Photodegradation of methylene blue dye on a catalyst mixture (Cu₂O and CuO) powder in aqueous medium

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Abstract: In this study, a powder of two stable forms of copper oxide (Cu_2O and CuO) was utilized for the photocatalytic degradation of Methylene blue (MB). Various attempts were made to determine the optimal conditions for degradation, including liquid-phase adsorption, initial dye concentration, catalyst weight loading, pH variation, H_2O_2, and NaI concentration. The results demonstrated that the photocatalytic degradation of MB by the Cu_2O-CuO mixture achieved efficiencies of 87.9% and 97.1%, respectively, in the presence of 0.01 M NaI and 2 mL of H_2O_2. A degradation rate of 97.92% was obtained at pH 12 after 2 hours. However, increasing the amount of dye is significantly reduced the degradation rate value, as the dye molecules blocked the light intensity required for photocatalyst activation. Liquid-phase adsorption studies showed that the adsorption efficiency of MB increased as its initial concentration decreased.

Additionally, an acidic medium (pH 2) was found to be optimal for adsorption at 95.69%. The addition of NaI to the reaction medium significantly enhanced the adsorption of MB on the catalyst mixture. In addition, the powder X-ray diffraction (XRD) investigations showed the crystalline system of monoclinic CuO and cubic Cu_2O. The morphological analysis using Scanning Electron Microscopy (SEM) revealed irregular shapes of nanostructures. Furthermore, investigations on the catalyst weight effect were investigated.

Keywords: Methylene blue, Photocatalytic activity, Copper oxide, Solar irradiation, Degradation efficiency

1. Introduction

Environmental pollution has become a major global challenge due to the Industrial Revolution, leading to significant water contamination while improving the quality of life. This highlights the urgent need for adequate water remediation methods to remove pollutants [1]. Due to their chemical stability and poor biodegradability, organic dyes such as methylene blue (MB) are challenging to break down in wastewater [2].

Among the various water treatment methods, photocatalytic degradation has recently gained considerable attention for its ability to remove low concentrations of organic contaminants, such as bacteria in hospital wastewater, pharmaceuticals, pesticides, and dyes [3-5]. Photocatalysis is an environmentally friendly and cost-effective process that occurs when the photocatalyst absorbs photons with an energy more significant than its bandgap energy. This leads to the generation of electron-hole pairs, where the excited electrons from the valence band move to the semiconductor's conduction band, reacting with dissolved oxygen (O_2). The resulting holes can react with hydroxyl radicals (HO•) or iodide ions (I⁻), forming highly reactive species that participate in degrading organic dyes [6]. Including

oxidizing agents, such as hydrogen peroxide (H_2O_2) and sodium iodide (NaI), plays a critical role in enhancing the photocatalytic process. H_2O_2, for instance, can act as a hole acceptor, producing hydroxyl radicals that increase the degradation efficiency, while NaI contributes by scavenging holes and facilitating the formation of reactive iodine species. Both agents significantly improve the overall performance of the photocatalyst [7, 8].

Numerous studies have focused on photocatalytic degradation of organic compounds, particularly methylene blue. Kundan Jangam and colleagues have published works on the degradation of methylene blue using different photocatalysts such as $Zn_{1-x}Co_{0.5x}Mg_{0.5x}Fe_2O_4$, $Zn_{1-x}Co_xFeCrO_4$, $Zn_{1-x}Co_xFeMnO_4$ and $Ni_{0.25}Cu_{0.55}Zn_{0.20}Fe_2O_4$ [9-12]. They observed that the capacity of these materials to degrade methylene blue varied. Under solar irradiation, MB removal rates of 99% ($Zn_{1-x}Co_xFeMnO_4$)[9], 99.23% ($Zn_{1-x}Co_{0.5x}Mg_{0.5x}Fe_2O_4$) [10,] and 96.7% ($Zn_{1-x}Co_xFeCrO_4$)[11] were achieved after 20, 40 and 85 minutes, respectively. On the other hand, the $Ni_{0.25}Cu_{0.55}Zn_{0.20}Fe_2O_4$ catalyst produced an MB degradation rate of 95% after 50 minutes of treatment time [12]. In the same vein, Pramod, Agale

and colleagues [13] found that the best methylene blue photodegradation performance observed with 5% Sr doped in ZnO with a high degradation rate constant of 0.0389 min^{-1} comparatively to ZnO and Sr (1%, 3%, 7% and 8%) doped in ZnO.

Furthermore, copper oxides (CuO and Cu_2O) are among the catalysts that have attracted increasing interest due to their suitability as p-type semiconductors, active under visible light, with direct bandgaps of 1.3–1.7 eV for CuO and 2.1–2.3 eV for Cu_2O [14, 15]. Thanks to their small bandgaps and high natural abundance, these materials are widely used in solar cells, electrochemical water splitting, gas-sensing devices, lithium-ion battery electrodes, thin-film transistors, and photocatalysts [16, 17].

This work has been designed to evaluate the Cu_2O+CuO, in the form of powder, photocatalyst efficiency for degradation of MB in the presence of oxidizing species agents like NaI and H_2O_2. After confirming the structure of the catalyst, the experimental parameters influencing the optimization of the dye photodegradation reaction were systematically investigated. In each experiment, a liquid phase adsorption step was carried out before the photodegradation phase. To our knowledge, no similar research has been published to date. We hope that the results of this study will provide a green and efficient method for wastewater treatment of dye.

