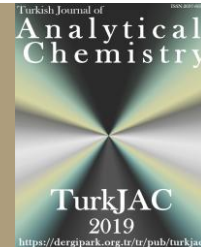




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Photocatalytic degradation of Reactive Orange 107 in wastewaters under UV irradiation using multiphase cobalt selenide (CoSe_x) nanocatalyst: Performance evaluation, kinetic assessment, and mechanistic insights

Murat Kıranşan^{1*} ¹ Gümüşhane University, Gümüşhane Vocational School, Department of Chemistry and Chemical Processing Technologies, 29100 Gümüşhane, Türkiye

Abstract

Dye contaminated wastewater remains an important environmental concern because conventional treatment processes often provide incomplete removal of persistent azo dyes, while the photocatalytic potential of multiphase cobalt selenides remains insufficiently explored. This study therefore aimed to develop and evaluate a newly synthesized multiphase cobalt selenide (CoSe_x) nanocatalyst for the photocatalytic degradation of Reactive Orange 107 (RO 107) in aqueous systems. The catalyst was characterized by XRD, FT-IR, SEM-EDX, HRTEM, N₂ adsorption-desorption and BJH analyses, and its performance was examined under different catalyst dosages, dye concentrations, pH values, irradiation sources, water matrices, and reuse cycles. The characterization results confirmed a highly crystalline and porous CoSe_x structure with well-defined morphology and homogeneous elemental distribution. Under optimized conditions of 1.0 g/L catalyst dosage, 25 mg/L RO 107, natural pH, and UV-C irradiation, 97.87% degradation was achieved within 120 min, while 5 mg/L RO 107 yielded 98.17% removal. The process followed pseudo-first-order kinetics, with k_{app} values of 0.0040–0.0417 min⁻¹ for catalyst dosage, 0.0043–0.0333 min⁻¹ for initial concentration, and 0.0049–0.0417 min⁻¹ for pH. UV-C outperformed UV-B and UV-A, and real water tests confirmed high activity despite matrix effects. After six cycles, efficiency decreased from 97.87% to 81.23%. Importantly, the material exhibited broad substrate applicability and retained substantial performance in chemically complex water matrices, supporting its potential environmental relevance. These results demonstrate the novelty, robustness, and practical applicability of multiphase CoSe_x as a reusable photocatalyst for advanced treatment of dye contaminated waters.

Keywords: Multiphase cobalt selenide (CoSe_x) nanocatalyst, RO 107 degradation, toxic dye, photocatalytic process, synergistic effect

1. Introduction

Industrial effluents containing synthetic dyes constitute a major environmental concern because colorants are extensively used in textile, leather, printing, paper, and dye-manufacturing industries [1]. Reactive dyes are especially problematic owing to their high water solubility, stable aromatic frameworks, chromophoric groups, and limited biodegradability. Even at low concentrations, these compounds can impart coloration to aquatic environments, restrict light penetration, suppress photosynthesis, lower dissolved oxygen, and adversely affect aquatic organisms [2,3]. Reactive Orange 107 (RO 107) contains azo linkages and sulfonated functional groups that enhance its solubility and stability [4]. Consequently, conventional treatment systems often fail to achieve complete removal.

Sulfonated reactive azo dyes are resistant to decolorization and mineralization, while anaerobic transformation may generate hazardous aromatic amine intermediates [5]. Therefore, efficient oxidative processes capable of disrupting the chromophoric structure and promoting degradation of organic intermediates are required for RO 107-contaminated wastewater [6].

Conventional methods, including coagulation-flocculation, adsorption, membrane separation, biological treatment, and chemical precipitation, involve incomplete mineralization, chemical demand, sludge generation, membrane fouling, and phase transfer rather than pollutant destruction [7–9]. Advanced oxidation processes (AOPs) are capable of generating highly

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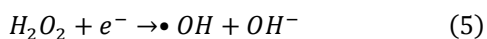
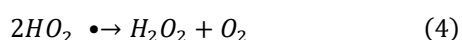
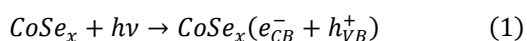
***Corresponding author:** murat.kiransan@gumushane.edu.tr

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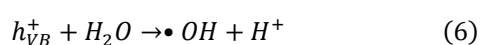
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reactive oxidative species that promote the transformation and degradation of persistent organic pollutants, and under sufficiently intensive reaction conditions, may ultimately lead to their partial or complete mineralization into CO_2 , H_2O , and inorganic species [10]. Among them, semiconductor photocatalysis is an approach in which irradiation activates the catalyst, generating conduction-band electrons and valence-band holes when photon energy equals or exceeds the band-gap energy [11]. These photogenerated electron-hole pairs initiate surface redox reactions and generate reactive oxygen species, including hydroxyl radicals ($\bullet\text{OH}$), superoxide radical anions, and hydroperoxyl radicals, which play key roles in the oxidative decomposition of dye molecules [12]. The photocatalytic activation of CoSe_x nanocatalyst under light irradiation and the subsequent formation of reactive oxygen species can be summarized by the following Eqs. (1–5).

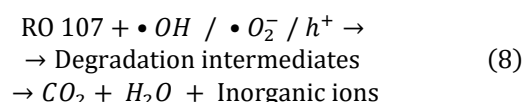


In this process, light irradiation promotes the excitation of electrons from the valence band to the conduction band of CoSe_x nanocatalyst, generating electron-hole pairs. The photogenerated conduction-band electrons react with dissolved oxygen to form superoxide radical anions, which are subsequently converted into hydroperoxyl radicals and hydrogen peroxide [13]. Finally, hydrogen peroxide can be further reduced by electrons to generate highly oxidative hydroxyl radicals ($\bullet\text{OH}$), which play a crucial role in the degradation of Reactive Orange 107 molecules. Meanwhile, the photogenerated holes in the valence band can directly oxidize RO107 molecules or react with water and hydroxide ions to generate hydroxyl radicals ($\bullet\text{OH}$), which can be summarized by the following Eqs. (6,7) [14–16].



The generated reactive oxygen species can attack the azo bond, aromatic rings, and auxochromic groups of RO107, leading to decolorization, fragmentation, ring

opening reactions, and progressive mineralization by the following Eq. (8) [17].



In this photocatalytic system, hydroxyl radicals ($\bullet\text{OH}$) are generally considered the most powerful oxidative species due to their high oxidation potential and non-selective reactivity toward organic pollutants. Superoxide ($\bullet\text{O}_2^-$) radicals contribute to photocatalytic oxidation by promoting oxygen activation, limiting electron-hole recombination, and sustaining radical reactions [18]. Photogenerated holes may oxidize RO 107 molecules adsorbed on the CoSe_x surface; therefore, degradation performance is governed by light harvesting, charge separation, surface reactivity, adsorption affinity, and ROS generation [19]. CoSe_x nanocatalyst have attracted interest because of their favorable electronic structure, potential visible-light response, and efficient charge transfer. Related metal selenide photocatalysts have demonstrated activity toward dye degradation, highlighting their potential in wastewater remediation [20]. Nanoscale CoSe_x nanocatalyst can provide abundant reactive sites and shorten charge-carrier migration pathways, thereby improving overall photocatalytic efficiency [21].

RO 107 degradation over CoSe_x nanocatalyst is controlled by catalyst dosage, initial dye concentration, pH, irradiation time, light source, water matrix, inorganic ions, and radical scavengers [22]. Catalyst loading influences active-site availability, although excessive amounts may induce aggregation, light scattering, and reduced photon penetration [23]. Likewise, elevated dye concentrations can hinder photon transport and intensify competition for surface sites, while pH regulates catalyst surface charge, dye speciation, adsorption, and ROS formation [24]. The novelty of this study lies in evaluating multiphase cobalt selenide (CoSe_x) as a photocatalyst for RO 107 degradation while linking catalyst structure, operating conditions, reaction kinetics and degradation mechanism. Unlike conventional studies focused on single phase metal oxides or common semiconductors, this work examines the benefits of coexisting cobalt selenide phases for charge carrier migration, reduced electron-hole recombination and enhanced ROS generation under UV irradiation. Its scientific contribution is strengthened by evaluating catalyst dosage, pollutant concentration, pH, irradiation source, water matrix, reusability, and radical scavenging behavior, together with kinetic and mechanistic analyses [25]. Integrating performance data with reactive species

and degradation pathway evaluation provides mechanistic insight and supports efficient treatment strategies for persistent reactive azo dyes in wastewater [26].

CoSe_x nanocatalysts were selected for this study because cobalt selenides combine favorable electronic characteristics, redox active cobalt centers, and composition dependent phase structures that are particularly advantageous for photocatalytic oxidation. More importantly, the coexistence of different cobalt selenide phases can generate interfacial regions that facilitate photogenerated charge migration and reduce electron-hole recombination, thereby increasing the availability of charge carriers for surface redox reactions and ROS generation. The nanoscale nature of CoSe_x also provides a high density of accessible surface-active sites and short charge transport pathways, which can promote interactions among the catalyst surface, dissolved oxygen, and RO 107 molecules. In addition, cobalt selenides remain considerably less explored than conventional TiO₂, ZnO or other metal-oxide based photocatalysts for reactive azo-dye treatment. Therefore, multiphase CoSe_x was chosen to investigate whether its phase heterogeneity and interfacial electronic interactions could provide a more effective photocatalytic platform for the degradation of persistent RO 107 in wastewater.

2. Material and method

2.1. Materials and equipment

All chemicals used in this study were of analytical grade and were obtained from Merck (Darmstadt, Germany) and Sigma-Aldrich (Germany). Cobalt(II) chloride hexahydrate (CoCl₂·6H₂O), N,O-bis(trimethylsilyl)acetamide (BSA), Reactive Orange (RO 107), sodium tetrahydroborate (NaBH₄), hydrazine hydrate (N₂H₄·H₂O), sodium dihydrogen phosphate (NaH₂PO₄), sodium bicarbonate (NaHCO₃), ethanol (C₂H₆O), ethylenediaminetetraacetic acid (EDTA, C₁₀H₁₆N₂O₈), chloroform (CHCl₃), tert-butanol ((CH₃)₃COH), and p-benzoquinone (C₆H₄O₂) were purchased from Sigma-Aldrich (Germany). Hydrochloric acid (HCl), sulfuric acid (H₂SO₄), sodium sulfate (Na₂SO₄), sodium chloride (NaCl), sodium fluoride (NaF), and sodium hydroxide (NaOH). Potassium iodide (KI) was also used as received from a commercial supplier without additional purification. Deionized water was used throughout all synthesis, modification, and catalytic degradation experiments. All aqueous solutions were freshly prepared prior to use. The chemicals were utilized for pH adjustment, radical scavenging experiments, and preparation of model pollutant solutions without any further treatment.

For catalyst synthesis and modification in the liquid phase, mixing procedures were performed using a magnetic stirrer (IKA RCT Basic, Germany) under controlled stirring conditions. The drying of synthesized materials was carried out in a laboratory oven (Santen SE 125), while calcination processes were conducted in a programmable muffle furnace (Protech laboratory oven) at the desired temperatures. All chemicals and catalyst samples were accurately weighed using an analytical balance (Sartorius BP1106, Germany) with a precision of ±0.1 mg. The concentration of Reactive Orange (RO 107) in the aqueous phase after photocatalytic degradation was determined by UV-Vis spectrophotometry (PerkinElmer Lambda 25, United Kingdom) by monitoring the characteristic maximum absorption wavelength of the dye. The pH of the reaction solutions was adjusted using dilute HCl or NaOH solutions and measured with a benchtop pH meter (Hanna pH-2221). Following each degradation experiment, the catalyst particles were separated from the suspension by centrifugation using a BOECO S-8 centrifuge. Artificial irradiation was provided by 8 W UV-A, UV-B, and UV-C lamps (Herolab GmbH, Germany), which were placed inside a quartz tube positioned at the center of the reactor.

2.2. Materials characterization

The structural, morphological, and physicochemical properties of the hydrothermally synthesized CoSe nanocatalysts were comprehensively characterized using advanced analytical techniques. Fourier-transform infrared spectroscopy (FT-IR, Bruker VERTEX 70v) was employed to identify surface functional groups and to elucidate possible interfacial interactions between CoSe nanoparticles. The crystalline structure and phase composition of the synthesized materials were analyzed by X-ray diffraction (XRD) using a PANalytical Empyrean diffractometer with Cu K α radiation (λ = 1.5406 Å). The surface morphology and microstructural features were examined using scanning electron microscopy (SEM, Zeiss Sigma 300). Detailed nanoscale structural analysis was further performed by High-resolution transmission electron microscopy (HT-TEM, Hitachi High-Tech HT7700).

