

# Sonochemical Analysis of Methylene Blue with Additives and ZnO Nanoparticles in Aqueous Medium

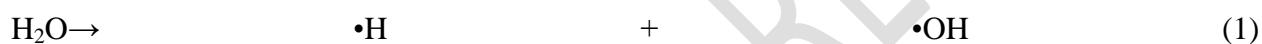
## Abstract

The use of ultrasound was found to be a very suitable and effective method for the degradation of hazardous dyestuffs. The degradation of dye molecules in aqueous media in the presence of various additives by ultrasonic irradiation was investigated in order to clarify the degradation mechanism. In this investigation, Methylene Blue (MB) have been used as a representative of azo dye and inorganic salts like NaCl and Na<sub>2</sub>SO<sub>4</sub> is used as additives where 10mg is taken from both of them in per litre of CCl<sub>4</sub> and 20mg for H<sub>2</sub>O<sub>2</sub> solutions respectively. The volume of all solutions was 100ml containing 25mg/L of MB.ZnO nanoparticle is also used for the investigation of degradation. The sonication of dye molecules were conducted for 0, 5, 15, 25 minutes. From the experiments it is clear that the acidic condition is favorable for dye degradation. Evaluating the results we have also found that all additives aided the degradation comparatively higher or lower the extent depending on their used amount in solution. The degradation mechanism was discussed in details adopting UV-vis spectra. So, it is a clear indication that azo dyes from waste water can be efficiently removed by using sonochemical irradiation method under acidic condition.

**Keywords:** Azo dye, Methylene Blue, Sonochemical Analysis, Additives, Decomposition.

**1. Introduction:** Organic dyes are utilized in many different industries, including optical data discs, food, cosmetics, pharmaceuticals, solar cells, and traditional textile manufacturing. For instance, MB is a significant synthetic dye that is utilized in water testing, sulfide analysis, medicine, and biology [1]. It also serves as a peroxide generator and a redox indicator. However,

they generally disrupt ecosystems and are poisonous, mutagenic, and carcinogenic to aquatic and human life [2-4]. It is necessary to create the technology for eliminating organic dyes from water. To get rid of these chemicals, numerous techniques including chemical, physical, and biological ones have been devised [4-6]. The potential for completely mineralizing organic pollutants to CO<sub>2</sub> and H<sub>2</sub>O has made advanced oxidation processes (AOPs) a hot topic of attention. In AOPs for wastewater treatment, ultrasonography has recently been employed [7-9]. The pyrolysis reactions that occur at and inside hot regions during collapsing bubbles and the radical reactions by OH and H radicals [10] that are generated by the pyrolysis of water are the two fundamental principles of sonochemical reactions.



Numerous studies have investigated the sonochemical degradation of phenolic compounds and dyes [4,11–17]. The creation of efficient additives to speed up the decomposition of organic molecules has been the focus of intensive research. Recent studies [17–19] have looked into how adding CCl<sub>4</sub> or C<sub>6</sub>F<sub>14</sub> affects sonochemical degradation. Although CCl<sub>4</sub> is one of the dangerous chemicals and is therefore highly regulated in usage, it is a valuable additive to speed up the sonochemical breakdown of the target organic molecules. According to Sponza et al. [18], the presence of 19 mg L<sup>-1</sup> C<sub>6</sub>F<sub>14</sub> increased the elimination rates of phenol in the wastewater from the olive mill. Zeng et al. [19] reported that the sonochemical degradation of phenol increased from 0.014 to 0.031 min<sup>-1</sup> or from 0.014 to 0.032 min<sup>-1</sup>, respectively, in the presence of 150 M CCl<sub>4</sub> or 1.5 M C<sub>6</sub>F<sub>14</sub>. According to studies [18,19], the action of CCl<sub>4</sub> or C<sub>6</sub>F<sub>14</sub> as a H atom scavenger is what causes these beneficial effects. Additionally, it has been noted that the use of certain chemicals can influence how quickly colours degrade [20-22]. On the other hand, metal oxide semiconductors have received much research into their potential as photocatalysts to purge water

and air of organic contaminants [23-26]. The active sites of electron-hole pairs are produced when the metal oxides are activated by the right amount of photon energy, and this increases the catalytic activity on the metal oxide surfaces. [27]. Due to its excellent stability and relatively straightforward preparation process, TiO<sub>2</sub> is regarded as the oldest, most prevalent, and optimal material among these metal oxides [28-31]. 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 been extensively studied as a photocatalyst for the degradation of various organic pollutants. Moreover, ZnO nanostructures are preferred over TiO<sub>2</sub> as photocatalyst alternatives for photodegradation due to their more favorable solar spectrum absorption, affordability, and nontoxicity [32]. In numerous studies, ZnO nanostructures demonstrated significant photocatalytic activity for the removal of organic pollutants, such as organic dyes [33]. As a result, we looked at how CCl<sub>4</sub>, H<sub>2</sub>O<sub>2</sub>, NaCl, Na<sub>2</sub>SO<sub>4</sub>, and ZnO nanoparticles affected the sonochemical degradation of MB in this study. Additionally, we have researched several parameters such aqueous temperatures, additive concentrations (CCl<sub>4</sub>, H<sub>2</sub>O<sub>2</sub>, NaCl, Na<sub>2</sub>SO<sub>4</sub>, and ZnO nanoparticle) to optimize the sonochemical breakdown rate of MB in water.

