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Efficient degradation of organic and inorganic contaminants in water using a ZnO-based heterojunction photocatalyst

Darlington C. Ashiegbu^a, Michael Enemuob^b and Herman Potgieter^{a,c}

^aSustainable and Innovative Metals and Minerals Extraction Technology (SIMMET) Laboratory, School of Chemical and Metallurgical Engineering, University of the Witwatersrand, Wits, South Africa; ^bDepartment of Energy and Mineral Engineering (EME), The Pennsylvania State University, University Park, Pennsylvania, USA; ^cDepartment of Natural Science, Manchester Metropolitan University, Manchester, UK

ABSTRACT

Access to clean water is essential for sustaining life, yet organic and inorganic contaminants pose significant risks to public health and ecosystems. In this study, a ZnO-BiOI heterojunction photocatalyst was synthesized and characterized for the degradation of methyl orange (MO), 2-chlorobiphenyl (2CBP), cyanide, and thiocyanate. Structural analyses (SEM-EDS, XRD, optical, and thermal techniques) revealed a highly porous, crystalline morphology. Under optimal conditions, the photocatalyst achieved complete removal of thiocyanate, cyanide, and MO within 30, 35, and 120 minutes, respectively, and 60% removal of 2CBP in 150 minutes. Photocatalytic performance was influenced by catalyst loading and initial contaminant concentration. For example, MO degradation increased from 59% to 100% as catalyst mass increased from 2.5 mg to 40 mg within 120 minutes. However, excess catalyst led to agglomeration and turbidity, reducing efficiency. Higher contaminant concentrations also diminished degradation due to active site saturation and light-screening effects. Kinetic studies showed pseudo-first-order behaviour, with half-lives of 12, 141, and 4 minutes for MO, 2CBP, and thiocyanate, respectively. This study highlights the importance of

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CONTACT Darlington C. Ashiegbu  darlingtonashiegbu1985@yahoo.com, darlington.ashiegbu@wits.ac.za  Sustainable and Innovative Metals and Minerals Extraction Technology (SIMMET) Laboratory, School of Chemical and Metallurgical Engineering, University of the Witwatersrand, Private Bag X3, Wits 2050, South Africa

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parameter optimization and demonstrates the potential of ZnO-BiOI heterojunctions as sustainable photocatalysts for industrial and environmental water treatment.

Introduction

Contemporary studies have increasingly focused on focused on renewable and sustainable energy sources. This trend is driven by the diminishing reserves of fossil fuels and the environmental repercussions associated with their extraction and consumption. The pervasive impact of impure water, laden with organic, inorganic, and microbial contaminants, has inflicted significant harm on both humans and ecosystems worldwide.

The textile industry plays a vital role in meeting consumer demands; however, it is one of the leading contributors to global environmental contamination, alongside its extensive consumption of fuels and chemicals (Desore & Narula, 2018). Among its environmental impacts, textile manufacturing significantly contributes to water pollution worldwide by discharging wastewater containing dyes. Inefficient dye-making processes result in substantial dye losses, with approximately 2 to 20% of these lost dyes being discharged into the environment as effluents (Lellis et al., 2019; Gnanasekaran et al., 2023). Such wastewater, mainly from printing and dyeing activities, is characterized by high concentrations of complex pollutants, elevated biochemical oxygen demand (BOD) and chemical oxygen demand (COD) levels, and weak biodegradability (Ochoa et al., 2016). Moreover, this effluent compromises water quality and also poses grave threats to aquatic ecosystems (Kaur & Singhal, 2014).

Polychlorinated biphenyls (PCBs) are synthetic chemicals known for their chemical stability and persistence in the environment (Hong et al., 1998). Despite their production and industrial use cessation, PCBs persist as hazardous pollutants in various environmental matrices. Prolonged exposure to PCBs can lead to chronic toxicity, adversely affecting organ systems, the central nervous system, and reproductive health (Dasary et al., 2010). The United States Environmental Protection Agency established stringent regulations, setting a zero maximum contaminant level goal and a maximum contaminant level of 0.5 ppb for PCBs in municipal water systems (Liang et al., 2014).

In addition to the textile industry, mining activities worldwide significantly contribute to water contamination, mainly by discharging effluents containing cyanides and thiocyanates. Gold mining operations have

historically utilized cyanidation as the major leaching method, resulting in the production of cyanide and thiocyanate-laden waste from the extraction of gold from low-grade ores (Budaev et al., 2015).

Several approaches have been proposed for addressing water contaminants, including biodegradation, incineration, solvent extraction, adsorption, and chemical treatment. However, these methodologies may not always yield satisfactory results (Jiang et al. 2017; Štrédllová & Cajthaml, 2022). Biodegradation, while effective, is often slow and requires careful monitoring (Wang et al., 2022). Solvent extraction, albeit effective, can be exorbitant and may involve the use of dangerous solvents. Although promising, adsorbents use requires vigilant monitoring to prevent saturation of the adsorbent and subsequent loss of efficacy (Jing et al., 2018; Štrédllová & Cajthaml, 2022). To address these challenges, innovative approaches are needed.