Textural properties, including specific surface area, pore volume, and pore size distribution, were evaluated by nitrogen adsorption-desorption measurements at 77 K using a Micromeritics 3Flex BET surface area analyzer. The specific surface area was calculated according to the Brunauer-Emmett-Teller (BET) method.

2.3. Synthesis of multiphase CoSe_x nanocatalyst

CoSe_x nanocatalyst were synthesized through a hydrothermal method using CoCl₂·6H₂O and selenium

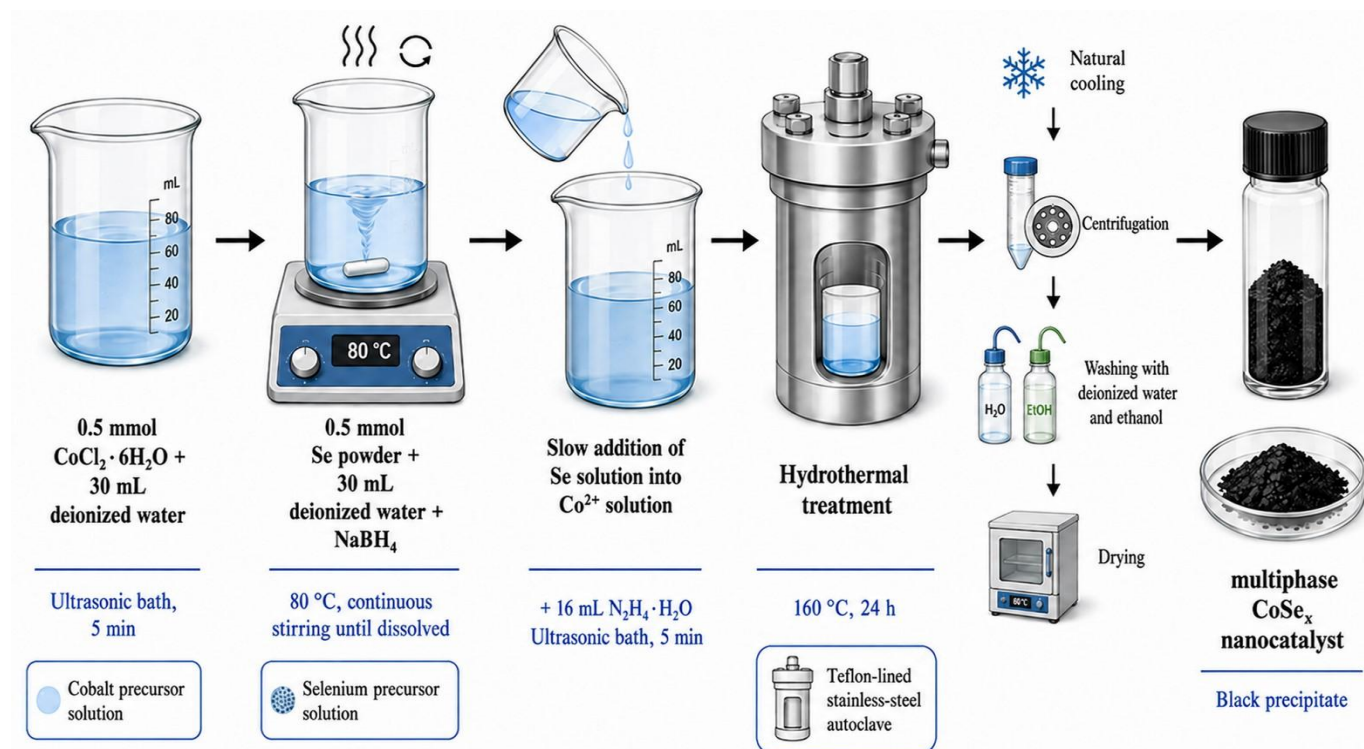


Figure 1. Schematic representation of the hydrothermal synthesis process of the multiphase CoSe_x nanocatalyst

powder as the Co and Se sources, respectively. Initially, 0.5 mmol of $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ was dissolved in 30 mL of deionized water and sonicated in an ultrasonic bath for 5 min to obtain a homogeneous cobalt precursor solution. Separately, 0.5 mmol of selenium powder was gradually added into 30 mL of deionized water in the presence of NaBH_4 as a reducing agent, and the mixture was heated at 80 °C under continuous stirring until complete dissolution was achieved. The addition of NaBH_4 facilitated the reduction of selenium powder into reactive selenide species, which subsequently interacted with Co^{2+} ions to initiate the formation of cobalt selenide nuclei. NaBH_4 was selected as the reducing agent because elemental selenium exhibits limited aqueous reactivity and requires activation to form reactive selenide species. NaBH_4 efficiently converts Se^0 into soluble $\text{NaHSe}/\text{HSe}^-$ species, promoting reaction with Co^{2+} , homogeneous nucleation, and multiphase CoSe_x formation during hydrothermal treatment. The selenium containing solution was then slowly introduced into the $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ solution under continuous stirring, followed by the addition of 16 mL of hydrazine hydrate ($\text{N}_2\text{H}_4 \cdot \text{H}_2\text{O}$). The resulting mixture was sonicated for an additional 5 min to enhance precursor dispersion and improve nucleation homogeneity. Subsequently, the final reaction mixture was transferred into a Teflon-lined stainless steel high-pressure reactor and subjected to hydrothermal treatment at 160 °C for 24 h [27]. Under these hydrothermal conditions, the elevated temperature and autogenous pressure promoted the nucleation, crystal

growth, and crystallization of CoSe_x nanocatalyst. After cooling, the product was filtered, repeatedly washed with deionized water, dried at 100 °C for 3 h, and calcined at 450 °C for 2 h to obtain the CoSe_x nanocatalyst as illustrated in Fig. 1 [28].

2.4. Experimental procedure for photocatalytic degradation

Reactive Orange 107 (RO 107), a representative azo dye frequently encountered in dye-contaminated domestic and hospital effluents, was selected as the target organic pollutant for the photolytic and photocatalytic degradation experiments.

Owing to its persistence and potential toxicity, even trace levels of RO 107 in aquatic environments may pose considerable risks to human health, including hepatic impairment, renal dysfunction, and other adverse physiological effects. The molecular structures and selected physicochemical characteristics of the dyes investigated in this work are summarized in Table 1.

Photocatalytic degradation tests were carried out in a cylindrical glass photoreactor with a total volume of 1000 mL. The irradiation source consisted of 8 W UV-A, UV-B, and UV-C lamps (Herolab, Germany), which were positioned inside a quartz sleeve placed along the central axis of the reactor to ensure efficient light distribution throughout the reaction medium. According to the manufacturer specifications, the UV-A lamp exhibits a maximum emission wavelength at 365 nm within the conventional UV-A spectral region of approximately

Table 1. Chemical structures and some properties of dyes used in this study

Name	Chemical Structure	Molecular Formula	M _w (g mol ⁻¹)	λ _{max} (nm)
Reactive Orange 107 (RO 107)		C ₁₆ H ₁₆ N ₄ Na ₂ O ₁₀ S ₃	566.49	410
Acid Orange 7 (AO7)		C ₁₆ H ₁₁ N ₂ NaO ₄ S	350.32	483
Reactive Blue 19 (RB19)		C ₂₂ H ₁₆ N ₂ Na ₂ O ₁₁ S ₃	626.54	592
Basic Yellow 2 (BY2)		C ₁₇ H ₂₂ N ₃ Cl	303.83	432
Malachite Green (MG)		C ₂₃ H ₂₅ ClN ₂	463.50	617
Congo Red (CR)		C ₃₂ H ₂₂ N ₆ Na ₂ O ₆ S ₂	696.66	497

315–400 nm, whereas the UV-B lamp has a maximum emission at 312 nm within the 280–315 nm range. The UV-C lamp provides short wave ultraviolet radiation with a dominant emission maximum at 254 nm, corresponding to the UV-C region of approximately 200–280 nm. Although the nominal electrical power of all lamps was identical (8 W), their emission wavelengths and irradiance characteristics differed. Therefore, the observed differences in photocatalytic activity should be interpreted not only in terms of lamp power but also with respect to photon energy, spectral distribution, and the ability of the emitted radiation to effectively excite the multiphase CoSe_x nanocatalyst. The photocatalytic process was initiated by switching on the UV lamp at the start of each experiment, as illustrated in Fig. 2.

Before irradiation, dark adsorption experiments were performed to evaluate the adsorption contribution and to clearly differentiate it from the actual photocatalytic degradation of RO 107. For a typical experiment, 1000

mL of RO 107 aqueous solution at a predetermined concentration was introduced into the reactor, followed by the addition of the required amount of CoSe_x nanocatalyst under natural pH conditions. Throughout the photocatalytic experiments, the reaction suspension was continuously agitated using a magnetic stirrer at a constant stirring speed of 150 rpm to maintain homogeneous dispersion of the CoSe_x nanocatalyst and to minimize external mass-transfer limitations. 10 mL were withdrawn from the reaction mixture at predetermined irradiation intervals of [e.g., 10–120 min] for quantitative monitoring of RO 107 degradation. After each sampling step, the catalyst particles were immediately separated from the collected suspension by centrifugation prior to UV-Vis spectrophotometric analysis at 410 nm. The reaction temperature was maintained at approximately 25 °C throughout the experiments to minimize possible thermal effects on the degradation process.

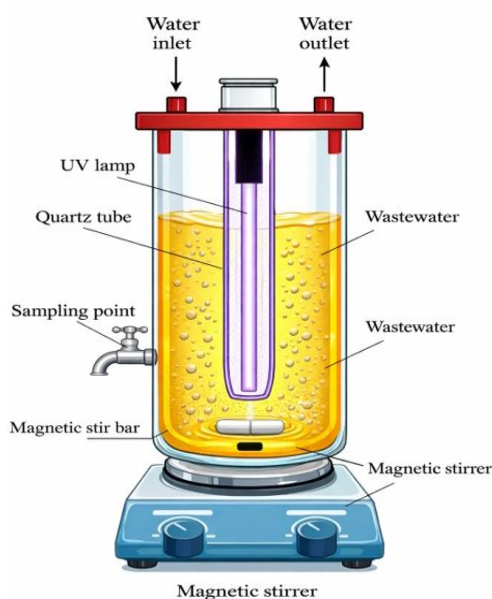


Figure 2. Schematic representation of the reactor used in photocatalytic degradation experiments.

Temperature control was achieved using an external cooling system, while the reaction temperature was periodically monitored using a calibrated thermometer. These controlled hydrodynamic, sampling, and thermal conditions ensured reliable comparison among individual photocatalytic experiments and improved the reproducibility of the obtained degradation data. The resulting suspension was magnetically stirred in the absence of light for a sufficient time to attain adsorption-desorption equilibrium between RO 107 molecules and the available active sites on the CoSe_x surface. After completion of the dark equilibration step, a known volume of suspension was collected and separated from the catalyst particles. The concentration obtained after dark adsorption equilibrium was taken as the initial concentration for the subsequent photocatalytic degradation experiments.

The degradation efficiency (%) was calculated based on the relative decrease in RO 107 concentration over time, enabling comprehensive evaluation of catalytic activity and operational stability. The dye degradation efficiencies were calculated using Eq. (9).

$$\text{Degradation efficiency (\%)} = [(C_0 - C_t) / C_0] \times 100 \quad (9)$$

Here, C_0 and C_t represent the initial concentration and the concentration at time t of the dye, respectively.

2.5. Kinetic study

The kinetic behavior was evaluated using the following equation derived from the simplified Langmuir-Hinshelwood model to Eq. (10).

$$-\ln(C_t / C_0) = k_{\text{app}} t \quad (10)$$

where C_0 and C_t represent the initial and time-dependent RO 107 concentrations, respectively, and k_{app} (min^{-1}) is the apparent pseudo-first-order rate constant obtained from the slope of the linear plots of $-\ln(C_t/C_0)$ versus irradiation time [30].

3. Results and discussion

3.1. Characterization of CoSe_x nanoparticles

The multiphase CoSe_x nanocatalyst used as a catalyst in the photocatalytic degradation of Reactive Orange 107 dye waste was synthesized as illustrated in Fig. 1. Subsequently, the synthesized multiphase CoSe_x nanocatalyst was characterized using various analytical techniques.

