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Recycling of Polyethylene Terephthalate to Bismuth-Embedded Bimetallic MOFs as Photocatalysts toward Removal of Cationic Dye in Water

Sana Karamat^a, Toheed Akhter^{a,}, Sadaf Ul Hassan^b, Muhammad Faheem^a, Asif Mahmood^c, Waheed Al-Masry^c, Shumaila Razzaque^d, Sadia Ashraf^a, Taewook Kim^e, Soo-Kyung Han^e, and Chan Ho Park^{e,*}*

^aDepartment of Chemistry, University of Management and Technology, C-II, Johar Town, 54770, Lahore, Pakistan.

^bDepartment of Chemistry, COMSATS University Islamabad, Lahore Campus, Lahore, Pakistan.

^cDepartment of Chemical Engineering, College of Engineering, King Saud University, Riyadh, 11421, King Saudi Arabia.

^dInstitute of Physical Chemistry, Polish Academy of Sciences, Kasprzaka, 44/51, 01-224 Warszawa, Poland.

^eDepartment of Chemical and Biological Engineering, Gachon University, Seongnam 13120, Republic of Korea.

KEYWORDS: Industrial Dye Removal, PET Waste Recycling, Bismuth-Embedded Photocatalysts, Green Synthesis, Metal-Organic Frameworks,

ABSTRACT

Our study presents a sustainable approach to fabricating efficient photocatalytic metal-organic frameworks (MOFs) by recycling polyethylene terephthalate (PET) waste from bottles. Through chemical depolymerization, recycled terephthalic acids (BDCs) obtained from PET waste were coordinated with copper (Cu) and nickel (Ni) to prepare a bimetallic Ni/Cu-MOF. After exploring various Ni:Cu ratios (1:3, 2:3, and 3:3), we determined that the 2:3 ratio represents the optimal metal combination (degradation efficiency 50–60% under direct sunlight). Subsequently, we integrated bismuth oxyiodide (BiOI) into the Ni/Cu-BDC MOF, yielding Ni/Cu-MOF@BiOI heterostructures. Thorough structural characterization via scanning electron microscopy and X-ray diffraction confirmed the morphology and composition of the prepared materials. Assessing the photocatalytic performance against MB degradation in water under solar irradiation, we systematically analyzed operational parameters such as pH, catalyst dosage, MB concentration, and irradiation time. Ni/Cu-MOF@BiOI heterostructures exhibited exceptional efficiency, degrading 99% of MB under sunlight in four hours. Our research presents a sustainable method for the synthesis of photocatalysts using recycled PET waste, along with optimized operational parameters for enhanced catalytic efficiency. This approach combines green synthesis, material hybridization, and thorough analysis, contributing significantly to sustainable materials for pollutant remediation.

1. Introduction

Polyethylene terephthalate (PET) is a transparent, mechanically strong, and inexpensive polyester widely used to prepare food packaging materials (especially beverage bottles), permanent press fabrics, X-ray films, and audio and video tapes¹. However, the extensive utilization of PET plastics in various applications has become a serious environmental concern because of their nonbiodegradable nature². Additionally, the toxic chemicals (e.g., phthalates, bisphenol A, and polyfluorinated compounds) used in PET manufacturing have adverse effects on human health, including eye irritation, breathing difficulties, and respiratory problems³. According to a 2015 report, the production of virgin plastic reached over 8,200 Mt, with 6,300 Mt of plastic waste generated. Only 9% of this waste was recycled, while 12% was incinerated, and the remaining 79% was disposed of in open environments or deposited in landfills⁴. By 2050, large amounts (approximately 12,000 Mt) of such waste are likely to be disposed of into the environment. Because PET is the major component of this waste plastic⁵, efficient recycling approaches for PET are urgently required to be studied and implemented; four such approaches can be adopted to recycle PET and other such polymers, including primary⁶, secondary or mechanical, tertiary or chemical, and quaternary process⁷.

Chemical processes are used to recycle post-consumer condensation polymers, including PET, polyurethanes, polyamides, and polyesters, because they generate reusable raw materials that can be converted into valuable materials⁸. For example, approximately 85% by weight of PET can be recycled into terephthalic acid, called 1,4-benzendicarboxylic acid, BDC, which can be used as a building block for chemical products⁷.

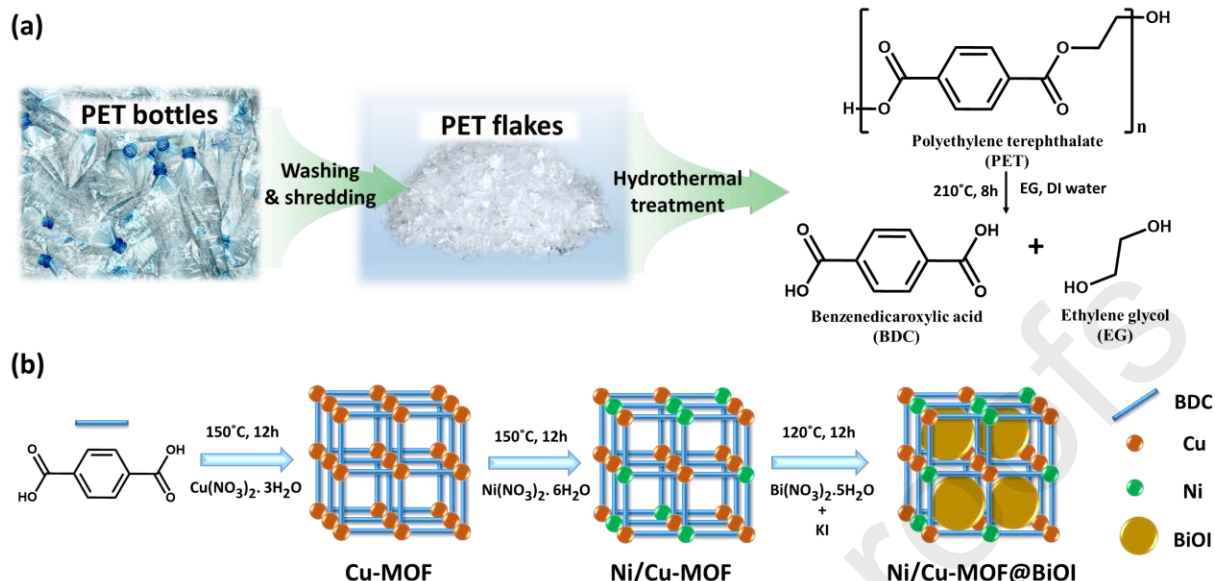
Metal-organic frameworks (MOFs) are porous materials that have drawn significant attention recently because of their potential use in numerous environmental applications, such as gas sensing, adsorption, drug delivery, and catalysis⁹. MOFs are constructed by connecting metals to organic linkers via strong coordination bonds¹⁰. Owing to their unique properties, such as tunable pore sizes, open metal sites, accessible surface areas, and ordered crystalline structures, MOFs are considered effective compounds for the photocatalytic degradation of organic pollutants¹¹. Chemical pollutants (e.g., pesticides, heavy metals, and dyes) are discharged into water bodies from the printing, papermaking, paint, and textile industries, causing serious environmental and health hazards¹². In the past few years, numerous single-metal MOFs have been reported for the efficient degradation of organic dyes, such as MIL-8¹³, MIL-101(Fe)¹⁴, MIL-88A(Fe)¹⁵, MIL-53(Fe)¹⁶, and Cu(BDC) MOFs¹⁷.

