes the combined influence of solution pH and catalyst loading on MO degradation using the BiOCl-CuO_{0.6%} material. The corresponding regression coefficients and model fit quality are illustrated in Figure 9a. The positive linear coefficient associated with catalyst concentration indicated that increasing photocatalyst dosage initially enhanced degradation efficiency. However, the negative quadratic term suggests the presence of an optimal catalyst loading, beyond which performance declines, in agreement with previous photocatalytic studies [51,52]. In contrast, all pH-related coefficients resulted negative, indicating that lower pH values favor MO degradation. Figure 9b presents the three-dimensional response surface plot, illustrating the combined effects of pH and catalyst dosage on degradation efficiency. The highlighted red region identifies the optimal operational domain, where mildly acidic conditions and moderate catalyst concentrations resulted in maximum photocatalytic performance.

According to the factorial statistical model, the optimal pH for efficient MO degradation using the BiOCl-CuO_{0.6%} material after 60 min of irradiation was approximately 4. At this pH, partial deprotonation of oxygen-containing functional groups in MO likely enhanced adsorption onto the photocatalyst surface. Considering that the experimentally determined isoelectric point of BiOCl-CuO_{0.6%} is 3.8, the catalyst surface remained slightly positively charged at pH 4, which promotes electrostatic attraction with the anionic dye species. This favorable interaction explains the high degradation rate observed under these conditions. At pH values below 4, the conversion yield decreased, likely due to electrostatic repulsion between protonated dye species and the positively charged catalyst surface. Conversely, under alkaline conditions, the catalyst surface became negatively charged,

leading to electrostatic repulsion with deprotonated MO molecules. This effect limited dye adsorption and reduced photocatalytic degradation efficiency [53,54]. It is important to note that the obtained model was validated by repeating the process three times under the optimal conditions determined, yielding a degradation rate of $47.73 \pm 3.3\%$ after 60 min of irradiation, which is consistent with the values predicted by the quadratic model.

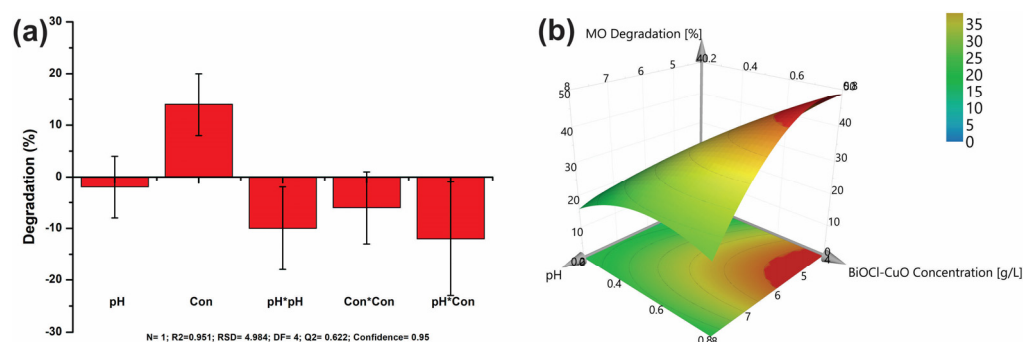


Figure 9. (a) Model coefficients and fit quality showing the effects of catalyst concentration and pH on degradation efficiency. Efficiency increases with catalyst dosage up to an optimum, then decreases, while lower pH values enhance degradation. (b) 3D response surface plot illustrating the combined influence of pH and catalyst dosage.

2.5. Kinetic Measurement and Mechanistic Approach

Photocatalytic degradation experiments were repeated under optimized conditions to investigate both kinetic behavior and degradation pathways. Kinetic profiles were obtained by HPLC, and degradation intermediates were identified using liquid chromatography coupled to tandem mass spectrometry (LC-MS/MS). Figure 10 presents the time-dependent degradation profile of MO at an initial concentration of 10 mg L^{-1} under optimal operating conditions. The appearance of additional chromatographic peaks during irradiation indicates that MO degradation proceeds through a stepwise mechanism involving the formation of transient intermediate species. The experimental data showed excellent agreement with a pseudo-first-order kinetic model, yielding a rate constant of 0.02 min^{-1} and a correlation coefficient of 0.98. It is worth noting that the photocatalytic experiments were performed at relatively low methyl orange concentrations (10 mg L^{-1}). Under these conditions, catalyst active sites and reactive oxygen species can be considered in excess relative to the pollutant, allowing the Langmuir–Hinshelwood expression to be simplified to a model based on the contaminant concentration. To verify the suitability of this model, the experimental data were also fitted using a pseudo-second-order kinetic expression. However, both models produced very similar correlation coefficients, with no significant improvement in fit quality for the second-order model (Table S2, Supporting Information).