3.1.1. XRD Analysis

As shown in Fig. 3 the crystalline structure of the synthesized multiphase CoSe_x nanocatalyst was examined by X-ray diffraction analysis. The XRD pattern displays several well resolved diffraction peaks at 2θ values of 23.55° , 26.52° , 29.75° , 33.89° , 41.43° , 43.66° , 45.48° , 48.39° , 51.80° , 55.72° , 56.14° , 61.44° , 61.68° , 65.35° , 68.58° and 71.63° , indicating the formation of a crystalline cobalt diselenide based structure. The reflections located at approximately 26.52° , 33.89° , 43.66° , 45.48° , 51.80° , 61.68° , 65.35° , 68.58° , and 71.63° can be tentatively indexed to the (111), (210), (220), (221), (311), (400), (410), (411), and (420) crystallographic planes of cubic CoSe₂, respectively. In addition, the diffraction features observed at 23.55° , 29.75° , 41.43° , 48.39° , 55.72° , and 56.14° may be associated with orthorhombic CoSe₂-related lattice planes, including (110), (101), (210), (211), (221), and (300), suggesting the possible coexistence of CoSe polymorphic domains. These reflections show good agreement with the lattice planes of orthorhombic CoSe nanocatalyst in JCPDS/PDF No. 53-0449 [31].

However, several low- and medium-angle reflections, particularly those at 23.55° , 29.75° , 41.43° , 43.66° , 45.48° , 51.80° , 55.72° , and 61.68° , may overlap with characteristic reflections of trigonal selenium, which has been reported to show diffraction peaks around 23.5° , 29.7° , 41.4° , 43.6° , 45.4° , 51.7° , 55.9° , and 61.5° . Therefore, the XRD pattern should be interpreted as confirming the formation of crystalline CoSe₂ nanocatalyst, while the possible contribution of residual selenium or Se-rich domains cannot be fully excluded solely from XRD analysis [32].

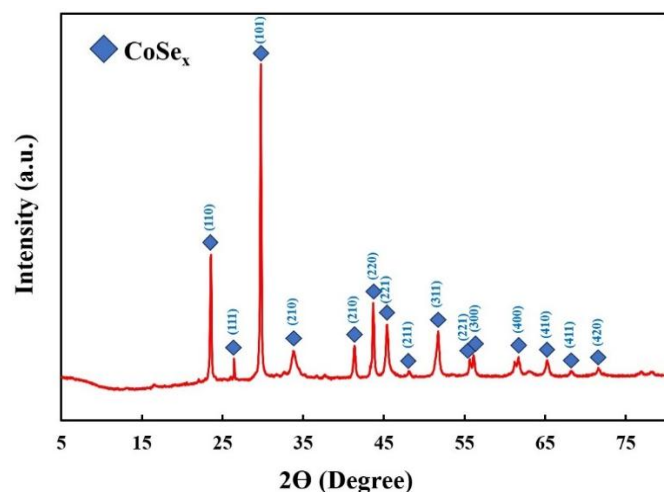


Figure 3. XRD diffractogram of the synthesized multiphase CoSe_x nanocatalyst.

The crystallite sizes of the multiphase CoSe_x nanocatalyst were quantitatively evaluated using the Debye–Scherrer equation. This is expressed as follows, Eq. (11).

$$d = (k\lambda)/(\beta \cos\theta) \quad (11)$$

Where k is the Debye–Scherrer constant (0.89), λ is the X-ray wavelength (0.15406 nm), β is the full width at half maximum (FWHM) of the diffraction peak in radians, and θ represents the Bragg diffraction angle. The crystallite size of the multiphase CoSe_x nanocatalyst phase was estimated from the diffraction peak located at $2\theta = 29.75^\circ$, which is associated with the crystalline structure of multiphase CoSe_x nanocatalyst, using the Debye–Scherrer equation. Based on this calculation, the average crystallite size of multiphase CoSe_x nanocatalyst was determined to be approximately 32.8 nm [33].

3.1.2. FTIR Analysis

As shown in Fig. 4, the FT-IR spectrum of the synthesized multiphase CoSe_x nanocatalyst exhibits the characteristic vibrational features expected for cobalt selenide-based nanostructures. A broad absorption band centered at 3416 cm⁻¹ can be assigned to the stretching vibration of surface hydroxyl groups (O–H) and physically adsorbed water molecules. The presence of this broad band indicates that the nanoparticle surface contains hydroxylated sites, which is common for nanomaterials exposed to ambient conditions and may be beneficial for interfacial interactions during catalytic applications [34].

In the low wavenumber region, the prominent absorption band observed at 664 cm⁻¹, together with the bands at 465 cm⁻¹ and 421 cm⁻¹, is associated with the metal–selenium lattice vibrations, confirming the formation of Co–Se bonds within the crystal framework. These bands are generally regarded as fingerprint

vibrations of cobalt selenide structures and provide strong evidence for the successful synthesis of multiphase CoSe_x nanocatalyst. Moreover, the absence of significant absorption bands in the higher wavenumber region related to organic functional groups suggests that the final product is relatively free from residual organic impurities or precursor related species. The FT-IR results verify the formation of multiphase CoSe_x nanocatalyst and indicate a chemically clean surface containing hydroxyl functionalities and characteristic Co–Se bonding environments [35].

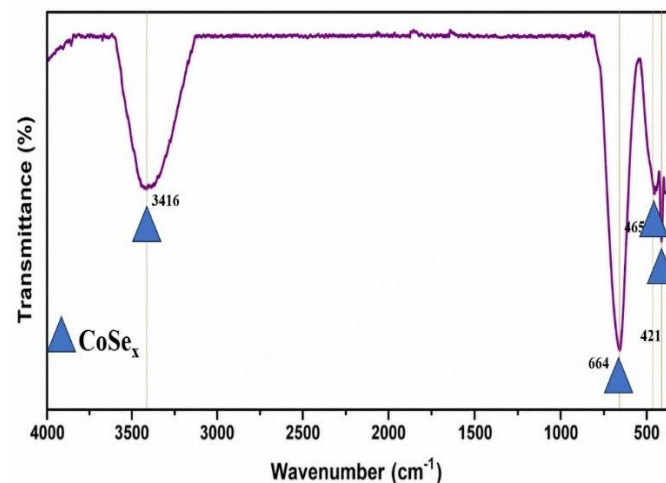


Figure 4. FT-IR spectra of the synthesized multiphase CoSe_x nanocatalyst.

3.1.3. SEM/EDX Analysis

The SEM micrographs of the synthesized multiphase cobalt selenide (CoSe_x) nanocatalyst are presented in Fig. 5(a–d). As observed in Fig. 5(a), the CoSe_x sample exhibits a heterogeneous morphology composed of compact, irregularly shaped nanostructured aggregates. The particles appear as densely packed crystalline blocks with partially faceted surfaces, indicating the formation of well developed multiphase CoSe_x domains during the synthesis process. In addition to the faceted particles, some flake like and rough textured agglomerates are also visible, suggesting that the nanoparticles tend to assemble into larger secondary structures due to high surface energy and interparticle interactions. The image recorded at higher magnification clearly reveals that the surface of the multiphase CoSe_x nanocatalyst is not smooth but rather rough and porous like, which may provide more accessible active sites for photocatalytic reactions [36].

As shown in Fig. 5(b), it further confirms the aggregated nature of the multiphase CoSe_x nanocatalyst at a broader morphological scale. The sample consists of interconnected clusters with flower-like, sheet-like and irregular granular features.

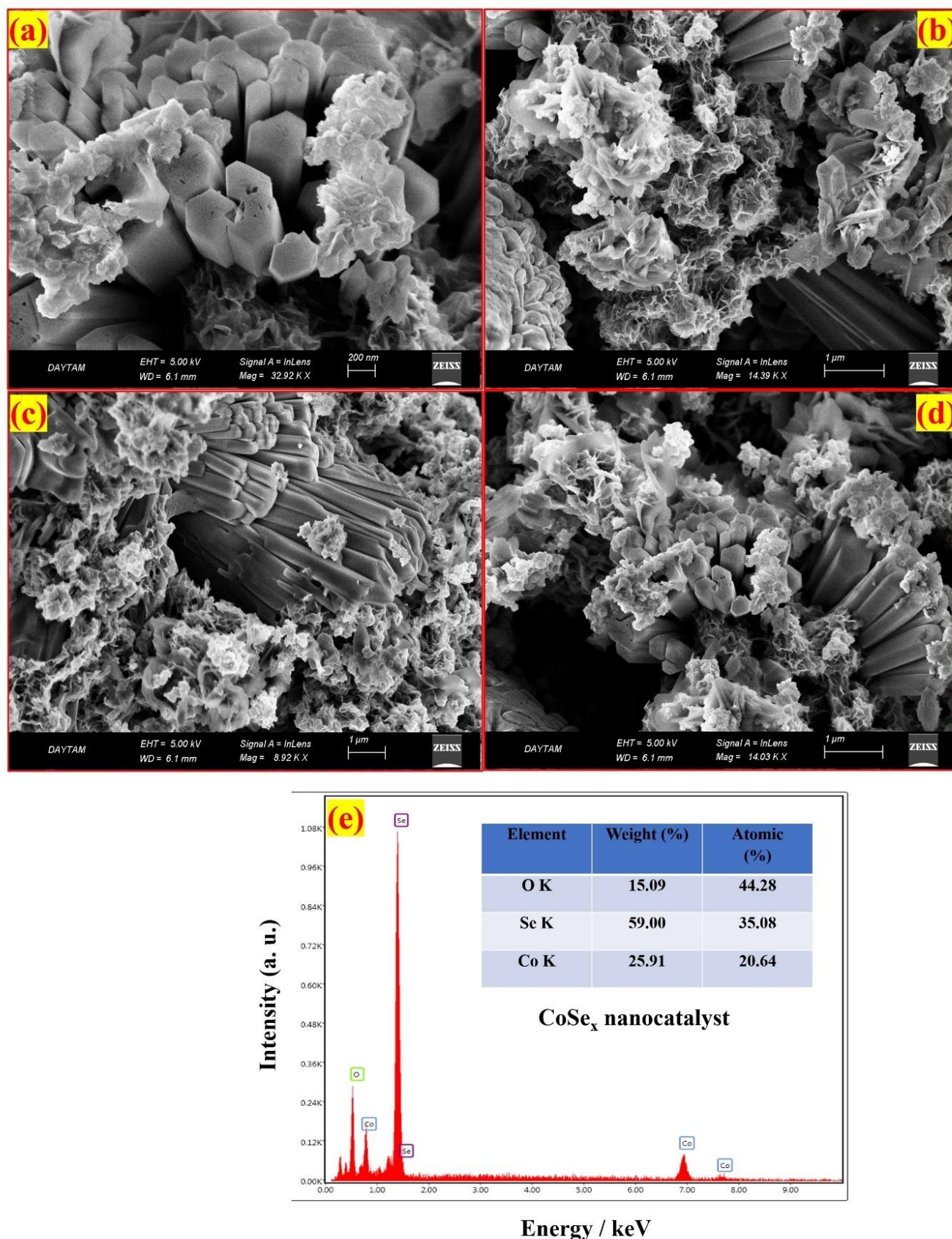


Figure 5. SEM images of (a–d) multiphase CoSe_x nanocatalyst, and EDX spectra of (e) multiphase CoSe_x nanocatalyst.

Such a hierarchical morphology can be advantageous for catalytic applications because it may enhance light harvesting, facilitate dye/catalyst contact, and improve the accessibility of reactive surface sites. The coexistence of compact crystalline regions and loosely assembled

porous aggregates suggests that the hydrothermal synthesis route promotes both crystal growth and particle self-assembly. This type of morphology is particularly beneficial for photocatalytic degradation processes, since surface roughness and interparticle

voids can increase the interaction between the pollutant molecules and the catalyst surface [37]. The EDX spectrum of the multiphase CoSe_x nanocatalyst is shown in Fig. 5(e), and the corresponding elemental composition is summarized in the inset table. The spectrum confirms the presence of the main constituent elements, namely Co and Se, indicating the successful formation of cobalt selenide nanocatalyst. The strong Se signal and distinct Co peaks demonstrate that both elements are incorporated into the synthesized material. According to the quantitative EDX results, the sample contains 59.00 wt.% Se and 25.91 wt.% Co, corresponding to 35.08 atomic% Se and 20.64 atomic% Co, respectively. The detection of oxygen with 15.09 wt.% and 44.28 atomic% may be attributed to surface-adsorbed oxygen species, hydroxyl groups, or slight surface oxidation of the nanoparticles during exposure to air. Importantly, no additional impurity-related elements are observed in the EDX spectrum, confirming the relatively high purity of the synthesized multiphase CoSe_x nanocatalyst [38].

3.1.4. HRTEM Analysis

As shown in Fig. 6, the HRTEM images of the synthesized multiphase CoSe_x nanocatalyst, provide detailed insight into their crystalline microstructure. As shown in Fig. 6(a, b), the multiphase CoSe_x nanocatalyst exhibits closely aggregated nanocrystalline domains with irregular and partially rounded morphologies. The overlapping contrast regions indicate that the particles

of the synthesized multiphase CoSe_x nanocatalyst. The clearly visible lattice fringes in Fig. 6(a) and Fig. 6(b) demonstrate the formation of ordered crystalline planes within the multiphase CoSe_x structure.

