

Efficiency of ZnO Nanoparticles and Various Additives on Sonodegradation of Methylene Blue

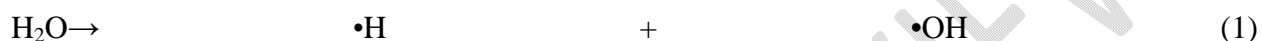
Abstract

Sonochemical method for the degradation of toxic dyestuffs is now considered as a promising technique. The dye molecule like Methylene Blue (MB) was degraded using ultrasound irradiation at different pH. The efficiency of various additives namely CCl_4 , H_2O_2 , NaCl and Na_2SO_4 with different doses for MB degradation was observed. The degradation efficiency of ZnO nanoparticles was also measured. The sonolysis of dye molecule was conducted for 0, 5, 15, 25 minutes and the extent of degradation was measured by UV-vis spectrophotometer. Acidic media is more efficient for degradation compared to basic media. 200 $\mu\text{M/L}$ doses H_2O_2 of 20 mM concentration showed highest efficiency (41.98%) to degrade the MB molecules. On the otherhand CCl_4 , Na_2SO_4 and ZnO nanoparticles also showed maximum 35.63%, 34.88% and 41.72% degradation efficiency respectively. From the result it is confirmed that the efficiency increases in the presence of additives and ZnO nanoparticles in comparison to the efficiency (18.88%) obtained without these additives.

Keywords: Additives, Azo dye, Degradation, Methylene Blue, Nanoparticles.

1. Introduction: Organic dyes are used in a wide range of sectors, including optical discs, food, cosmetics, medicines, solar cells, and traditional textile manufacturing. To ensure clean and safe water sources, it is critical to identify a method for extracting and discarding the organic dye chemicals used on a regular basis [1, 2]. Although there are numerous types of dyes, azo dyes represent for 70% of total dye production globally [3]. These compounds are distinguished by the azo bond chromophore group ($-\text{N}=\text{N}-$), which is related with aromatic structures and functional groups such as $-\text{NH}_2$ and $-\text{SO}_3\text{H}$ [4, 5]. These dyes are widely used in the food, textile, paper, leather, and pharmaceutical industries because of their exceptional properties and low cost [6]. The effects of various dye compounds on human health vary. When azo dyes and their intermediates degrade, they can cause damage, mutagenesis, and carcinogenesis, posing a major risk to human health [7]. For example, MB is a major synthetic dye used in water testing, sulfur analysis, medicine, and biology [8]. It also functions as a peroxide producer and redox indicator. However, they generally disturb ecosystems and are toxic, mutagenic, and carcinogenic to both

aquatic and human life [9-11]. It is important to develop a technology to remove this dye from water. Numerous chemical, physical, and biological approaches have been developed to remove these compounds [11-13]. Advanced oxidation processes (AOPs) have received a lot of attention due to their ability to totally mineralize organic contaminants to CO₂ and H₂O. Ultrasonography has lately been used in alternative operating procedures for wastewater treatment [14-16]. The two main concepts of sonochemical reactions include pyrolysis reactions that occur at and inside hot regions during collapsing bubbles, as well as radical reactions by OH and H radicals produced by water pyrolysis [17].



Several research have looked at the sonochemical degradation of phenolic chemicals and dyes [11, 18-24]. The development of efficient additives to accelerate the decomposition of organic molecules has been the subject of extensive investigation. Recent research investigated how adding CCl₄ or C₆F₁₄ impacts sonochemical degradation [24-15]. Although CCl₄ is a toxic chemical and hence heavily controlled in use, it is an effective addition for speeding up the sonochemical breakdown of the target organic molecules. Sponza et al. found that 19 mg L⁻¹ C₆F₁₄ boosted the rate of phenol removal in olive mill wastewater [25]. According to Zeng et al., the sonochemical degradation of phenol rose from 0.014 to 0.031 min⁻¹ or from 0.014 to 0.032 min⁻¹ in the presence of 150 M CCl₄ or 1.5 M C₆F₁₄ [26]. According to research the action of CCl₄ or C₆F₁₄ as a H atom scavenger is responsible for these positive benefits [25, 26]. Furthermore, it has been observed that the usage of specific chemicals can affect how quickly colors deteriorate [27-29]. Metal oxide semiconductors, on the other hand, have been extensively studied for their potential as photocatalysts for the removal of organic pollutants from water and air [30-33]. When the metal oxides are activated by the appropriate quantity of photon energy, active sites of electron-hole pairs form, increasing catalytic activity on the metal oxide surfaces [34]. TiO₂ is considered the oldest, most common, and best material among these metal oxides due to its outstanding stability and relatively simple fabrication technique [35-38]. Zinc oxide (ZnO), a metal oxide with an exciton binding energy of 60 m eV and a rather broad band gap of 3.37 eV, has received substantial research as a photocatalyst for the breakdown of numerous organic contaminants. Furthermore, ZnO nanostructures are recommended over TiO₂ as photocatalyst alternatives for photodegradation due to their better solar spectrum absorption, lower cost, and nontoxicity [39]. Numerous studies have shown that ZnO nanostructures have