To place the performance of the BiOCl-CuO catalyst in context, a qualitative comparison with representative high-performance photocatalysts reported in the recent literature was conducted (Table S3, Supporting Information). The comparison includes visible-light-driven heterojunction systems based on g- C_3N_4 , MOF-derived catalysts, and other oxide semiconductors. Although direct quantitative comparison among studies is limited by differences in experimental conditions, such as light intensity, catalyst loading, and pollutant concentration, the present BiOCl-CuO system exhibits competitive degradation efficiency considering its relatively low CuO content, simple synthesis route, and good operational stability. These features highlight its potential as a scalable and structurally simple alternative within the family of visible-light photocatalysts.

LC-MS/MS analysis of the initial solution ($t = 0 \text{ min}$) revealed a dominant molecular ion signal at $m/z = 304$, corresponding to MO under acidic conditions. After irradiation, the intensity of this parent ion decreased significantly and was accompanied by the emergence

of new fragment signals at $m/z = 290$, 276, and 255. These spectral features indicate progressive molecular breakdown through peripheral bond cleavage, leading to the formation of two major degradation pathways (Figure 11). The first pathway started with demethylation (left pathway), whereas the second pathway is associated with desulfonation (right pathway). The latter transformation is expected to release HSO_4^- into the aqueous phase [55], which is consistent with the slight decrease in solution pH observed during photocatalytic treatment and the progressive discoloration of the reaction medium. Based on relative signal intensities and temporal evolution, the ions detected at $m/z = 276$ and 255 were assigned to the dominant intermediate species formed during MO degradation. These degradation routes are consistent with the mechanisms previously reported by Watchaure et al. [55]. Furthermore, cleavage of the azo bond is commonly observed during advanced oxidation processes, thereby promoting aromatic ring opening and further oxidation. At advanced reaction stages, this degradation sequence may ultimately lead to near-complete mineralization, yielding CO_2 and H_2O , along with minor amounts of HSO_4^- and NO_3^- as secondary products.

To identify the dominant reactive oxygen species (ROS) involved in MO degradation, scavenger experiments were conducted using selective quenching agents. Fixed scavenger concentrations were selected based on values widely reported in the literature to ensure a sufficient molar excess relative to the target reactive species and, therefore, effective inhibition of the corresponding reaction pathway [56–58]. These experiments were designed to qualitatively identify the dominant ROS rather than to establish quantitative dose–response relationships. To avoid competitive or synergistic effects, each experiment was performed with a single scavenger, a strategy commonly used for reliable ROS identification in heterogeneous photocatalytic systems [59].