The HRTEM images also reveal that the lattice fringes are not randomly distributed but extend over several nanocrystalline regions, suggesting good crystallinity and successful crystal growth. The coexistence of highly ordered fringe regions and darker overlapping zones indicates that the multiphase CoSe_x nanocatalyst is composed of multiple crystalline domains with different orientations [39]. This polycrystalline and aggregated architecture may be advantageous for photocatalytic applications, because interfacial boundaries and structural defects can act as active sites for charge separation and surface redox reactions. These findings support the structural results obtained from XRD analysis and demonstrate that the synthesized multiphase CoSe_x nanocatalyst possesses a well-developed nanocrystalline framework, which may contribute positively to its photocatalytic activity by facilitating electron transport and providing active surface sites for reactive oxygen species generation [40, 41].

3.1.5. Nitrogen adsorption–desorption isotherms, BJH pore size distribution, and BET textural properties

As shown in Fig. 7(a), the N₂ adsorption–desorption isotherms of the synthesized multiphase CoSe_x

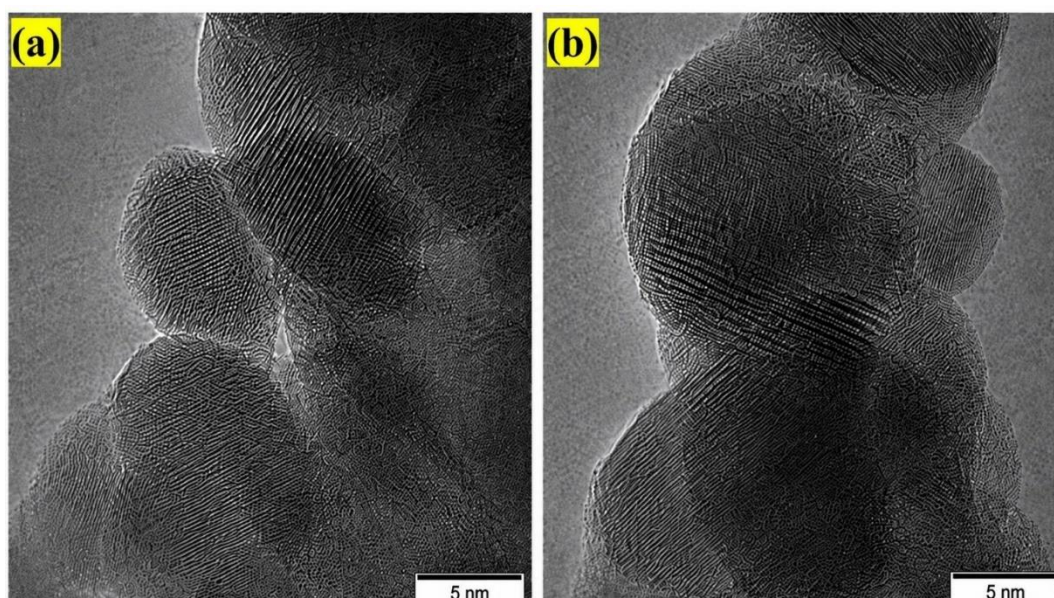


Figure 6. FHR-TEM images of (a, b) multiphase CoSe_x nanocatalyst.

are assembled into compact clusters, which is commonly observed for nanoscale metal chalcogenides due to their high surface energy and strong interparticle interactions. Despite this aggregation, the particles display well-resolved lattice fringes, confirming the crystalline nature

nanocatalyst, while the corresponding textural parameters are summarized in Table 2. The isotherm displays a continuous increase in the adsorbed nitrogen volume over the entire relative pressure range, followed by a pronounced uptake at high relative pressure values

close to $P/P_0 = 1.0$. This sharp increase can be attributed to capillary condensation within mesopores and interparticle voids formed by the aggregation of multiphase CoSe_x nanocatalyst. The presence of a visible hysteresis loop between the adsorption and desorption branches further confirms the mesoporous character of the material. Such hysteretic behavior is generally associated with pore filling and emptying processes occurring in mesoporous networks, indicating that the synthesized multiphase CoSe_x nanocatalyst possesses accessible porous channels and interparticle spaces [42].

The BET surface area of the multiphase CoSe_x nanocatalyst was determined to be $14.7246 \text{ m}^2/\text{g}$, indicating the presence of a moderately developed surface texture. In contrast, the Langmuir surface area was calculated as $19.6516 \text{ m}^2/\text{g}$, suggesting that the surface of the material contains a high number of adsorption-accessible sites under the assumptions of the Langmuir model. The micropore surface area and micropore volume were found to be $1.5624 \text{ m}^2/\text{g}$ and $0.0008 \text{ cm}^3/\text{g}$, respectively. These values indicate that, although microporous contributions exist, the overall pore structure is predominantly governed by mesoporous and interparticle void regions rather than purely microporous channels [43].

The total pore volume obtained from the adsorption branch was $0.0492 \text{ cm}^3/\text{g}$, whereas the desorption branch gave a slightly higher value of $0.0465 \text{ cm}^3/\text{g}$. This difference is consistent with the hysteresis behavior observed in the isotherm and may be related to delayed evaporation or pore-network effects during the desorption process. The average pore diameters calculated from adsorption and desorption data were 13.3228 nm and 12.5042 nm , respectively, both of which fall within the mesoporous range. Similarly, the BJH average pore diameters were determined as 12.8062 nm for adsorption and 11.6024 nm for desorption, further confirming the mesoporous nature of the synthesized multiphase CoSe_x nanocatalyst [44]. Fig. 7(b) shows the BJH pore size distribution of the multiphase CoSe_x nanocatalyst. The curve exhibits a broad distribution extending from small mesopores to larger pore domains, with a major pore population in the mesoporous region. The pore volume increases markedly at lower pore diameters, reaches a maximum in the intermediate mesopore range, and then decreases at larger pore sizes before showing a secondary increase at high pore diameters. This broad distribution suggests the formation of a hierarchical porous structure composed of mesopores and larger interparticle voids. Such a pore architecture is most likely generated by the irregular assembly and partial agglomeration of primary multiphase CoSe_x nanocatalyst during the hydrothermal synthesis process [45].

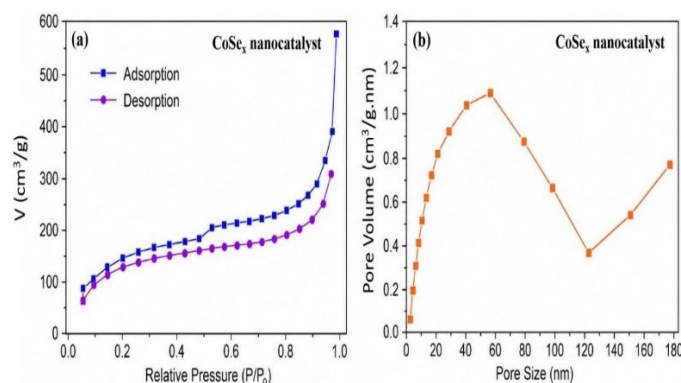


Figure 7. (a) Nitrogen adsorption-desorption isotherms of multiphase CoSe_x nanocatalyst and (b) BJH pore size distribution of the samples multiphase CoSe_x nanocatalyst.

As a result, the N_2 adsorption-desorption and BJH analyses demonstrate that the synthesized multiphase CoSe_x nanocatalyst possesses a mesoporous and hierarchically assembled porous structure. The combination of a measurable BET surface area, mesoporous average pore diameter, and accessible pore volume is highly favorable for photocatalytic applications. These textural properties can enhance pollutant adsorption, promote diffusion of Reactive Orange 107 molecules into the catalyst surface region, and facilitate the interaction between dye molecules and photoinduced reactive species. Therefore, the porous structure of multiphase CoSe_x nanocatalyst is expected to contribute positively to their photocatalytic performance by improving mass transfer, increasing surface accessibility, and supporting efficient surface redox reactions under irradiation [46].

Table 2. Surface area and porosity characteristics of multiphase CoSe_x nanocatalyst.

Textural characteristics	Value
BET surface area(m^2/g)	14.7246
Langmuir surface area(m^2/g)	19.6516
Micropore surface area(m^2/g)	1.5624
Micropore volume(cm^3/g)	0.0008
Total pore volume (Adsorption) (cm^3/g)	0.0492
Total pore volume (Desorption) (cm^3/g)	0.0465
Average pore diameter (Adsorption) (nm)	13.3228
Average pore diameter (Desorption) (nm)	12.5042
BJH average pore diameter (Adsorption) (nm)	12.8062
BJH average pore diameter (Desorption) (nm)	11.6024

3.2. Removal of RO 107 by photocatalytic degradation process

This section systematically optimizes the multiphase CoSe_x nanocatalyst-assisted photocatalytic degradation of RO 107 by investigating the effects of key operational parameters, including the initial RO 107 concentration, catalyst dosage, water matrix, solution pH, irradiation source, and radical scavengers. In addition, the degradation performance of the CoSe_x nanocatalyst

toward different toxic dyes was evaluated to assess its broader applicability. Successive reuse experiments were also conducted to determine the operational stability, recyclability, and long-term performance of the catalyst under repeated photocatalytic cycles.

3.2.1. Effect of CoSe_x nanocatalyst dosage

The effect of multiphase CoSe_x nanocatalyst dosage on the photocatalytic degradation of RO 107 under UV-C irradiation is presented in Fig. 8(a). The degradation efficiency increased markedly with increasing catalyst dosage from 0.1 to 1.0 g/L. At the lowest catalyst loading of 0.1 g/L, only 38.22% degradation was achieved after 120 min, indicating that the limited number of available active sites was insufficient for efficient photon absorption and reactive oxygen species (ROS) generation. Increasing the catalyst dosage to 0.2, 0.4, 0.6, and 0.8 g/L enhanced the degradation efficiency to 49.87%, 56.51%, 67.35%, and 75.13%, respectively. This progressive improvement can be attributed to the increased availability of photocatalytically active CoSe_x surface sites, which facilitates greater UV-C light harvesting, more efficient electron–hole pair formation, and enhanced production of oxidative radicals responsible for RO 107 degradation [47]. A substantial increase in degradation efficiency was observed when the CoSe_x dosage was raised to 1.0 g/L, reaching 97.87% after 120 min. This result demonstrates that 1.0 g/L provides sufficient active sites and an optimal catalyst

The marginal enhancement beyond 1.0 g/L suggests that the photocatalytic system approaches a saturation point, where additional catalyst particles do not significantly contribute to the degradation process. At higher catalyst loadings, excessive particle concentration may also promote light scattering, UV-C shielding, and partial agglomeration, thereby limiting the effective activation of the catalyst surface. Therefore, considering both degradation performance and catalyst economy, 1.0 g/L can be regarded as the optimum multiphase CoSe_x nanocatalyst dosage for the photocatalytic degradation of RO 107 [48].

