

Article

A New 2D Metal-Organic Framework for Photocatalytic Degradation of Organic Dyes in Water

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Abstract: Two-dimensional (2D) metal-organic frameworks (MOFs) are fascinating photocatalytic materials because of their unique physical and catalytic properties. Herein, we report a new (E)-4-(3-carboxyacrylamido) benzoic acid [ABA-MA] ligand synthesized under facile conditions. This ABA-MA ligand is further utilized to synthesize a copper-based 2D MOF via the solvothermal process. The resulting 2D MOF is characterized for morphology and electronic structural analysis using advanced techniques, such as proton nuclear magnetic resonance, Fourier-transform infrared spectroscopy, ultraviolet-visible spectroscopy, and scanning electron microscopy. Furthermore, 2D MOF is employed as a photocatalyst for degrading organic dyes, demonstrating the degradation/reduction of methylene blue (MeBl) dye with excellent catalytic/photodegradation activity in the absence of any photosensitizer or cocatalyst. The apparent rate constant (k_{ap}) values for the catalytic degradation/reduction of MeBl on the Cu(II)-[ABA-MA] MOF are reported to be 0.0093 min^{-1} , 0.0187 min^{-1} , and 0.2539 min^{-1} under different conditions of sunlight and NaBH_4 . The kinetics and stability evaluations reveal the noteworthy photocatalytic potential of the Cu(II)-[ABA-MA] MOF for wastewater treatment. This work offers new insights into the fabrication of new MOFs for highly versatile photocatalytic applications.

Keywords: 2D MOF; photocatalytic degradation; methylene blue; waste water treatment



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1. Introduction

Globally, water contamination has appeared as a severe issue [1]. There are several types of water contaminants, including nitroarenes [2], pesticides [3], heavy metals [4], organic dyes [5], and fertilizers [6]. Among them, dyes are extremely harmful to humans [7], plants [8], and aquatic life [9]. Water contamination is mainly caused by the use of different organic dyes in the leather [10], textile [11], printing [12], pulp [13], and paper [14] industries. The only way to resolve this situation is to ban these industries or eliminate the organic dyes by electro/photodegradation [15]. However, these industries contribute to wider daily life demands and cannot be excluded. Consequently, eliminating organic dyes from water using photocatalysts is the only solution. In order to resolve this issue, a variety of materials, including polymers [16], ligands [17], inorganic nanoparticles [18–20], hybrid microgels [21–23], and metal-organic frameworks (MOFs) [24,25], have been investigated. The ligands and organic polymers remove these dyes from water through adsorption. However, incomplete elimination of these dyes and a large consumption of adsorbents (ligands and polymers) are the main drawbacks of these adsorbents. Furthermore, it takes a longer time to remove dyes through adsorption. Therefore, ligands and organic polymer adsorbents are ineffective for wastewater purification. The primary disadvantages of using

metal nanoparticles are their instability and lack of easily recyclable properties. Therefore, MOFs are promising substances capable of removing toxic organic dyes from water (without any disadvantage) due to their versatile porosity and catalytic properties [26–28].

The synthesis and design of MOFs have advanced significantly over the past decades [29]. These materials provide enormous chemical and structural variability as well as a wide range of applications [30–33]. The essential features affecting the performance of a material are selectivity, permeability, and operating stability [34,35]. Microstructural engineering is also required to control the orientation of MOF crystal formation at the mesoscopic level to improve performance. It is challenging to develop facile synthetic techniques with great accuracy over their microstructural structure at meso- and microscopical levels for optimal performance [35]. The properties of MOFs as an adjustable version (chemical tunability), with unparalleled high surface area, high porosity with flexible pore sizes, robustness, and structural diversity make them suitable for various applications such as sensing, drug delivery, gas storage, magnetic separation, separation, electrochemical energy storage, catalysis, and degradation of toxic organic dyes from aqueous mediums [36–40]. Additionally, MOFs have been utilized as unique precursors for creating inorganic functional materials with previously unimaginable design potential, such as carbons, metal-based compounds, and their composites [41].