Compared to single-metal MOFs, MOFs with two or more metals in their structure have demonstrated high catalytic activities owing to the synergistic effects of different metals¹⁸. In this regard, the photocatalytic performance of various bimetallic MOFs for the degradation of various organic dyes has been explored, including Zn/Zr MOFs, Cu/Fe MOF, and Fe/Ti MOF-NH₂ for the degradation of rhodamine B¹⁹, MB^{18, 20}, and orange II²¹, respectively, and Fe/Ni_x MOF for the decomposition of methylene blue (MB) and methyl orange¹⁸. The combination of metals in MOFs has been reported to significantly affect the catalytic performance of the MOFs aiming for the degradation of pollutants in water. For instance, Liu *et al* reported the enhanced photocatalytic performance of Fe/Cu-BDC MOF compared to that of pure Cu-BDC MOF²².

In the domain of photocatalytic degradation, advanced oxidation processes (AOPs) have been used as techniques for the treatment of water contaminated with organic pollutants²³. AOPs involve the generation of highly reactive hydroxyl radicals to degrade recalcitrant compounds into harmless byproducts²⁴. Recent studies have investigated innovative approaches to enhance the efficiency of AOPs in water treatment. For instance, electrochemical oxidation modeling of atrazine, a widely used herbicide, has been explored to assess process parameters, intermediate formation, and kinetic constants, offering insights into optimizing treatment processes²⁵. Furthermore, the combination of ozone with ultraviolet (UV) irradiation and hydrogen peroxide (H_2O_2) has demonstrated efficacy in degrading micropollutants from various sources, highlighting the potential of synergistic AOPs for water remediation²⁶. Moreover, the utilization of self-heating magnetic nanocatalysts has shown promise in improving the degradation of wastewater, underscoring the importance of novel catalysts in enhancing AOPs for practical applications²⁷. Likewise, several adsorbents have been used to remove organic pollutants from the water²⁸.

An effective strategy to further enhance the AOP-based photocatalytic performance for removing pollutants from the water is to tailor the hybrid photocatalytic system. These hybrid materials have been reported to be efficient photocatalysts, including $TiO_2/Al_2O_3@Cu(BDC)$ composite²⁹, $B-TiO_2/MIL-100(Fe)$ composite³⁰, and $Ag_2CrO_4/Cu(BDC)$ composites³¹. Such hybrid structures facilitate the separation of photoinduced charge carriers, increase the surface area, and increase the visible-light response, which improves the photocatalytic performance. The coupling of BiOI with bimetallic MOF to prepare heterostructure photocatalysts has been reported for various photocatalytic applications³². In the context of water treatment, AOP-based photocatalytic degradation has shown considerable potential in addressing the challenges posed by organic pollutants. By integrating insights from studies such as those mentioned above, this research aims to contribute to developing sustainable and effective strategies for mitigating environmental pollution caused by PET waste and organic contaminants in water sources. To the best of our knowledge, no other study has reported the dual benefit of addressing land pollution through the green synthesis of photocatalysts by recycling plastic waste, while simultaneously achieving efficient degradation of pollutants in industrial wastewater under direct sunlight irradiation.

Herein, we demonstrate the green synthesis of bismuth-embedded Ni/Cu bimetallic MOFs as photocatalysts using PET waste bottles as shown in Scheme 1. As a building block of the MOF, recycled BDC was obtained via the chemical depolymerization of waste PET. The obtained BDC was coordinated with the metal atoms Cu and Ni to prepare MOFs with various Ni:Cu ratios (Ni/Cu-MOF). To enhance catalytic performance, caged bismuth in Ni/Cu-MOF structures, called Ni/Cu-MOF@BiOI, was subsequently formed by adding BiOI to Ni/Cu-MOF as a filler, for the first time. The structures of the Cu-BDC coordinated MOF (Cu-MOF), Ni/Cu-MOF, and Ni/Cu-MOF@BiOI heterostructures were confirmed using XRD and SEM, and FTIR and UV–visible spectroscopy. The photocatalytic performance of these heterostructures was evaluated by monitoring the degradation of MB in an aqueous solution as a function of time under solar light, depending on the pH, catalyst dosage, and MB concentration in the solution. Our study represents a sustainable approach to MOF synthesis utilizing recycled PET waste, through the combination of bimetallic Ni/Cu-MOF and BiOI. Also, systematic exploration and optimization of operational parameters analyzes to enhance photocatalytic efficiency. This amalgamation of green synthesis techniques, material hybridization, and comprehensive analysis renders our study significant in the field of sustainable materials for pollutant removal.



Scheme 1. (a) Recycling of terephthalic acid (BDC) from waste polyethylene terephthalate (PET) bottles via hydrothermal treatment based depolymerization. (b) Synthesis of Cu-MOF, Ni/Cu-MOF, and Ni/Cu-MOF@BiOI.

2. Experimental section

2.1. Materials

Copper nitrate trihydrate ($\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$, 99.5%), nickel nitrate hexahydrate ($\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, 98%), ethylene glycol (EG, 99.9%), *N,N* dimethylformamide (DMF, 99.8%), potassium iodide (KI, 99%), bismuth nitrate pentahydrate ($\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$, 71%), and ethanol (99.9%) were purchased from Sigma-Aldrich and used as received. Terephthalic acid (BDC) was extracted from PET waste bottles and used as an organic linker. PET bottles were collected from household waste bins and washed thoroughly with distilled water; their caps, rings, and labels were removed before BDC extraction.

2.2. Recycling of BDC from waste PET bottles via depolymerization

The recycling of BDC was carried out in a 100-mL Teflon-lined stainless-steel autoclave using a previously reported method with slight modification³³. The washed PET waste bottles were shredded into small flakes. The PET flakes (0.5 g) were placed in an autoclave containing 5 mL ethylene glycol and 35 mL distilled water. The reaction mixture was heated at 210 °C for 8 h. After cooling to room temperature, the precipitate was centrifuged and washed multiple times with distilled water and ethanol. The final product was dried at 80 °C for 6 h to obtain white crystalline BDC powder in 65% yield; the recycled BDC was used for the synthesis of the MOFs.

2.3. Synthesis of Cu-MOF and Ni doped Cu-MOF (Ni/Cu-MOF)

The Cu-MOF and Ni/Cu-MOF were synthesized using a typical hydrothermal method. For this purpose, 0.5 g recycled BDC was dissolved in 10 mL DMF, and 1.068 g of $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ was

dissolved in 40 mL of distilled water, followed by addition to the BDC solution. This mixture was stirred for 30 min at room temperature and then transferred to a 100-mL Teflon-lined stainless-steel autoclave. The autoclave was then placed in an oven and heated to 150 °C for 12 h. The reaction mixture was allowed to cool to room temperature (around 30 °C), resulting in the formation of precipitates, which were filtered and washed twice with DMF and ethanol. The final light-blue product was then dried for 12 h at 120 °C. The Ni-doped Cu-MOF was synthesized following the same procedure as that used for the Cu-MOF; the only difference was the addition of different ratios of $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and $\text{Cu}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$. The Ni to Cu ratios were adjusted to 1:3, 2:3, and 3:3, yielding 1:3 Ni/Cu-BDC, 2:3 Ni/Cu-BDC, and 3:3 Ni/Cu-MOF, respectively.

