Original Research Article

Photolytic Degradation of Methylene Blue: Influence of pH, H_2O_2, NaI, and NaCl on Wastewater Treatment Efficiency

ABSTRACT

In Ivory Coast, dyes are widely used in traditional textile dyeing. It's a lucrative business that is attracting more and more people. Unfortunately, the wastewater from these textile dyeing units is discharged directly and continuously into the immediate environment. This poses a risk to human health and the environment. This work investigated the degradation of methylene blue (MB), a model dye, by photolysis. The effects of the following parameters were studied: initial dye concentration, pH, H_2O_2, NaI, NaCl, and NaCl combined with H_2O_2 or NaI. The experiments were monitored using a UV-visible spectrophotometer. The results showed that MB can be effectively degraded by direct photolysis in a basic medium and at very low concentrations. Additionally, NaI and H_2O_2 had a very significant positive effect (83.77 % and 92 %) in contrast to NaCl (6.23 %). Furthermore, the treatment of MB solution was enhanced when NaCl was combined with NaI or H_2O_2 with a degradation rate of 88.1 and 84.9 %, respectively. The kinetic study revealed that the UV irradiation of MB can be described by both zero-order and first or second-order kinetics. In conclusion, the UV/H_2O_2, UV/NaI, UV/NaCl+H2O2, and UV/NaCl+NaI systems represent very interesting alternative processes for the treatment of wastewater containing dyes at neutral pH.

Keywords: Advanced oxidation process; Methylene Blue dye; inorganic ions; UV light

1. INTRODUCTION

Dyes are aromatic organic compounds that absorb light and produce colour in the visible spectrum (Abd-Elhamid et al. 2020, Benkhaya et al. 2020). They are used in a variety of sectors, including the textile, pharmaceutical, and food industries. Unfortunately, a significant portion of these dyes is discharged daily into water bodies after use (Soltani et al. 2013), contributing significantly to environmental pollution.

In Ivory Coast, traditional textile dyeing is a thriving informal sector that attracts an increasing number of people due to its financial benefits. Most artisans involved in this sector acquire their skills through family traditions passed down over generations or by learning from master artisans. However, artisans typically lack access to crucial information, such as the supplier, country of origin, expiration date, usage guidelines, and the effects of dyes on human health and the environment. They are generally sold in simple plastic packaging and are handled by artisans without adequate protective measures, such as masks, gloves, or goggles. Moreover, wastewater from these dyeing activities is frequently discharged directly onto the ground or

into the sewerage system without prior treatment, posing severe pollution risks to the environment and human health. The dyes used in this sector are known to be non-biodegradable, resistant to conventional methods of pollutant degradation, toxic, and with some being carcinogenic (Contreras et al. 2019, Sun et al. 2019). In addition, the discharge of dye-containing wastewater results in aesthetic pollution and eutrophication. This affects aquatic life by promoting excessive algae growth, reducing oxygen levels required to sustain aquatic ecosystems (Gemeay et al. 2003). The dye effluents are also mutagenic and toxic to various microbiological and fish species (Daneshvar et al. 2003). This highlights the urgent need to identify and implement effective solutions for treating wastewater containing these harmful dyes to mitigate their adverse environmental and health impacts. Methylene blue (MB), one of the most commonly used and studied dyes, presents significant challenges to conventional degradation technologies. While biological wastewater treatment is considered environmentally friendly and cost-effective, are often ineffective for treating dye effluents due to the complex and poorly biodegradable nature of dyes (Allouche et al.2017, Bedin et al. 2016, Derakhshan et al. 2013, Han et al. 2013, Jalal et al.2024, Kumar et al. 2017) . Adsorption is another widely used method due to its simplicity, relatively low cost, and effectiveness in reducing toxicity (Liu et al. 2016, Nassar et al. 2016). However, this technology has the disadvantage of generating secondary pollution that is potentially dangerous for the environment and human health (Kumar et al. 2017).