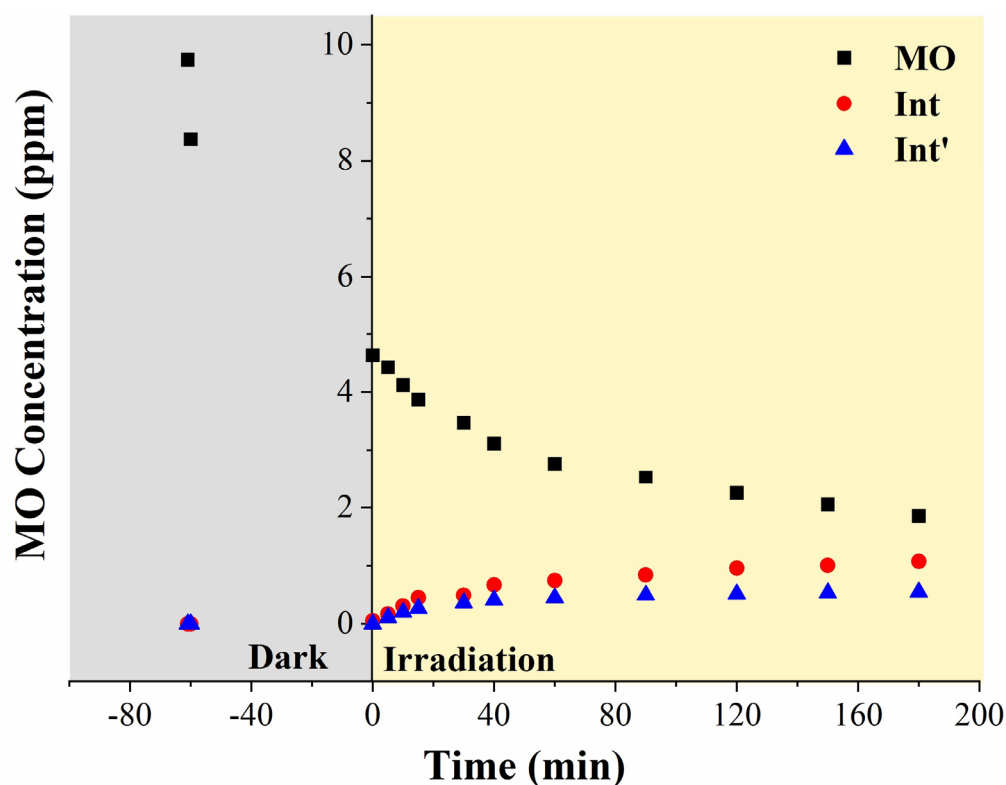


Figure 10. Evolution of MO concentration during its photocatalytic degradation by $\text{BiOCl-CuO}_{0.6\%}$, pH = 4, and 0.8 g L^{-1} .

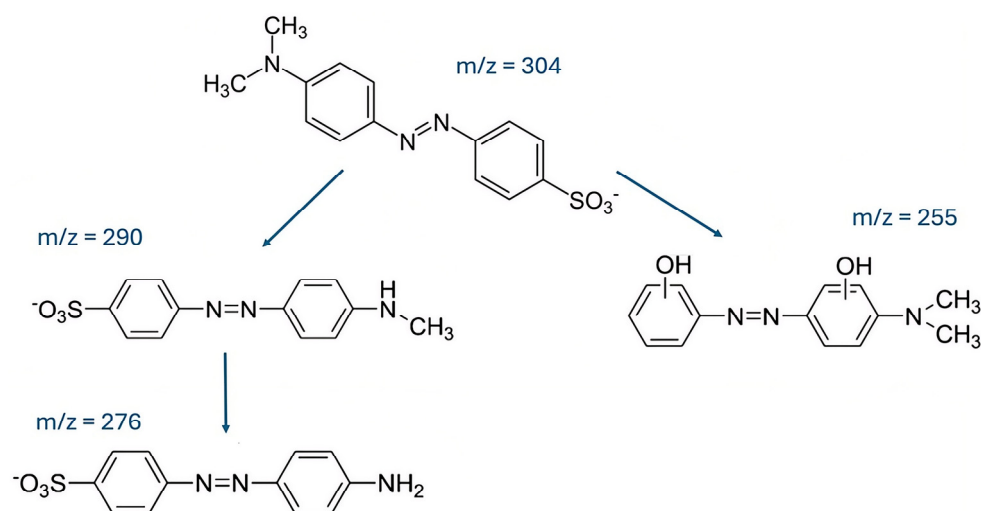


Figure 11. First stages of the proposed degradation mechanism of MO inferred from the mass-fragmentation pattern of mass spectra.

Kinetic results obtained under different scavenging conditions are presented in Figure 12. In the absence of scavengers, the highest apparent rate constant ($\sim 0.022 \text{ min}^{-1}$) was obtained, confirming the strong photocatalytic activity of the BiOCl-CuO_{0.6%} material. The addition of isopropanol (IPA), a selective $\bullet\text{OH}$ scavenger, resulted in a drastic decrease in degradation rate ($k < 0.002 \text{ min}^{-1}$), indicating the dominant role of hydroxyl radicals in the oxidation process [39,60]. In contrast, oxalic acid (OA), used as a photo-hole (h^+) scavenger, produced a moderate decrease in activity ($\sim 0.013 \text{ min}^{-1}$), indicating a secondary contribution of photo-generated holes [19]. The presence of *p*-benzoquinone (BQ), a superoxide radical ($\bullet\text{O}_2^-$) scavenger, partially inhibited the reaction ($\sim 0.0055 \text{ min}^{-1}$), suggesting that $\bullet\text{O}_2^-$ species are involved but play a less dominant role [61]. These results demonstrated that the photocatalytic degradation mechanism of the BiOCl-CuO heterostructures was primarily governed by $\bullet\text{OH}$ radicals, followed by photo-generated holes and, to a lesser extent, superoxide radicals. This hierarchy of reactive species reflects efficient interfacial charge separation within the heterojunction structure, enabling multichannel ROS generation and enhancing overall pollutant removal efficiency [62].