The apparent pseudo-first-order kinetic parameters for the photocatalytic degradation of RO 107 at different CoSe_x nanocatalyst dosages are presented in Fig. 8(b). The kinetic data showed that the degradation process followed the apparent pseudo-first-order model with high correlation coefficients, as evidenced by R² values ranging from 0.9573 to 0.9856. These high R² values confirm the good linearity of the kinetic plots and indicate that the degradation of RO 107 under UV-C irradiation was well described by the pseudo-first-order kinetic model. The apparent rate constant (k_{app}) increased progressively with increasing multiphase CoSe_x nanocatalyst dosage. At low catalyst loadings of 0.1 and 0.2 g/L, the k_{app} values were 0.0040 and 0.0057 min⁻¹, respectively, indicating a relatively slow degradation rate due to the limited number of available photocatalytic active sites and insufficient reactive

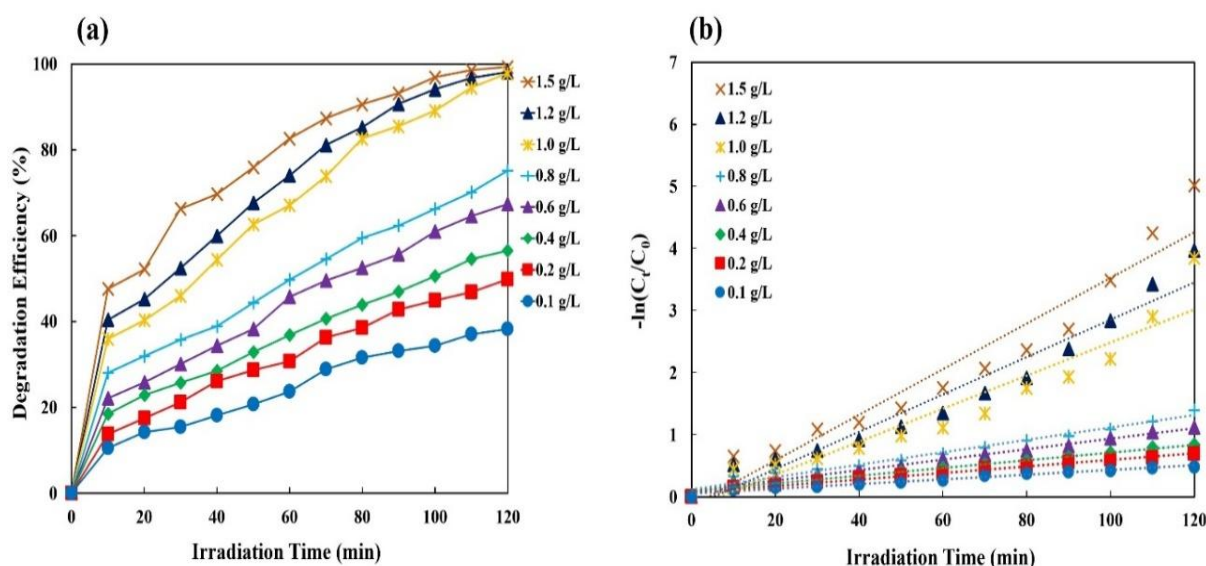


Figure 8. (a) The effect of CoSe_x nanocatalyst dosage on the degradation of RO 107 the photocatalytic degradation process, (b) Apparent pseudo-first-order reaction kinetics (Experimental conditions: Initial dye concentration: 25 mg/L, pH for RO 107: Natural pH, Irradiation source: UV-C, Irradiation time: 120 min)

pollutant interaction for near complete degradation of RO 107 under the applied experimental conditions. Further increases in catalyst dosage to 1.2 and 1.5 g/L resulted in only slight improvements, with degradation efficiencies of 98.10% and 99.33%, respectively (Fig. 8(a)).

oxygen species generation. Increasing the catalyst dosage to 0.4, 0.6, and 0.8 g/L enhanced the k_{app} values to 0.0069, 0.0093, and 0.0115 min⁻¹, respectively (Table 3.a). This improvement can be attributed to the greater availability of illuminated CoSe_x nanocatalyst surface

sites, which promotes photon absorption, electron-hole pair formation, and the subsequent generation of oxidative radicals such as $\bullet\text{OH}$ and $\bullet\text{O}_2^-$ [49].

A further increase in the CoSe_x nanocatalyst dosage resulted in a more pronounced enhancement in the reaction rate, with k_{app} values reaching 0.0320, 0.0330, and 0.0417 min^{-1} at 1.0, 1.2, and 1.5 g/L, respectively. Although the highest k_{app} value was obtained at 1.5 g/L, the degradation efficiency results indicated that near complete RO 107 removal was already achieved at 1.0 g/L. Therefore, considering both kinetic acceleration and catalyst economy, 1.0 g/L can be regarded as the optimum CoSe_x nanocatalyst dosage for the photocatalytic degradation of RO 107 under the applied UV-C irradiation conditions [50].

The slight decrease in R^2 values at higher catalyst dosages, particularly at 1.0–1.5 g/L, may be associated with rapid degradation at the initial reaction stage and the near complete removal of RO 107 toward the end of the irradiation period. Nevertheless, all R^2 values remained sufficiently high, confirming the reliability of the pseudo-first-order kinetic model for describing the CoSe_x nanocatalyst assisted photocatalytic degradation process [51].

3.2.2. Effect of initial RO 107 concentration

The effect of the initial RO 107 concentration on the photocatalytic degradation performance of the CoSe_x nanocatalyst under UV-C irradiation is presented in Fig. 9(a). The degradation efficiency was strongly dependent on the initial dye concentration. At relatively low RO 107 concentrations of 5, 15, and 25 mg/L, very high degradation efficiencies of 98.17%, 98.06%, and 97.87% were achieved after 120 min, respectively. These

results indicate that, at low pollutant concentrations, the available photocatalytically active CoSe_x nanocatalyst surface sites and generated ROS were sufficient to effectively oxidize RO 107 molecules. However, a gradual decrease in degradation efficiency was observed as the initial RO 107 concentration increased beyond 25 mg/L. When the dye concentration was increased to 45 and 75 mg/L, the degradation efficiency decreased to 88.15% and 74.55%, respectively. This decline became more pronounced at higher concentrations, reaching 67.59%, 47.56%, and 40.81% for 100, 125, and 150 mg/L RO 107, respectively (Fig. 9(a)). The reduced photocatalytic performance at elevated dye concentrations can be attributed to several factors, including the saturation of active sites on the CoSe_x nanocatalyst surface, increased competition among dye molecules for ROS, and the inner filter effect caused by the intense color of the solution. At higher RO 107 concentrations, the penetration of UV-C photons into the reaction medium is restricted, thereby reducing the effective photoactivation of the catalyst and limiting electron-hole pair generation [52].

The apparent pseudo-first-order kinetic parameters for the photocatalytic degradation of RO 107 at different initial dye concentrations under UV-C irradiation are presented in Fig. 9(b). The kinetic data exhibited good agreement with the pseudo-first-order model, as confirmed by the high correlation coefficients, with R^2 values ranging from 0.9452 to 0.9916. These results indicate that the photocatalytic degradation of RO 107 over the CoSe_x nanocatalyst can be reliably described by apparent pseudo-first-order kinetics under the investigated experimental conditions. The apparent rate constant (k_{app}) decreased progressively with increasing

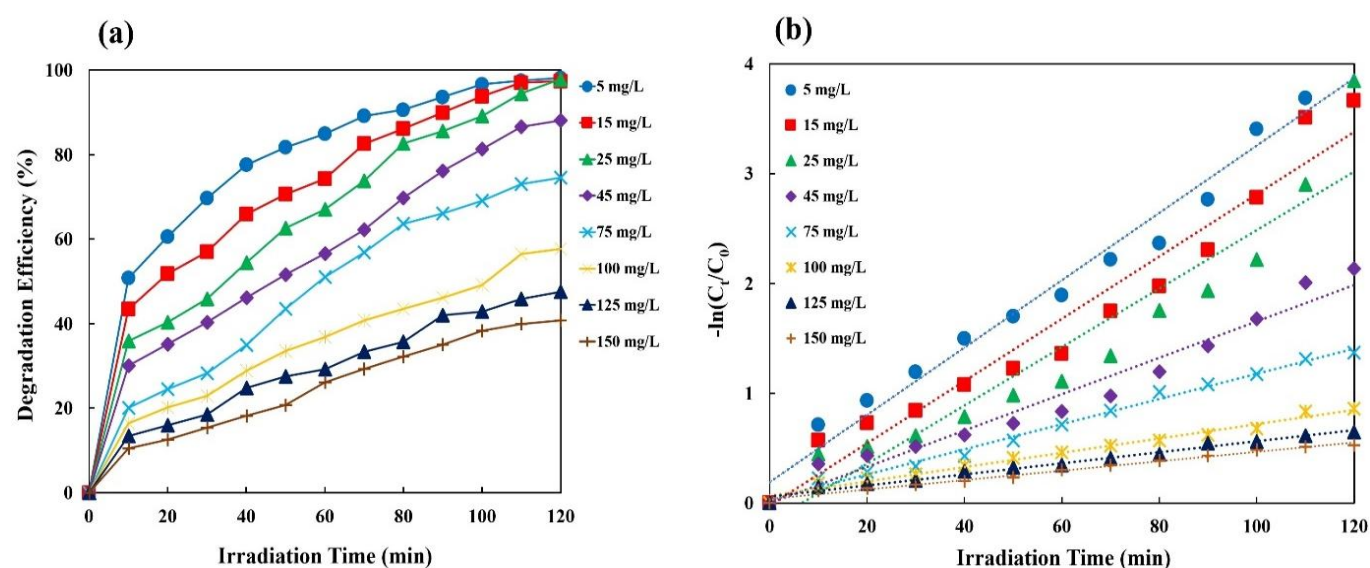


Figure 9. (a) Effect of initial dye concentration on the degradation of RO 107 by photocatalytic degradation process, (b) Apparent pseudo-first-order reaction kinetics. (Experimental conditions: Catalyst dosage: 1.0 g/L, pH for RO 107: Natural pH, Irradiation source: UV-C, Irradiation time: 120 min)

initial RO 107 concentration [53]. At low dye concentrations of 5, 15, and 25 mg/L, the k_{app} values were 0.0333, 0.0328, and 0.0320 min^{-1} , respectively (Table 3.b), demonstrating rapid photocatalytic oxidation due to the sufficient availability of active CoSe_x nanocatalyst surface sites and ROS relative to the number of dye molecules in solution. Under these conditions, UV-C photons can effectively penetrate the reaction medium, promoting efficient catalyst photoactivation, electron hole pair generation, and radical mediated degradation reactions [54].

As the initial RO 107 concentration increased from 45 to 150 mg/L, a continuous decrease in k_{app} was observed. The k_{app} value declined from 0.0177 min^{-1} at 45 mg/L to 0.0114, 0.0071, 0.0053, and 0.0043 min^{-1} at 75, 100, 125, and 150 mg/L, respectively (Table 3.b). This reduction in the reaction rate can be attributed to the increased number of dye molecules competing for the limited photocatalytic active sites and oxidative radical species. In addition, higher RO 107 concentrations may intensify the light screening effect of the colored solution, thereby reducing UV-C photon penetration and limiting the effective activation of CoSe_x nanocatalyst. Consequently, the formation rate of ROS such as $\bullet\text{OH}$ and $\bullet\text{O}_2^-$ becomes insufficient to maintain rapid degradation at elevated pollutant loadings [55].

3.2.3. Effect of pH

The influence of solution pH on the photocatalytic degradation of RO 107 over the multiphase CoSe_x nanocatalyst under UV-C irradiation is shown in Fig. 10(a). The degradation efficiency was strongly affected by the initial pH of the reaction medium. Under highly acidic conditions, the photocatalytic performance was considerably suppressed, with only 44.78% degradation achieved at pH 2 after 120 min. When the

pH was increased to 4, the degradation efficiency improved to 70.65%, indicating that excessive proton concentration in strongly acidic media negatively affects the photocatalytic oxidation of RO 107. A remarkable enhancement in degradation efficiency was observed at the natural pH of RO 107 solution, corresponding to pH 5.5, where 97.87% degradation was achieved within 120 min. Further increases in pH resulted in slightly higher degradation efficiencies, reaching 98.37%, 98.88%, and 99.33% at pH 6, 8, and 10, respectively (Fig. 10(a)). These results demonstrate that the CoSe_x nanocatalyst exhibits excellent photocatalytic activity under near neutral and alkaline conditions, while acidic conditions significantly inhibit the degradation process [56]. The lower degradation efficiency under acidic conditions may be attributed to unfavorable surface charge interactions between the catalyst surface and RO 107 molecules, as well as the reduced availability of hydroxyl ions (OH^-) required for hydroxyl radical ($\bullet\text{OH}$) formation. In contrast, under near neutral and alkaline conditions, the increased presence of OH^- ions can facilitate the generation of highly reactive $\bullet\text{OH}$ radicals, thereby accelerating the oxidative degradation of RO 107. Moreover, the improved catalyst–pollutant interaction and enhanced radical mediated oxidation at higher pH values contribute to the near complete removal of the dye. Although the highest degradation efficiency was obtained at pH 10, the difference between natural pH and alkaline conditions was relatively small. Therefore, considering practical applicability, chemical free operation, and reduced pH adjustment costs, the natural pH of RO 107 solution can be regarded as the most suitable operating condition for the CoSe_x assisted photocatalytic degradation process [57,58].