Today, Advanced Oxidation Processes (AOPs) represent a promising alternative based on the generation of highly reactive oxidant species that can effectively degrade all kinds of organic compounds (Ling et al. 2016, Wen et al. 2019). These technologies are used to remove toxic organic compounds such as MB (Khan et al. 2022, Zhang et al. 2019). Photocatalytic degradation is one of the AOPs commonly used for dye degradation (Deepika et al. 2023, Chih-Chi et al. 2018, Venkatraman et al. 2020). In this process, a semiconductor used as a photocatalyst absorbs light and uses the photon energy to contribute significantly to the degradation of organic compounds (Bickley et al. 1991, Shen et al. 2017). However, the photocatalytic activity of the semiconductor depends on its band gap and its ability to generate electron-hole pairs that give rise to free radicals that undergo secondary reactions (Lou et al. 2014). According to the literature, the semiconductors ZnO, CdS, TiO_2, and their composites are widely used for the photocatalytic degradation of dyes, especially methylene blue (Dinda et al. 2023, Enéderson et al. 2010, Ranfang et al. 2014, Velanganni et al. 2018). In the case of direct photolysis, the energy from the light is absorbed directly by the organic compound, resulting in its molecular decomposition (Bendjama et al. 2019). The main disadvantage of this method is that it requires a very long degradation time and generally leads to conversion of the parent compound sometimes producing more toxic intermediates (Aziz et al. 2020, Zhou et al. 2009). However, it appears that the direct photolysis of MB alone is insufficient to significantly degrade it under UV light irradiation (Rashad et al. 2016). Indeed, the literature reports that the degradation rate of MB after 10h under solar irradiation was 7.9 % (Siong et al. 2019). But, using the UV/H_2O_2 system for the degradation of organic compounds allows very high degradation rates to be achieved compared to simple UV irradiation (Sari et al. 2010). Photolysis in the presence of H_2O_2 can lead to mineralisation of organic compounds (Ae-Jung et al. 2022). However, the effectiveness of this process is heavily reliant on the concentration of H_2O_2. Using an excessive concentration of H_2O_2 can inhibit the process by consuming hydroxyl radicals (Bingliang et al. 2022, Fenglian et al. 2010). Also, the degradation of compounds by UV/NO_3^- and UV/Cl^- processes has been reported in the literature (Deng et al. 2014, Sicheng et al. 2022, Zhiquan et al. 2022). However, work on the degradation of compounds employing the UV/NaI or UV/NaI+NaCl system is still in its infancy to the best of our knowledge.

The purpose of the present work was: (1) evaluate the influence of different parameters on the UV photolysis of MB, such as the concentration of MB, NaI, NaCl, pH and the amount of

H_2O_2; (2) explore the synergistic effect of NaI and NaCl, and H_2O_2 and NaCl on MB photolysis degradation. We hope that this work will be useful for future research in this field.

2. MATERIAL AND METHODS

2.1. Reagents

Methylene blue (Purity >98.0) was obtained from Aladdin Chemicals Co. Ltd. (Shanghai, China). Hydrogen peroxide (H_2O_2) was produced by SCHARLAU. Sodium chloride (NaCl) and sodium iodide (NaI) were manufactured by Merck. The solid products and reagents are stored at the ambient temperature and protected from light. The pH of the electrolyte was adjusted using sodium hydroxide (Prolabo) and Sulfuric acid (Fluka), and pH was recorded with Banté pH meter using a combination pH electrode. The calibration of the electrode was performed using buffer solutions of pH 4.0, 7.0 and 9.0. Solutions were prepared with distilled water. All the experiments were performed at laboratory temperature.

2.2. Experimental procedure

The photolysis measurements were performed with a Suntest sun simulator (ORIGINAL HANAU) (**Fig. 1**), equipped with a 1500 W xenon lamp. The radiations emitted by this lamp were not filtered. A 100 mL of MB solution, prepared in distilled water, was introduced into the solar simulator. The first sample (2 mL) is collected at t=0, then the solar simulator is switched on and the chronometer is started. Samples of approximately 2 mL are taken, without any filtration, at different well-defined times, and their absorbance at 665 nm was recorded using a HACH DR 6000 UV-vis spectrophotometer. The concentration of MB degraded during photolysis was quantified via a calibration curve obtained by measuring the absorbance of MB solutions with known concentrations.