Photocatalysis has come into view as a powerful tool in environmental remediation, utilizing light to drive chemical reactions and degrade pollutants. A photocatalyst utilizes light energy to catalyse reactions on its surface. During this mechanism, the photocatalytic material captures incident light energy in the form of photons, typically ultraviolet (UV) or visible light, and uses this energy to initiate chemical transformations. The key principle behind photocatalysis is the exposure to photons which initiates charge carrier generation within the photocatalyst. These photoexcited electrons and holes possess high reactivity and can engage in oxidation-reduction reactions either with molecules adsorbed on the catalyst surface or within the surrounding medium. This leads to the degradation of contaminants, the activation of molecular oxygen for oxidation reactions, or the reduction of specific compounds. Photocatalysis has found widespread applications in addressing environmental pollution, especially through the breakdown of organic contaminants in aquatic and atmospheric systems (Ashiegbu & Potgieter, 2024). It presents multiple benefits in contrast to traditional treatment systems, including its ability to operate under mild conditions, its effectiveness in mineralizing a wide range of organic compounds, and its potential for solar-driven processes, utilizing the clean and inexhaustible energy of the sun. Moreover, photocatalysis is environmentally friendly, as it does not require the use of additional chemicals and can utilize renewable energy sources.

In this investigation, we applied an efficient, rapid, and direct method for degrading water contaminants through the synthesis of a heterojunction photocatalyst composed of ZnO and BiOI. The ZnO-BiOI heterojunction was selected for this study due to its synergistic properties that address the limitations of individual photocatalysts. ZnO stands out as a low-cost material with notable chemical robustness and high photocatalytic

efficiency; however, its efficiency is hindered by the fast recombination of photogenerated charge carriers and a wide bandgap that restricts light absorption to the UV region (Ferreira et al., 2021). Conversely, BiOI exhibits excellent visible-light absorption due to its narrow bandgap and layered structure, but its standalone photocatalytic activity is limited by poor charge mobility (Yu et al., 2024). Integrating ZnO with BiOI in a heterostructure enhances photocatalytic activity by promoting efficient separation of photoinduced charge carriers, reducing electron-hole recombination, and broadening absorption of light within the visible range (Ashiegbu et al., 2023). Previous studies have shown these synergistic effects to improve organic pollutants' degradation efficiency significantly (Alaveh & Samadi, 2024; Xiao et al., 2020; Zhang et al., 2018; Zhu et al., 2023). Such advantages make the ZnO-BiOI heterojunction a highly promising photocatalyst for addressing environmental challenges, including the treatment of cyanide in mining wastewater. This configuration aims to leverage the synergistic effects of these materials in photocatalytic degradation. Additionally, the degradation kinetics of the photodegradation experiments have been investigated by fitting the degradation reactions to a kinetic model, allowing for a deeper understanding of the photocatalytic degradation process.

Materials and methods

Chemicals

Various chemical reagents were utilized in this study, such as 2-chlorobiphenyl, potassium iodide, bismuth nitrate pentahydrate, zinc acetate dihydrate, and ethanol. These chemicals were sourced from Sigma-Aldrich and Associated Chemical Enterprises. Additionally, potassium thiocyanate, ferric chloride, and sodium cyanide were received from Associated Chemical Enterprises, while the University of the Witwatersrand provided methyl orange, hydrochloric acid, and ammonium hydroxide. The rhodanine indicator was obtained from DRD Gold. A water purification system from Millipore was utilized for all sample preparations. It is important to note that all solvents and chemicals utilized in the experiments were of analytical reagent (AR) grade and did not require further purification prior to use.

Materials preparation and synthesis

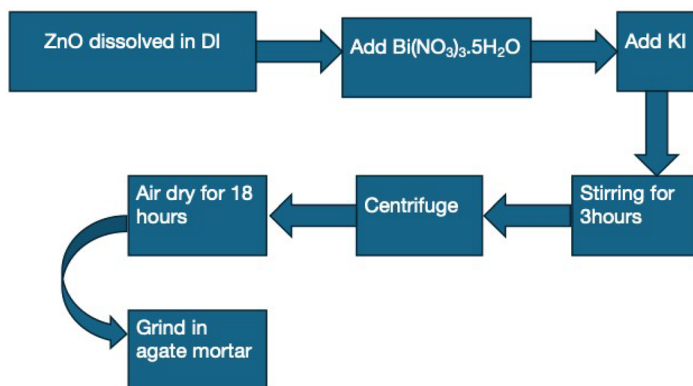
As detailed in the study by Ashiegbu and Potgieter (2024), the synthesis of heterostructure began with the preparation of ZnO through the sol-gel method using zinc acetate dihydrate. The process involved introducing a

mixture of zinc acetate dehydrate into a reactor attached to a reflux apparatus submerged in a water bath. Refluxing occurred for 30 minutes at 60°C with continuous stirring, during which oxalic acid, dissolved in alcohol, was slowly added to form gels. Subsequently, refluxing continued for another 60 minutes at 50°C. Following completion of the reflux process, the xerogel was cooled to room temperature and then oven-dried overnight at 80°C. After drying, the sample underwent calcination at 500°C in a furnace to yield ZnO nanoparticles.

To create the ZnO–BiOI heterojunction, pristine ZnO was suspended in water before 10.43 g of $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$, dissolved in alcohol, was introduced into the mixture. KI (3.57 g), initially solubilized in deionized water, was subsequently added in a controlled manner while stirring the mixture for an additional 3 hours. Once stirring ceased, the suspension underwent centrifugation and was left to air dry for 18 hours. The resulting dried material was gathered, ground, and transformed into the ZnO–BiOI heterojunction (Scheme 1).