Lastly, the stability of the optimized BiOCl-CuO_{0.6%} heterostructure was evaluated by conducting three consecutive photocatalytic degradation cycles under identical operating conditions. After each cycle, the catalyst was recovered, washed, and reused. The results indicate that the MO degradation efficiency remained close to 50% after 60 min of irradiation across all cycles, confirming the good short-term stability of the photocatalytic system. Only a slight decrease in activity was observed upon reuse. The corresponding apparent pseudo-first-order rate constants were 0.010, 0.0098, and 0.0091 min^{-1} for the first, second, and third cycles, respectively, demonstrating minimal kinetic decay and good operational stability of the heterostructure.

It should be noted that reliable long-term stability assessment requires prior optimization of solution pH and heterojunction composition, as these parameters directly influence interfacial robustness and structural integrity [19,63]. While the present reuse experiments confirm short-term operational stability, future work will focus on extended cycling tests and complementary analyses to evaluate potential CuO leaching, surface deactivation, and structural modifications induced by prolonged operation.

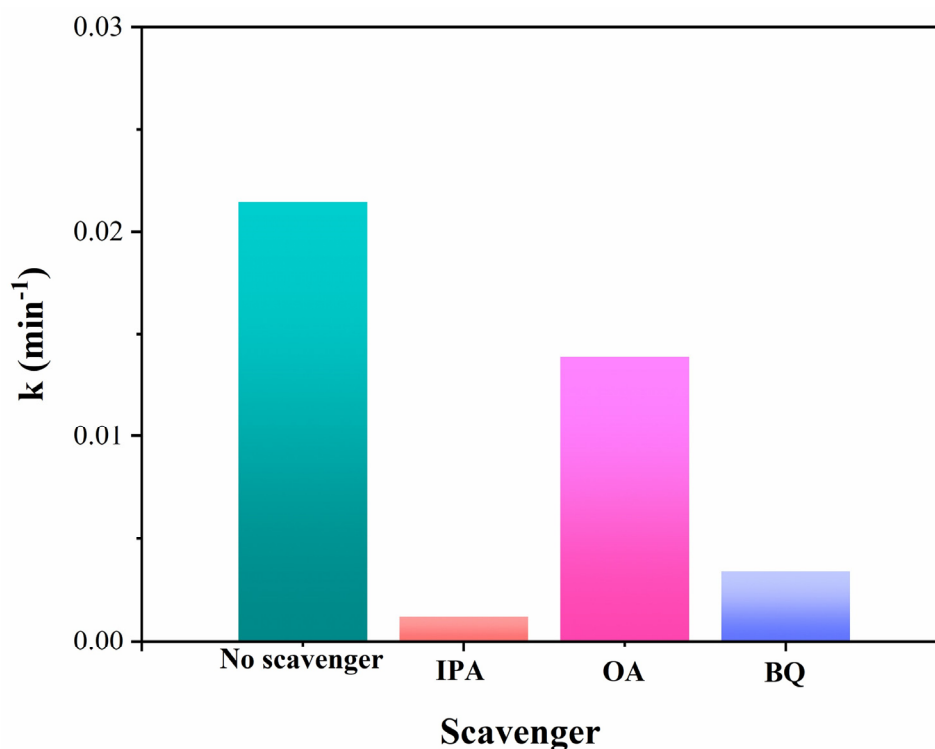


Figure 12. Photocatalytic efficiency on MO degradation by BiOCl-CuO_{0.6%} without and with different scavengers.

3. Materials and Methods

All chemical reagents used in this study were supplied by Merck (Darmstadt, Germany) and were of analytical grade. Copper(II) nitrate trihydrate (Cu(NO₃)₂·3H₂O), sodium hydroxide (NaOH), bismuth nitrate pentahydrate (Bi(NO₃)₃·5H₂O), potassium chloride (KCl), ethylene glycol, and absolute ethanol were used as precursor materials and solvents for photocatalyst synthesis. Deionized water (DIW) was used throughout all synthesis, washing, and purification procedures.