The calibration curve obtained is represented by a straight line described by the equation 1:

$$\textbf{Absorbance} = 0.2304\ C + 0.081 \quad \textbf{(1)}$$

Then, the percentages of degradation in the absence and presence of oxidants were calculated using the equation 2:

$$\%\textbf{Degradation} = \frac{C_0 - C_t}{C_0} \times 100 \quad \textbf{(2)}$$

Where C_0 is the initial concentration of MB, while C_t, denotes its concentration after irradiation for a time t.

Experimental conditions, including the initial MB concentration, pH, NaI, NaCl, H_2O_2, NaI+NaCl and NaCl+H_2O_2 were adjusted as needed to explore their influence on the MB photolysis. The kinetics of MB photodegradation were determined by fitting the experimental data to a pseudo- first-order kinetic model (Equation 3) (Wang et al. 2021). The obtained R^2 values indicated that the degradation process in this study followed a pseudo-first-order kinetic model.

$$ln\left(\frac{C_t}{C_0}\right) = -k_{obs}t \quad \textbf{(3)}$$

Where C_0 and C_t are the initial and different time concentrations of the MB, respectively. k_{obs} represents the first-pseudo-order constant.

Fig.1. Experimental setup used for photodegradation of MB

3. RESULTS AND DISCUSSION

3.1 MB UV-Vis absorption spectrum

The colour of MB depends on its chromophoric and auxochromic groups. The chromophore group is the part of the molecule responsible for absorbing light (Khan et al. 2022). In the case of MB compound, the N-S conjugated system on the central aromatic heterocycle is the main chromophore, allowing it to absorb specific wavelengths, contributing to its blue colour. The auxochrome group does not absorb light directly, but modifies the chromophore's absorption. It influences the absorption wavelength and can also affect the intensity and stability of the colour. In MB, amine groups (-NH) and other substituents can act as auxochromes, enhancing the effect of the chromophore.

The UV-Vis absorption spectrum of BM in solution, presented in Fig.2, exhibits a localized intense peak at 665 nm attributed to the monomer form of the MB, and a shoulder peak at 610 nm associated with a dimer form of the dye studied (Wang et al. 2021). Indeed, the peak at 665 nm will be the peak that will allow us to follow the concentration of methylene blue. Furthermore, the 295 nm peak is associated with substituted benzene rings.

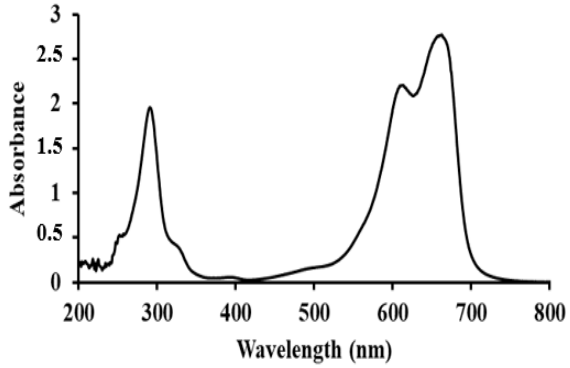

Fig.2. UV-visible absorption spectrum of methylene blue at pH=6.01

3.2. Effect of MB concentration

The effect of MB initial concentration was investigated in the range of 3 to 15 mg/L at unadjusted pH of 6.01 during 4 hours of UV-C irradiation. The results obtained, shown in **Fig.3 (A)**, revealed a decreasing of the degradation rate of MB when increasing the initial concentration. The concentration removal determined after 4 hours of UV-C irradiation are 71.99, 34.38, 18.2 and 3.52 %, respectively, for 3, 5, 10 and 15 mg/L (**Fig.2 (B)**). The K_{obs} values decreased also from 0.33 to 0.009 h^{-1} when MB concentration increased from 3 to 15 mg/L (Table 1). It appears that increasing the initial concentration has an inhibitory effect of the performance of photolysis. This can be explained by the fact that more oxidation products could be formed with the increase of MB in photolysis process, and which could scavenge reactive radicals. Furthermore, the addition of excess MB could enhance an internal filtering effect, so that the penetration of photons entering the solution would be significantly reduced, leading to an apparent decrease in the proportion of the incident UV flux absorbed by MB molecule (Wang et al. 2021).