2. Materials and methods

2.1. Material and reagent
Methylene blue (98% purity), the model compound used in this work, was purchased from Aladdin Chemicals Co. Ltd. (Shanghai, China) and used without further purification. The copper oxide-based adsorbent was obtained from Prolabo. Sodium iodide (NaI) and hydrogen peroxide (H_2O_2) were provided by Riedel-de Haen and Scharlau, respectively. pH was adjusted using aqueous sulfuric acid (H_2SO_4, Fluka) and sodium hydroxide (NaOH, Prolabo) solutions. The distilled water was used throughout the experiments.

2.2. Experimental methods
The photocatalytic degradation of methylene blue (MB) was studied under simulated solar irradiation using a SunTest Original Hanau device equipped with a Phillips UV-C lamp (55 W). The catalyst, a mixture of CuO and Cu_2O powders, was prepared by grinding copper oxide pellets. The grains were ground in a porcelain creuset until they were reduced to powder. For each experiment, 25 mg of this homogeneous mixture was introduced into a reactor (100 mL) containing MB. Before activating the solar simulator, the mixture was kept in a dark environment for 30 minutes to establish adsorption equilibrium between MB and the photocatalyst. The adsorption was continuously stirred in the dark. The photoreactor (SunTest) was then illuminated for 04 h (240 minutes). Samples of the MB solution (3 mL) were collected at predefined time intervals and stored in a refrigerator at 4 °C. The sample marked as t=-0,5h represents the initial adsorption phase, while t= 0h marks the end of this phase and the beginning of the photocatalytic degradation phase. The experimental parameters studied include the effects of the initial concentration, catalyst mass, pH, the presence of NaI, and the presence of H_2O_2.

A series of experiments was carried out to study the Effect of the initial dye concentration, varying the MB concentration between 3 and 15 mg/L in the presence of 25 mg of photocatalyst. Concerning the Effect of the initial pH of the solution, pH values from 2 to 12 were studied using 25 mg of photocatalyst with a dye concentration of 10 mg/L. For the Effect of iodide ions, we chose concentrations of 0.005 and 0.01 M NaI, using 25 mg/L of photocatalyst at free pH. Finally, the Effect of H_2O_2 was analyzed by varying the volume of H_2O_2 from 0.1 to 2 mL for 10 mg/L MB, without imposing a pH. In addition, the catalyst weight of the MB degradation was investigated.
For each experiment, catalysts were immediately separated from MB samples through centrifugation before absorbance was recorded.

The CuO and Cu_2O catalyst mixture used in this study was characterized by scanning electron microscopy (SEM) and X-ray diffraction (XRD).

2.3. Analysis technique
MB samples were analyzed using a UV-visible spectrophotometer, with the maximum absorption wavelength observed at 668 nm. The MB concentration was determined from the calibration curve using Equation 1.

$$\text{Absorbance} = 0.2304\,[MB] + 0.081 \text{ with } R^2 = 0.9901 \quad (1)$$

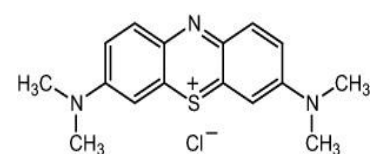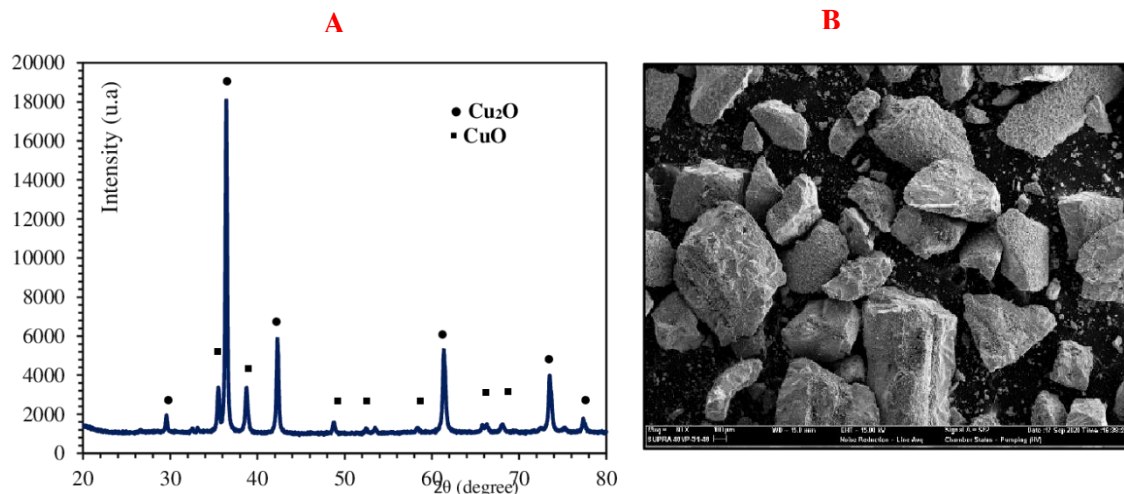The molecular structure of MB is shown in Figure 1.