Different forms of MOFs, including 2D sheets/bilayers and 3D extended networks, have been designed and used for various applications based on the geometry and connecting properties of the precursors [42,43]. Two-dimensional MOFs have distinctive features and are employed in multiple applications, such as energy conversion and storage, catalysis, and sensing [44]. These materials are excellent candidates for electrochemical applications due to their large specific surface area, tunable structure, porous network, availability of metal active sites, and efficient mass transport properties. Therefore, the appropriate alignment of several donor sites for metal coordination at certain sites is essential to regulate the size, shape, and morphology of MOFs [45,46].

In order to create MOFs, it is necessary to choose the correct metal centers to combine with organic linkers. Copper-based MOFs have received much attention due to the discovery of straight chain secondary building units (SBU), which are advantageous energetically under reaction conditions [47]. Additionally, after activation, the coordinated guest molecules in copper straight chain SBUs can be used in their carboxylic groups to create open sites for Cu(II) ions that are advantageous for applications involving gas storage, adsorption, and catalysis [34,48,49]. Therefore, we selected a unique bidentate ligand to prepare a 2D Cu(II) carboxylate MOF with both carboxyl coordination bonds to copper. A bifunctional carboxylic ligand paired with copper was employed to generate an extended 2D structural framework via copper carboxylate straight chain linkages. In a typical synthesis, a new carboxylic group-containing ligand was synthesized using 4-aminobenzoic acid (4ABA) and maleic anhydride (MA) in acetic acid at room temperature. Then the synthesized ligand (4ABA–MA) was used to form a (Cu(II)–[4ABA–MA]) MOF with copper (II) ions in equimolar condition. The resultant 2D MOF (Cu(II)[4ABA–MA]) was applied as a catalyst in the photocatalytic and catalytic degradation/reduction of methylene blue (MeBl) from an aqueous medium.

2. Results and Discussion

The 4ABA–MA was synthesized by mixing the solutions of 4ABA and MA with gentle stirring in an acidic medium at room temperature (24 °C) (Figure 1) [50]. The acidic medium and low-temperature conditions were used to avoid the cyclization by nitrogen atoms of an amino group. In the acidic condition, the possibility of electron donation from the nitrogen atom of the amino group to maleic anhydride is reduced. Still, the reaction occurs due to the high basicity of the amino group and less stability of maleic anhydride. Upon conversion of the closed ring of maleic anhydride to an open chain after reaction, the electronegativity of the nitrogen atom of the amide group decreases due to the electron withdrawing carbonyl group, which is directly attached to the nitrogen atom in the product (in the form of the

amide). Therefore, the nitrogen of the amide group will not attack the carboxylic carbon atom to form a cyclic product in the acidic medium at a low temperature. Then the Cu(II)–[4ABA–MA] MOF was synthesized by the solvothermal process in DMF solvent at a pH of 6.7. Due to the acidic nature of carboxylic groups, deprotonation occurred, and carboxylic groups of 4ABA–MA were converted into carboxylate ions. The electron-donating capacity of 4ABA–MA towards the Cu(II) ions increases due to deprotonation, resulting in MOF formation.