significant photocatalytic activity for removing organic contaminants, such as organic dyes [40]. Therefore, in this work we have investigated the efficiency of additives like CCl_4 , H_2O_2 , NaCl , Na_2SO_4 , and ZnO nanoparticles on the sonolytic degradation of MB at certain concentration and pH.

2. Experimental

2.1 Materials and equipments: Methylene Blue ($\text{C}_{16}\text{H}_{18}\text{ClN}_3\text{S}$), Merck Life Science Private Limited, Godraj, Vadhroli East, Mumbai-400079, Sodium Chloride (NaCl), Ranbaxy Fine chemicals Limited A-3, New Delhi-110020 (ISO 9001: 2000 certified company), Sodium sulphate (Na_2SO_4), Merck Specialities Private Limited, Worli, Mumbai-400018, Hydrogen peroxide (H_2O_2), Carbon tetrachloride (CCl_4), Merck, D-6100 Darmstadt, FR. Germany. The sonicator machine used in this work is shown in figure 1.



Fig. 1: Sonicator bath used in sonochemical degradation.

2. 2 Preparation of Solutions

MB solutions with a concentration of 25 mg/l were prepared. In 100 ml of distilled water, solutions of the inorganic salts NaCl and Na₂SO₄ were prepared using 36 and 13.9 grams of each salt, respectively, based on their maximum saturation points. One liter of distilled water was mixed with 1.02 mg and 2.04 ml of H₂O₂ to make 10 mM/l and 20 mM/l H₂O₂ solutions, respectively. A little syringe is used to prepare the 200, 400, and 600 μM/l CCl₄. Water soluble dyes can absorb and reflect light, reducing the water's clarity naturally. Normally, dye effluent contains between 10 and 50 mg/l, although 1.0 mg/l dye solutions are visible and may be considered as pollutants [41, 42].



Fig. 2: Methylene blue solution

3. Results and Discussion

3.1 Degradation percentage of MB at various pH

The degradation percentages of MB without additives used in sonochemical irradiation process under various situations are presented and discussed below. Figure 3 depicts the degradation

efficiency of MB at different pH. NaOH and H₂SO₄ solutions were used to change the solution's pH.

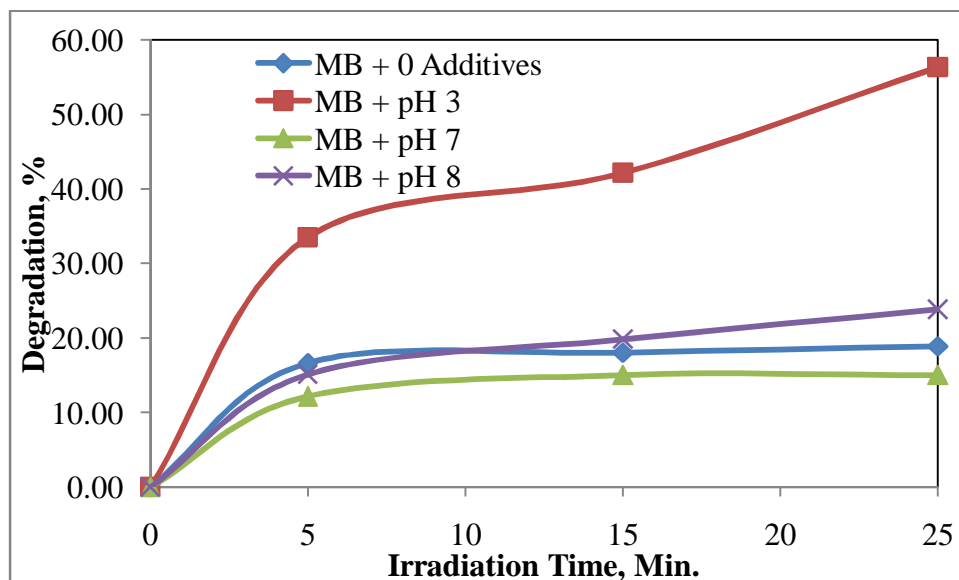


Fig. 3: Degradation efficiency for pure MB at various pH.