Photocatalytic evaluation

The photo-activity of the heterostructure photocatalysts was evaluated by subjecting them to simulated solar radiation in a batch process, during which the degradation of 2-chlorobiphenyl (2CBP), methyl orange, cyanide, and thiocyanate compounds was monitored. In a standard procedure, 100 mL of deionized water containing the desired concentration of methyl orange (10 ppm), 2-chlorobiphenyl (10 ppm), cyanide (40 ppm), and thiocyanate (40 ppm) was prepared and placed in individual 150 mL beakers. These beakers were positioned on a stirrer plate, which was placed 20 cm away from the light source, and the initial concentrations



Scheme 1. Synthesis of ZnO–BiOI heterojunction.

of the pollutants were noted. Following a 30-minute equilibration period in the dark to allow the pollutants and photocatalysts to interact, the suspensions were stirred magnetically to ensure proper dispersion of the photocatalysts. The pH of each suspension was then adjusted using HCl and NH_4OH as necessary. The photocatalytic system was irradiated using an AM 1.5G 100mW/cm² solar radiation simulator, continuously stirring the suspensions throughout the experimental period. At specific time intervals, samples were extracted from the mixture using a syringe and filtration through a 0.22 μm membrane filter to eliminate photocatalyst particles. Post-filtration, the samples were then analysed using a Shimadzu 1800 spectrophotometer to determine the removal efficiency of the heterojunction photocatalyst. The characteristic wavelengths of thiocyanate ions (SCN^-) and methyl orange were utilized for analysis. In the case of 2-chlorobiphenyl (2CBP), a GC-MS process was employed, while free cyanide concentration was determined using the silver nitrate titration (SNT) protocol in the presence of rhodanine as an indicator. To maintain free cyanide in its ionic form and prevent the formation of toxic hydrogen cyanide gas, the pH of the cyanide (CN^-) solution was consistently adjusted to above 11. This is because cyanide exists predominantly as HCN at a pH below 10, a volatile and highly toxic gas which poses significant environmental and safety risks (Jaszczak et al., 2017). By maintaining a pH above 11, the equilibrium shifts toward the ionic form, CN^- , ensuring a safer experimental environment and preserving the integrity of the cyanide solution for accurate photocatalytic degradation studies.

Results and discussion

Characterization

Scanning Electron Microscopy (SEM) analysis was conducted to investigate the morphological features of the synthesized ZnO-BiOI heterojunction using a Carl Zeiss Sigma FE-SEM. The SEM images of the heterojunction, presented in Figure 1a, reveal a heterogeneous mix of nanoparticle shapes, including rod-like, spherical, and irregular forms, indicative of a non-uniform surface morphology without a distinct orientation. The ZnO nanoparticles (Figure 1b) exhibit a highly porous, sponge-like morphology with noticeable agglomeration. This characteristic can be attributed to the high-temperature synthesis process (500 °C), which resulted in the total degradation of the organometallic precursor and the formation of a dense microstructure. For the as-synthesized BiOI catalyst, as shown in Figure 1c, irregular, plate-like morphologies were observed. This morphology is likely influenced by the hydrothermal