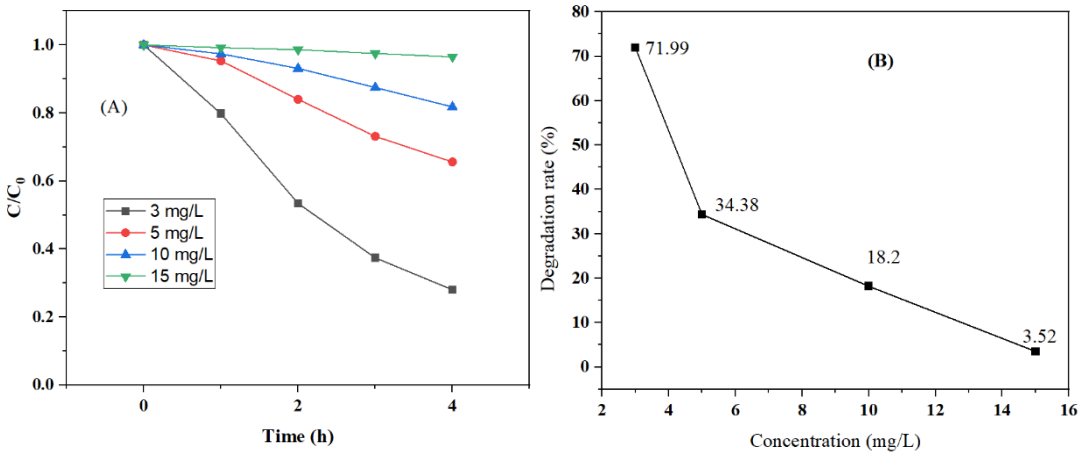

Fig.3. (A) Effect of MB concentration on degradation versus time; (B) MB concentration reduction rate for different initial MB concentrations after 4 hours; pH = 6.01

3.3. Initial pH Effect

The effect of pH on the direct MB photolysis was performed at different pH values (3.1; 6.8 and 11.06) for 10 mg/L of MB solution with a volume of 100 mL during 04 hours of treatment. Figure 4 (A) exhibits a difference in the reactivity of MB as a function of the initial pH of the medium. The rate of degradation was rapid at pH 11.06 compared to pH 6.01 and pH 3.1. The removals obtained increased from 0.85 to 24.87%, and the k_{obs} increased from 0.017 to 0.065 when pH increased from 3 to11.06 showing the enhancement of MB degradation with increasing pH. As pH 3.1 is lower than pKa 3.8 (Khan et al. 2022), MB is mainly in protonated form, which could limit its interaction with photons emitted by light. At pH 6.01, degradation is significantly improved because the compound is no longer in the protonated form and therefore reacts more readily with light than at pH 3.1. At alkaline pH, the degradation percentage reaches its maximum (24.87%). This can be explained by the fact at this pH, MB is deprotonated, which increases its reactivity with free radicals, leading to a higher degradation rate. Furthermore, alkaline conditions can promote the formation of hydroxyl

radicals, which are powerful oxidants, thereby improving MB degradation. $OH^{\bullet}$ radicals will in turn react with each other to form peroxide (H_2O_2) which plays a prominent role in the degradation process (equations 4-6) (Khan et al. 2022).