Figure 1. Molecular structure of MB

3. Results and Discussion

3.1. Copper oxides characterization
Figure 2. A shows the X-ray diffraction patterns of the powder obtained from the copper pellets. Diffraction peaks can be seen at 2θ= 36; 38.9, 49, 53, 58, 66 and 68.8°C. These values correspond to the (-111), (111), (-202), (020), (202), (-311), and (220) crystal planes characteristic of the CuO monoclinic structure according to JCPDS data (80-0076) [18, 19]. According to JCPDS No. 05-0667, the diffraction peaks at 2θ values of 29.8, 36.8, 42.5, 61.8, 73.8, and 78.2 °C

corresponding to the (110), (111), (200), (211), (220), (311) and (222) crystal planes are characteristic of the Cu_2O cubic structure [18, 20]. These results indicate that the obtained powder contains CuO and Cu_2O particles.

Figure 2. B shows the scanning electron microscope (SEM) image of the catalysts obtained after crushing the copper-based pellets. As can be seen, the $CuO+Cu_2O$ particles are irregularly distributed and have irregular shapes. Their size ranges from 10 to 40 nm, indicating that they are nanoparticles.

A

B

Figure 2. XRD (A) and SEM (B) characterization of copper oxides

3.2. Liquid-phase adsorption of MB
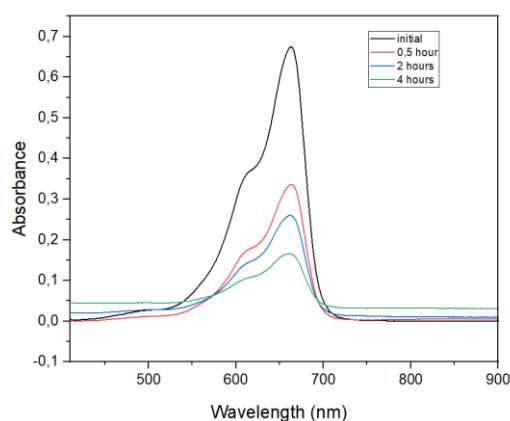
Liquid-phase adsorption studies were carried out for different concentrations of MB in a solution containing the catalyst mixture of CuO and Cu_2O. This phase aimed to assess the adsorption efficiency of the catalysts, as the degradation rate of dyes in heterogeneous photocatalysis can depend on their adsorption capacity onto the catalyst surface [21]. Figure

3 (a) shows the result obtained after 0.5 hours under dark conditions, where MB is adsorbed onto the photocatalysts. However, the percentage of adsorption decreases as the concentration of MB increases. At pH 2, 6.01, 9.01, and 12, equilibrium adsorption tests revealed that significant adsorption of the dye occurred at acidic pH levels (Figure 3(b)).
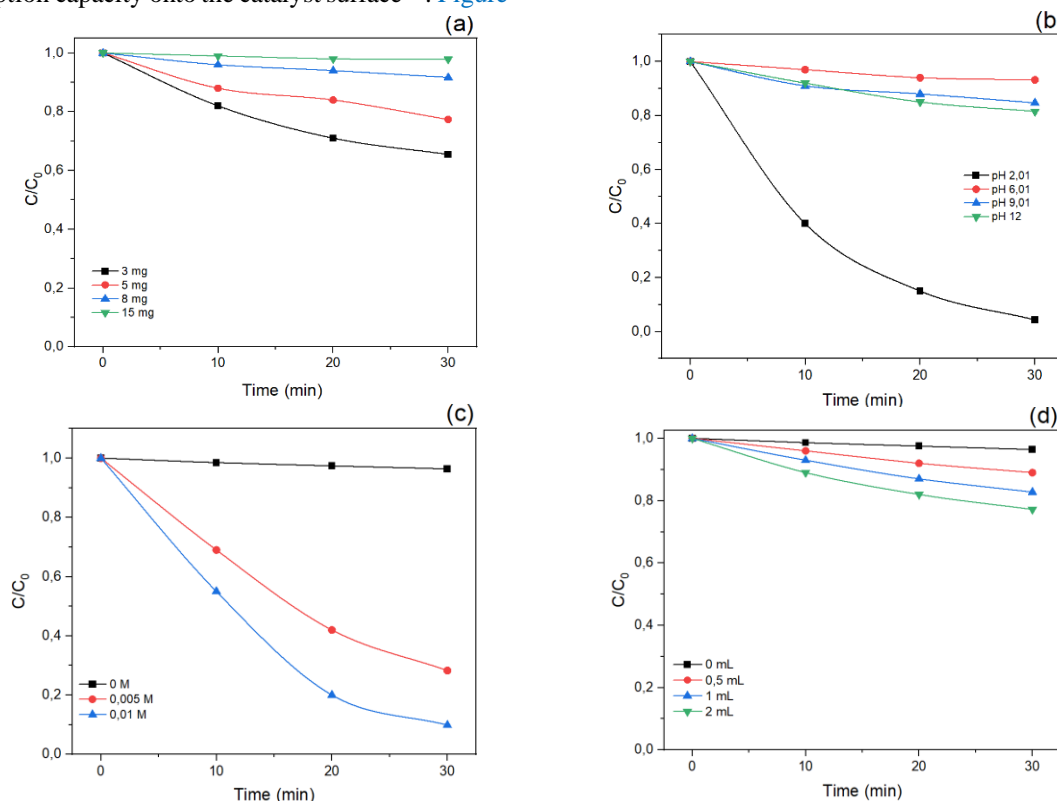
Figure 3. Liquid phase adsorption at different concentrations of MB (a), for different pH values (b), at different amounts of NaI (c) and varying amounts of H_2