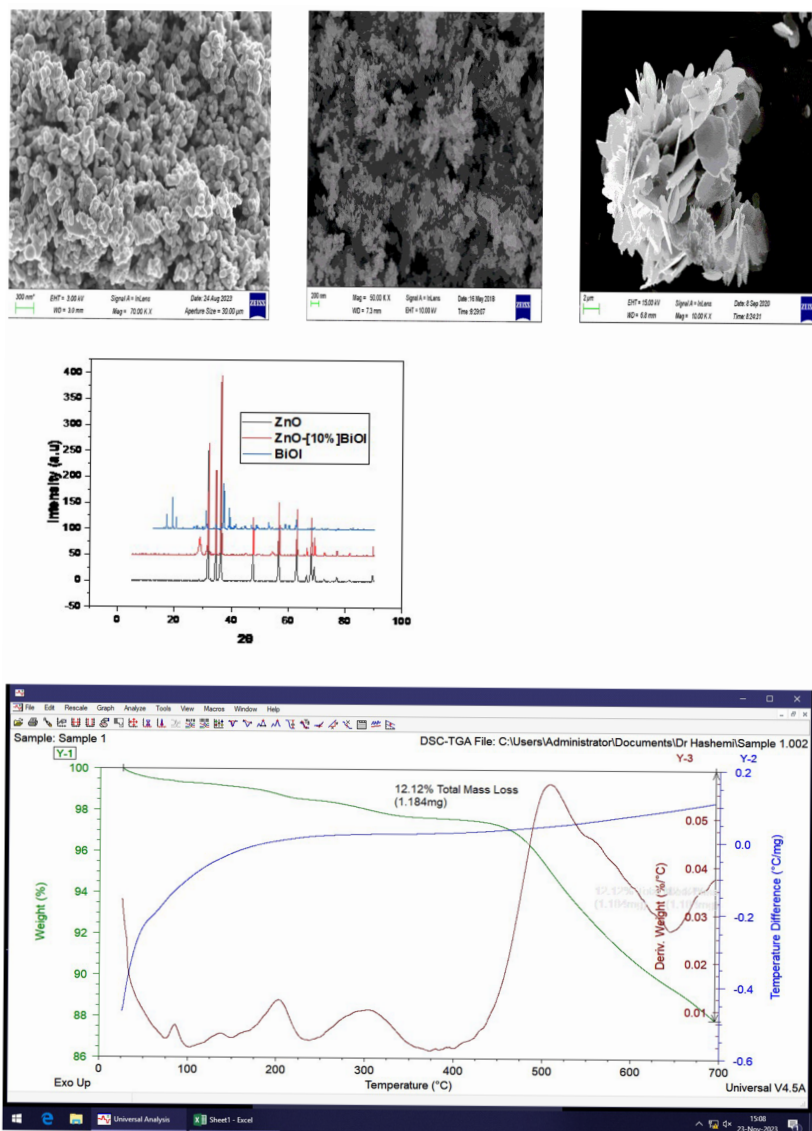


Figure 1. (a) SEM micrograph of the heterojunction photocatalyst (b) SEM image of pure ZnO (c) SEM image of pure ZnO (d) XRD patterns of pristine ZnO, BiOI and the prepared heterostructure (e) Thermogravimetric analysis of the heterostructure (f) Surface area and textural characteristics ZnO (g) Surface area and textural characteristics BiOI (h) Analysis of surface area alongside textural characteristics of the heterostructure.

synthesis method and the choice of low-viscosity solvents, which facilitated a high ion diffusion rate during crystal growth. Therefore, the solvent properties and synthesis conditions are critical in shaping the final

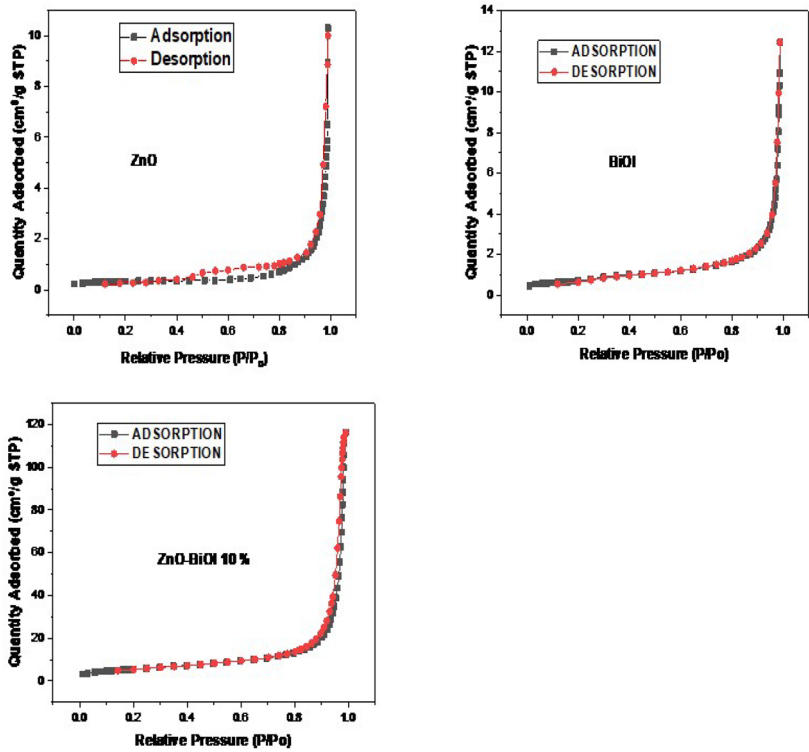


Figure 1. Continued.

Table 1. Elemental composition analysis of the synthesized heterostructure.

Element	Weight %	Atomic %
O	16.16	47.10
Zn	68.52	48.88
I	4.11	1.51
Bi	11.21	2.50
Total	100.00	

morphology of the BiOI nanoparticles. These distinct morphological features are expected to serve a vital function in the photocatalytic performance of the ZnO-BiOI heterojunction.

SEM energy-dispersive X-ray spectroscopy (EDS) analysis of the ZnO-BiOI heterojunction revealed its chemical composition. Zinc emerged as the primary constituent, constituting 68.52 wt% of the heterojunction, followed by oxygen at 16.16 wt%, bismuth at 11.21 wt%, and iodine at 4.11 wt%, as depicted in Table 1. This elemental verified that the synthesized catalyst contained the intended elements in the correct stoichiometric proportions, with no detectable impurities.

X-ray diffraction (XRD) analysis was used to examine the structural properties of the synthesized materials, namely ZnO nanoparticles, BiOI photocatalyst, and the ZnO-BiOI heterostructure, as shown in [Figure 1d](#). The XRD profile of ZnO nanoparticles exhibited distinct and well-defined peaks at 2θ angles of 31.7° , 34.4° , 36.1° , 47.3° , 56.3° , 62.6° , 66.3° , 67.9° , and 69.1° . These reflections align with the (100), (002), (101), (102), (110), (103), (200), (112), and (201) lattice planes characteristic of hexagonal ZnO, corresponding to the wurtzite crystal structure identified in JCPDS card no. 01-075-6445. The sharpness and intensity of these peaks suggest a highly crystalline nature, which can be linked to the high thermal treatment conditions used in the material preparation. No secondary phases or impurity peaks were detected, indicating the complete conversion of precursors and high material purity. The crystallite size, estimated from the most intense diffraction peaks using the Debye-Scherrer equation, was approximately 37.6 nm, confirming the nanoscale dimensions of the ZnO particles. For the BiOI photocatalyst, the XRD pattern revealed strong reflections indicative of a tetragonal crystal structure, as referenced by JCPDS card no. 00-010-0445. Key peaks appeared at 10° , 30° , 34° , 46° , and 56° , which correspond to the (001), (102), (110), (200), and (212) planes, respectively. Additionally, secondary phases such as $\text{Bi}_5\text{O}_7\text{I}$ and $\text{Bi}_7\text{O}_9\text{I}_3$ were observed, likely formed due to the extended hydrothermal synthesis carried out in a Teflon-lined autoclave. The sharpness of the peaks again confirmed the enhanced crystallinity of the sample. The average crystallite size of BiOI, derived via the Debye-Scherrer method, was found to be around 40 nm. The composite ZnO-BiOI heterostructure displayed diffraction peaks representative of both ZnO and BiOI phases. The ZnO phase retained its characteristic reflections at 2θ values of 31.7° , 34.4° , 36.1° , 47.3° , 56.3° , 62.6° , 66.3° , 67.9° , and 69.1° , corresponding to its hexagonal structure. Meanwhile, the BiOI-related peak around 29° was assigned to the (102) plane, signifying successful integration of BiOI into the heterostructure (Tong et al., 2017; Zeng et al., 2020). The presence of distinct crystalline peaks representing the presence of both ZnO and BiOI, along with the absence of any extraneous reflections, confirms the successful integration of the two components and the high phase purity of the resulting hybrid composite (Ashiegbu et al., 2023). The heterostructure also exhibited pronounced crystallinity, and its average crystallite size was determined to be approximately 31 nm using the Debye-Scherrer formula, reaffirming its nanostructured nature.