$$MB^{+} + OH^{-} \rightarrow MB^{*} + {}^{\bullet}OH \quad (4)$$

$$2\,{}^{\bullet}OH \rightarrow H_2O_2 \quad (5)$$

$$MB^{*} + H_2O_2 \rightarrow \text{products} \quad (6)$$

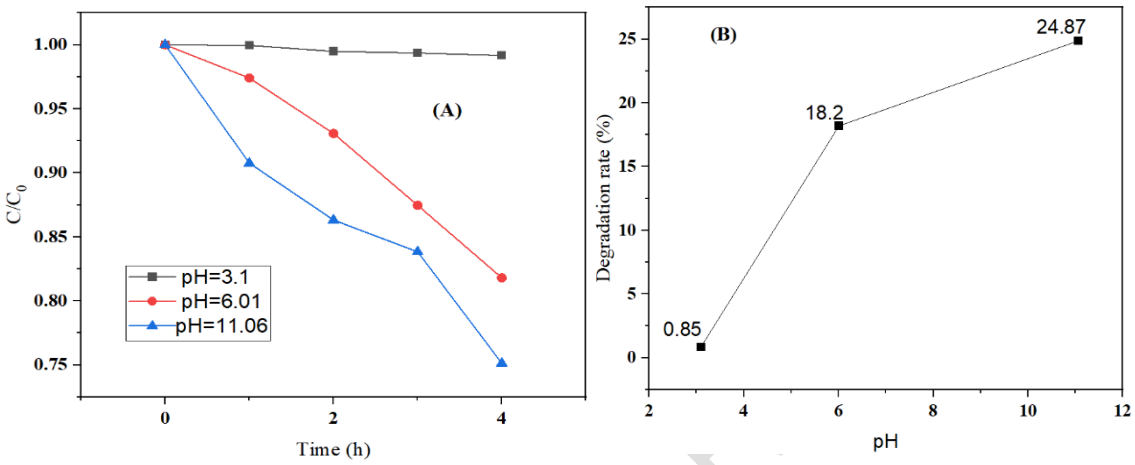

Fig.4. (A) Effect of pH on MB degradation versus time; (B) MB concentration reduction rate for different pH over a period of 4 hours; [MB] = 10 mg/L

3.4. Effect of H_2O_2

Photolysis reactions involve the generation of highly active $OH^{\bullet}$ radicals. The radicals formed during direct photolysis are considered to be oxidants for various chemicals. For this purpose, hydrogen peroxide's influence on MB degradation during the photolysis process was investigated in a solution containing 10 mg/L of MB for 4 h of irradiation. The degradation of MB at pH 6.01 (unadjusted) was followed as a function of irradiation time for different amounts of H_2O_2 within the range between 0 and 1 mL.

Fig.5 depicts the degradation efficiency of MB solution as a function of the volume of H_2O_2 added to the solution. H_2O_2 had a strong positive effect on the degradation of MB. The percentage of MB degradation are 88.82 and 92 % by adding 0.5 and 1 mL of H_2O_2, respectively, which surpassed that obtained without hydrogen peroxide (18.2 %) by 4.88 and 5.05 times, respectively. This means that H_2O_2 significantly promotes the photolysis of MB degradation under the conditions we work in, as reported in the literature (Wenhui et al. 2019) . This behavior is attributed to the significant quantity of the powerful and unselective radicals ($OH^{\bullet}$) produced in the UV/H_2O_2 (Equation 7). These radicals attack the molecule and produce the molecule radicals, $MB^{\bullet}$ in our case (Equation 8) (Hanadi et al. 2021, Ali et al. 2024). These MB radicals undergo further oxidation and are converted into reaction intermediates that can lead to CO_2, H_2O, NO_x, SO_x, and HCl as described by Mohammad A. Ali and collaborators (equation 8) (Ali et al. 2024). In fact, the intermediates products of MB included 2-amino-5-(N-methyl formamide)benzene sulfonic acid (m/z =230), 2-amino-5-(methyl amino)-hydroxybenzene sulfonic acid (m/z = 218), benzenesulfonic acid (m/z= 158), phenol (m/z = 94) and other (Ali et al. 2024, Yang et al. 2017).