Furthermore, the amount of MB adsorbed onto the CuO + Cu$_2$O catalyst surface with the addition of I$^-$ ions at natural pH was higher than that without I$^-$ ions (Figure 3 (c)). This enhanced adsorption of MB dye in an acidic medium can be attributed to the increased solubility of divalent metal oxides, which rises with the square of the hydrogen ion activity [22]. The catalyst surface's adsorption capacity increases as the solution's pH decreases, leading to greater MB dye adsorption. The significant adsorption effect in the presence of I$^-$ can be explained by the strong influence of the overall surface charge, which affects the adsorptive properties of CuO + Cu$_2$O particles. MB, which is a cationic pollutant, is strongly adsorbed at its natural pH due to the relatively more negative surface charge caused by the adsorption of I$^-$ ions onto the surface of the photocatalyst particles. Liquid phase adsorption was also performed with different amounts of H$_2$O$_2$, as shown in Figure 3 (d). Notably,

MB adsorption onto the catalyst did not increase significantly with increasing volumes of H$_2$O$_2$ compared to NaI.

3.2. Photocatalytic degradation of MB

The catalytic efficiency of the CuO+Cu$_2$O mixture was evaluated by its photocatalytic activity in degrading MB dye, as shown in Figure 4. This figure illustrates the Effect of dye absorption in an aqueous solution under visible light irradiation for 4 hours, following 0.5 hours of adsorption onto the catalyst surface. Since MB dye was relatively stable in aqueous solution under visible light irradiation, a reduction in absorbance indicates degradation of the leading dye chromophores [23]. Therefore, the degradation of MB is attributed to the photocatalytic reaction of CuO+Cu$_2$O, and the amount of dye degradation as a function of irradiation time is displayed in Figure 4.

Figure 4. Absorption spectra of a solution of MB under solar light illumination

Figure 5. Photodegradation at different concentrations of MB

3.2.1. Effect of initial dye concentrations

Different initial concentrations of MB were used to study the Effect of increasing initial dye concentration on the degradation rate, ranging from 3 to 15 mg/L in the presence of 25 mg of CuO + Cu$_2$O catalyst under irradiation. As shown in Figure 5, increasing the dye concentration from 3 to 15 mg/L significantly reduces the degradation rate from 71% to 5%. This reduction occurs because the number of active catalyst sites
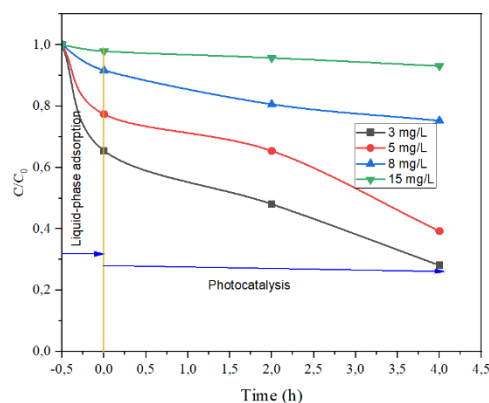
3.2.2. Effect of catalyst weight loading

The Effect of catalyst loading on the degradation of MB was investigated in the dark during 0.5 hours of experience followed by 04 hours of UV irradiation. The catalyst masses explored were 25, 50, and 100 mg/L for a fixed MB concentration (10 mg/L) in 100 mL of solution. Figure 6. A displays the dye elimination kinetics in the dark and under artificial solar irradiation. It can be seen that the rate of BM degradation decreases as the mass of the catalyst increases. The best methylene blue dye removal kinetics were obtained with a catalyst mass of 25 mg. This is confirmed by the methylene blue degradation rates obtained after 4.5 hours of treatment (in the dark

remains constant, meaning the number of adsorbed molecules is the same regardless of concentration. As the concentration of dye molecules increases, the generation of $OH_{ads}^{\bullet}$ Radicals are hindered, and the light intensity reaching the catalyst for excitation decreases [24, 25]. Consequently, the generation of electron-hole pairs diminishes, decreasing dye degradation due to a lack of oxidizing species.

and under irradiation), which are 40, 19; 29.32 and 4.29%, respectively, for 25, 50 and 100 mg of CuO-Cu$_2$O (Figure 6.B). Under our experimental conditions, an increase in the mass of the catalyst appears to harm the elimination of methylene blue.

Indeed, an increase in the mass of the catalyst increases the number of active sites available for the degradation of the organic compound. However, beyond a certain threshold in the mass of the catalyst, the solution can become turbid, reducing the light penetration into the solution [9, 10, 26].

In addition, increasing the mass of the catalyst can promote particle agglomeration, reducing the specific surface area available for adsorption and

photocatalytic reactions. A lower specific surface area means fewer active sites are available for the methylene blue molecules. In addition, secondary reactions such as the recombination of electron-hole pairs may occur as the mass of the catalyst increases [18].
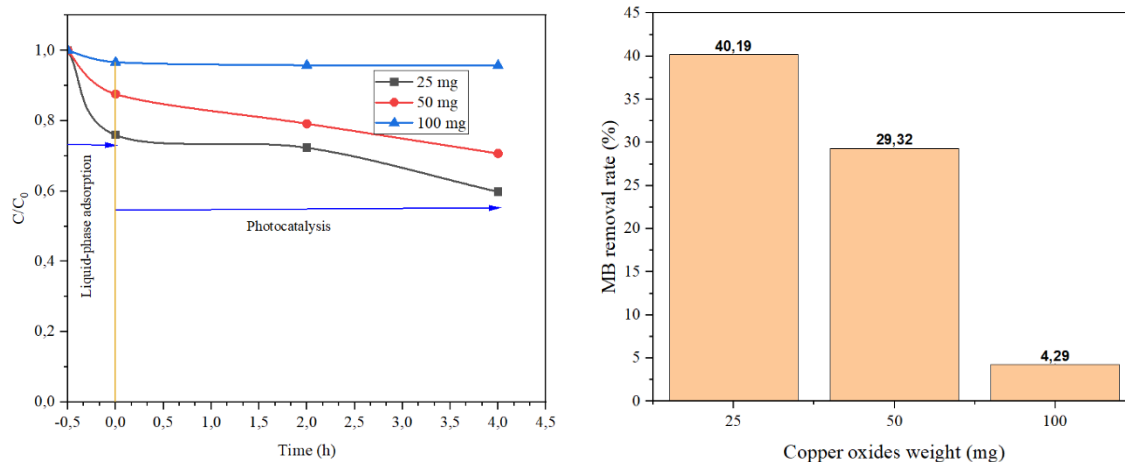