The weight percentage curve ([Figure 1e](#)) exhibits a gradual decrease across the entire heating range. Notably, between temperatures of 485°C and 575°C , the curve steepens, indicating a heightened rate of decomposition for the heterojunction during this temperature range. This observation aligns with the derived weight percentage curve, where the highest

peak occurs at 513 °C, representing the temperature corresponding to the maximum decomposition rate. Importantly, this temperature falls within the range of 485 °C to 575 °C, further emphasizing the correlation between the two curves and confirming that this temperature range fosters the fastest decomposition rate for the heterojunction (Azadi & Habibi-Yangjeh, 2015).

The optical attributes of the samples were analyzed using a UV-Vis spectrophotometer, with spectra recorded in the range of 200–900 nm at ambient conditions. The bandgap energies determined using Tauc plots derived from the Kubelka-Munk function, as expressed by Eq. (1):

$$\alpha h\nu = A(h\nu - E_g)^n \quad (1)$$

here, α is the absorption coefficient, A is a proportionality constant, h represents Planck's constant, ν is the photon frequency, E_g denotes the bandgap energy, and n is $\frac{1}{2}$ or 2 depending on whether the electronic transition is direct or indirect, respectively. The bandgap values were calculated by extending the linear region of the $(\alpha h\nu)^2$ versus $h\nu$ plot. The absorption spectra and corresponding Tauc plots for the composites are presented in [Supplementary Information 1a, 1b, and 1c](#). The absorption maxima for ZnO and the ZnO-BiOI composite were observed at 373 nm and 378 nm, respectively. The integration of BiOI into ZnO resulted in a slight red shift in the absorption spectrum of the heterostructure, a phenomenon consistent with observations reported in prior studies (Yan et al., 2022; Ashiegbu et al., 2022).

The calculated bandgap for pure ZnO was 3.37 eV, while the ZnO-BiOI composite presented a narrower bandgap of 3.0 eV. This bandgap reduction, attributed to the coupling of BiOI into ZnO, aligns with the detected red shift in the absorption spectrum of the heterojunction material, enhancing its optical response in the visible light region.

The surface area and textural properties of the synthesized materials were assessed using nitrogen (N_2) adsorption-desorption isotherms. As per the classification defined by IUPAC, the undoped ZnO sample exhibited a Type V isotherm with a characteristic H3 hysteresis loop, suggesting weak adsorbate-adsorbent interactions typically linked with non-rigid aggregates of plate-like particles. This sample displayed a relatively low specific surface area of 1.93 m²/g ([Figure 1f](#)). In contrast, the as-prepared BiOI photocatalyst showed a Type IV isotherm with minimal hysteresis, indicating a mesoporous structure interspersed with macropores. Its specific surface area was slightly higher at 2.61 m²/g ([Figure 1g](#)). Remarkably, the ZnO-[10%]BiOI heterostructure exhibited a significant enhancement in surface area, measured at 19.79 m²/g. The corresponding N_2 adsorption-desorption isotherm also followed a Type IV profile but lacked

prominent hysteresis, consistent with a mesoporous material with improved textural properties (Figure 1h). These results confirm that coupling ZnO with BiOI not only influences the crystallographic structure but also substantially improves surface characteristics, which are crucial for photocatalytic performance.

Photocatalytic study

Figure 2a and b illustrate the photodegradation efficiency plots of methyl orange and 2-chlorobiphenyl by the synthesized heterojunction. Notably, 5 mg of ZnO-BiOI successfully degraded 40 ppm of CN^- within 35 minutes of simulated solar light irradiation, as shown in Figure 1d. In comparison, the same catalyst dose achieved complete degradation of SCN^- in less than 30 minutes, as presented in Figure 1c. This performance surpasses that reported by Mediavilla et al. (2019), who observed complete cyanide degradation after 5 hours under simulated solar light using commercial undoped titania (TiO_2) as the catalyst. Moreover, the ZnO-BiOI heterostructure exhibited remarkable efficiency, completely destroying MO