$$H_2O_2 + h\vartheta \rightarrow 2\,OH^{\bullet} \quad (7)$$

$$OH^{\bullet} + MB \rightarrow \text{intermediates} \rightarrow CO2 + H_2O + NO_x + SO_x + HCl \quad (8)$$

However, we note a slight increase of the MB degradation percentage when the amount of H_2O_2 passed from 0.5 to 1 mL, which means a higher amount of H_2O_2 may result in a reduction of the UV/H_2O process efficacy due to the generation of $HO^{\bullet}_2$ and O_2 instead of $OH^{\bullet}$ (Equations 9-10), which are less powerful than hydroxyl radicals.

$$H_2O_2 + OH^{\bullet} \rightarrow HO^{\bullet}_2 + H_2O \quad (9)$$

$$HO^{\bullet}_2 + OH^{\bullet} \rightarrow O_2 + H_2O \quad (10)$$

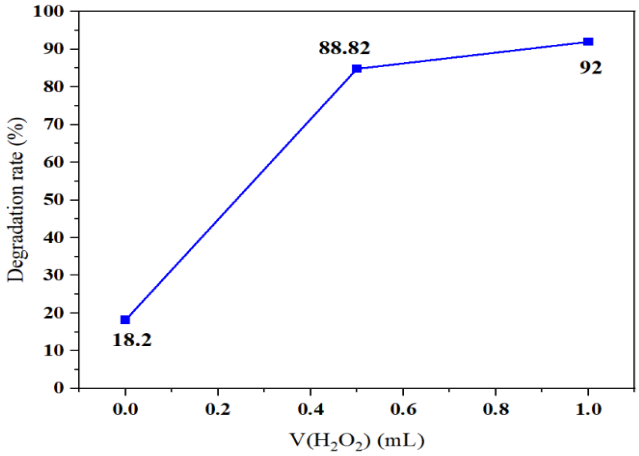

Fig.5. MB concentration removal for different H_2O_2 volume over a period of 4 hours; [MB] = 10 mg/L

3.5. Effect of NaI

The effect of sodium iodide (NaI) on the photolysis degradation of 10 mg/L of methylene blue solution was conducted at an unadjusted pH of 6.01 over 4 hours of treatment. Different NaI concentrations (0.075 and 0.01 M) were used to evaluate the MB degradation kinetics. As shown in **Fig.6(A)**, iodide ions contributed to the degradation of MB. After 4 h, degradation percentage of 77.48 % and 83.77 % were achieved for 0.0075 M and 0.01 M NaI, respectively. These percentages are 4.26 and 4.60 times higher than the 18.2% obtained from photolysis without NaI. K_{obs} determined, 0.708 and 0.854 h^{-1} for 0.0075 and 0.01 M NaI, respectively, that are higher than that in These results suggested a strong participation of the reactive of intermediates species from I^- in the degradation of MB. I^- might absorbs photons leading to its dissociation into $I^{\bullet}$ which then react with methylene blue, leading to degradation reactions (Equation 11) (Tang et al. 2021, Xu et al. 2024). Furthermore, iodide radicals can combine to form I_2, which can subsequently react with I^- to form I_3^- (Equations 12-13) (Kalmár et al. 2014, Tang et al. 2021, Xu et al. 2024). In a further step, $I^{\bullet}$ can react with I^- to form $I_2^{\bullet-}$, the latter being less potent than $I^{\bullet}$ (Grebel et al. 2010, Kalmár et al. 2014) (Equation 14).