2.4. Synthesis of Ni/Cu-MOF@BiOI composites

Ni/Cu-MOF@BiOI composites were synthesized, aiming for improved photocatalytic activity under visible-light irradiation, by a previously reported method with some modifications³⁴. Moreover, the 2:3 Ni/Cu-MOF was selected for the preparation of the composites because it exhibited relatively higher photocatalytic activity than the 1:3 and 3:3 Ni/Cu-MOF. First, 0.9702 g of $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ and 0.3984 g of KI were separately dissolved in 30 mL of ethylene glycol, and the solutions were stirred separately for 30 min at room temperature (around 30 °C). Subsequently, 0.06 g of Ni/Cu-MOF were added to a $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ solution, followed by stirring for 15 min. The dropwise addition of KI solution into the above reaction mixture yielded a light-green suspension, which was stirred for 1 h, transferred into a Teflon-lined autoclave, and heated at 120 °C for 12 h. Subsequently, the reaction mixture was allowed to cool to room temperature where the product was precipitated. The precipitate obtained was filtered and washed repeatedly with distilled water. The light-green powder obtained was heated overnight to dryness. The prepared composites were given labeled as Ni/Cu-MOF@BiOI-10 and Ni/Cu-MOF@BiOI-15 (with MOF:BiOI ratios of 90:10 and 85:15, respectively).

2.5. Characterizations

X-ray diffraction (XRD) patterns of synthesized samples were obtained using an X-ray diffractometer (Bruker D2-Phaser) with $2\theta = 10\text{--}80^\circ$ using Cu $K\alpha$ radiation at $\lambda = 0.15406$ nm and operated at room temperature to analyze the structural properties. A scanning electron microscope (Nova 450 NanoSEM) was used to examine the crystal morphology of all samples. The elemental compositions of the prepared samples were measured using energy-dispersive X-ray analysis (EDX). Fourier transform infrared (FTIR, Bruker Alpha Platinum ATR) spectra of all samples were obtained in the range of $4000\text{--}400\text{ cm}^{-1}$. The absorption spectra of the photocatalytically degraded methylene blue (MB) solutions were recorded using a UV-visible spectrophotometer (Metash UV-9000).

2.6. Photocatalytic activity

Photocatalytic degradation of MB was conducted using the synthesized catalysts under direct sunlight irradiation. To prepare the 100 mL of the solution with a certain concentration of MB and photocatalyst in a vessel, a stock solution of MB (100 ppm) in water and powder of MOF photocatalysts were used. Before light irradiation, the MB solution was kept in the dark for 30 min with continuous stirring to achieve an adsorption-desorption equilibrium. The sample was then transferred to a Petri dish and exposed to direct sunlight. All the samples were covered with

transparent glass sheets during irradiation to minimize evaporation. After irradiation for the required period, the decrease in MB concentration in all samples was analyzed using a UV–visible spectrophotometer. This process was repeated thrice to obtain the average photocatalytic efficiency of the catalyst. The MB degradation efficiency (η) was calculated using the following equation-1.³⁵

$$\eta = \left[1 - \left(\frac{C_t}{C_0} \right) \right] \times 100\% \text{ (Equation – 1)}$$

Where C_0 and C_t are the initial MB concentration and concentration at time t , respectively.

To enhance the catalytic performance of the photocatalysts, we explored the effect of various parameters on the photodegradation of MB in the presence of catalysts. These parameters included variations in pH (ranging from 3 to 9), dye concentration (ranging from 10 to 40 ppm), and catalyst amount (ranging from 100 to 1200 ppm).

3. Results and discussions

3.1. Synthesis of MOFs

The recycled BDC, Cu-MOF, Ni/Cu-MOFs, and Ni/Cu-MOF@BiOI composites were analyzed by UV–visible spectroscopy. Figure 1a shows the UV–visible spectra of recycled and commercial BDC with $\lambda_{\max}$ of 240 nm; the spectra are in good agreement with the previously reported results¹. Both spectra matched well, indicating that BDC was successfully extracted by the depolymerization of waste PET. The UV–vis spectra of the Cu-MOF and Ni/Cu-MOFs are presented in Figure 1b; here, the absorption bands at 210 nm and 250 nm were attributed to $\pi-\pi^*$ and $n-\pi^*$ transitions, respectively. Hypochromic shift in $n-\pi^*$ transition was observed as the concentration of dopant Ni metal increases. This can be attributed to the coordination of the lone pair of electrons on oxygen with Ni atoms, making them unavailable for $n-\pi^*$ transitions.

As shown in Figure 1c, the Ni/Cu-MOF exhibits an absorption edge at approximately 378 nm, whereas the Ni/Cu-MOF@BiOI-15 composite has an absorption edge at approximately 401 nm (Figure 1d). The prepared composites extend the light absorption to the visible region, which in turn leads to improved photocatalytic activity, as can be inferred from the results.

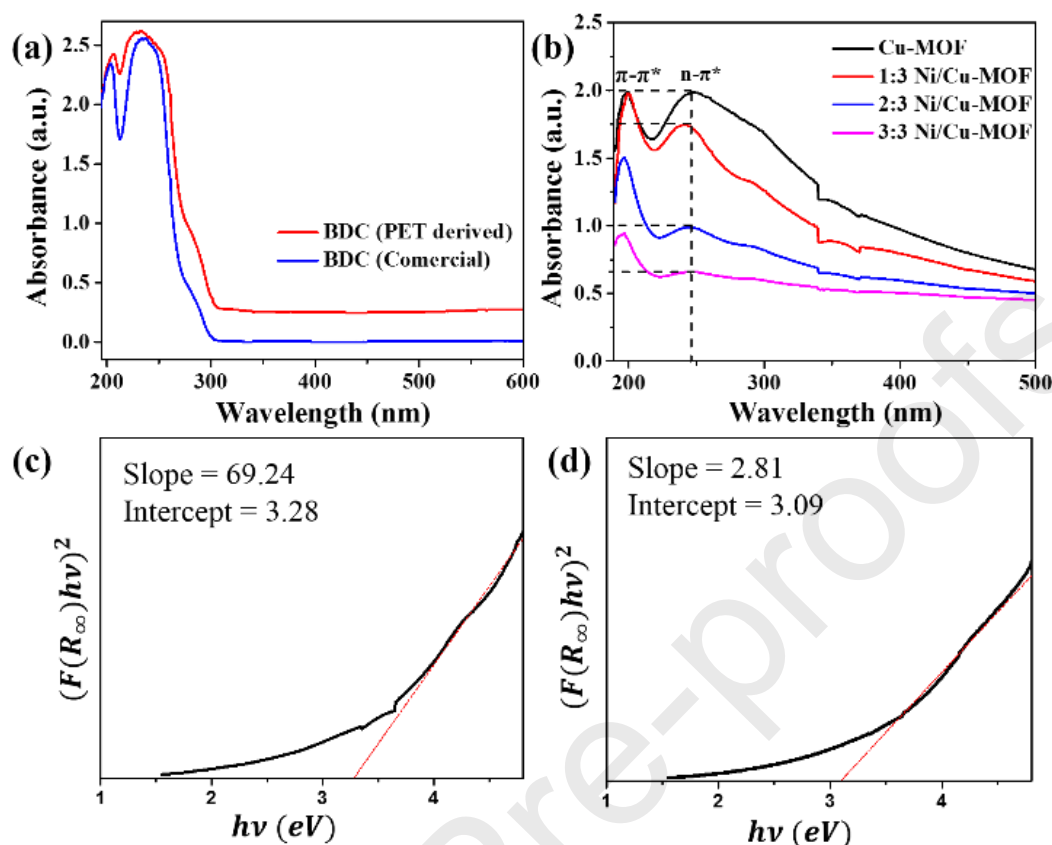


Figure 1. UV–Visible spectra of (a) recycled terephthalic acid (BDC) and commercial BDC; (b) Cu-MOF and Ni/Cu-MOFs; (c) 2:3 Ni/Cu-MOFs (d) Ni/Cu-MOF@BiOI-15.