Figure 6. (A) Evolution of the MB removal rate during treatment. **(B)** MB removal rate after adsorption and UV irradiation treatment.

3.2.3. Effect of initial pH

A degradation test for MB was performed under irradiation after a 0.5 hour equilibration adsorption phase at pH 2.01, 6.01, 9.01, and 12, as shown in Figure 7. For the test, 25 mg catalyst was added to 100 mL of aqueous dye solutions with an initial 10 mg/L concentration. For both pH values of 2 and 12, notable changes in UV-vis spectra during photocatalytic degradation of MB are shown in Figure 5. During solar light irradiation, the characteristic absorption band of the dye (668 nm) gradually decreases, and the solution becomes almost colorless after 2 hours of irradiation in the case of pH 12 (The solution became colorless during liquid phase adsorption for pH 2). Under acidic conditions, the degradation rate of

58.5% can be attributed to the high adsorption of MB onto the catalyst surface. Thus, photocatalysis and adsorption exhibit a remarkable synergistic effect on dye degradation. At high pH values, OH_{ads}^- ions adsorbed onto the surface of the photocatalyst particles act as efficient traps for the photogenerated holes [27] (Equation 2). As a result, $OH_{ads}^\bullet$ Radical generation increases progressively on the catalyst surface, providing significant power to degrade the pollutants, ultimately accelerating MB dye degradation. Table 1 shows that at pH equal to 12 a 97.92% degradation is observed after 2 hours under irradiation.

$$OH_{ads}^- \;+\; h^+ \quad\rightarrow\quad OH_{ads}^\bullet \tag{2}$$
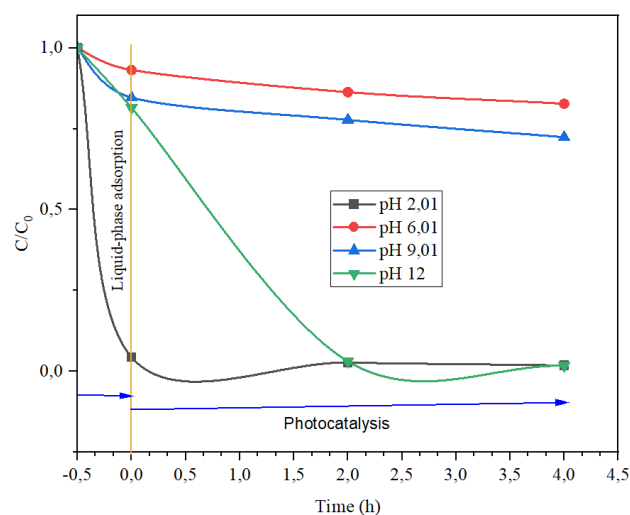
Figure 7. Photodegradation for different pH values

Table 1. Degradation rate at different pH as a function of time.

| pH	Adsorption rate (%) after 30 minutes	Photodegradation rate (%) after 2 hours
2.01	95.69	58.5
6.01	6.15	11.2
9.01	15.3	14.51
12	18.51	97.92

3.2.4. Effect of the presence of I⁻ ions

The photocatalytic degradation of dye was also studied using various initial concentrations of NaI (0,005 and 0.01 M), with 25 mg of catalyst and an initial dye concentration of 10 mg/L. Heterogeneous photocatalysis primarily occurs at the interfacial layers between molecules, so the adsorption properties of the reactants on the photocatalyst surface are crucial for driving the chemical reaction. The presence of I_{ads}^- ions on the surface of the CuO+Cu$_2$O catalyst creates an environment that not only increases the number of active sites for dye-semiconductor interactions but also generates $I_{ads}^\bullet$ Radicals are oxidizing and reactive species (Figure 8) (Equation 3). Iodide ions act as hole scavengers by adsorbing onto the catalyst surface and interacting with photogenerated holes to form iodine radicals (I·). These radicals enhance the dye degradation process by increasing the production of reactive species. This mechanism is similar to other halide ions, where forming radicals boosts the photocatalytic reaction [7].