From the graph it is found that the efficiency at pH 3 is 56.33% at pH 7 is 15.06% and at pH 8 is 23.82% where the efficiency for raw solution without changing the pH is 18.88% i. e. acidic media is more efficient for degradation than basic media. There is a considerable chance of enhancing degradation efficiency using additives that maintain an acidic environment during sonochemical breakdown. Previous research has shown that sonochemical degradation efficiency is higher in an acidic environment [27-29].

3.2. Efficiency of CCl₄ for sonochemical degradation of MB

The efficiency of CCl₄ at 200, 400, and 600 μM/L concentrations on the sonochemical degradation of MB is represented in figure 4.

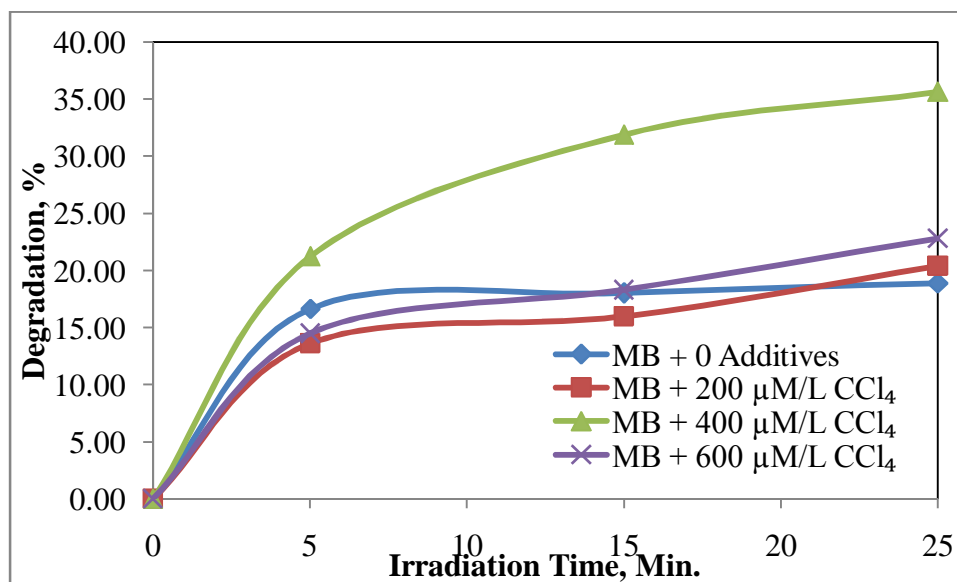
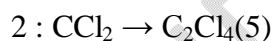
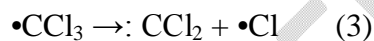
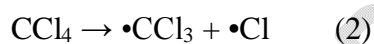


Fig. 4: Efficiency of CCl₄ for the degradation of MB

In presence of CCl₄, the highest efficiency of MB degradation is 35.63% when 400 μM/L CCl₄ was present. In the presence of 600 μM/L CCl₄ the efficiency is 22.80% and at 200 μM/L the efficiency of degradation is 20.39%. We suggest that active Cl radicals or related species are formed during CCl₄ sonolysis, and that these radicals or species could be beneficial in the breakdown of MB, though some researchers' claims that CCl₄ could act as a H atom scavenger [26]. According to previous research [24, 43-46], the following responses might occur:



The radicals that form, which contain chlorine (Cl, CCl₃, CCl₂, and Cl₂) and so on, may speed up the breakdown of MB in an aqueous solution. Merouani et al. [20] reported that 200 mg L⁻¹ of CCl₄ increased the sonochemical degradation rate of rhodamine B at 300 kHz by 21 times. According to Okitsu et al., adding 100 ppm CCl₄ increased the sonochemical breakdown rate of MO at 200 kHz by 41 times [38]. The effectiveness of CCl₄ for MB degradation discovered in this investigation is consistent with these findings. Another study found that the presence of

CCl_4 improves the sonolytic breakdown. From the above discussion, though CCl_4 has high toxicity it can be used as an additive [47].