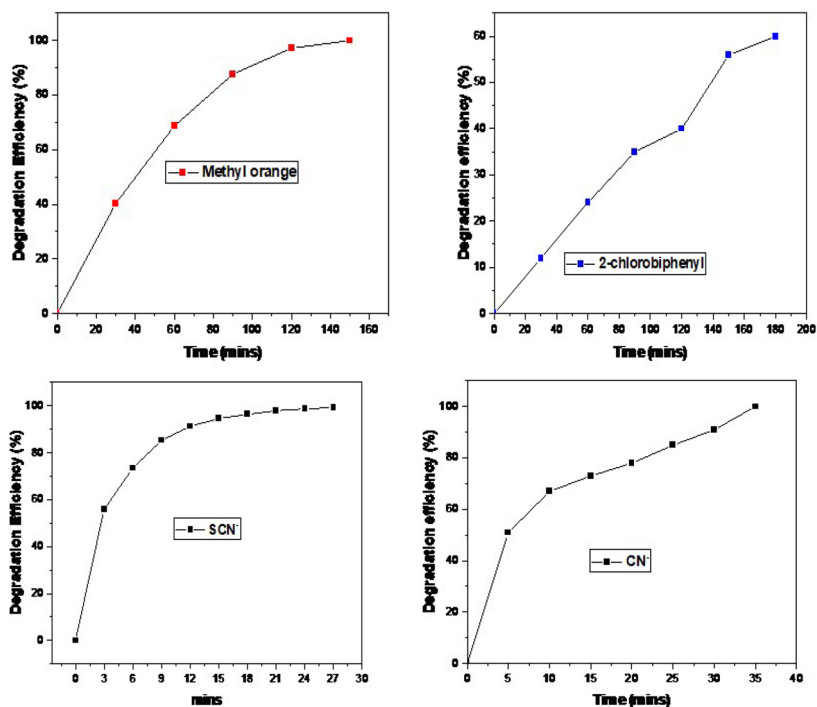


Figure 2. Photodegradation efficiency plots of (a) Methyl orange (b) 2-chlorobiphenyl (c) SCN^- (d) CN^- .

within 120 minutes and achieving a 60% degradation of 2-chlorobiphenyl within 180 minutes. A previous study by Regraguy et al. (2022) achieved 75% degradation efficiency when they applied TiO_2 photocatalyst in the degradation of MO dye. These results underscore the exceptional photocatalytic activity and efficiency of the synthesized heterojunction.

Effect of heterojunction-photocatalyst mass

The mass of the ZnO-BiOI photocatalyst significantly influences the efficiency of photocatalytic removal for methyl orange (MO), 2-chlorobiphenyl (2CBP), thiocyanate (SCN^-), and cyanide. Catalyst mass determines the availability of active sites, which facilitate pollutant adsorption, light absorption, and the development of oxidative reactive species (Rangarajan et al., 2022). However, both insufficient and excessive catalyst dosages can hinder photocatalytic performance, as observed in this study and supported by previous literature. For MO degradation, varying the catalyst dose from 2.5 mg to 40 mg showed a direct correlation between increased catalyst mass and improved degradation efficiency. While 2.5 mg achieved only 59% degradation in 180 minutes, 40 mg resulted in 100% degradation within 120 minutes (Figure 3a). This improvement is ascribed to the higher quantity of accessible active sites for photon absorption and pollutant interaction. Similar trends were observed for 2CBP degradation, where raising the catalyst mass from 35 mg to 150 mg enhanced pollutant decrease resulting from enhanced production of hydroxyl radicals. However, agglomeration and turbidity effects reduced photocatalytic activity beyond optimal loading, in agreement with the results reported by Ahmed et al. (2011) and Malik et al. (2022). The degradation of SCN^- further highlights the impact of catalyst mass (Figure 3c). At 2.5 mg, approximately 60% SCN^- removal was achieved in 27 minutes, whereas 15 mg enabled complete degradation within 12 minutes. The increase in active sites and improved electron-hole pair formation contributed to the enhanced performance, as Bahrami and Nezamzadeh-Ejhi (2015) reported. Similarly, for cyanide abatement, raising the catalyst mass from 5 mg to 15 mg led to complete degradation within 15 minutes (Figure 3d). However, at 25 mg, the removal process was delayed stemming from an overloaded catalyst system, which caused solution turbidity and reduced light penetration.

The study demonstrates the critical role of optimizing catalyst mass to balance active site availability with efficient light absorption. While increasing the catalyst dose enhances degradation efficiency up to an optimal point, excessive dosages can diminish performance due to agglomeration and light shielding effects. These findings emphasize the importance of determining the appropriate catalyst loading for each target