This twofold Effect led to an increase in the photodegradation processes. As the initial concentration of NaI increases, the degradation efficiency also improves (Figure 9). Figure 10 shows that the blue color of the solution disappeared after 01 hour. Under visible light illumination, in the presence of I_{ads}^- ions, the CuO + Cu$_2$O catalyst degraded 80.33 and 87.94% of MB after 01 hour, respectively, for 0.005 and 0.01M of NaI.

$$I_{ads}^- \; + \; h^+ \qquad \rightarrow \qquad I_{ads}^\bullet \qquad (3)$$
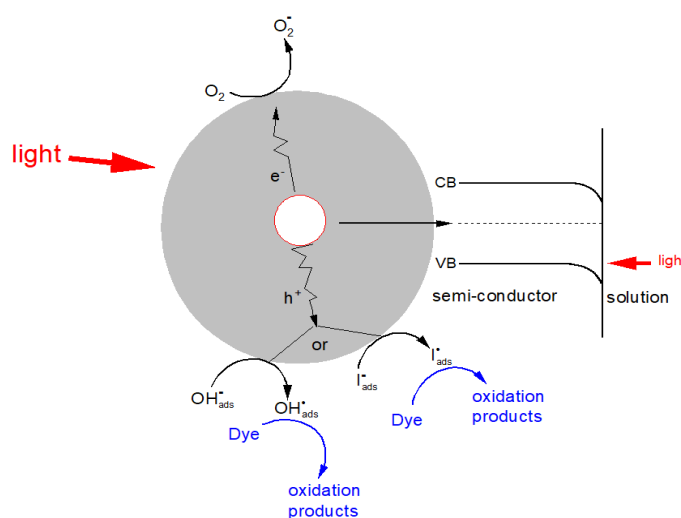
Figure 8. Mechanism for the photocatalytic activity on the surface of the semiconductor under the irradiation of light.
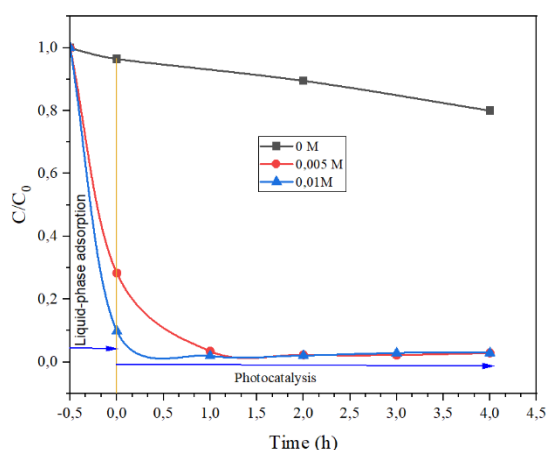
Figure 9. Photodegradation at different amount of NaI
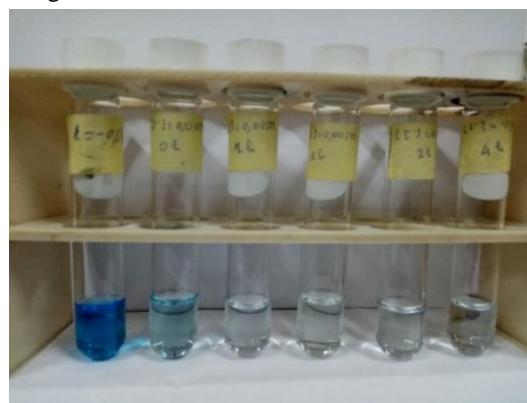
Figure 10. Color solution evolution under irradiation in the presence of I⁻

The amount of H_2O_2 for effective degradation of MB was investigated by using different dosages of H_2O_2, ranging from 0.1 mL to 2 mL, as shown in Figure 11. The dye's photodegradation rate increased with increasing the initial volume of H_2O_2. The removal of dye MB rose from 29% at 0.1 mL to 97.1% at 2 mL. This observation suggests that total degradation of the pollutant can be achieved by gradually increasing the amount of hydrogen peroxide. The high degradation rate can be attributed to the generation of $OH_{ads}^{\bullet}$ Radicals on the photocatalyst surface. Indeed, hydrogen peroxide acts as a highly effective electron acceptor, preventing the recombination of electron-hole pairs, which is a key factor in improving photocatalytic efficiency. Upon exposure to visible light, H_2O_2 decomposes to produce reactive hydroxyl radicals ($OH\cdot_{ads}$) (Equation 4), which are powerful

oxidizing agents that significantly contribute to the breakdown of organic pollutants such as methylene blue (MB). These radicals drive the degradation process by attacking the dye molecules on the catalyst's surface [8, 28, 29].

$$H_2O_2 \quad \rightarrow \quad OH_{ads}^{\bullet} \;+\; OH_{ads}^{\bullet} \qquad (4)$$

The results show that adding NaI and H_2O_2 significantly accelerates methylene blue (MB) degradation. However, a comparison of the efficiency of NaI and H_2O_2 in the degradation of methylene blue reveals different reaction kinetics for each species. Iodide ions (I^-) act as potent agents, inducing rapid degradation of the dye. In contrast, hydrogen peroxide (H_2O_2) induces a slower, gradual degradation. These observations are confirmed by photolysis studies on MB (figure not shown).
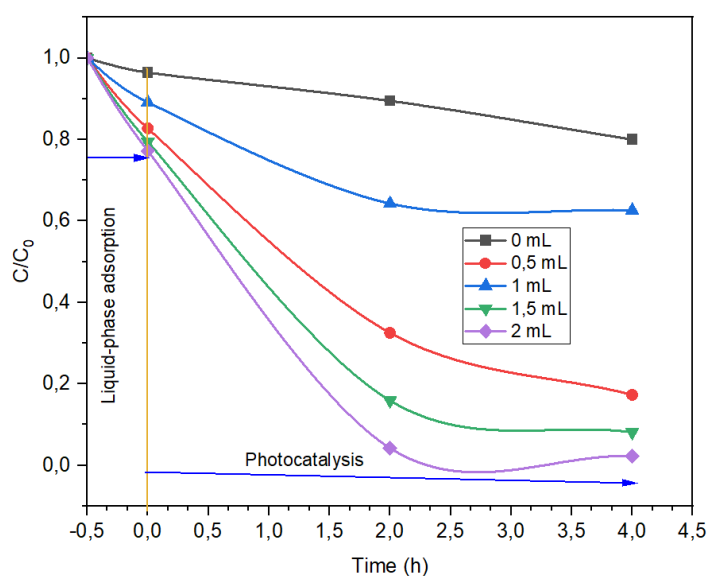