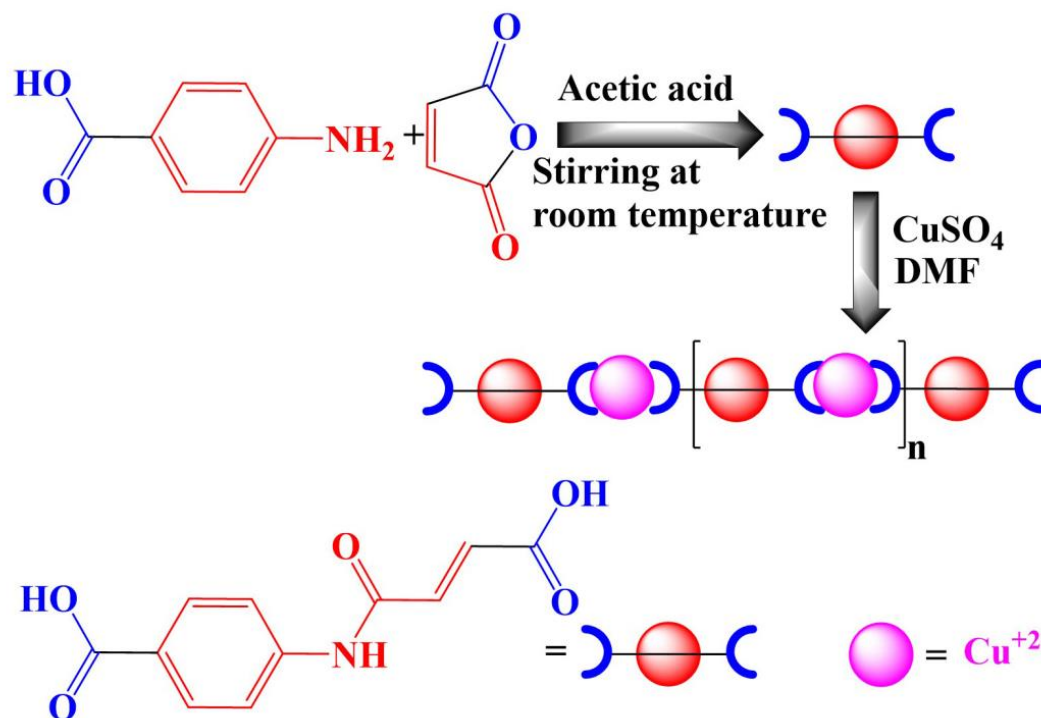


Figure 1. Schematic illustration of Cu(II) synthesis-[ABA–MA] MOF.

The chemical structural investigations of 4ABA–MA were performed via proton NMR (Figure 2a). The two protons of both carboxylic groups appeared at 11.21 and 10.68 ppm. The carboxylic group, produced by the opening of maleic anhydride, appeared at 11.21 ppm, which is more de-shielded than other carboxylic groups (directly attached to the aromatic ring) due to the resonance effect. Therefore, the protons of both carboxylic groups appeared at different positions. The other protons of aromatic rings and acyclic parts appeared in the 6.96 to 7.96 ppm region. One proton of the amide group merged with the solvent peak in the range of 3.00 to 4.00 ppm. The ¹H NMR analysis confirmed the formation of 4ABA–MA. Moreover, the functional group identification and conversion from 4ABA–MA and the Cu(II)–[4ABA–MA] MOF was investigated via FTIR. The O–H, N–H, and C–H stretching peaks of carboxylic groups in 4ABA–MA appeared at 3153 cm^{−1}, 3116 cm^{−1}, and 2867 cm^{−1}, respectively (Figure 2b). The stretching peak of the C=O group appeared at 1722 cm^{−1} and 1714 cm^{−1} in both 4ABA–MA and the Cu(II)–[4ABA–MA] MOF. This shifting in the carbonyl stretching peak position of carboxylic groups indicated the involvement of this group in complex formation. The different FTIR spectra of 4ABA–MA and Cu(II)–[4ABA–MA] indicated the formation of the MOF.