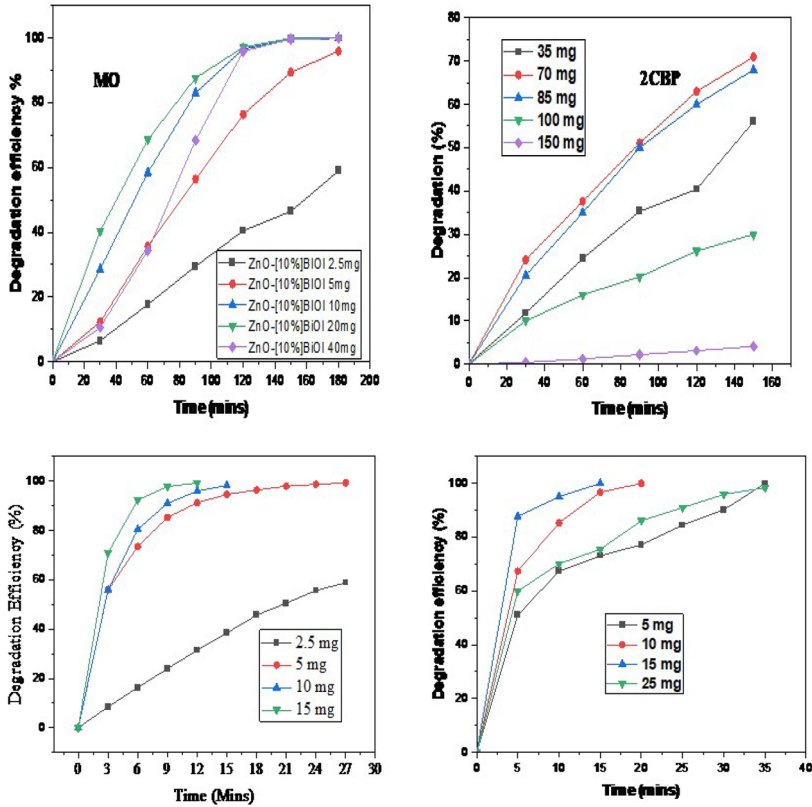


Figure 3. Influence heterojunction mass on the photodegradation of (a) Methyl orange (b) 2-chlorobiphenyl (c) SCN^- (d) CN^- .

pollutant to achieve maximal photocatalytic efficiency while maintaining cost-effectiveness.

Effect of contaminant concentration

The starting levels of contaminants has a crucial influence on the efficiency of their photocatalytic degradation using the ZnO-BiOI heterojunction. For methyl orange (MO), 2-chlorobiphenyl (2CBP), thiocyanate (SCN^-), and cyanide, degradation efficiency was observed to decrease as the initial contaminant concentration increased, highlighting the importance of optimizing this parameter to enhance photocatalytic performance.

In the case of MO, degradation efficiency decreased from 100% at lower concentrations (5–20 ppm) to 82% at 40 ppm within the same reaction time (Figure 4a). This decline is linked to the saturation of active sites on the photocatalyst surface and the increased optical density of the solution, which limits light penetration and photon interaction with the heterojunction (Kader et al., 2022). Similarly, for 2CBP, as the

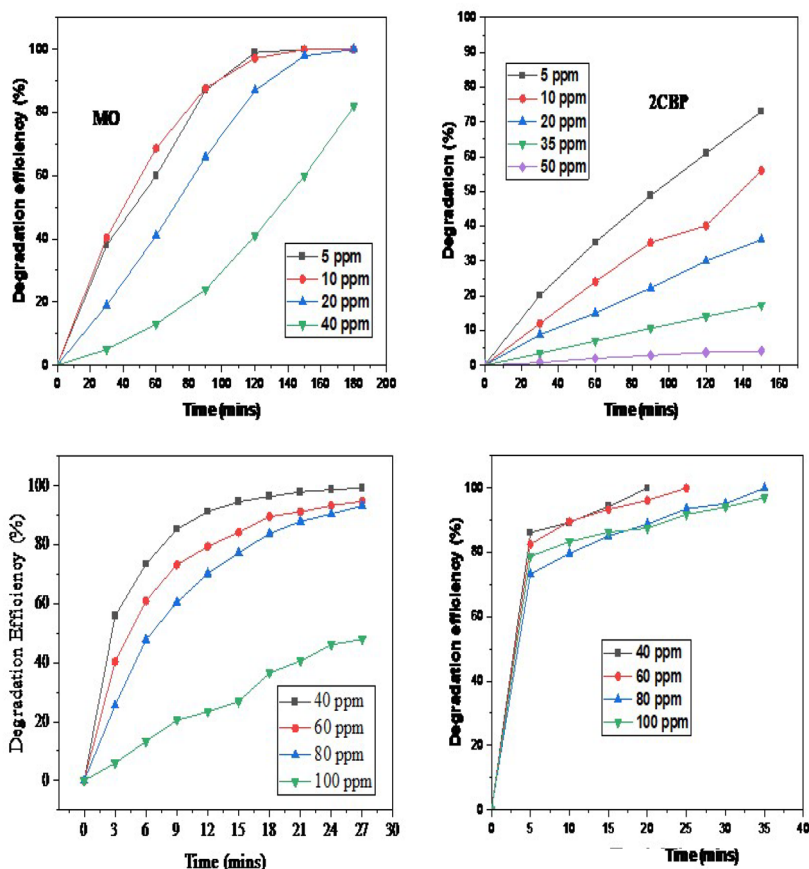


Figure 4. Influence of contaminant concentration on the photodegradation process (a) Methyl orange (b) 2-chlorobiphenyl (c) SCN⁻ (d) CN⁻.

concentration increased from 5 ppm to 50 ppm, photodegradation efficiency declined due to a higher number of pollutant molecules occupying the reaction sites on the catalyst, impeding photon access and slowing the degradation rate (Figure 4b).