$$I^- + h\vartheta \rightarrow I^{\bullet} + e_{aq}^- \quad (11)$$

$$2I^{\bullet} \rightarrow I_2 \quad (12)$$

$$I_2 + I^- \rightarrow I_3^- \quad (13)$$

$$I^{\bullet} + I^- \rightarrow I_2^{\bullet-} \quad (14)$$

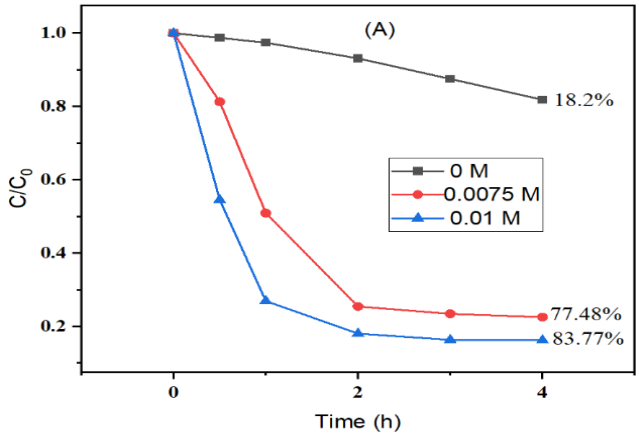

Fig.6. (A) Evolution of MB concentration (10 mg/L) over time for different NaI concentrations and (B) Comparison of C_{MB} evolution in the presence of NaI and H_2O_2

3.6. Effect of NaCl and NaCl combined with H_2O_2 or NaI

Cl^- ions are commonly found in water bodies (Luo et al. 2020), and can influence the pollutant removal processes. **Fig.7(A)** displays the influence of Cl^- ions on the photolysis of MB. The investigations were performed in 10 mg/L of MB solution at unadjusted pH. Cl^- had an inhibitory effect on the photodegradation of MB and the removal efficiency decreased from 18.2 % (absence of Cl^-) to 6.2% (presence of Cl^-).

The inhibitory effect of chloride ions can be explained by their reaction with hydroxyl radicals which could lead to the generation of other less reactive inorganic radical species ($Cl^{\bullet}$, $Cl_2^{\bullet}$ and $HOCl^{-\bullet}$) (Hilla et al. 2007, Kambiré et al. 2022, Lu et al. 2005). Chloride ions can also influence the optical properties of the solution, affecting the way light is absorbed and, consequently, the efficiency of photolysis of MB. Cl^- ions have been recognized as inhibitors, along with other inorganic ions such as SO_4^{2-}, NO_3^-, HCO_3^-, and H_2PO_4/HPO_4^{2-} ions, for the degradation of organic compounds by photolysis (Hilla et al. 2007, Wen et al. 2019).
Experiments were conducted by adding, to 10 mg/L MB + 0.01 M NaCl, 1 mL H_2O_2 and 0.01 M NaI separately to the mixture. According to the results obtained (**Fig.7 (B)),** it's evident that the presence of NaI or H_2O_2 significantly improves the removal of MB during photolysis treatment. After 4 h of treatment, the rates obtained were 84.9 % and 88.1 % in the presence of H_2O_2 and NaI, respectively. The coexisting I^- and Cl^- synergistically affect the removal of MB in the UV/Cl^--I^- system compared to when NaI (83.77 %) and NaCl (6.2 %) were present alone in the reaction medium. This improvement could be explained by the fact that hydroxyl radicals react more rapidly with iodide ions to form the reactive intermediates species (RIS) of iodine compared with chloride ions, which can contribute to the degradation of MB (Equations 15-17). Furthermore, as iodine is photosensitive, I_2 could be formed in the reaction medium and react with chloride ions to form Cl_2 (equation 18), which is a powerful oxidant.

$$OH^{\bullet} + I^- \leftrightarrow IOH^{\bullet-} \quad k_1=1.6*10^{10}\ M^{-1}s^{-1} \quad (15)$$

$$OH^{\bullet} + 2I^- \leftrightarrow I_2^{\bullet-} + OH^- \quad k_2=1.4*10^{10}\ M^{-1}s^{-1} \quad (16)$$

$$OH^{\bullet} + Cl^- \leftrightarrow ClOH^{\bullet-} \quad k_3= 4.3*10^{9}\ M^{-1}s^{-1} \quad (17)$$

$$Cl^- + I_2 \rightarrow 2I^- + Cl_2 \quad (18)$$

However, when NaCl and H_2O_2 are simultaneously present in the medium, a slight decrease in the efficiency of MB degradation was observed compared to the case where H_2O_2 (92 %) alone was present in the medium. This finding is consistent with the works of Muruganandham (Muruganandham and Swaminathanm 2004) who demonstrated that the presence of chloride ions resulted in a slight decrease in the degradation rate of reagent orange 4 by UV/H_2O_2.