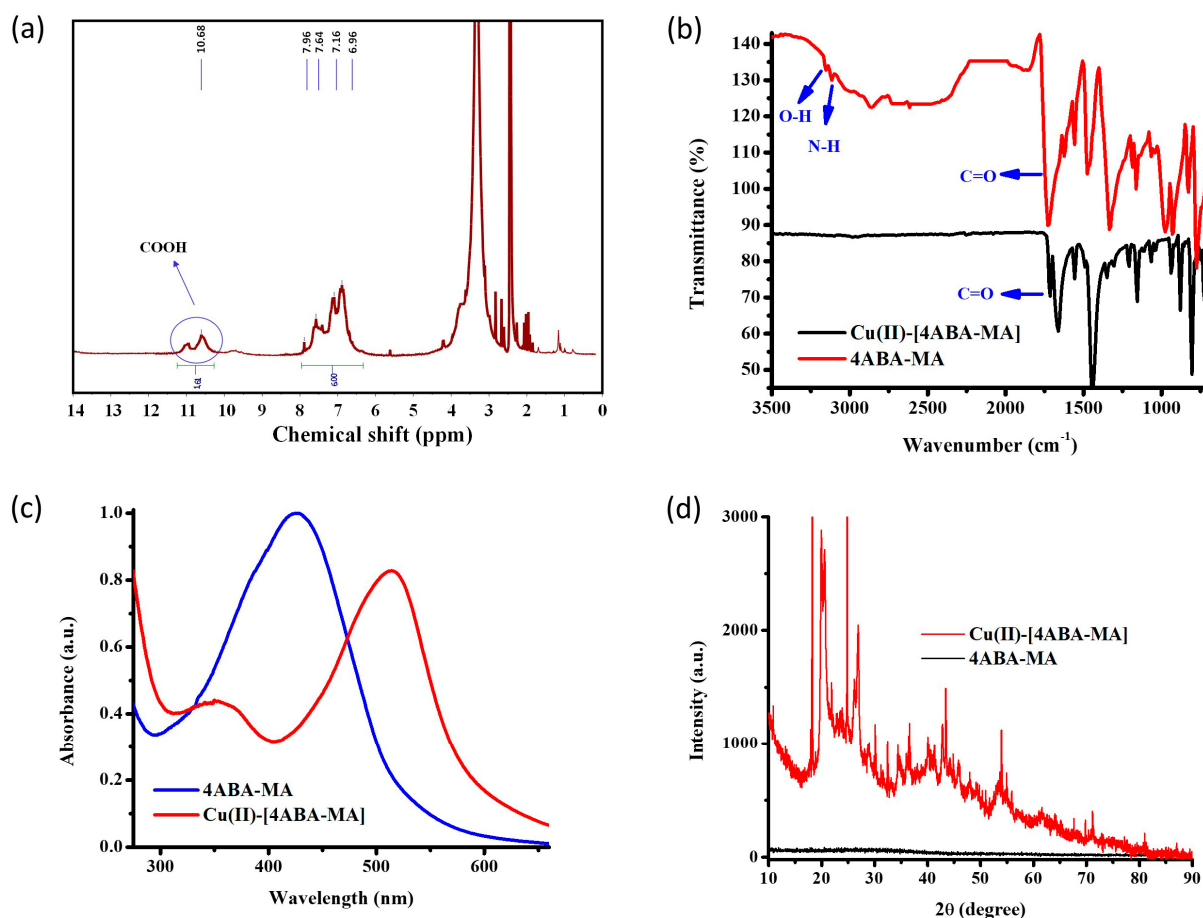


Figure 2. Chemical structural characterization of 2D MOF: (a) ^1H NMR spectrum of 4ABA-MA in DMSO and (b) FTIR of 4ABA-MA and Cu(II)-[4ABA-MA] MOF. (c) UV-visible spectrum of 4ABA-MA and Cu(II)-[4ABA-MA] (d) PXRD of 4ABA-MA and Cu(II)-[4ABA-MA] MOF.

The complex formation of 4ABA-MA with copper metal ions was further investigated by UV-visible spectrophotometry (Figure 2c). For this purpose, two separate solutions of both 4ABA-MA and Cu(II)-[4ABA-MA] were prepared in DMF solvent. The λ_{max} of 4ABA-MA appeared at 425 nm and Cu(II)-[4ABA-MA] at 515 nm. This shifting in the value of λ_{max} of 4ABA-MA after adding the copper salt confirmed the formation of a Cu(II)-[4ABA-MA] 2D MOF. The degree of crystallinity of both 4ABA-MA and Cu(II)-[4ABA-MA] was examined with XRD (Figure 2d). The 4ABA-MA do not show any crystallinity, while a high crystallinity is observed in Cu(II)-[4ABA-MA], which indicates the formation of the complex of 4ABA-MA with copper ions as a Cu(II)-[4ABA-MA] MOF.

Furthermore, the morphology of the Cu(II)-[4ABA-MA] MOF was determined by SEM and elemental mapping analysis. The SEM images show the Cu(II)-[4ABA-MA] MOF exists in a 2D hexagonal shape with a smooth surface (Figure 3a,b). Two-dimensional morphology arises from the 2D complexation of 4ABA-MA. There are two carboxylic groups in the 4ABA-MA structure at 180° with respect to each other. Therefore, the 4ABA-MA shows complexation from both sides to form the Cu(II)-[4ABA-MA] MOF, forming a 2D hexagonal structure. Additionally, the elemental mapping analysis of the Cu(II)-[4ABA-MA] MOF was performed, which reveals the composition of the catalysts. Carbon, nitrogen, oxygen, and copper elements are found in the Cu(II)-[4ABA-MA] MOF.