3.3 Efficiency of H_2O_2 for MB degradation

Sonolysis of MB with 20, 100 and 200 μL doses of H_2O_2 at two different concentration 10 mM and 20 mM were carried out and the degradation efficiency is demonstrated in figure 5. It is observed from the figure that highest degradation efficiency showed by 200 μL of 10 mM H_2O_2 is 25.97% (fig. 5 a) and 200 μL of 20 mM H_2O_2 is 41.98% (fig. 5 b) after 25 minutes irradiation i. e. higher doses and higher irradiation time increases the efficiency of degradation. The generation of free radicals as active species explains the H_2O_2 reaction process for dye discolouration.



According to research, the US/UV/ H_2O_2 technique is the most successful in decomposing malachite green because it incorporates ultrasound to facilitate H_2O_2 scission in addition to photolysis [48]. Another recent study assessed the impact of introducing hydrogen peroxide at concentrations of 0.05, 0.10, and 0.15 M. The treatment with 0.10 M H_2O_2 and 45 W was effective and energy-efficient, removing 62.9% of the water's absorbance [49]. Sonolysis with 400 μL of H_2O_2 has been shown to improve methyl orange elimination efficiency [27]. When compared to previous research, it is clear that a variety of uses for hydrogen peroxide (H_2O_2) have emerged in the field of water treatment due to its relative safety and convenience of use.