3.1. Synthesis of Photocatalyst Materials

3.1.1. CuO

CuO nanoparticles were synthesized following a previously reported method [17]. Briefly, 1 g of Cu(NO₃)₂·3H₂O was dissolved in 400 mL of DIW in a flat-bottom flask. The solution was heated under continuous stirring. When the temperature reached 328 K, 0.4 g of NaOH was added, leading to the formation of a black precipitate. The suspension was then maintained at 343 K for 15 min and subsequently allowed to cool to room temperature. The precipitate was washed with DIW and ethanol in eight alternating cycles. Solid recovery was performed by centrifugation at 4000 rpm for 5 min using a DLAB centrifuge (Beijing, China). The collected material was dried in a vacuum oven (Vacucell 55 Eco Line oven, BMT, Prague, Czech Republic) at 333 K for 1 h.

3.1.2. BiOCl

BiOCl was synthesized using the reported method of Mera et al. [15]. First, 0.3 g of Bi(NO₃)₃·5H₂O was dissolved in 40 mL of ethylene glycol under constant stirring. In parallel, 0.3 g of KCl was dissolved in 40 mL of ethylene glycol to prepare a homogeneous solution. The KCl solution was then added dropwise to the bismuth precursor solution under gentle stirring. The resulting mixture was transferred to a 100 mL Teflon-lined stainless-steel reactor (Parr Instrument Company, Moline, IL, USA) and heated at 428 K

for 18 h in an oven (Quimis, Valparaíso, Chile). After cooling to room temperature, the suspension was decanted and filtered to remove ethylene glycol. The solid product was washed with DIW and ethanol in four alternating cycles. The purified powder was dried at 333 K for 1 h in a vacuum oven and subsequently stored in an amber flask wrapped with aluminum foil to minimize light exposure.

3.1.3. BiOCl-CuO Heterostructures

The BiOCl-CuO heterostructure was synthesized by incorporating CuO nanoparticles during the solvothermal synthesis of BiOCl, following the reported procedures by Song et al. [17] and Li et al. [16]. $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ (0.3 g) was dissolved in 40 mL of ethylene glycol under vigorous stirring. In parallel, the desired amount of CuO was dispersed in 10 mL of ethylene glycol, and 0.3 g of KCl was dissolved in 40 mL of ethylene glycol. Both the CuO suspension and the KCl solution were added dropwise to the bismuth precursor solution while stirring was maintained. The resulting mixture was transferred to a Teflon-lined stainless-steel reactor and heated at 440.5 K for 18 h. Washing, solid recovery, and drying procedures were carried out following the same protocol used for BiOCl synthesis.

The reproducibility of the solvothermal synthesis was evaluated by carrying out three independent preparations for each material (BiOCl, CuO, and BiOCl-CuO) under identical experimental conditions. No statistically significant variation in photocatalytic performance was observed among replicates, confirming the high reproducibility of the solvothermal protocol.

High gravimetric yields were consistently obtained, typically ranging from 90 to 95%. These values were mainly attributed to high precursor conversion and minimal material loss during washing and drying steps. The yields obtained are consistent with those reported for BiOCl-based materials and BiOX heterostructures synthesized using similar solvothermal routes [15,27].

3.2. Material Characterization

The morphology of BiOCl, CuO, and BiOCl-CuO heterostructures containing 0.6, 3.4, and 10% CuO was examined using scanning electron microscopy (SEM) with a SU-3500 microscope (Hitachi, Hitachinaka, Japan). Energy-dispersive X-ray spectroscopy (EDS, Hitachi, Hitachinaka, Japan) was used to confirm the presence of CuO nanoparticles on the BiOCl surface. Measurements were performed at an accelerating voltage of 15 kV under a vacuum pressure of 60 Pa. High-resolution field-emission SEM images of the BiOCl-CuO_{0.6%} sample were acquired using a JSM-7800F microscope (JEOL Ltd., Tokyo, Japan). Phase composition and crystallinity were analyzed by X-ray diffraction (XRD) using a Bruker D4 diffractometer (Bruker AXS GmbH, Ettlingen, Germany) equipped with a Lynxeye detector. Measurements were conducted with a Cu K α radiation and a Ni K β filter over a 2θ range of 3 to 70° using a step size of 0.020°. Diffraction patterns were indexed using ICDD cards 01-083-7690 (BiOCl) and 01-076-7800 (CuO).