## 2. Experimental

**2.1 Materials and equipments:** Methylene Blue (C<sub>16</sub>H<sub>18</sub>ClN<sub>3</sub>S), Merck Life Science Private Limited, Godraj One, 8<sup>th</sup> Floor, pirojshanagar, Eastern Express highway, Vadhroli East, Mumbai-400079, Sodium Chloride (NaCl), RANBAXY Fine chemicals Limited A-3, Okhla industrial area, phase-I, New Delhi-110020 (ISO 9001: 2000 certified company), Sodium sulphate (Na<sub>2</sub>SO<sub>4</sub>), Merck Specialities Private Limited, Shiv Sagor Estate `A` DrAnnic Besant Road, Worli, Mumbai-400018, Hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>), Merck KGaA, 64271 Darmstadt, Germany, Carbon tetrachloride (CCl<sub>4</sub>), Merck, D-6100 Darmstadt, FR. Germany.



**Fig. 1:** Sonicator bath used in sonochemical degradation.

## 2. 2 Preparation of Solutions

25 mg/l solutions of MB were prepared. In 100 ml of distilled water, solutions of the inorganic salts NaCl and Na<sub>2</sub>SO<sub>4</sub> were produced using 36 and 13.9 grams of each salt, respectively, according to their greatest saturation points. One liter of distilled water has been mixed with 1.02 mg and 2.04 milligrams of H<sub>2</sub>O<sub>2</sub>, respectively, to create 10 mg/l and 20 mg/l H<sub>2</sub>O<sub>2</sub> solutions. Using a tiny syringe, the 200, 400, and 600 μM/L CCl<sub>4</sub> is adjusted. Dyestuffs in water can absorb and reflect light, decreasing the transparency of the water naturally. Normally, dye effluent includes between 10 and 50 mg/L, though 1.0 mg/L dye solutions are visible and might be considered as contaminants and objectionable [34, 35].



**Fig. 2:**Prepared methylene blue solution

### **3. Results and Discussion**

#### **3.1 Sonochemical Degradation of MB under various pH**

Based on the first-order kinetics model function, exponential curves are represented in the figure as solid curves.

$$x = ae^{-kt} \dots \dots \dots (1)$$

Where, the constant 'a' is primary concentration of MB, 25mg/l, k is a fitting parameter need to be optimized and t is the degradation time. The degradation rates of MB without additives using sonochemical irradiation processes in different conditions are shown and discussed below. NaOH and H<sub>2</sub>SO<sub>4</sub> Solutions have been used to maintain the pH of the solution.