Figure 11: Photodegradation at different amounts of H_2O_2

4. Conclusion

In this study, the photocatalytic activity of MB dye under light irradiation was examined. The results demonstrated higher photocatalytic activity when MB dye is strongly adsorbed onto the catalyst surface during liquid-phase adsorption. In an essential medium (pH 12), a degradation rate of 98% was obtained after 2 hours, likely due to the increased generation of $OH_{ads}^{\bullet}$ Radicals. Under optimized conditions, the degradation rate further improved with an increase in NaI concentration up to 0.01 M, probably due to the excess formation of $I_{ads}^{\bullet}$ Radicals. Additionally, the introduction of hydrogen peroxide proved beneficial in enhancing the photodegradation rate of MB dye. However, it is essential to note that the efficiency of hydrogen peroxide depends on the volume added. The high efficiency of $CuO + Cu_2O$ photocatalyst for MB dye photodegradation suggests

its potential application for degrading other dye commercial pollutants. A mass of 25 mg of catalyst gives the best BM degradation rate.

References

1- M. Soleiman, R.R. Mahmood, G. Mehrorang, D. Kheibar, H. Shaaker, Sonochemical-assisted synthesis of CuO/Cu2O/Cu nanoparticles as an efficient photocatalyst for simultaneous degradation of pollutant dyes in a rotating packed bed reactor: LED illumination and central composite design optimization, Ultrason. Sonochem., 2018, 40, 601-610. https://doi.10.1016/j.ultsonch.2017.08.007

2- P.O. Oladoye, T.O. Ajiboye, E.O. Omotola, O.J. Oyewola. Methylene blue dye: Toxicity and potential elimination technology from wastewater. Results Eng. 2022, 16, 100678. https://doi.org/10.1016/j.rineng.2022.100678.

3- S. Olga, V. Vincenzo, R. Luigi, S. Diana, Photocatalytic activity of a visible light-active structured photocatalyst developed for municipal wastewater treatment. J. Cleaner Prod., 2018, 175, 38-49. https://doi.10.1016/j.jclepro.2017.11.088

4- N.C. Meng, J. Bo, W.K.C. Christopher, S. Chris, Recent developments in photocatalytic water treatment technology: A review. Water Res., 2010, 44 (10), 2997-3027. https://doi.org/10.1016/j.watres.2010.02.039

5- H. Yujie, B.S. Nora, H.H.R. Huub, A.M.L. Alette, Degradation of pharmaceuticals in wastewater using immobilized TiO2 photocatalysis under simulated solar irradiation. Appl. Catal., B, 2016; 182: 132-141. https://doi.org/10.1016/j.apcatb.2015.09.015

6- J. Nahi, R. Asha, R. Raveendran, B. Beena, Efficient photocatalytic degradation of organic dye from aqueous solutions over zinc oxide-incorporated nanocellulose under visible light irradiation. Main Group Met. Chem., 2020, 43, 84-91. https://doi.org/10.1515/mgmc-2020-0009.

7- J.M. Coronado, F. Fresno, M.D. Hernández-Alonso, R. Portela. Design of advanced photocatalytic materials for energy and environmental applications, Book, Springer, pp 5–33, 2013.

8- H.H. Tran, T.M. Cao, V.V. Pham, Progress in design strategies for photocatalytic hydrogen peroxide generation, Top. Catal., 2024, 67, 1085–1100. https://doi.org/10.1007/s11244-024-01936-6.

9- K. Jangam, K. Patil, S. Balgude, S. Patange, P. More. Synthesis and characterization of magnetically separable Zn1-xCoxFeMnO4 nanoferrites as a highly efficient photocatalyst for degradation of dye under solar light irradiation. J. Phys. Chem. Solids 2021, 148, 109700. https://doi.org/10.1016/j.jpcs.2020.109700.

10- More K. Jangam, K. Patil, S. Balgude, S. Patange, P. More. Magnetically separable Zn1-xCo0.5xMg0.5xFe2O4 ferrites: stable and efficient sunlight-driven photocatalyst for environmental remediation. RSC Adv., 2020, 10, 42766. https://doi.org/10.1039/D0RA08172H.

11- K. Jangam, S. Balgude, H. Pawar, S. Patange, P. More. Effect of cobalt substitution in Zn1-xCoxFeCrO4 ferrichromate: emerging light absorber for degradation of model textile dye. Surf. Interfaces 2022, 33, 102189

12- K. Jangam, A. Nair, K. Patil, S. Balgude, A. Kulkarni, P. More. Magnetically separable Ni0.25Cu0.55Zn0.20Fe2O4 ferrite as a highly efficient photocatalyst for environmental remediation. Functionalized Nanomaterials Based. Devices for Environmental Applications, Micro and Nano Technologies, 2021, 329-347. https://doi.org/10.1016/B978-0-12-822245-4.00013-1.