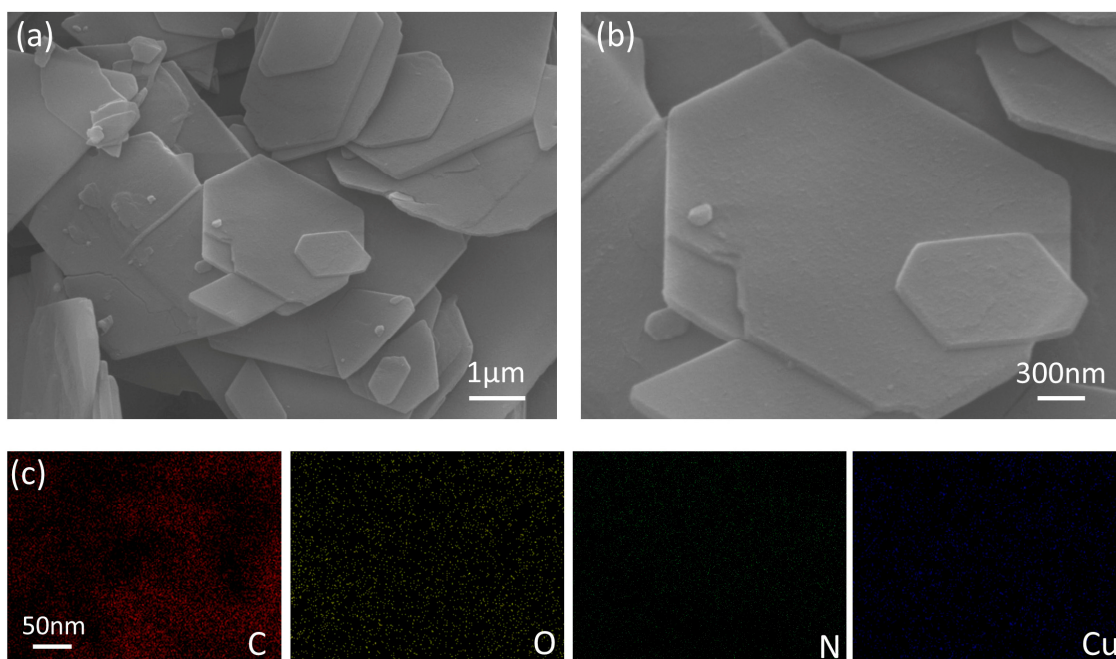


Figure 3. Morphology analysis. (a,b) SEM images and (c) elemental mapping analysis of Cu(II)-[4ABA-MA].

The photocatalytic performance of Cu(II)-[4ABA-MA] was investigated against MeBl via UV-visible spectrophotometry. The catalytic efficiency of Cu(II)-[4ABA-MA] was determined under different conditions, such as in the absence or presence of sunlight and with or without NaBH₄ (reductant). Firstly, 0.1 g of Cu(II)-[4ABA-MA] was added to the 100 mL of (0.05 mM) MeBl solution in the absence of NaBH₄ and light, and the solution run in a UV-visible spectrophotometer. The UV-visible spectra show a decline in the $\lambda_{\max}$ value for the peak at 656 nm without additional peaks under different conditions (Figure 4a). This spectrum indicates that the Cu(II)-[4ABA-MA] has efficiently degraded the MeBl in 270 min. Similarly, the degradation of MeBl was also monitored in the presence of sunlight (Figure 4b). The peaks of MeBl decreased continuously, resulting in the form of degradation of MeBl. However, it is found that the degradation of MeBl is much faster in the presence of sunlight than in dark conditions. The MeBl is degraded in 120 min in the presence of sunlight compared to 270 min under dark conditions [51]. These results demonstrate the higher photocatalytic efficiency of the Cu(II)-[4ABA-MA].