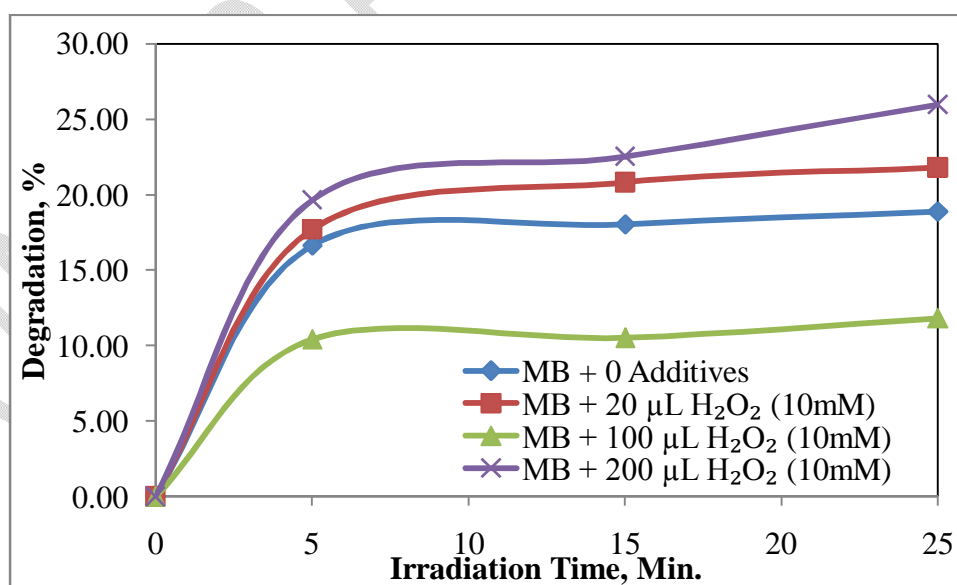


Fig. 5 a: Efficiency of H_2O_2 (10mM) for the degradation of MB

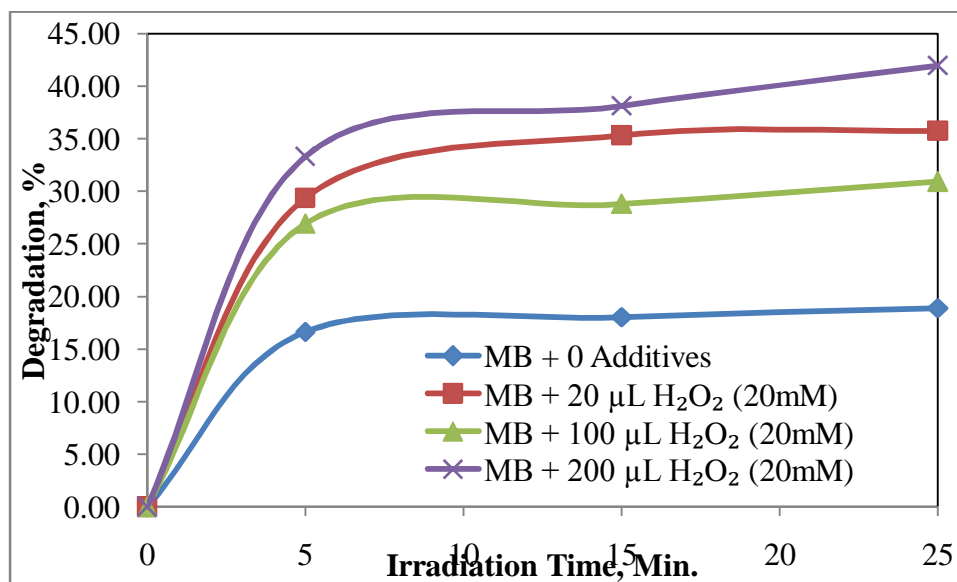


Fig. 5 b: Efficiency of H₂O₂(20mM) for the degradation of MB

3. Efficiency of NaCl and Na₂SO₄ for the degradation of MB: 10 ml and 20 ml NaCl and Na₂SO₄ were added in to the MB solution in order to find the efficiency of the inorganic salts on dye degradation. Figure 6 and 7 represents the observed result. It is seen in the figure that highest degradation (34.88%) obtained by 20 ml Na₂SO₄ indicates the addition of Na₂SO₄ improved the degradation efficiency for MB. On the other hand the addition of NaCl caused it to decrease as compared to the degradation of pure MB. Previous research has demonstrated that in synthetic dye solutions containing a variety of Na₂SO₄ and NaCl mixer, Na₂SO₄ had a more modest effect on decolorization efficiency than NaCl. A higher concentration of Na₂SO₄ did not impede the decolorization process and even boosted the effectiveness of reactive bright red K-2BP in dye solutions with comparable salt or Na⁺ concentrations [50]. Furthermore, the degradation rate has accelerated due to the increased salt concentration. Following comparison, it can be concluded that Na₂SO₄ outperforms NaCl in terms of MB degradation. Uddin et al. published a study in 2016 on the sonochemical degradation of 4-chlorophenol, phenol, catechol, and resorcinol in the absence and presence of Na₂SO₄ or NaCl [51]. The rate of phenolic compound decomposition adhered to a pseudo-first order rate constant [52]. Another study conducted by Monira et al. found that the effectiveness of methyl orange degradation increased in the presence of a 20 ml Na₂SO₄ solution.