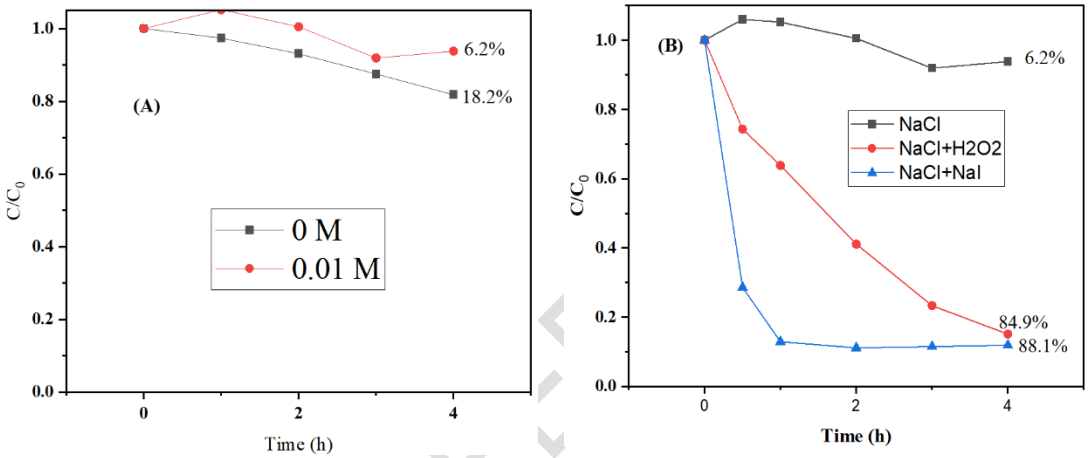

Fig.7. (A) Evolution of MB concentration (10 mg/L) over time in the presence of 0.005 M NaCl, (B) Effect of NaCl+ H_2O_2 (1 mL) and NaCl+NaI (0.01 M) combination

Table 1. Pseudo-first order rate describing MB oxidation in various conditions

Parameters	MB concentration (mg/L)				Initial pH			H_2O_2 (mL)		NaI (M)		NaCl (M)
	3	5	10	15	3.1	6.01	11.06	0.5	1	0.0075	0.01	0.01
k_{obs} (h-1)	0.33	0.111	0.051	0.009	0.017	0.051	0.065	0.488	0.62	0.708	0.854	-
R^2	0.994	0.98	0.974	0.986	0.977	0.975	0.961	0.994	0.964	0.989	0.92	-

4. CONCLUSION

Photolysis under artificial solar irradiation was employed for the degradation of the widely used model dye. The initial concentration of MB significantly influences the performance of the process used in that 71.99 % of the degradation rate is achieved for low MB concentrations (3 mg/L) versus 3.52 % when the concentration is very high (15 mg/L). The effect of pH shows that the photolysis degradation of MB is easier in a basic medium due to the production of hydroxyl radicals generated by hydroxide ions. Hydrogen peroxide strongly contributes to the photolytic degradation of MB (from 18.2 % for 0 mL to 91 % for 1 mL of H_2O_2). I^- ions significantly enhance the degradation kinetics of MB. Photolytic degradation of methylene blue

in the presence of NaI leads to almost important degradation of the initial compound by reducing the experiment time. On the other hand, the presence of NaCl leads to a very low degradation of the initial compound (6.2 %). However, combined with H_2O_2 and NaI, MB degradation rates of more than 84 % are achieved. Most of the experiments performed in this work can be described, in a general way, by the pseudo-zero, 1 and 2-order kinetic models. In conclusion, the degradation of MB by photolysis of H_2O_2, NaI, NaCl+H_2O_2, and NaCl+NaI allows an efficient oxidation of the organic compound.

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