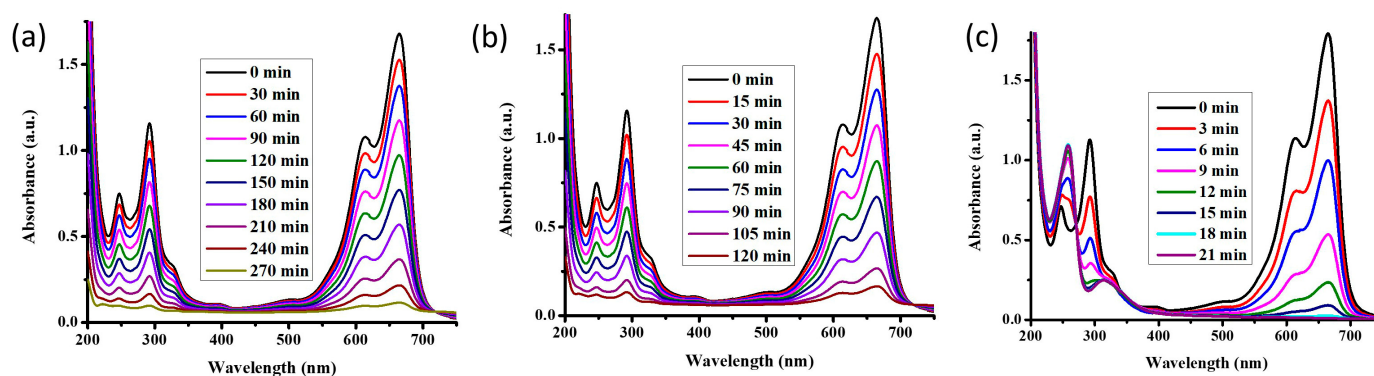


Figure 4. Catalytic and photocatalytic degradation/reduction of MeBl on Cu(II)-[4ABA-MA] MOF; (a) in the absence of both sunlight and NaBH₄, (b) in the presence of sunlight but the absence of NaBH₄, (c) in the presence of NaBH₄ but the absence of sunlight.

Additionally, the degradation of MeBl was also examined in sunlight and NaBH_4 (Figure 4c) [52,53]. In total, 0.3 g of NaBH_4 and 0.1 g of Cu(II)-[4ABA-MA] were added into the (0.05 mM) solution of MeBl and the spectrum recorded. A similar decline is observed in the λ_{max} value at 665 nm, while new peaks appeared (Figure 4c). The decline in the peak at 665 nm and appearance at some other place indicated the reduction of MeBl in the absence of NaBH_4 . Such peaks did not appear in the absence of NaBH_4 . These results suggest that the Cu(II)-[4ABA-MA] MOF degraded the MeBl into CO_2 and H_2O in the absence of NaBH_4 , but this catalyst reduced the MeBl into some other component. Further research on the separation and purification of these components could provide additional information and mechanisms for this reduction process. The reduction rate of MeBl in the presence of NaBH_4 is very high; it takes merely 21 min to completely degrade the dyes in water. Similar behaviour was reported by Melinte et al. [54], where bimetallic (Ag/Au) nanoparticles loaded a crosslinked polymer system for the catalytic and photocatalytic reduction of 4-nitrophenol. Different peaks appeared in the case of catalytic reduction, while there was no peak in the photocatalytic reaction. Therefore, based on similar observations in our results, a similar hypothesis shows the possible mechanism for photocatalytic degradation.

A kinetic study of catalytic and photocatalytic degradation of MeBl was performed to determine the degradation mechanism. The pseudo-first-order kinetic equation was applied to evaluate the apparent rate constant (k_{ap}) in the presence and absence of NaBH_4 and the presence and absence of sunlight. A plot of $\ln(A_t/A_0)$ vs time determines the reaction rate. The value of $\ln(A_t/A_0)$ decreases slowly with respect to time in the absence of both sunlight and NaBH_4 (Figure 5a). This behaviour shows that the Cu(II)-[ABA-MA] MOF has low catalytic efficiency in the absence of sunlight and it increases in the presence of sunlight with a linear relationship between the $\ln(A_t/A_0)$ and time. In the presence of sunlight, the electrons can easily be transferred from ground level to excited results to support the capacity of the electron donor-acceptor process. Therefore, the catalytic performance is higher in the presence of sunlight. The reduction of MeBl rapidly occurred in the presence of NaBH_4 . It is a fact that NaBH_4 is a strong reducing agent. Therefore, the MOF provided the surface area for the catalytic reduction reaction of MeBl, resulting in the reduction of MeBl forming new compounds, which are evidenced by the appearance of new peaks in UV-visible spectra [55,56]. The value of k_{ap} was found to be 0.0093 min^{-1} , 0.0187 min^{-1} , and 0.2539 min^{-1} in the absence of both sunlight and NaBH_4 and the presence of only sunlight, and only NaBH_4 , respectively, for the catalytic degradation/reduction of MeBl in the Cu(II)-[ABA-MA] MOF.