13- P. Agale, V. Salve, S. Mardikar, S. Patange, P. More. Synthesis and characterization of hierarchical Sr-doped ZnO hexagonal nanodisks as an efficient photocatalyst for the degradation of methylene blue dye under sunlight irradiation. Appl. Surf. Sci. 2024, 672, 160795

14- F. El-Sayed, V. Ganesh, M.S.A. Hussien, T.H. AlAbdulaal, H.Y. Zahran, I.S. Yahia, M.S. Abdel-Wahab, S. Mohd, B. Yugandhar, Facile synthesis of Y2O3/CuO nanocomposites for photodegradation of dyes/mixed dyes under UV- and visible light irradiation. J. Mater. Res. Technol., 2022, 19, 4867-4880. https://doi.org/10.1016/j.jmrt.2022.06.163

15- M.R.C. Alfaro, D. Sanchez-Martinez, L.M. Torres-Martínez, CuO thin films deposited by DC sputtering and their photocatalytic performance under simulated sunlight. Mater. Res. Bull., 2020, 122, 110678. https://doi.org/10.1016/j.materresbull.2019.110678

16- J. Denghui, X. Jianbin, W. Liqiong, Z. Wei, Z. Yuegang, L. Xinheng, Photocatalytic performance enhancement of CuO/Cu2O heterostructures for photodegradation of organic dyes: Effects of CuO morphology, Appl. Catal., B, 2017, 211, 199-204. https://doi.10.1016/j.apcatb.2017.04.034

17- V. Scuderi, G. Amiard, S. Boninelli, S. Scalese, M. Miritello, P.M. Sberna, G. Impellizzeri, V. Privi-Tera, Photocatalytic activity of CuO and Cu2O nanowires, Mater. Sci. Semicond. Process., 2016, 242, 89-93. https://doi:10.1016/j.mssp.2015.08.008

18- O. Kambiré, Y.P.A. Chia, Y.U. Kouakou, F. Yeo, L. Ouattara, Photocatalytic degradation of methyl orange in an aqueous solution in the presence of copper oxide, J. Chem., Biol. Phys. Sci., 2023, 13 (4), 401-412. https://doi.10.24214/jcbps.A.13.4.40112

19- D. Manyasree, P.M. Kiran, R. Ravikumar. CuO nanoparticles: Synthesis, characterization, and their bactericidal efficacy. Int. J. App. Pharm. 2017, 9(6), 71-74

20- C. H. Voon, B.Y. Lim, S.C.B. Gopinath, Y. AL-Douri, K.L. Foo, M.K. Md Arshad, S.T. Ten, A.R. Ruslinda, U. Hashim, V.C.S. Tony. Fabrication of Cu2O nanostructured thin film by anodizing. Mater. Sci.-Pol. 2018, 36 (2), 209-216.

21- J. Wiszniowski, D. Robert, J. Surmacz-Gorska, K. Miksch, J.-V. Weber, Photocatalytic decomposition of humic acids on TiO2: Part I: Discussion of adsorption and mechanism, J. Photochem. Photobiol., A, 2022, 152 (1-3): 267-273. https://doi.org/10.1016/S1010-6030(02)00022-9.

22- D.J. Wesolowski, S.E. Ziemniak, L.M. Anovitz, M.L. Machesky, P. Bénézeth, D.A. Palmer, Chapter 14: Solubility and surface adsorption characteristics of metal oxides. Aqueous systems at elevated temperatures and pressures, 2004,

493-595. https://doi.org/10.1016/B978-012544461-3/50015-6.

23- W.Z. Tang, A. Huren, UV/TiO2 photocatalytic oxidation of commercial dyes in aqueous solutions. Chemo-
sphere, 1995, 31 (9), 4157-4170. https://doi.org/10.1016/0045-6535(95)80015-D

24- A.K. Subramani, K. Byrappa, S. Ananda, L.M.L. Rai, C. Ranganathaiah, M. Yoshimura, Photocatalytic degradation of indigo carmine dye using TiO2 impregnated activated carbon, Bull. Mater. Sci., 2007, 3 (1), 37-41. https://doi.org/10.1007/s12034-007-0007-8

25- M.A. Behnajady, N. Modirshahla, R. Hamzavi, Kinetic study on photocatalytic degradation of C.I. acid yellow 23 by ZnO photocatalyst, J. Hazard. Mater., 2006, 133(1-3), 226-232. https://doi.org/10.1016/j.jhazmat.2005.10.022

26- Z. Othman, A. Sinopoli, H.R. Mackey, and K.A. Mahmoud. Efficient Photocatalytic Degradation of organic Dyes by AgNPs/TiO2/Ti3C2Tx MXene Composites under UV and Solar Light. ACS Omega 2021, 6, 33325-33338.

27- P.S. Kumar, M. Selvakumar, S.G. Babu, S.K. Jaganathan, S. Karuthapandian, S. Chattopadhy-Ay, Novel CuO/chitosan nanocomposite thin film: facile hand-picking recoverable, efficient and reusable heterogeneous photocatalyst, RSC Adv., 2015, 5(71), 57493-57501. https://doi.org/10.1039/C5RA08783J

28- P.C. Heimenz, R. Rajagopalan, Principles of colloid and surface
chemistry, third edition, revised and expanded, Marcel Dekker, 1978, 671.

29- F. D. Serant, «Influence des nitrates sur la photolyse et le traitetment d'oxydation avancée H202/UV de matières organiques», pH thesis, Université de Rennes, France, 1996.