The apparent pseudo-first-order kinetic parameters for the photocatalytic degradation of RO 107 at different

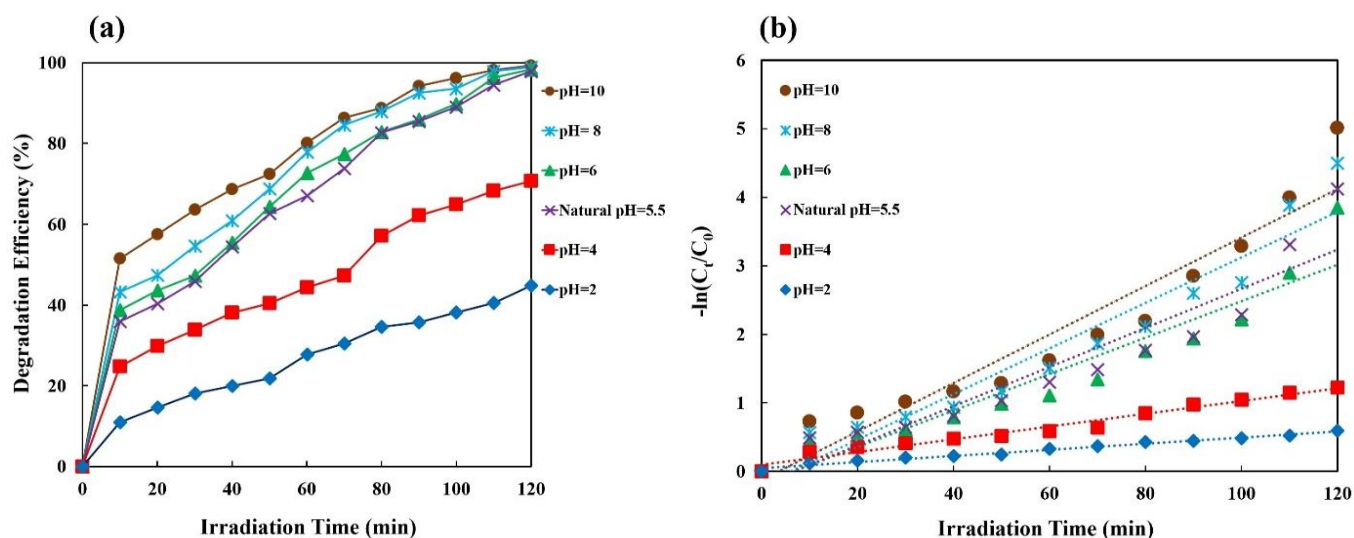


Figure 10. (a) The effect of pH on the degradation of RO 107 the photocatalytic degradation process, (b) Apparent pseudo-first-order reaction kinetics. (Experimental conditions: Initial dye concentration: 25 mg/L, Catalyst dosage: 1.0 g/L, Irradiation source: UV-C, Irradiation time: 120 min)

solution pH values under UV-C irradiation are presented in Fig. 10(b). The kinetic data showed good compatibility with the pseudo-first-order model, as confirmed by the relatively high correlation coefficients, with R^2 values ranging from 0.9300 to 0.9850. These results indicate that the CoSe_x nanocatalyst assisted photocatalytic degradation of RO 107 can be adequately described by apparent pseudo-first-order kinetics under the investigated pH conditions. The apparent rate constant (k_{app}) increased markedly as the solution pH shifted from strongly acidic to alkaline conditions. At pH 2, the lowest k_{app} value of 0.0049 min⁻¹ was obtained, indicating that the degradation reaction proceeded slowly under highly acidic conditions [59].

This limited kinetic performance can be attributed to the unfavorable catalyst–pollutant interaction, reduced availability of hydroxyl ions, and suppressed formation of •OH radicals. When the pH was increased to 4, the k_{app} value increased to 0.0102 min⁻¹, suggesting that the inhibition observed under strong acidic conditions was partially alleviated. A substantial enhancement in the reaction rate was observed at the natural pH of RO 107 solution, where the k_{app} value reached 0.0320 min⁻¹. Further increases in pH resulted in higher k_{app} values of 0.0343, 0.0374, and 0.0417 min⁻¹ at pH 6, 8, and 10, respectively (Table 3.c). This improvement can be mainly associated with the increased concentration of OH⁻ ions in the reaction medium, which facilitates the formation of highly reactive •OH radicals and accelerates the oxidative degradation of RO 107 [60,61].

3.2.4. Effect of different process on RO 107 degradation

The comparative evaluation of different processes clearly demonstrates the superior photocatalytic performance of the multiphase CoSe_x nanocatalyst toward RO 107 degradation under UV-C irradiation. As shown in Fig. 11(a), the photocatalytic process achieved a degradation efficiency of 97.87% within 120 min, whereas adsorption and direct photolysis resulted in considerably lower removal efficiencies of 43.43% and 40.97%, respectively. The limited removal observed in the adsorption experiment indicates that RO 107

molecules can interact with the surface of the CoSe_x nanocatalyst; however, adsorption alone is insufficient to ensure effective pollutant elimination [62]. Similarly, the relatively low photolytic degradation confirms that UV-C irradiation in the absence of the catalyst cannot provide adequate oxidative degradation of RO 107 under the investigated conditions (Fig. 11(a)).

The remarkable enhancement obtained in the photocatalytic system can be attributed to the synergistic interaction between UV-C irradiation and the CoSe_x nanocatalyst surface. Upon light activation, CoSe_x nanocatalyst promotes the generation and separation of photogenerated electron–hole pairs, which subsequently participate in the formation of reactive oxygen species such as •OH radicals and superoxide radical anions. These highly reactive species are mainly responsible for the oxidative cleavage of the chromophoric and aromatic structures of RO 107, leading to efficient dye degradation. Therefore, the much higher degradation efficiency achieved in the photocatalytic process confirms that RO 107 removal is not governed solely by physical adsorption or direct photolysis, but predominantly by catalyst mediated photocatalytic oxidation [63].

3.2.5. Effect of UV radiation region

The effect of different UV irradiation regions on the photocatalytic degradation of RO 107 in the presence of the multiphase CoSe_x nanocatalyst as shown in Fig. 11(b). The degradation efficiency was strongly influenced by the irradiation wavelength, following the order UV-C > UV-B > UV-A. After 120 min of reaction, the highest degradation efficiency was achieved under UV-C irradiation (97.87%), while lower efficiencies were obtained under UV-B (89.17%) and UV-A (80.69%) irradiation (Fig. 11(b)). This trend clearly indicates that shorter wavelength UV light provides more effective activation of the CoSe_x nanocatalyst, thereby promoting a higher photocatalytic degradation performance [64]. The superior efficiency observed under UV-C irradiation can be attributed to its higher photon energy, which facilitates more efficient excitation of electrons from the

Table 3. RO 107 degradation rate constants with regression coefficients for parameters such as catalyst dosage concentration, initial RO 107 concentration and effect of pH.

Catalyst dosage concentration (g/L)	(a)		(b)			(c)		
	k_{app} (min ⁻¹)	R^2	Initial dye concentration (mg/L)	k_{app} (min ⁻¹)	R^2	pH	k_{app} (min ⁻¹)	R^2
0.1	0.0040	0.9777	5	0.0333	0.9821	2	0.0049	0.9850
0.2	0.0057	0.9852	15	0.0328	0.9452	4	0.0102	0.9715
0.4	0.0069	0.9806	25	0.0320	0.9654	5.5	0.0320	0.9654
0.6	0.0093	0.9856	45	0.0177	0.9624	6	0.0343	0.9433
0.8	0.0115	0.9769	75	0.0114	0.9919	8	0.0374	0.9300
1.0	0.0320	0.9654	100	0.0071	0.9827	10	0.0417	0.9519
1.2	0.0330	0.9679	125	0.0053	0.9835			
1.5	0.0417	0.9573	150	0.0043	0.9875			

valence band to the conduction band of CoSe_x nanocatalyst, resulting in enhanced generation of electron-hole pairs and ROS [65].

In contrast, the relatively lower degradation efficiencies under UV-B and especially UV-A irradiation suggest that the reduced photon energy limits catalyst activation and decreases the production of oxidative radicals responsible for dye decomposition. Nevertheless, the appreciable degradation obtained under UV-B and UV-A irradiation still confirms the photoresponsive nature of the CoSe_x nanocatalyst across a broad UV region. These findings demonstrate that the photocatalytic performance of CoSe_x nanocatalyst is highly dependent on the irradiation source, and that UV-C irradiation provides the most favorable conditions for the efficient degradation of RO 107. Overall, the results highlight the important role of irradiation energy in

determining the extent of photocatalytic activity and further confirm the strong potential of CoSe_x nanocatalyst for the treatment of dye contaminated wastewater [66].

3.2.6. Effect of water matrix

The effect of the water matrix on the photocatalytic degradation of RO 107 using the CoSe_x nanocatalyst is illustrated in Fig. 11(c). Prior to their use in the photocatalytic experiments, the real water samples were subjected to a mild physical pretreatment to remove coarse suspended solids without substantially altering their native chemical composition. The collected samples were first allowed to settle and were then filtered through a 0.45 µm membrane filter. Following filtration, the samples were stored at approximately 4 °C in clean, tightly sealed containers and were brought to room

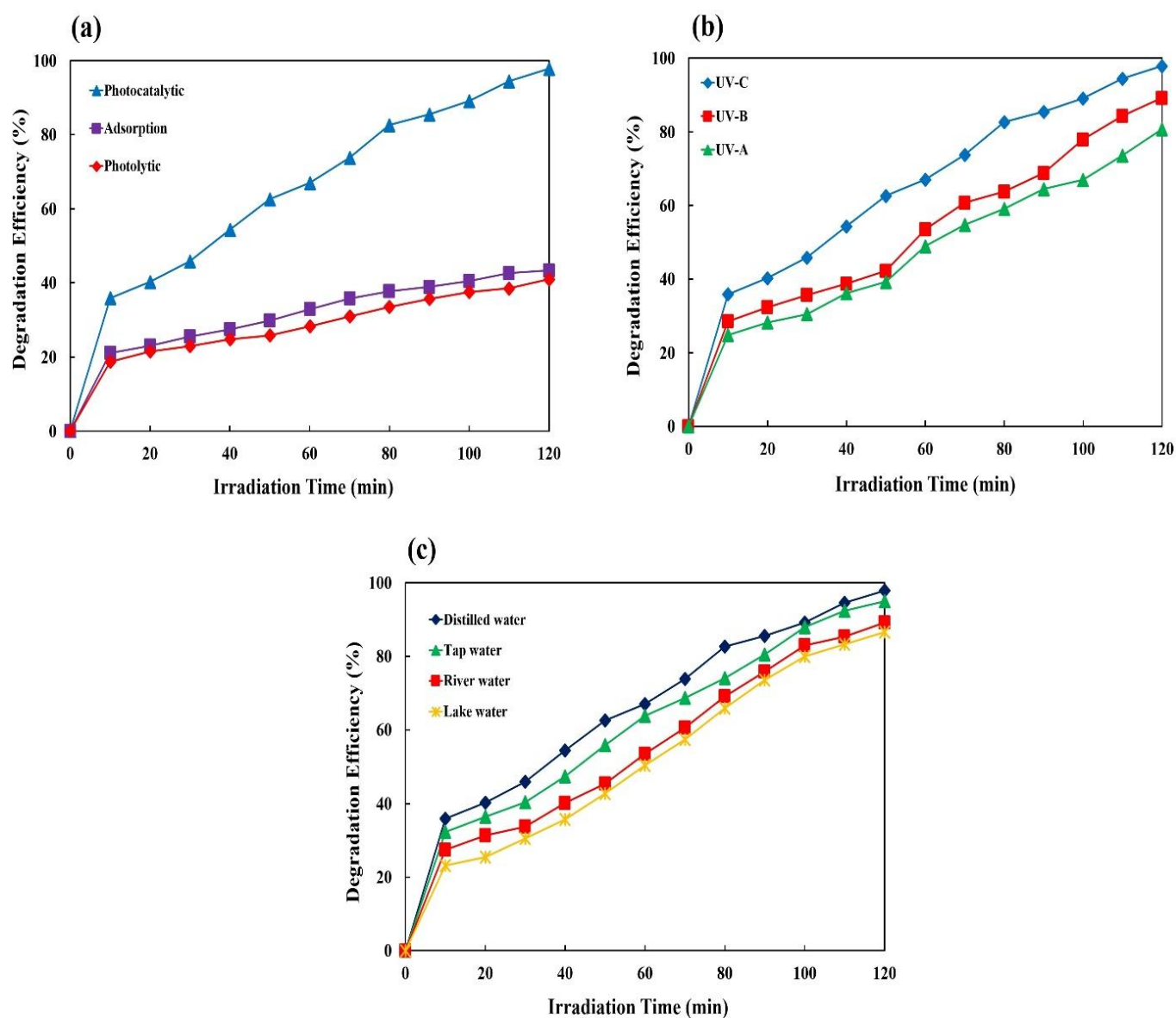


Figure 11. (a) Degradation effect of RO 107 by photocatalytic degradation process of different processes, (b) Degradation effect of RO 107 by photocatalytic degradation process of different irradiation, (c) Effect of water matrix (Experimental conditions: Initial dye concentration: 25 mg/L, Catalyst dosage: 1.0 g/L, pH for RO 107: Natural pH, Irradiation source: UV-C, UV-B, UV-A, Irradiation time: 120 min)

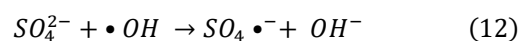
temperature before use. No chemical pretreatment, pH adjustment, ionic-strength modification, or disinfectant addition was performed. Thus, the naturally occurring dissolved inorganic ions and organic matter were largely retained, allowing the influence of the actual water matrix on the photocatalytic degradation performance of RO 107 to be evaluated under environmentally relevant conditions. The obtained results reveal that the degradation efficiency was strongly influenced by the type of aqueous medium, decreasing in the order of distilled water > tap water > river water > lake water. After 120 min of UV-C irradiation, the highest degradation efficiency was observed in distilled water (97.87%), whereas lower efficiencies were recorded in tap water (94.92%), river water (89.16%), and lake water (86.58%) (Fig. 11(c)). This trend clearly indicates that the presence of dissolved inorganic ions, natural organic matter, and other background constituents in real water samples adversely affects the photocatalytic performance of the CoSe_x nanocatalyst [67].