The FTIR spectra of the recycled BDC, Cu-MOF, and Ni/Cu-MOFs (Ni:Cu = 1:3, 2:3, and 3:3) are illustrated in Figure 2 and are in agreement with previously reported data³⁶. In these spectra, most of the absorption bands of the recycled BDC and MOFs (Cu-MOF and Ni/Cu-MOFs: Ni:Cu = 1:3, 2:3, and 3:3) correspond well with each other, with slight shifts in the absorption bands. The FTIR spectrum of BDC has a broad absorption band in the 3200–2500 cm^{-1} range that can be attributed to O–H stretching vibration. This band was absent in the spectra of all MOFs samples, indicating that the carboxylic groups were completely coordinated with the metal in the MOFs³⁷. Similarly, the C=O stretching band at 1664 cm^{-1} in the BDC spectrum shifted to a lower frequency of 1564 cm^{-1} in the MOFs spectra owing to the deprotonation of the carboxylic acid groups³⁶.

Additionally, for both BDC and the as-prepared MOFs, the C=C stretching band of the aromatic rings occurred at approximately 1490 cm^{-1} . The band at 1290 cm^{-1} was attributed to the C–O–C stretching vibration in both BDC and MOFs. Furthermore, the bands at 737 cm^{-1} in the case of the Cu-MOF and Ni/Cu-MOFs originated from Cu–O stretching vibrations³⁸. Likewise, the band at approximately 680 cm^{-1} , in the spectra of Ni/Cu-MOFs, can be attributed to Ni–O stretching vibrations³⁹. These results confirm that all samples were successfully synthesized.

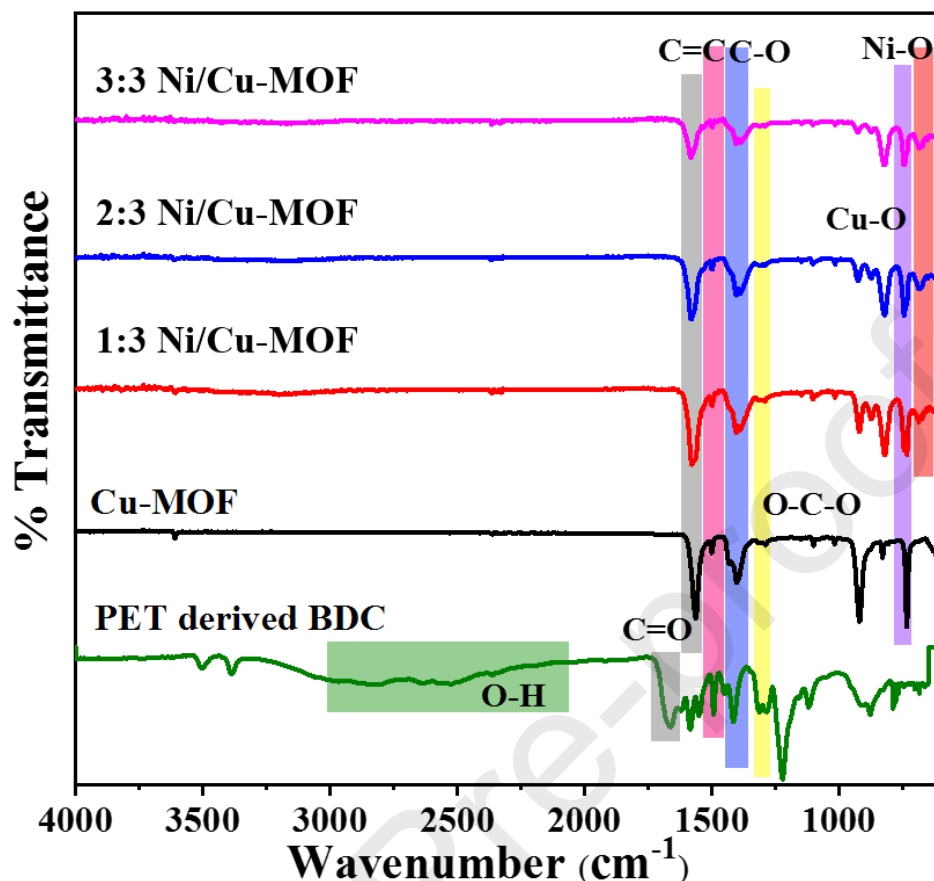


Figure 2. FTIR spectra of recycled terephthalic acid (BDC), Cu-MOF, and Ni/Cu-MOFs (Ni:Cu = 1:3, 2:3, and 3:3).

The XRD diffractograms of Cu-MOF, Ni/Cu-MOFs (Ni:Cu = 1:3, 2:3, and 3:3), and Ni/Cu-MOF@BiOI-15 are shown in Figure 3. The XRD diffractogram of Cu-MOF displayed the different diffraction peaks at $2\theta = 13.8^\circ$, 15.7° , 19.6° , 30.0° , 37.0° , and 42.5° . These peaks are related to the (222), (333), (420), (422), (773), and (882) crystal planes, respectively, and are consistent with previously reported literature⁴⁰. The XRD pattern of the Cu-MOF evidently matches well with that of the Ni/Cu-MOF. After doping with various amounts of Ni, the Cu-MOF diffraction peaks remained unchanged, indicating that the crystal structure remained unchanged. This may be because Ni^{2+} and Cu^{2+} ions have similar radii of 0.069 and 0.073 nm, respectively, and because Ni^{2+} has been partially substituted for Cu^{2+} in the Cu-MOF structure, as described in the literature⁴¹. On the other hand, the XRD pattern of Ni/Cu-MOF@BiOI-15 exhibited the diffraction peaks at $2\theta = 26.02^\circ$, 32.80° , 46.88° , and $54.62.0^\circ$ that can correspond to the (102), (110), (200), and (212) crystal planes, respectively. The XRD patterns were devoid of any additional peaks, demonstrating the high purity and crystallinity of the samples.