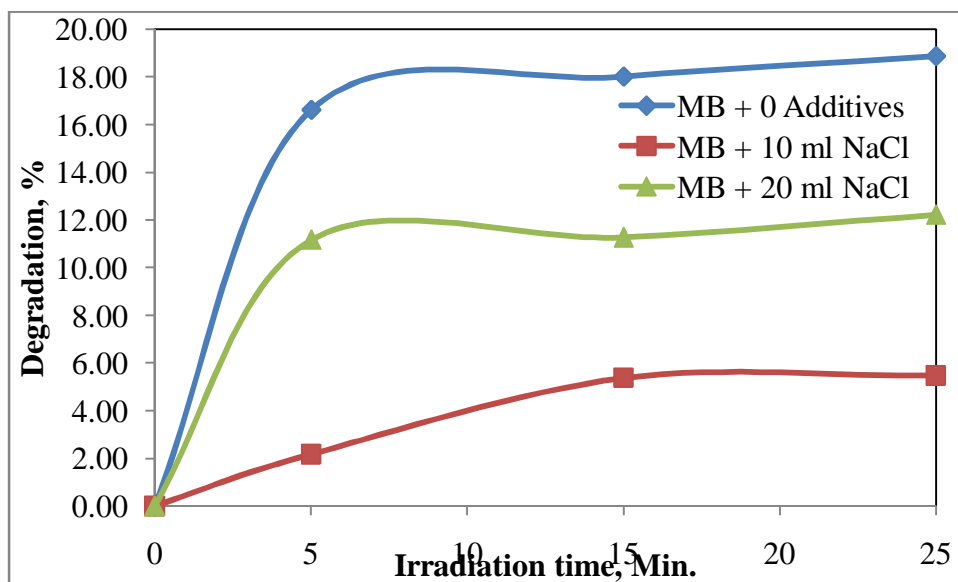


Fig. 6: Effect of NaCl on the degradation of MB

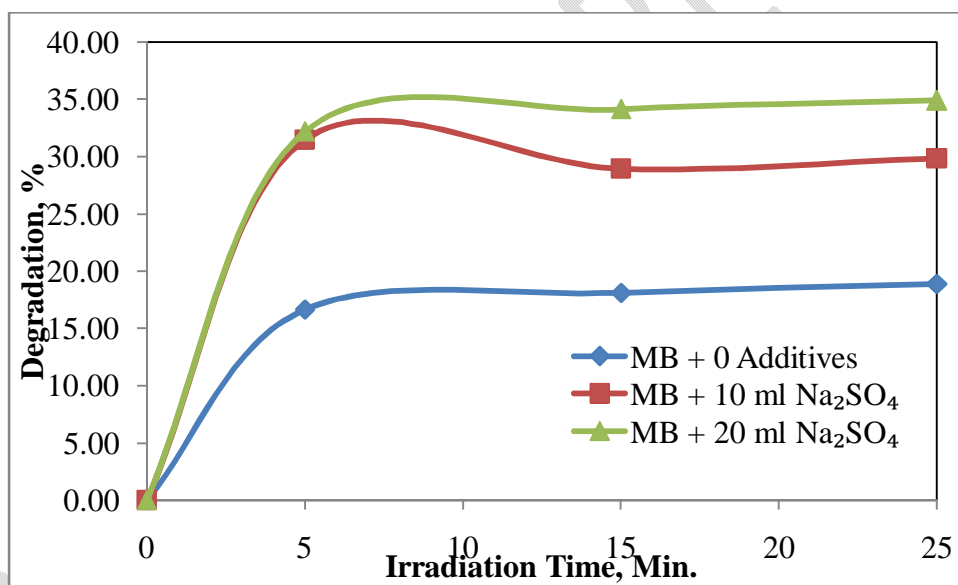


Fig. 7: Effect of Na₂SO₄ on the degradation of MB

3.5 Effect of ZnO nanoparticle on MB degradation: Figure 8 displays the ultrasonic degradation efficiency of ZnO nanoparticle for MB. The efficiency of degradation is up to 41.73% after 25 minutes sonication. Due to advantageous spectrum absorption, porous nature and crystalline structure ZnO nanoparticle increases the degradation efficiency. Maedeh Asgharian et al. observed the maximum efficiency to degrade MB in presence of rGO/ZnO/Cu

compound in presence of 25 mg photocatalyst doses[53].ZnO nanoparticle is also showed one of the highest degradation efficiency of MB in this work.

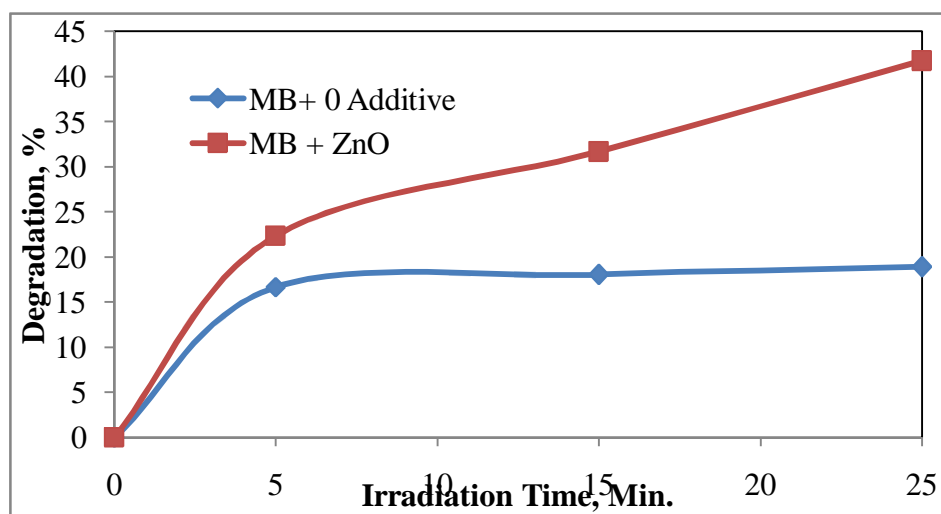


Fig. 8: Efficiency of ZnO on the degradation of MB

4. Conclusions

The ultrasonic degradation efficiency of CCl_4 , H_2O_2 , NaCl , Na_2SO_4 and ZnO nanoparticle for MB degradation was studied at different pH, doses and concentration. The efficiency of degradation was higher at low pH compared to higher pH. 400 $\mu\text{M/L}$ dose of CCl_4 is more efficient to degrade the MB compared to other doses. On the other hand highest degradation efficiency obtained by H_2O_2 at 200 μL doses with 20 mM concentration. H_2O_2 also showed the highest degradation efficiency than the other additives used in this study. Furthermore, Na_2SO_4 increases the degradation percentages of MB But NaCl decreases the degradation percentages in compared to the degradation occurred for pure MB. ZnO nanoparticle enhanced the degradation efficiency considerably. Therefore, all these additives and nanoparticles except NaCl are appropriate for sonolytic degradation of methylene blue in aqueous medium.

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