A comparable trend was observed for SCN⁻, where degradation efficiency decreased from 100% at 40 ppm to approximately 45% at 100 ppm (Figure 4c). The reduction in efficiency at higher concentrations can be attributed to the light-screening effect caused by increased solution turbidity, as well as the overwhelming of catalytic sites by SCN⁻ molecules (Sudarsh et al., 2023). This phenomenon reduces the availability of hydroxyl radicals and reactive oxygen species (ROS), critical for pollutant degradation (Al-Abidy & Al-Nayili, 2022). For cyanide, degradation efficiency was similarly influenced by initial concentration. While over 85% degradation was achieved within 5 minutes at 40 ppm, increasing the

concentration to 100 ppm resulted in slightly lower efficiencies within the same reaction time, requiring 35 minutes for 97% degradation (Figure 4d). The decline in efficiency at higher cyanide concentrations is due to the excessive surface accumulation of cyanide ions on the photocatalyst, which inhibits charge carrier generation and ROS production (Baeissa, 2015). These observations underscore the critical role of optimizing initial contaminant concentrations in photocatalytic processes. Excessive

Table 2. Degradation efficiency, R^2 values, first-order kinetics, and half-lives ($t_{1/2}$) for the photodegradation of methyl orange, 2-chlorobiphenyl, thiocyanate, and cyanide using the heterojunction photocatalyst.

Contaminant	Degradation efficiency (%)	R^2	k (min^{-1})	$t_{1/2}$ (min)
Methyl orange	100	0.85	0.0587	11.9
2-chlorobiphenyl	60	0.969	0.0049	141
SCN^-	100	0.997	0.188	3.7
CN^-	100	0.973	0.0597	11.6

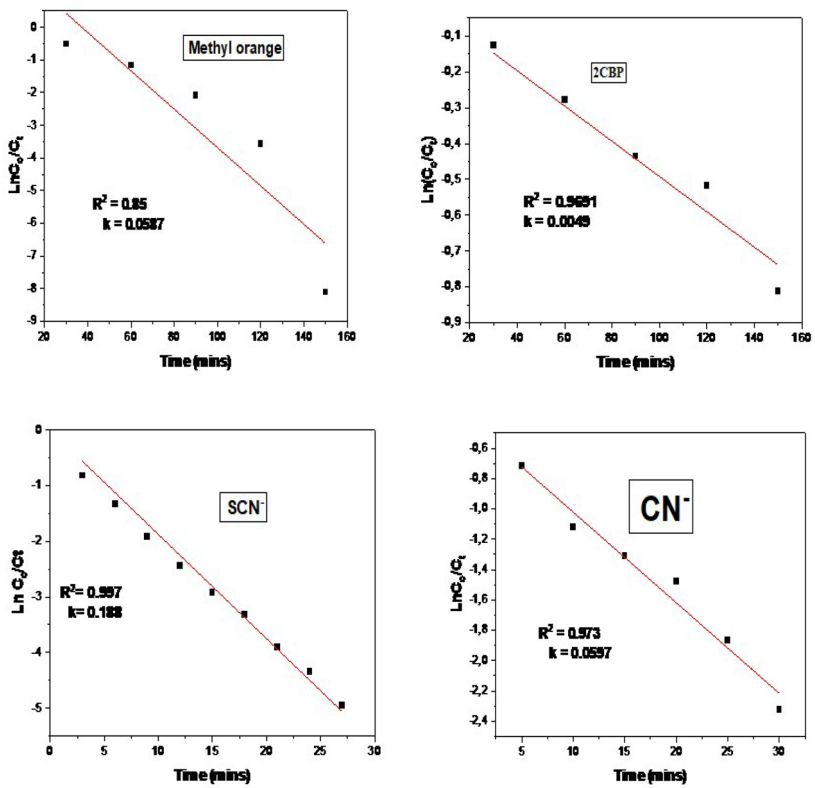


Figure 5. Plots based on pseudo-first-order kinetics for (a) methyl orange (b) 2-chlorobiphenyl (c) SCN^- (d) CN^- .

pollutant levels saturate active sites, hinder light penetration, and reduce ROS generation, thereby limiting degradation efficiency. The results align with previous studies and emphasize the importance of balancing pollutant load and catalyst activity to achieve effective photocatalytic degradation (Lubis et al., 2019; Zargaran et al., 2020; Dolatabadi et al., 2022).

Kinetics study

A pseudo-first-order kinetic model accurately describes the rate dynamics of the photodegradation process involving all the investigated reactions. Table 2 outlines the kinetic response consistent with a first-order reaction, demonstrated by the linear transformation $\ln(C_0/C_t)$ plotted against time. The table also provides the heterostructures' apparent reaction rate constants (k) and corresponding half-life ($t_{1/2}$) values. Analysis reveals that the concentration of MO is halved to its initial level within approximately 12 minutes when utilizing ZnO-BiOI, whereas it takes about 141 minutes for 2-chlorobiphenyl. Furthermore, SCN^- levels are diminished to half their initial concentration in just 4 minutes under similar conditions (Figure 5).

Conclusion

This study involved the fabrication of a heterojunction photocatalyst through a straightforward and direct synthesis process. The synthesized heterostructure underwent characterization using advanced characterization instruments. Subsequently, the prepared heterostructure was employed in the treatment of methyl orange dye, 2-chlorobiphenyl, thiocyanate ions, and cyanide ions. When subjected to irradiation using artificial solar light, the heterostructure demonstrated remarkable removal capabilities, facilitating the breakdown of 40 ppm CN^- within 35 minutes, 40 ppm SCN^- in under 30 minutes, 60% degradation of 2-chlorobiphenyl, and complete degradation of methyl orange dye. The pseudo-first-order kinetic model was determined to fit the photodegradation reactions best. Specifically, the CN^- level was observed to halve in approximately 12 minutes when applying the heterostructure, whereas it took about 141 minutes for 2-chlorobiphenyl degradation.

Disclosure statement

No potential conflict of interest was reported by the author(s).

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