X-ray photoelectron spectroscopy (XPS, Physical Electronics Inc., Chanhassen, MN, USA) measurements were carried out using a Physical Electronics VersaProbe II system with monochromatic Al K α radiation. Fourier transform infrared (FTIR) spectra (Agilent Technologies, Santa Clara, CA, USA) were recorded using an Agilent Cary 630 spectrometer in transmission mode over the range of 5000–220 cm^{-1} , with a resolution of 4 cm^{-1} and 32 scans. Specific surface area was determined from nitrogen adsorption-desorption isotherms at −196 °C using the Brunauer-Emmett-Teller (BET) method. Samples were degassed at 150 °C for 16 h prior to analysis. Pore size distribution was calculated using the Barrett-Joyner-Halenda method, and pore volume was obtained from distribution curves using a NOVA 1000e analyzer (QuantaChrome, Boynton Beach, FL, USA). The isoelectric point was determined by dynamic light scattering, using a Zetasizer Nano ZS

(Malvern Instruments, Malvern, UK). Optical properties, including band gap energy, were evaluated by diffuse reflectance UV–Vis spectroscopy using a Thermo Scientific Evolution 220 spectrophotometer (Thermo Fisher Scientific (Waltham, MA, USA)) equipped with an integrating sphere.

3.3. Photocatalysis Tests

The photocatalytic performance of the base materials (CuO and BiOCl) and BiOCl–CuO heterostructures was evaluated in batch mode using methyl orange (MO) as a model pollutant under visible-light irradiation. Experiments were carried out in a glass reactor equipped with a water-cooling jacket to keep a constant temperature of 293 K. The reactor was placed inside a closed black box to eliminate interference from external light sources.

A Xe lamp (VIPHID, 6000 K, 12 V, 35 W) was used as the light source and positioned above the reactor at a fixed distance of 5 cm from the solution surface. The lamp was isolated from the reaction medium using a cylindrical Pyrex glass jacket, which allows transmission of UV-visible radiation while protecting the lamp from direct contact with the suspension. The emission spectrum of the xenon lamp spans approximately 380–900 nm, corresponding to simulated solar radiation with dominant intensity in the visible region [15,64]. The average irradiance measured at the reactor surface was 65 mW cm^{-2} . This irradiation configuration was maintained constant throughout all experiments to ensure reproducible photon flux and comparable operating conditions. Continuous magnetic stirring, together with the reactor geometry, ensured homogeneous light distribution within the suspension and minimized light-shielding effects during photocatalytic operation.

In a typical experiment, 0.1 g of the photocatalyst was dispersed in 250 mL of a 10 mg L^{-1} MO aqueous solution and stirred in the dark for 60 min to reach adsorption–desorption equilibrium. Afterward, irradiation was initiated, and aliquots were withdrawn at regular time intervals over a total reaction time of 240 min. The collected samples were filtered out using a $0.22 \text{ }\mu\text{m}$ hydrophilic polyvinylpyrrolidone membrane and subsequently analyzed by high-performance liquid chromatography (HPLC, Agilent Technologies, Santa Clara, CA, USA).

HPLC measurements were carried out using an Agilent 1260 Infinity II system equipped with a UV-Vis diode array detector and a C-18 column operating under isocratic conditions. The mobile phase consisted of 60% methanol and 40% ammonium acetate buffer (pH = 6.6) at a flow rate of 0.70 mL min^{-1} . MO was detected at 464 nm, with a total runtime of 7 min. The injection volume was set to $10 \text{ }\mu\text{L}$. Photocatalytic degradation efficiency was calculated using Equation (3).

$$\text{Deg\%} = \frac{C_0 - C_t}{C_0} \times 100 \quad (3)$$

where C_0 corresponds to the initial MO concentration after adsorption–desorption equilibrium, and C_t represents the concentration at a given irradiation time as determined by HPLC. To identify the optimal CuO loading for maximum MO degradation, BiOCl–CuO heterostructures with CuO contents ranging from 0 to 10.0% were synthesized and systematically evaluated.

Optimization of Operating Conditions

The BiOCl–CuO material exhibiting the highest photocatalytic activity toward MO degradation was first identified and subsequently selected for process optimization studies. This catalyst (BiOCl–CuO_{0.6%}) was used to evaluate the effects of catalyst loading and pH on photocatalytic performance. MO aqueous solutions were prepared in DIW at varying catalyst concentrations, while pH was adjusted using 0.1 mol L^{-1} hydrochloric acid and

0.1 mol L^{−1} NaOH solutions. Solution pH was monitored using a Hanna HI2002 pH meter (Hanna, Santiago, Chile).