The superior degradation efficiency in distilled water can be attributed to the absence of competing species that may consume ROS or occupy the active sites of the catalyst surface. In contrast, the reduced performance in tap, river, and lake water is most likely associated with matrix induced interference, where coexisting ions and naturally occurring organic substances act as radical scavengers or light screening agents, thereby limiting the generation and utilization of oxidative species responsible for RO 107 degradation [68]. The more pronounced decline observed in river and lake water further suggests that the complexity of natural water matrices plays a critical role in suppressing photocatalytic activity. Nevertheless, despite this inhibitory effect, the CoSe_x nanocatalyst still maintained relatively high degradation efficiencies in all tested water matrices, demonstrating its promising applicability for the treatment of dye contaminated waters under more realistic environmental conditions [69].

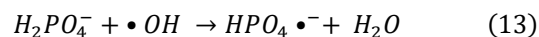
3.2.7. Effect of inorganic ions

The influence of inorganic ions on the photocatalytic degradation of RO 107 over the CoSe_x nanocatalyst was investigated to elucidate the dominant reactive species involved in the degradation mechanism, and the results are presented in Fig. 12(a). In the absence of any ions, the CoSe_x/UV-C system exhibited a high degradation efficiency of 97.87% after 120 min, confirming the strong photocatalytic activity of the catalyst. However, the introduction of different inorganic salts caused a noticeable decrease in RO 107 degradation, with efficiencies decreasing in the following order, without ions (97.87%) > Na₂SO₄ (92.51%) > NaH₂PO₄ (86.78%) >

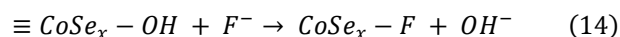
NaF (81.46%) > NaHCO₃ (79.13%) > NaCl (68.59%) > KI (56.04%) (Fig. 12(a)). This inhibition trend clearly demonstrates that the photocatalytic degradation of RO 107 is mainly governed by ROS and photogenerated charge carriers produced on the CoSe_x surface under UV-C irradiation [70]. The weakest inhibitory effect was observed in the presence of Na₂SO₄, where the degradation efficiency remained relatively high at 92.51%. This suggests that SO₄²⁻ ions have limited competition with RO 107 molecules for reactive oxidative species under the investigated conditions. The possible interaction of sulfate ions with •OH radicals can be expressed as follows Eq. (12).



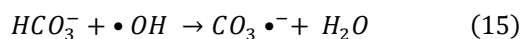
Although this reaction may partially consume •OH radicals, the generated sulfate radical species can still participate in oxidation reactions; therefore, the overall photocatalytic degradation efficiency is only slightly reduced [71]. A more pronounced decrease was observed in the presence of NaH₂PO₄, which reduced the degradation efficiency to 86.78%. Phosphate species may suppress photocatalytic activity by scavenging hydroxyl radicals (•OH) and competing for active sites on the CoSe_x surface as follows Eq. (13) [72].



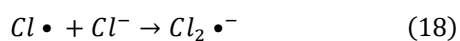
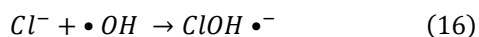
In addition, phosphate adsorption on the catalyst surface may limit the interaction between RO 107 molecules and photogenerated reactive species, thereby decreasing the effective degradation rate. The addition of NaF further reduced the degradation efficiency to 81.46%. Fluoride ions may strongly interact with surface metal sites of the CoSe_x nanocatalyst, leading to partial blockage of photocatalytically active centers [73]. This surface interaction can inhibit the formation of surface-bound •OH radicals by restricting the availability of adsorbed water and hydroxyl groups as follows Eq. (14).



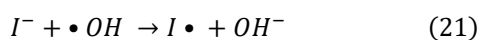
As a result, the reduced number of accessible active sites decreases the generation of ROS and suppresses RO 107 degradation. In the presence of NaHCO₃, the degradation efficiency decreased to 79.13%, indicating a significant scavenging effect of bicarbonate ions toward •OH radicals. Bicarbonate can rapidly react with •OH to form carbonate ions species, which are generally less reactive and more selective than •OH radicals as follows Eq. (15) [74].



This conversion decreases the concentration of highly oxidative $\bullet OH$ radicals in the reaction medium, thereby limiting the degradation of RO 107. NaCl caused a stronger inhibition, reducing the degradation efficiency to 68.59%. Chloride ions can react with $\bullet OH$ radicals and photogenerated holes, producing chlorine-based radical species with lower oxidative efficiency toward RO 107 compared with $\bullet OH$ as follows Eqs. (16–19) [75].



The formation of chlorine radical species and the consumption of hydroxyl radicals ($\bullet OH$) decrease the availability of highly reactive oxidants, resulting in a substantial reduction in photocatalytic performance. The most significant inhibition was observed in the presence of KI, where the degradation efficiency decreased sharply from 97.87% to 56.04%. This pronounced suppression indicates that photogenerated holes and surface-bound hydroxyl radicals ($\bullet OH$) play a dominant role in the degradation of RO 107. Iodide ions are highly effective scavengers of h^+ and $\bullet OH$, as represented by the following Eqs. (20–23) [76].



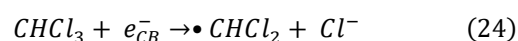
The strong consumption of photogenerated holes and hydroxyl radicals ($\bullet OH$) by iodide ions markedly inhibits the oxidative degradation pathway, confirming that h^+ and $\bullet OH$ are among the principal reactive species in the CoSe_x/UV-C photocatalytic system. As a result, the scavenger experiments provide important mechanistic evidence for the photocatalytic degradation of RO 107 over the CoSe_x nanocatalyst. The inhibition trend indicates that the degradation process is mainly driven by photogenerated holes and hydroxyl radicals ($\bullet OH$), while superoxide radicals may also contribute to the

oxidative transformation of the dye [77,78]. The strong inhibitory effects of KI, NaCl, and NaHCO₃ confirm the critical role of charge carriers and radical mediated oxidation in RO 107 degradation. Therefore, the superior performance of the CoSe_x nanocatalyst can be attributed to its ability to efficiently generate and utilize ROS under UV-C irradiation, promoting the oxidative cleavage of RO 107 and its subsequent degradation into smaller intermediates [79].

3.2.8. Effect of organic ions

The role of organic ions in the photocatalytic degradation of RO 107 over the CoSe_x nanocatalyst was investigated to identify the dominant reactive species involved in the oxidation mechanism, and the results are presented in Fig. 12(b). In the absence of any ions, the CoSe_x/UV-C system achieved a high degradation efficiency of 97.87% within 120 min, confirming the strong photocatalytic activity of the catalyst [80]. However, the addition of organic ions decreased the degradation efficiency to different extents, following the order: without ions (97.87%) > chloroform (91.30%) > EDTA (79.96%) > t-butanol (73.87%) > benzoquinone (66.17%). This inhibition trend clearly demonstrates that the degradation of RO 107 is mainly controlled by radical mediated photocatalytic oxidation rather than by direct photolysis or adsorption alone [81].

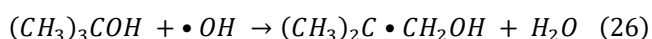
The weakest inhibitory effect was observed in the presence of chloroform, where the degradation efficiency decreased slightly from 97.87% to 91.30%. Chloroform can act as an electron ion by consuming photogenerated electrons from the conduction band, as represented by the following Eq. (24) [82].



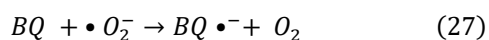
The relatively limited decrease observed in the presence of chloroform suggests that direct electron consumption is not the primary limiting factor in RO 107 degradation. However, the partial inhibition indicates that photogenerated electrons still contribute indirectly to the degradation mechanism by reducing dissolved oxygen to form $\bullet O_2^-$ radicals. The addition of EDTA reduced the degradation efficiency to 79.96%, indicating the important role of photogenerated holes in the photocatalytic oxidation process [83]. EDTA is widely recognized as an effective hole ions and can suppress hole-mediated oxidation according to the as represented by the following Eq. (25).



The decrease in degradation efficiency in the presence of EDTA confirms that h^+_{VB} species participate directly in RO 107 oxidation and also contribute indirectly to $\bullet OH$ formation through the oxidation of H_2O or OH^- on the catalyst surface. A more pronounced inhibition was observed with t-butanol, which decreased the degradation efficiency to 73.87%. Since t-butanol is a typical hydroxyl radical scavenger, this result demonstrates the significant contribution of $\bullet OH$ radicals to RO 107 degradation [84]. The scavenging reaction can be expressed as represented by the following Eq. (26).



The considerable suppression caused by t-butanol indicates that hydroxyl radicals are one of the main oxidative species responsible for the cleavage of azo linkages, chromophoric groups, and aromatic rings in the RO 107 molecule. The strongest inhibitory effect was obtained in the presence of benzoquinone, where the degradation efficiency decreased markedly to 66.17%. Benzoquinone is an efficient scavenger of superoxide radical anions, and its reaction with $\bullet O_2^-$ can be represented as by the following Eq. (27) [85].



The substantial reduction in degradation efficiency after benzoquinone addition indicates that $\bullet O_2^-$ radicals play a crucial role in the CoSe_x/UV-C photocatalytic system. This result suggests that the reduction pathway initiated by photogenerated electrons and dissolved oxygen is highly important for RO 107 degradation. The consumption of $\bullet O_2^-$ by benzoquinone limits the

formation of secondary oxidative species such as $HO_2\bullet$, H_2O_2 , and $\bullet OH$, thereby significantly suppressing the overall degradation efficiency [86].

As a result, the organic ions experiments provide strong mechanistic evidence for the photocatalytic degradation pathway of RO 107 over the CoSe_x nanocatalyst. The inhibition order indicates that superoxide radical anions are the most influential reactive species, followed by $\bullet OH$ radicals and photogenerated holes, whereas the direct contribution of photogenerated electrons is comparatively lower [87]. Therefore, the degradation of RO 107 in the CoSe_x/UV-C system can be mainly attributed to the synergistic action of $\bullet O_2^-$, $\bullet OH$, and h^+ species. These reactive species promote the oxidative cleavage of the dye structure and facilitate its transformation into smaller degradation intermediates, confirming the efficient radical-mediated photocatalytic activity of the CoSe_x nanocatalyst [88].