Finally, the structural stability of the Cu(II)-[4ABA-MA] was analyzed by PXRD analysis after photocatalytic evaluation. Similar peaks in PXRD were found before and after catalytic degradation, which demonstrates that the structure of the Cu(II)-[4ABA-MA] remains intact without any changes (Figure 5b). Furthermore, the photocatalytic activity of the Cu(II)-[ABA-MA] MOF was compared with the different photocatalysts on a similar dye degradation system. It is obvious that the photocatalytic activity of Cu(II)-[4ABA-MA] is superior in terms of the apparent rate constant value compared to recently reported catalysts (in Table 1). Additionally, the structural robustness of Cu(II)-[4ABA-MA] is another vital factor for long-term applications. These results indicate that MOF-based photocatalysts are effective for efficient dye degradation due to their versatile structure tunability and porosity and can be utilized for various dyes by altering the ligand or metal centers. Moreover, MOFs show more morphological flexibility and robustness than traditional metal-oxide-based catalysts under different pH conditions. Therefore, these results determine the remarkable potential of the Cu(II)-[4ABA-MA] -based 2D MOF as a dye degradation photocatalyst for wastewater treatment.

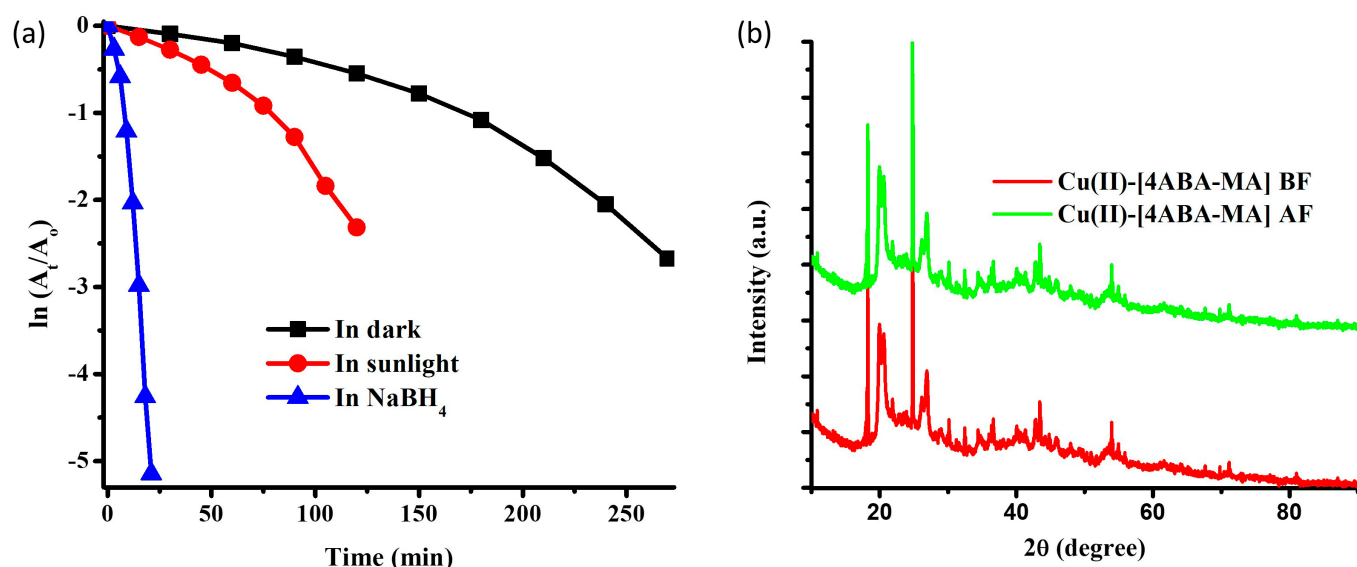


Figure 5. Photocatalytic performance of Cu(II)-[4ABA-MA] MOF (a) Degradation kinetics under different conditions (the black line represents the absence of both sunlight and NaBH₄ and the red line represents the presence of sunlight but the absence of NaBH₄, while the blue line represents the presence of NaBH₄ but the absence of sunlight). (b) XRD spectra of Cu(II)-[4ABA-MA] MOF before (red color) and after (green color) photocatalytic degradation of MeBl.