A central composite design (CCD) was followed to systematically investigate the selected operational parameters. Catalyst loadings ranging from 0.1 to 0.8 g L^{−1} and pH values between 4 and 9 were evaluated. Experimental runs were generated using Modde Pro 13 software (Sartorius, Göttingen, Germany), and the corresponding conditions are summarized in Table 5.

Table 5. CCD of experiments obtained using MODDE 13 software.

Sample Number	pH	BiOCl–CuO0.6% Concentration (g L ^{−1})
1	4	0.2
2	8	0.2
3	4	0.8
4	8	0.8
5	3.2	0.5
6	8.8	0.5
7	6	0.08
8	6	0.9
9	6	0.5
10	6	0.5
11	6	0.5

Response surface methodology (RSM) was applied using a two-factor experimental design, where pH and catalyst loading were selected due to their direct influence on catalyst-contaminant interactions, surface active-site availability, and optical efficiency in slurry photocatalytic systems. Potential light-shielding effects at high catalyst dosages were also considered. To isolate the influence of these variables and build a robust statistical model, all remaining experimental parameters, including initial MO concentration, reaction temperature, solution volume, stirring conditions, irradiation time, reactor geometry, and irradiance measured at the reactor plane, were kept constant throughout the design runs.

Accordingly, the developed model is valid and predictive within the evaluated experimental domain defined in Table 5 and under the controlled conditions described herein. Extrapolation of the model to different operational ranges, such as higher initial MO concentrations or different temperatures, should be approached with caution. These variables may alter kinetic regimes, adsorption contributions, and photon absorption efficiency, thereby affecting the overall system response [43].

3.4. Determination of the Photocatalytic Reaction Mechanism and Degradation Kinetics

To evaluate overall degradation performance, photocatalytic experiments were carried out under the optimized conditions described in Section 3.3. The kinetic behavior of MO was determined and fitted using a pseudo-first-order reaction model, as expressed by Equation (4).

$$-r_{\text{MO}} = k_1 C_{\text{MO}} \quad (4)$$

Furthermore, degradation intermediates were identified using high-performance liquid chromatography coupled to a triple quadrupole mass spectrometer (HPLC–MS/MS, Agilent Technologies, Santa Clara, CA, USA) [65]. Chromatographic separation was achieved using an Infinity 1200 Agilent Technologies system equipped with a Zorbax SB C18 column (150 mm × 4.6 mm, 5 µm particle size). The mobile phase consisted of a 70:30 (v/v) acetonitrile:0.1% formic acid mixture, delivered at 0.4 mL min^{−1} under isocratic conditions, with a total analysis time of 10 min. Ionization was performed by electrospray ionization, using N₂ as the drying gas at 300 °C and a flow rate of 11 L min^{−1}. The capillary voltage

was set to 4000 V, and the nebulizer pressure was maintained at 15 psi. Mass spectrometric analysis was performed using an Agilent Technologies 6420 system.

The most stable degradation byproducts were investigated through irradiation experiments conducted under optimized conditions. Mass spectra of the initial sample ($t = 0$ min) were first recorded in SCAN mode to establish the fragmentation profile of the parent compound. The characteristic MO signal at m/z 328 was monitored. After irradiation ($t = 180$ min), additional SCAN spectra were acquired to identify new signals potentially associated with degradation byproducts. To further confirm intermediate species, single ion monitoring mode was applied to both initial and irradiated samples, focusing on the target m/z signals associated with degradation products.

To elucidate the photocatalytic reaction mechanism, quenching experiments were carried out using selective radical scavengers. A 10 mg L^{-1} MO solution was prepared, and a total volume of 1 L was divided into four 250 mL aliquots. Each aliquot was treated with a specific scavenger: 136 μL of isopropanol (IPA) as a hydroxyl radical ($\bullet\text{OH}$) scavenger, oxalic acid (OA) as a hole (h^+) scavenger at a final concentration of 20 mmol L^{-1} , and *p*-benzoquinone (BQ) as a superoxide radical ($\bullet\text{O}_2^-$) scavenger at a final concentration of 10 mmol L^{-1} . Kinetic profiles obtained in the presence of scavengers were compared with those from the control experiment using a pseudo-first-order kinetic model.