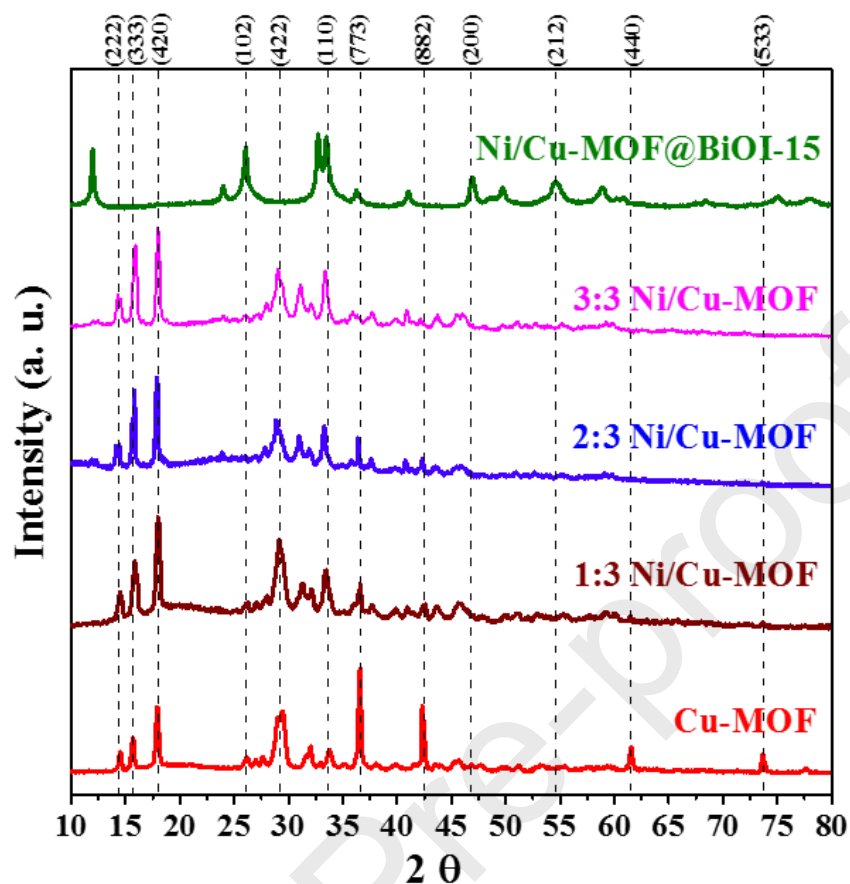


Figure 3. X-ray diffraction (XRD) of Cu-MOF, Ni/Cu-MOFs (Ni:Cu = 1:3, 2:3, and 3:3), and Ni/Cu-MOF-15.

Figure 4a and 4c illustrates SEM images of the Cu-MOF and Ni/Cu-MOF at different resolutions, and demonstrates the regular and crystalline structures of the MOF, with crystal sizes ranging from 100–200 nm; the images confirm the successful synthesis and homogeneous assembly of the MOFs. In addition, the prepared Cu-MOF exhibited a rod-like or long bar-like structure. The Ni/Cu-MOF was formed by ordered stacking of these rods, exhibiting a clear doping effect. These results are in good agreement with reported data^{40, 41}. The EDX spectra of Cu-MOF and Ni/Cu-MOF are shown in Figure 4b and 4d, respectively. These spectra indicated the presence of Cu, O, C, and Ni in the Cu-MOF and Ni/Cu-MOF, confirming the successful synthesis of the MOFs. Similarly, morphologies of Ni/Cu-MOF@BiOI-15 heterostructure in SEM images are presented in Figure 4e. The rod-like morphology of the heterostructure was maintained with an expanded diameter.

Moreover, the EDX spectrum shown in Figure 5f confirms the presence of Co, Ni, Bi, and I in the Ni/Cu-BDC MOF@BiOI heterostructures. Additionally, the percentage of atomic elements of each sample from the EDX analysis in Figure 5b, 5d, and 5f were summarized in Table 1. The Cu-BDC MOF clearly contains 36% of Cu without Ni, whereas the Ni/Cu-MOF contains 22% of Ni and 11% of Cu. The Ni/Cu-MOF@BiOI-15 showed high contents of Bi and iodine atoms due to the embedded BiOI.

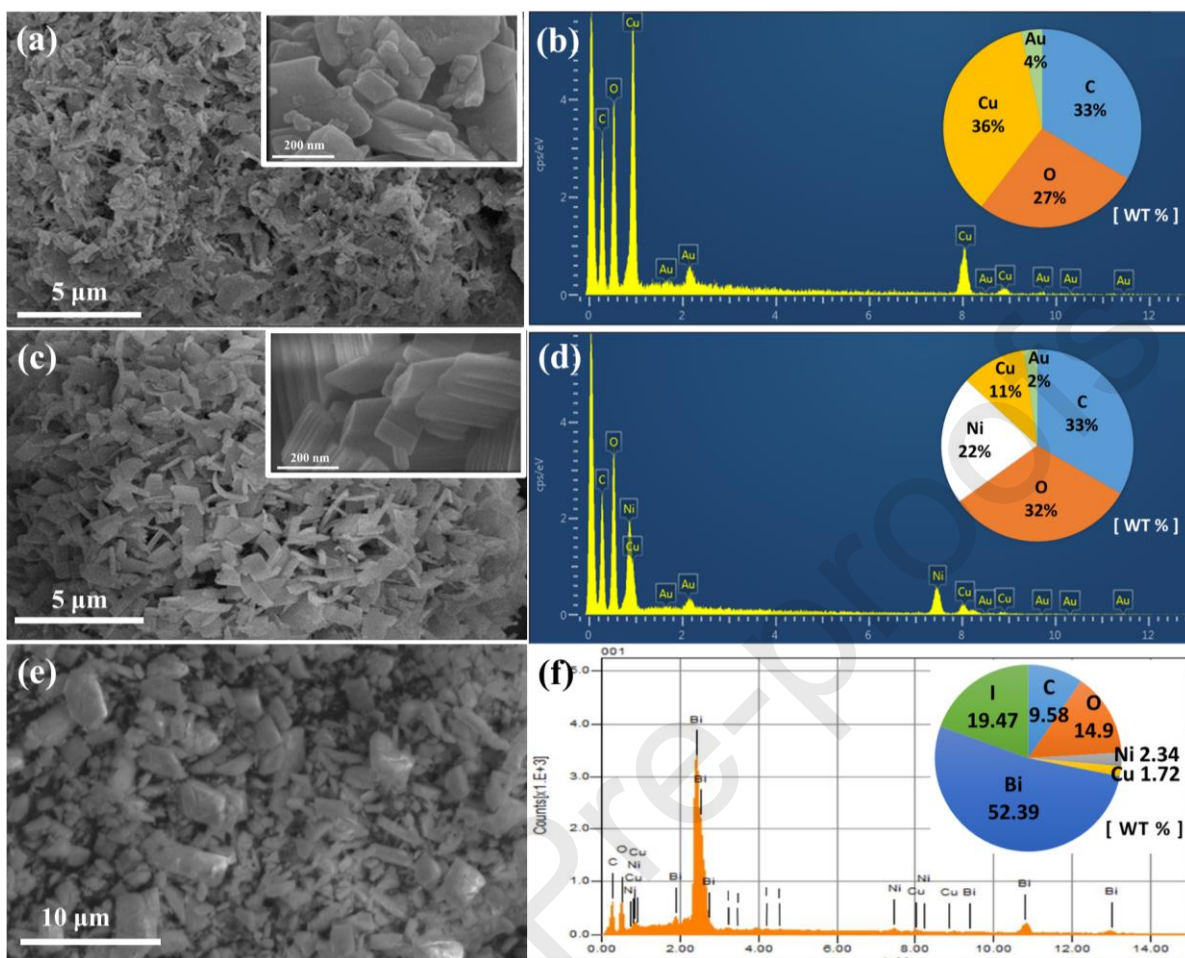


Figure 4. SEM image of (a) Cu-MOF, (c) Ni/Cu-MOFs, and (e) Ni/Cu-MOF@BiOI-15; EDX spectra of (b) Cu-MOF, (d) Ni/Cu-MOF, and (f) Ni/Cu-MOF@BiOI-15.