3.2.9. Reusability of the CoSe_x nanocatalyst in the photocatalytic degradation of RO 107

The reusability and operational stability of the CoSe_x nanocatalyst were evaluated through six consecutive photocatalytic degradation cycles of RO 107 under the optimized reaction conditions, and the results are presented in Fig. 13(a). In the first cycle, the CoSe_x nanocatalyst exhibited a high degradation efficiency of 97.87% after 120 min of UV-C irradiation, confirming its strong initial photocatalytic activity toward RO 107 removal. After repeated use, the degradation efficiency gradually decreased to 94.12%, 88.73%, 86.89%, 82.27%, and 81.23% in the second, third, fourth, fifth, and sixth cycles, respectively. Although a progressive decline was observed, the catalyst still retained approximately 83%

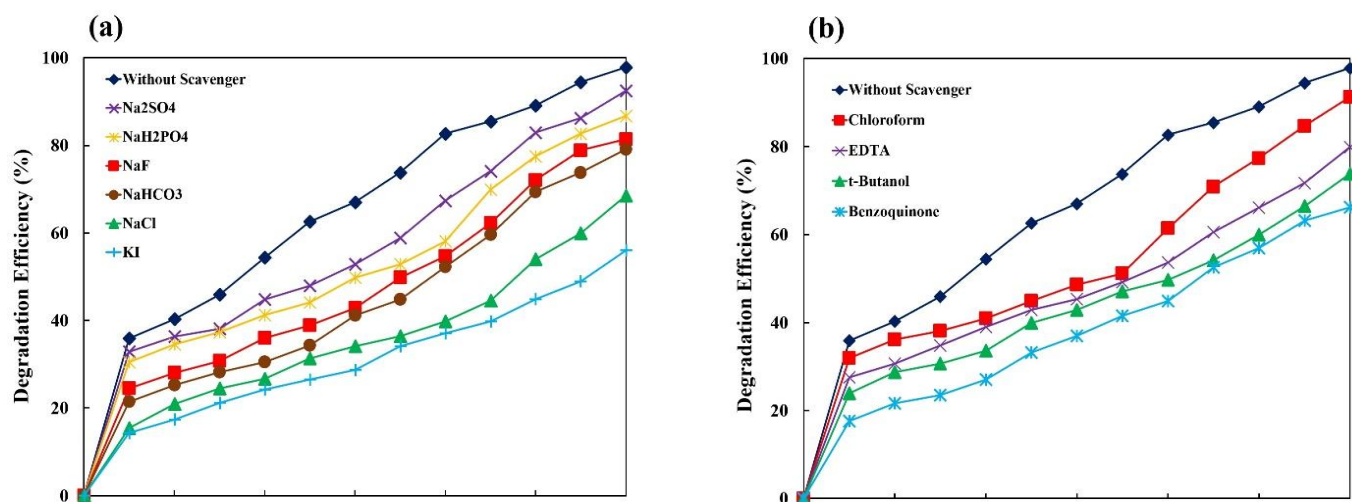


Figure 12. (a) Effect of inorganic ions on the degradation of RO 107 by photocatalytic degradation process, (b) Effect of organic ions on the degradation of RO 107 by photocatalytic degradation process. (Experimental conditions: Initial dye concentration: 25 mg/L, Catalyst dosage: 1.0 g/L, pH for RO 107: Natural pH, Ions concentration: 25 mg/L, Irradiation source: UV-C, Irradiation time: 120 min)

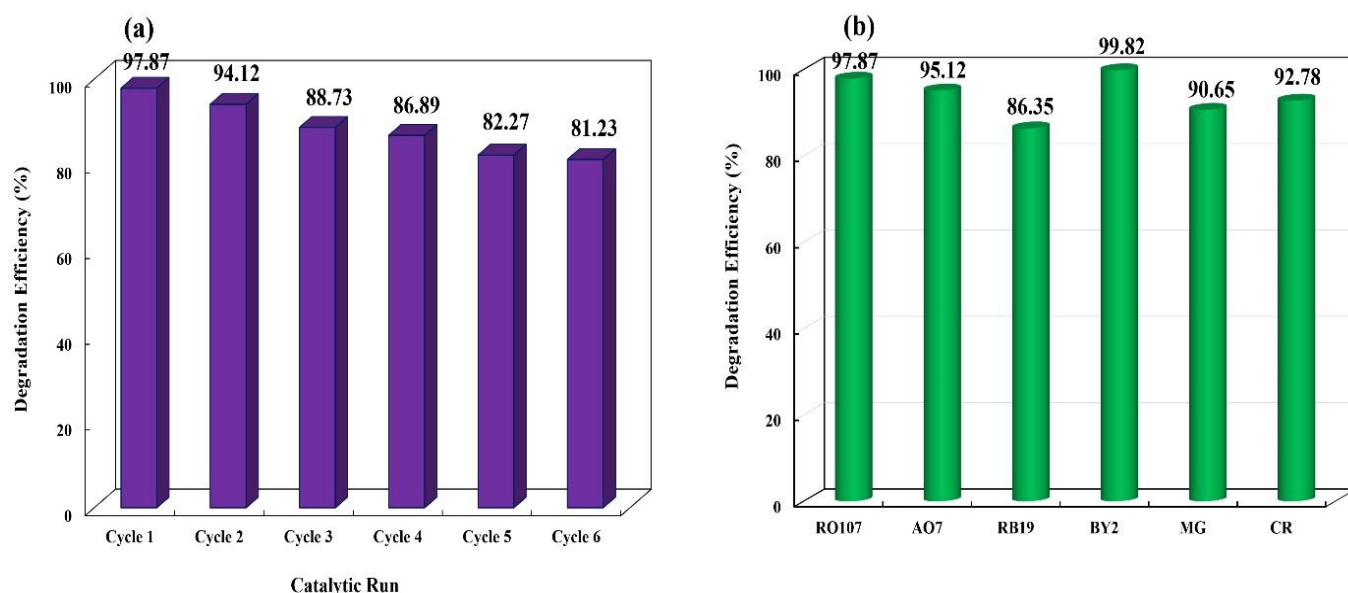


Figure 13. (a) Reusability of the CoSe_x nanocatalyst by photocatalytic degradation process, (b) Effect of photocatalytic degradation different dyes in the presence of CoSe_x nanocatalyst. (Experimental conditions: Initial dye concentration: 25 mg/L, Catalyst dosage: 1.0 g/L, pH for RO 107: Natural pH, Irradiation source: UV-C, Irradiation time: 120 min)

of its initial photocatalytic performance after six successive cycles, indicating acceptable reusability and stability (Fig. 13(a)). The decrease in degradation efficiency during repeated cycles may be attributed to partial catalyst loss during the recovery and washing steps, possible blockage of active surface sites by adsorbed dye molecules or degradation intermediates, and a reduction in the availability of photoactive sites after prolonged irradiation [89]. In addition, the accumulation of organic residues on the catalyst surface may hinder light absorption and suppress the efficient generation of reactive oxygen species. Nevertheless, the relatively high degradation efficiency maintained even after the sixth cycle demonstrates that the CoSe_x nanocatalyst possesses good recyclability and can be repeatedly applied for RO 107 degradation without severe activity loss. These findings highlight the practical potential of CoSe_x nanocatalyst as a reusable photocatalyst for the treatment of dye contaminated wastewater [90].

3.2.10. Effect of multiphase CoSe_x nanocatalyst on different dye contaminants

The applicability of the multiphase CoSe_x nanocatalyst toward the photocatalytic degradation of different dye molecules was investigated under identical experimental conditions, and the results are presented in Fig. 13(b). The degradation efficiencies obtained after 120 min of UV-C irradiation followed the order BY 2 (99.82%) > RO 107 (97.87%) > AO 7 (95.12%) > CR (92.78%) > MG (90.65%) > RB 19 (86.35%). These results clearly demonstrate that the CoSe_x nanocatalyst exhibits high photocatalytic activity toward a broad range of organic dyes, although the degradation performance

varies depending on the molecular characteristics of the target pollutant. The nearly complete removal of BY 2 and the very high degradation efficiencies achieved for RO 107 and AO 7 indicate that these dye molecules are more susceptible to oxidative attack under the applied photocatalytic conditions (Fig. 13(b)).

The differences observed among the tested dyes can be attributed to variations in their molecular structure, aromatic complexity, chromophoric groups, molecular size, and affinity toward the catalyst surface. In particular, dyes with more complex and stable structures may exhibit greater resistance to photocatalytic oxidation, resulting in comparatively lower degradation efficiencies, as observed for RB 19 and, to a lesser extent, MG. In addition, differences in adsorption behavior and the accessibility of reactive sites on the dye molecules may influence their interaction with the photogenerated ROS [91]. Despite these variations, the consistently high degradation efficiencies obtained for all tested dyes confirm the versatile and effective nature of the CoSe_x nanocatalyst. Overall, these findings highlight the strong potential of CoSe_x nanocatalyst as a promising photocatalyst for the treatment of wastewater containing structurally diverse dye contaminants [92].

3.2.11. Comparison of RO 107 photocatalytic degradation with other reported methods

As summarized in Table 4, the photocatalytic performance of the multiphase CoSe_x nanocatalyst compares favorably with several previously reported catalytic systems for RO 107 degradation. Under UV-C irradiation, CoSe_x nanocatalyst achieved a degradation efficiency of 97.87% at an initial RO 107 concentration of 25 mg/L using a catalyst dosage of 1.0 g/L within 120 min.

Table 4. Comparison of catalytic activity of CoSe_x nanocatalyst with some reported catalyst in the degradation of RO 107.

Catalyst	RO 107 concentration (mg/L)	Catalyst dosage (g/L)	Degradation efficiency (%)	Reaction time (min)	Degradation technique	References
CuO _n -La ₂ O ₃ /γ-Al ₂ O ₃	200	0.70	94.03	90	UV-C photocatalysis	[93]
SrSnO ₃	100	0.67	98.0	600	UV-C photocatalysis	[94]
CaSnO ₃	10	0.67	51.0	300	UV-C photocatalysis	[95]
(Co,Mn)Fe ₂ O ₄ @TiO ₂	10	0.60	76.3	960	UV-C photocatalysis	[96]
Ni _{0.5} V _{0.5} Fe ₂ O ₄	10	0.33	45.0	100	UV-C photocatalysis	[97]
CoSe _x nanocatalyst	25	1.0	97.87	120	UV-C photocatalysis	This work

This performance was markedly higher than those reported for CaSnO₃ (51.0%), (Co,Mn)Fe₂O₄@TiO₂ (76.3%), and Ni_{0.5}V_{0.5}Fe₂O₄ (45.0%), despite differences in the experimental conditions. Although SrSnO₃ exhibited a slightly higher degradation efficiency of 98.0%, this value was obtained after a substantially longer irradiation period of 600 min, indicating that CoSe_x provides comparable removal performance within a considerably shorter treatment time. Similarly, the CuO_n-La₂O₃/γ-Al₂O₃ system achieved 94.03% degradation at a considerably higher initial RO 107 concentration of 200 mg/L. As a result, the comparative results demonstrate that multiphase CoSe_x possesses strong photocatalytic activity and provides an advantageous balance between degradation efficiency and irradiation time. Nevertheless, direct comparison among different studies should be interpreted cautiously because catalyst loading, pollutant concentration, reactor configuration, irradiation intensity, and other operating conditions vary considerably. These findings nevertheless highlight the potential of multiphase CoSe_x as an efficient photocatalyst for the treatment of RO 107 containing wastewaters.

4. Conclusions

In this study, a multiphase CoSe_x nanocatalyst was successfully synthesized by a hydrothermal method and systematically evaluated for the photocatalytic degradation of Reactive Orange 107 (RO 107) under UV irradiation. Structural and morphological characterization by XRD, FT-IR, SEM/EDX, HRTEM, N₂ adsorption-desorption, BET, and BJH analyses confirmed the formation of crystalline, aggregated nanostructures with accessible surface features suitable for photocatalytic reactions. Photocatalytic performance was strongly governed by catalyst dosage, initial dye concentration, solution pH, irradiation wavelength, and water matrix. Increasing the catalyst loading from 0.1 to 1.0 g/L enhanced RO 107 degradation from 38.22% to 97.87%, while only marginal improvements were observed at higher dosages, indicating near saturation of active photocatalytic sites. Under optimum conditions of 1.0 g/L catalyst, 25 mg/L RO 107, natural pH 5.5, UV-C irradiation, and 120 min reaction time, the system

achieved 97.87% degradation. The apparent pseudo-first-order rate constant increased from 0.0040 to 0.0417 min⁻¹ with increasing catalyst dosage. High degradation efficiencies above 97% were achieved at 5–25 mg/L RO 107, whereas increasing the dye concentration to 150 mg/L reduced removal to 40.81% because of active site competition and limited photon penetration. Solution pH significantly affected activity, with degradation increasing from 44.78% at pH 2 to 99.33% at pH 10. The CoSe_x/UV-C system outperformed adsorption and direct photolysis, and irradiation efficiency followed UV-C > UV-B > UV-A. Water matrix experiments revealed moderate inhibition in tap, river, and lake waters relative to distilled water. Ions tests identified superoxide radicals, photogenerated holes, and hydroxyl radicals as key reactive species involved in RO 107 oxidation. The catalyst retained approximately 83% of its initial activity after six reuse cycles and also exhibited high activity toward several structurally different dyes. These results establish important structure–performance relationships and provide mechanistic evidence supporting cobalt selenide photocatalysis for advanced wastewater treatment. As a result, multiphase CoSe_x nanocatalyst an efficient, reusable and mechanistically versatile photocatalytic platform for treating persistent azo-dye contaminants in water and related wastewaters.

CRediT authorship contribution statement

Murat Kıranşan: Original draft, Writing-review & editing, Supervision, Resources, Validation, Methodology, Investigation, Formal analysis, Visualization, Data curation, Software, Conceptualization, Funding acquisition.

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Declaration of competing 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.

Declaration of generative AI in scientific writing

During the preparation of this work, the authors used ChatGPT to improve the readability and language of the manuscript. After using this tool/service, the authors reviewed and edited the content as needed and took full responsibility for the content of the published article.

Data availability

All data generated or analyzed during this study are included in this published article. More information is available from the corresponding author.

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