4. Conclusions

BiOCl-CuO heterostructures synthesized via a solvothermal route demonstrated high efficiency for methyl orange degradation, with photocatalytic performance primarily governed by CuO loading and interfacial dispersion. Moderate CuO content promoted intimate interfacial contact and uniform distribution of the active phase, whereas excessive loading resulted in uneven surface coverage and reduced effective surface area, which hindered charge transport and photocatalytic activity.

Photocatalytic operating conditions were optimized using response surface methodology based on a central composite design, covering catalyst concentrations from 0.1 to 0.8 g L^{-1} and pH values between 4 and 9. Under these conditions, the BiOCl-CuO0.6% heterostructure exhibited optimal performance. Degradation kinetics followed a pseudo-first-order model. Mass spectrometric analysis revealed transient degradation intermediates consistent with demethylation and desulfonation as initial transformation pathways, followed by progressive oxidative breakdown. Radical scavenging experiments identified hydroxyl radicals as the dominant reactive species, whereas superoxide radicals played a secondary role.

Overall, the results highlight that precise control of CuO dispersion and interfacial quality, rather than simply increasing CuO content, is a critical design parameter for achieving high photocatalytic efficiency in BiOCl-CuO systems. Future research should therefore focus on advanced interface engineering strategies, including controlled CuO deposition, post-synthesis treatments to minimize nanoparticle agglomeration, co-doping or ternary heterostructure configurations to extend light absorption and suppress charge recombination, and immobilization on high-surface-area supports to improve catalyst dispersion, adsorption capacity, and interfacial charge transport. This work represents the first comprehensive study integrating kinetic modeling, intermediate identification, and statistical optimization through response surface methodology for BiOCl-CuO heterostructures. The findings provide mechanistic insight and practical guidelines that support the rational design and potential large-scale application of BiOCl-CuO-based photocatalysts for environmental remediation.

Supplementary Materials: The following supporting information can be downloaded at <https://www.mdpi.com/article/10.3390/molecules31050754/s1>, Figure S1. Nitrogen adsorption–desorption isotherms at 77K for: □ CuO, ○ BiOCl, △ BiOCl–CuO_{0.6}, ◇ BiOCl–CuO_{3.4}, ▽ BiOCl–CuO₁₀. Filled symbols: adsorption; empty symbols: desorption data; Table S1. Wavelengths of vibration modes of functional groups found in the FTIR spectrum of synthesized materials; Figure S2. Jacketed Batch reactor for photocatalytic tests; Table S2. Coefficients of Determination for the modeling of the Methyl Orange degradation kinetic data; Table S3. Comparative photocatalytic performance of BiOCl–CuO and representative high-performance photo-catalysts reported in the literature [66–71].

Author Contributions: M.F.M.G., A.F.J., N.J.A. and A.C.M.: Developed the investigation, experimentation, and characterization of the physicochemical and morphological properties. J.C.D.-Á., A.S.-L. and J.U.-V.: carried out the characterization of the structural properties. M.F.M.G., A.F.J., N.J.A. and A.C.M.: wrote the original draft. M.F.M. and R.M.-R.: reviewed and edited the manuscript. All authors have read and agreed to the published version of the manuscript.

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Data Availability Statement: The authors confirm that the data supporting the findings of this study are available within the article. In addition, the datasets used and/or analyzed during the current study are available from the corresponding author on reasonable request.

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Conflicts of Interest: The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Abbreviations

The following abbreviations are used in this manuscript:

AOPs	Advanced Oxidation Processes
BET	Brunauer–Emmett–Teller
BJH	Barrett–Joyner–Halenda
BiOCl	Bismuth oxychloride
BiOX	Bismuth oxyhalide (X = Cl, Br, I)
BQ	<i>p</i> -Benzoquinone
C _B	Conduction Band
CCD	Central Composite Design
CuO	Copper(II) oxide
DIW	Deionized Water
D _p	Pore diameter
EDS	Energy Dispersive X-ray Spectroscopy
E _{CB}	Conduction band edge potential
E _g	Band gap energy
E _{VB}	Valence band edge potential
h ⁺	Photogenerated hole
HP	Heterogeneous Photocatalysis
IPA	Isopropanol
JCPDS	Joint Committee on Powder Diffraction Standards
MO	Methyl Orange
OA	Oxalic Acid
•OH	Hydroxyl radical

$\bullet\text{O}_2^-$	Superoxide radical
RSM	Response Surface Methodology
S_{BET}	Specific surface area determined by BET method
V_{B}	Valence Band
V_{p}	Pore volume

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