Table 1. Element analysis of Cu-MOF, Ni/Cu-MOF, and Ni/Cu-MOF@BiOI-15

Element	Cu-MOF	Ni/Cu-MOF	Ni/Cu-MOF@BiOI-15
	[wt%]	[wt%]	[wt%]
C	33	33	9.58
O	27	32	14.90
Ni	-	22	2.34

Cu	36	11	1.72
Au	4	2	-
Bi	-	-	52.39
I	-	-	19.47

3.2. Photocatalytic activity of MOFs

The photocatalytic activities of Cu-MOF, Ni/Cu-MOFs, Ni/Cu-MOF@BiOI-10, and Ni/Cu-MOF@BiOI-15 for MB degradation were evaluated with respect to time under the irradiation of sunlight (Figure 6a). Before irradiation, an aqueous solution of MB (10 ppm) and the photocatalyst (6 ppm) was stirred for 30 min in the dark to achieve adsorption–desorption equilibrium. In most cases of MOF samples, an initial decrease in dye concentration occurs during the mixing process in the dark, attributed to the formation of a complex between the dye molecule and the MOF, along with partial catalytic reactions. The reaction mixture was then irradiated with direct sunlight, as shown in Figure S1. During the irradiation, aliquots were collected at 0, 60, 120, 180, and 240 min. Any change in the MB concentration during irradiation was examined by UV–visible spectroscopic analysis of the collected samples.

Figure 6a shows MB degradation in the presence of the photocatalysts as a function of irradiation time, whereas the degradation efficiencies of all catalysts are shown in Figure 6b. As shown in Figure 6a and b, Cu-MOF and Ni/Cu-MOFs (Ni:Cu = 1:3, 2:3, and 3:3) could only degrade approximately 50–60% of MB after 240 min of irradiation; thus, these photocatalysts were not highly active under solar light. The low photocatalytic activity can be attributed to their low absorption in the visible region of sunlight. Compared to monometallic and bimetallic MOFs, Ni/Cu-MOF@BiOI-10 and Ni/Cu-MOF@BiOI-15 displayed significantly higher degradation efficiencies of 97% and 98.5%, respectively. The improved photodegradation efficiencies of both composites can be attributed to the separation of photoinduced electron–hole pairs, resulting in higher photocatalytic activity⁴². Similarly, higher photocatalytic activity of MOF@BiOI-15 than MOF@BiOI-10 was due to higher amount of BiOI in the former case.

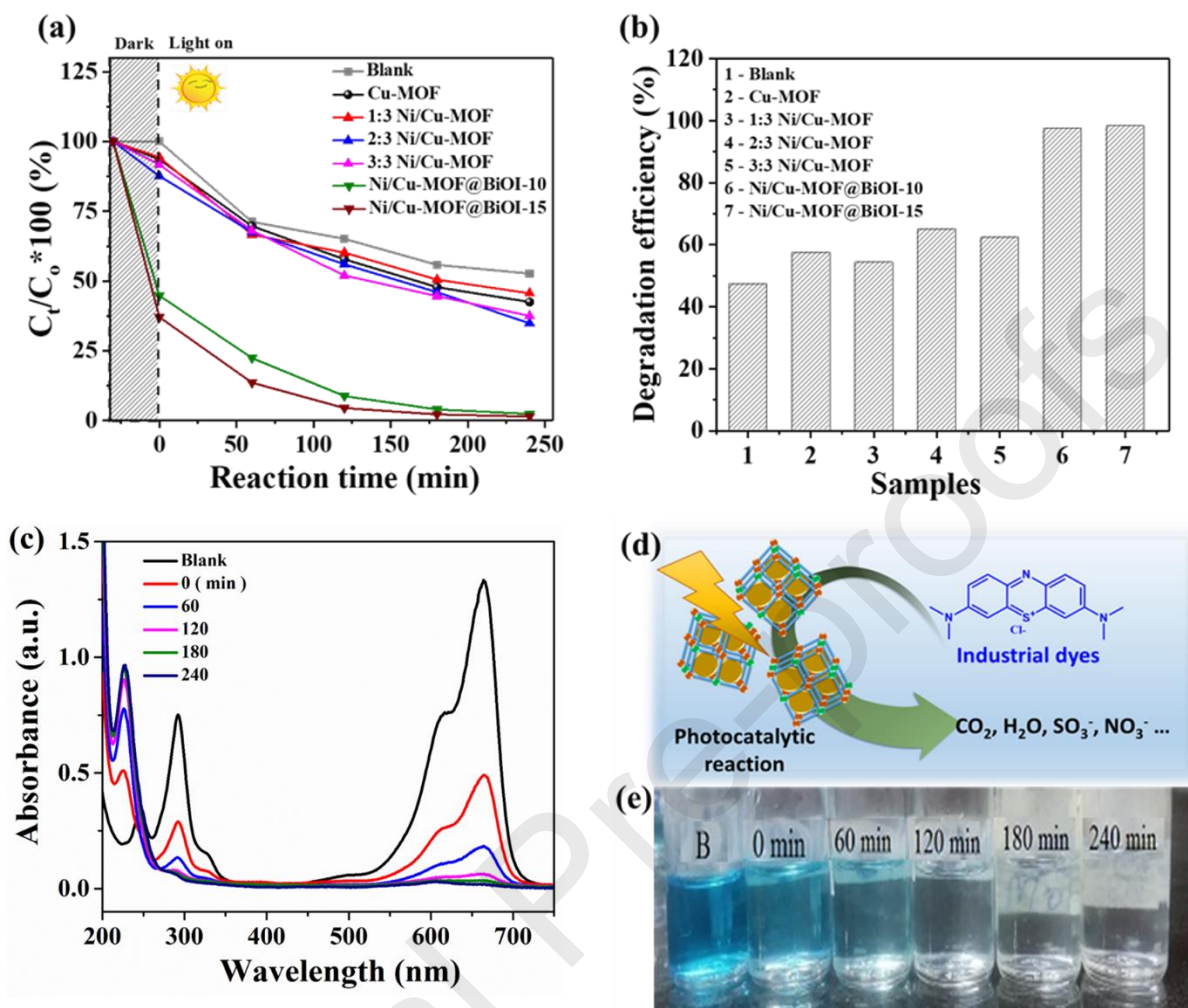


Figure 5. (a) Photodegradation of methylene blue (MB) as a function of time under sunlight irradiation in the presence of catalysts (600 ppm); and (b) degradation efficiency of all catalysts after 240 min of irradiation. (c) UV-vis spectra demonstrating MB degradation in aqueous solution in the presence of Ni/Cu-MOF@BiOI-15 at different irradiation times (blank = MB degradation in the absence of Ni/Cu-MOF@BiOI-15). (d) Illustration of the photocatalytic removal of industrial dyes using MOFs. (e) Discoloration of aqueous solution of MB during degradation process. During irradiation, temperature was 30-35 °C, solar radiation intensity was 240 W/m², and relative humidity was about 35 %. Petri dishes were covered with a transparent glass plate to minimize water evaporation during the experiment.