Table 1. Comparison of photocatalytic activity of Cu(II)-[4ABA-MA] MOF with other systems.

Catalyst	Abbreviations	Substrate	Apparent Rate Constant (k_{ap}) (min ⁻¹)	Refs
TiO ₂ particles	TiO ₂	MeBl	0.0021	[57]
TiO ₂ composite	TiO ₂ -P(ABSA)	MeBl	0.0138	[57]
Ag-doped ZnO	Ag@ZnO	MeBl	0.0059	[58]
Zinc oxide	ZnO	MeBl	0.0084	[59]
Copper (II)-[4-benzoic acid-maleic anhydride]	Cu(II)-[4ABA-MA]	MeBl	0.0187	This work

3. Materials and Methods

3.1. Materials

Maleic anhydride (MA) (C₄H₂O₃, 99%), 4-aminobenzoic acid (4ABA) (99%), acetic acid (99%), copper(II) sulfate pentahydrate (CuSO₄·5H₂O) (98%), and methylene blue (MeBl) were purchased from Sigma-Aldrich. De-ionized water was used for the catalytic and photocatalytic performance of copper(II)-[4ABA-MA].

3.2. Synthesis of 4ABA-MA and Cu(II)-[4ABA-MA]

The equimolar (0.1 mM) solutions of MA and 4ABA were prepared separately in two beakers in 20 mL acetic acid. Then, 4ABA solution was added dropwise into MA solution with gentle stirring at room temperature (24 °C). After mixing the solutions, the reaction was continued for 12 h with gentle stirring to complete the reaction. The yellow color precipitation indicated the formation of the 4ABA-MA ligand. The product was filtered and washed with water to remove the acetic acid molecules. The ligand was dried at 70 °C in an oven. Then this synthesized product was used to form MOF with Cu(II) ions. For this purpose, an equimolar solution of copper sulphate and 4ABA-MA was made in DMF solvent and then mixed at room temperature. This mixture was then added into a Teflon cylindrical autoclave and heated at 110 °C for 24 h. After completing the reaction, the product was cooled at room temperature and dried in an oven. The greenish crystalline Cu(II)-[4ABA-MA] product was formed.

3.3. Characterization Techniques

The synthesized 4ABA was characterized with NMR (400 MHz, Bruker's Avance Neo Technology, Billerica, MA, USA) technique. The Cary 630 FTIR spectrometer was used to identify the functional groups from MOF. The Bruker D2 Phaser powder X-ray diffraction (PXRD) technique was used for crystal structure analysis of 2D MOF. The UV-Vis spectrophotometer (V-780 UV-Vis/NIR) was used at room temperature. The MOF was also analyzed by Field Emission Scanning Electron Microscope (SEM) (FEI Nova 450 NanoSEM).

3.4. Electrocatalytic Application

The synthesized Cu(II)-[4ABA-MA] was used as a catalyst for the degradation of MeBl dyes from an aqueous medium. The catalytic efficiency of Cu(II)-[4ABA-MA] MOF was observed with and without NaBH₄. The performance of MOF was also investigated in the presence and absence of light in an aqueous medium. The same amount (0.01 g) of MOF was used for the catalytic degradation of 100 mL (0.05 mM) MeBl solution.

4. Conclusions

In this study, we report a new ligand synthesized using ABA and MA in the acid medium under ambient conditions. The 2D Cu(II)-[4ABA-MA] MOF was prepared using the newly synthesized ligand by the solvothermal process and employed as a photocatalyst in wastewater treatment. The 2D MOF showed excellent performance as a dye degradation catalyst in aqueous media, demonstrating the highly effective photocatalyst. Kinetic studies show that the Cu(II)-[ABA-MA] MOF has promising photocatalytic properties for the degradation/reduction of MeBl in the Cu(II)-[ABA-MA] MOF. Structural stability evaluation further demonstrates the practical applications of the Cu(II)-[ABA-MA] MOF in wastewater treatment. This study presents insightful designs and applications of Cu-based MOFs for waste treatment under mild conditions.

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