Figure 5c-e shows MB degradation in the presence of the Co/Ni-MOF@BiOI-15 photocatalyst (10 ppm MB in 600 ppm catalyst dissolved solution). In Figure 5c, the peak intensity declined constantly as the irradiation time increased, and the solution became colorless upon exposure to visible light. Furthermore, no new absorption bands were observed in the spectra, demonstrating complete degradation of MB without the formation of any intermediate³³. Regarding the result in Figure 5, the photocatalytic performances of pure Cu-MOF and the Ni/Cu-MOF for MB degradation under solar-light irradiation were relatively low. The performance of dye removal was improved up to 13 % in Cu and Ni based bimetallic system with relatively high ratio of Ni

composition than Cu. Furthermore, the Ni/Cu-MOF@BiOI heterostructure exhibited considerably high MB photodegradation of 98.5%, shown 71% and 51% enhancement compared to the Cu-MOF and 2:3 Ni/Cu-MOF, respectively in comparison of final efficiency (after 240 min). The expansion of the absorption wavelength range of the photocatalyst to the visible-light region and the reduction in electron-hole pair recombination rationally elevates the photocatalytic performance. Based on the results, the mechanism hypothetically is following: i) The electron-hole pairs were separated by photon absorption of photocatalysts. ii) The separated electrons and holes well contribute to induce the redox reaction with H₂O and O₂ in solution owing to the large surface area of the MOFs, generating the active superoxide anion and hydroxyl radical. iii) The active moieties degrade the cationic dyes (Figure S2).

Table 2 presents a comparison of the catalytic performances of the different photocatalysts for MB degradation. In accordance with these results, our Ni/Cu- MOF@BiOI-15 composite exhibited considerable photocatalytic activity. For example, with a degradation efficiency of more than 90% at dosage of 1200 mg/L achieved in about five mins, it surpassed catalysts like Fe₂TiO₅ nanoparticles, Ag₃PO₄/MnFe₂O₄ NCs, AC-Bi/TiO₂ NCs, MOF-5@rGO, SnO₂/TiO₂ nanocomposites, CoFe₂O₄-gC₃N₄, and Ag₂Co₃O₄ nanosheets. It is also important to mention here efficient degradation of MB using Ni/Cu- MOF@BiOI-15 composite was achieved under direct sunlight irradiation in pure environmental conditions.

Therefore Ni/Cu-MOF@BiOI-15 was selected for investigating effects of various parameters on the photodegradation performance. It is widely documented in the literature that the by-products of methylene blue (MB) photodegradation include water and CO₂. Readers are encouraged to refer to the existing literature for a detailed explanation of the photodegradation mechanism of MB⁴³⁻⁴⁵.

Table 2. Photocatalytic performance of various catalyst applied for degradation of methylene blue (MB) under solar light.

Photocatalysts	Catalyst dosage (mg/L)	Time (min)	MB degradation (%)	References
Fe ₂ TiO ₅ nanoparticles	500	240	53	43
Ag ₃ PO ₄ /MnFe ₂ O ₄ NCs	500	82	98	42
AC-Bi/TiO ₂ NCs	800	100	97	46
MOF-5@rGO	500	20	93	47
SnO ₂ /TiO ₂ nanocomposites	500	50	90	48

CoFe ₂ O ₄ -gC ₃ N ₄	500	45	100	49
Ag ₂ Co ₃ O ₄ nanosheets	416	90	88.4	50
	600	240	98.5	
Ni/Cu-MOF@BiOI-15				This work
	1200	<5	95	

3.2.1. Effect of pH

Because the pH significantly influences the oxidation capacity of free radicals and regulates the electrostatic interaction of photocatalyst surfaces with dyes during the photocatalytic process, the photodegradation of dyes depends on the pH of the medium¹⁹. Batch experiments were performed to evaluate the effect of pH on the photocatalytic degradation of MB, and the results are presented in Figure 6a. The pH of the MB solution was adjusted to 3, 5, 7, and 9 using HCl or NaOH. As shown in Figure 8a, Ni/Cu-MOF@BiOI-15 exhibited 98% degradation of MB within 120 min at pH 3. With an increase in pH value, MB degradation decreased; at pH 9, MB degradation was 93%, whereas MB degradation was 97% and 95% at pH 5 and 7, respectively. At pH > 10, the reaction almost completely stopped.

This result is comparable to that of the Fenton reaction, which is often performed under acidic conditions. One probable explanation is that for photocatalysts, the potential of the valence-band hole decreases as the pH increases, weakening the oxidizing ability of the hole and decreasing the rate at which hydroxyl radicals are produced¹⁵.

3.2.2. Dye concentration

The effect of increasing MB concentration on the photodegradation efficiency of Ni/Cu-MOF@BiOI-15 is presented in Figure 6b. This Figure shows that when the concentration of MB increased, the photocatalytic activity of Ni/Cu-MOF@BiOI-15 reduced. This can be attributed to the high MB concentration, which prevented the penetration of solar light into the solution, making the photocatalyst surface less accessible to light⁴⁴. As shown in Figure 6c, as the concentration of MB increased from 10 mg/L to 40 mg/L, the photodegradation efficiency of Ni/Cu-MOF@BiOI-15 decreased from 97.6% to 32.1%. Consequently, the high MB concentration had a negative impact on the photodegradation efficiency of Ni/Cu-MOF@BiOI-15.

3.2.3. Catalyst dosage

The MB photodegradation performance of Ni/Cu-MOF@BiOI-15 as a function of catalyst dosage is shown in Figure 6d. The photocatalytic activity of Ni/Cu-MOF@BiOI-15 was significantly enhanced by increasing its concentration from 0.1 g/L to 1.2 g/L. This can be attributed to the greater availability of active sites at higher catalyst dosages, which led to the generation of more photoexcited electron-hole pairs and rapid dye degradation⁵¹. Moreover,

higher catalyst dosages decreased the photocatalytic performance possibly due to agglomeration of the catalyst at higher concentrations, which hinders solar light access to the active sites of the catalyst.

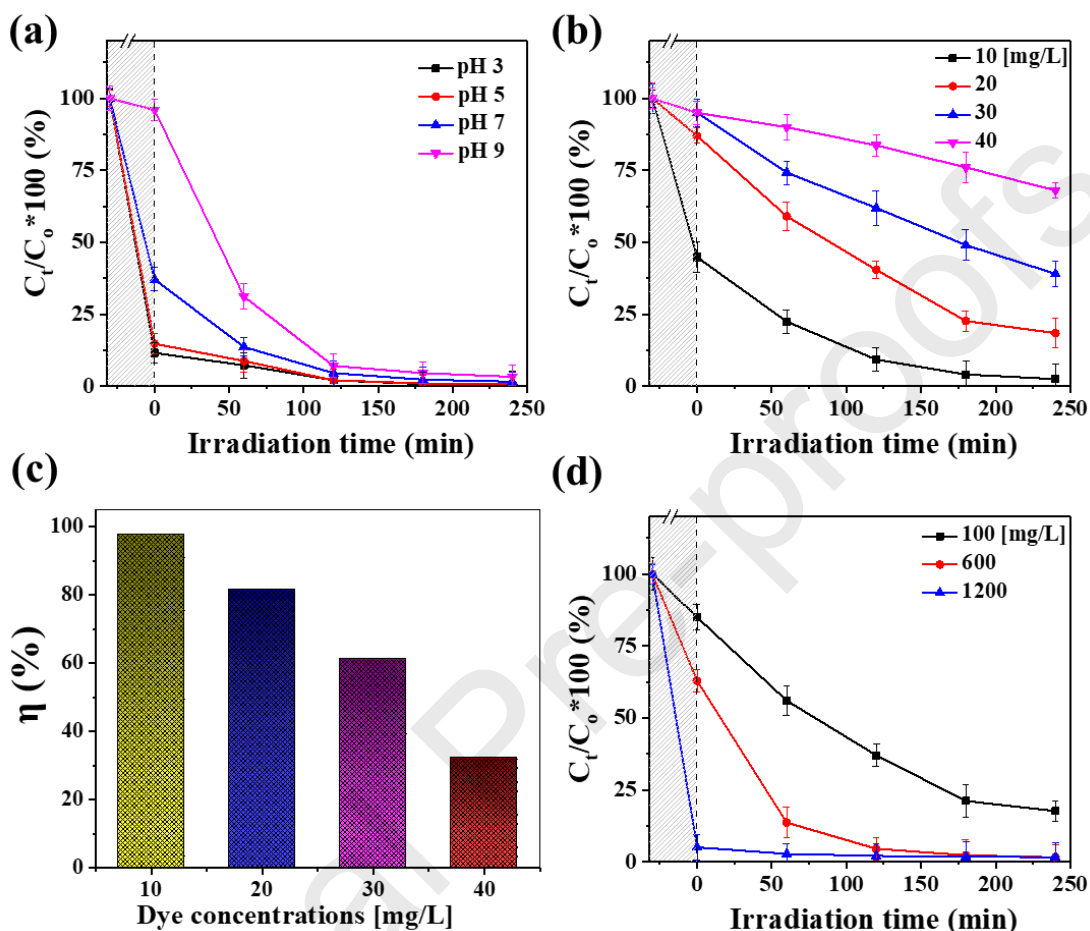


Figure 6. Effects of (a) pH (b) methylene blue (MB) concentration, and (d) catalyst dosage on the photodegradation activity of Ni/Cu-MOF@BiOI-15 over time; (c) Degradation efficiency depending on the concentration of MB. (d) Degradation behavior over time along with the catalyst dosage. During irradiation, temperature was 30-35 °C, solar radiation intensity was 240 W/m², and relative humidity was about 35 %. Petri dishes were covered with a transparent glass plate to minimize water evaporation during the experiment.

3.3 Photocatalyst reusability evaluation

The assessment of recyclability of a photocatalyst holds significant importance in evaluating its suitability for industrial applications. To investigate the recyclability of the synthesized photocatalyst, Ni/Cu-MOF@BiOI-15, it was recovered through centrifugation after each cycle of MB degradation. Subsequently, the recovered photocatalyst underwent washing with ethanol and drying under vacuum before the next MB degradation cycle under optimized conditions of pH, catalyst amount, and MB concentration. Remarkably, as illustrated in Figure 7, the photocatalytic efficiency of Ni/Cu-MOF@BiOI-15 remained consistent over ten successive cycles, underscoring its potential as a stable and efficient photocatalyst.

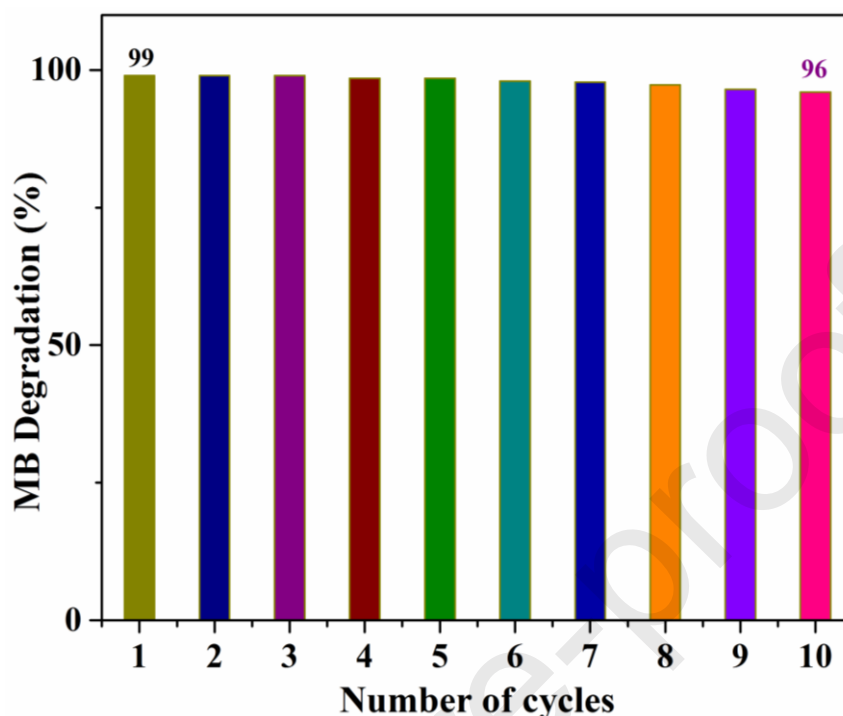


Figure 7. The reusability of Ni/Cu-MOF@BiOI-15 photocatalyst in methylene blue (MB). During irradiation, temperature was 30-35 °C, solar radiation intensity was 240 W/m², and relative humidity was about 35 %. Petri dishes were covered with a transparent glass plate to minimize water evaporation during the experiment.

4. Conclusions

In summary, various MOF photocatalysts were successfully synthesized through a solvothermal route and characterized using diverse analytical techniques. Comparative analysis among these photocatalysts, specifically Cu-MOF, Ni/Cu-MOF with varying Ni:Cu ratios (1:3, 2:3, and 3:3), Ni/Cu-MOF@BiOI-10, and Ni/Cu-MOF@BiOI-15, revealed the superior photocatalytic activity of the latter two toward methylene blue under solar light irradiation, in comparison to Cu-MOF. The incorporation of BiOI into the bimetallic MOF mitigated the recombination of electron-hole pairs and extended the absorption spectrum into the visible range, thereby enhancing the photodegradation of methylene blue. Furthermore, the study of the parameters revealed that the rate of photocatalytic degradation of MB was directly proportional to the catalyst loading and inversely proportional to the dye concentration. An acidic pH of 3 was identified as the optimal condition for MB degradation. These findings suggest an efficient photocatalyst based on the recycled building blocks for the treatment of industrial wastewater, which can be a clue how we should treat plastic waste for the environment.

Supporting Information

The conditions under which the samples were irradiated are given in supporting information.

Corresponding Author

Toheed Akhter, Department of Chemistry, School of Science, University of Management and Technology, Johar Town, Lahore, Pakistan; Email Address: toheed.akhter@umt.edu.pk. Chan Ho Park, Department of Chemical and Biological Engineering, Gachon University, 1342 Seongnam-daero, Seongnam 13120, Republic of Korea; Email Address: chhopark@gachon.ac.kr.

Author Contributions

Conceptualization, Toheed Akhter and Sana Karamat.; methodology, Sana Karamat; validation, Toheed Akhter, Sadaf Ul Hassan, and Chan Ho Park; formal analysis, Sana Karamat; investigation, Sana Karamat; resources, Asif Mahmood, Waheed Al-Masry; writing-original draft preparation, Toheed Akhter, Shumaila Razzaque, and Muhammad Faheem; writing-review and editing, Taewook Kim, Soo-Kyung Han, Sadia Ashraf, Chan Ho Park; and; supervision, Toheed Akhter and Chan Ho Park; All authors have read and agreed to the published version of the manuscript.

Notes

There are no conflicts to declare.

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Declaration of interests

☐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.

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