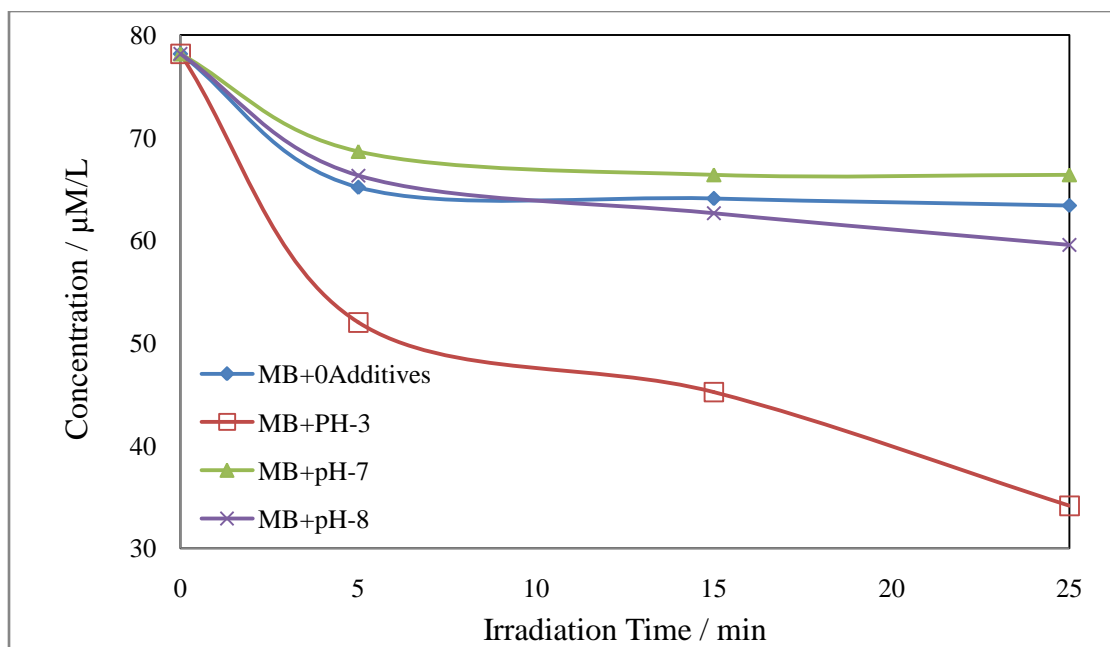
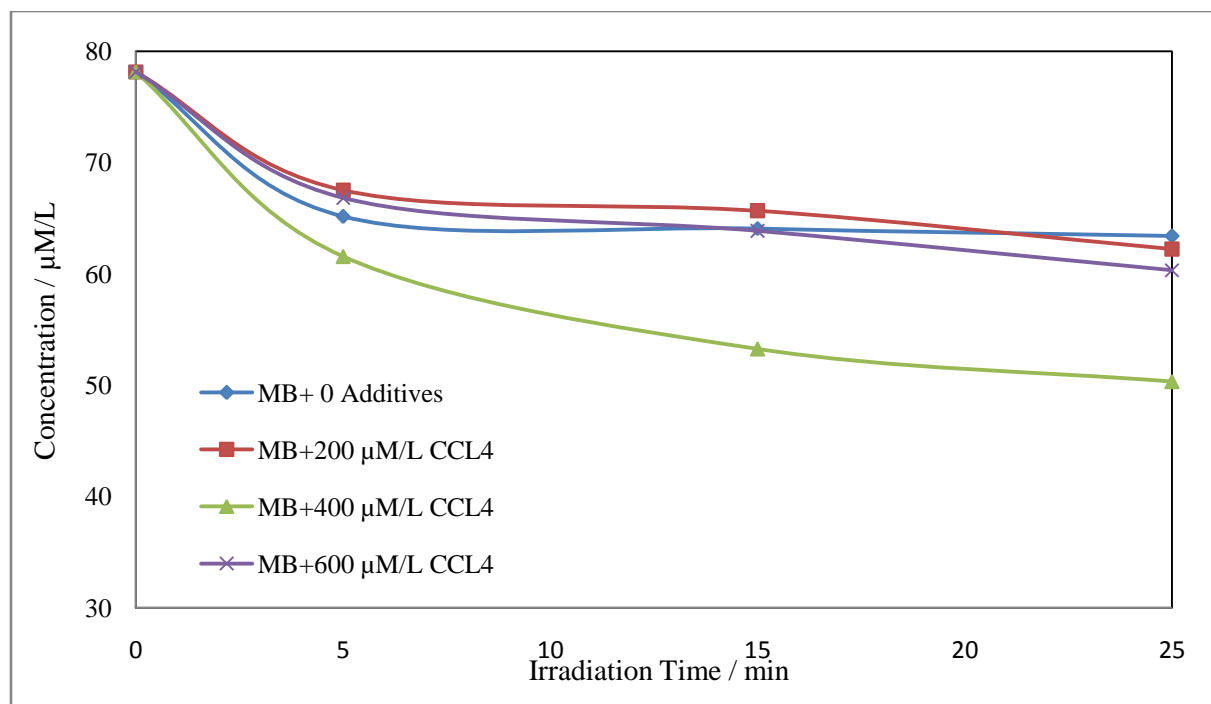


Fig. 3: Sonochemical degradation of pure MB at different time for various pH.

Figure-3 shows the degradation rate of MB in acidic condition of pH: 3 is higher than that of the neutral, i.e. pH: 7 and basic condition, viz. pH: 8. With additives where the acidic condition is maintained in the sonochemical degradation, there is a high possibility of an increased of degradation rate of MB.

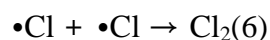
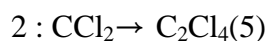
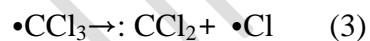
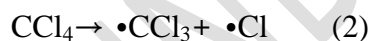
### 3.2. Effect $\text{CCl}_4$ on sonolytic degradation of MB

We examined the effect of  $\text{CCl}_4$  at 200, 400, and 600  $\mu\text{M/L}$  concentrations on the sonochemical degradation of MB. The result is represented in Fig. 4.



**Fig. 4: Effect of CCl<sub>4</sub> on the degradation of MB**

In presence of CCl<sub>4</sub>, the rate of MB degradation rose initially and increased highly when 400 µM CCl<sub>4</sub> was present. In the presence of 600µM/L CCl<sub>4</sub>, the rate is also greatly increased; however, at 200µM/L, the rate of degradation first sharply declines before increasing with increasing sonication time, with the exception at 25 minutes. Our findings indicate that active Cl radicals or related species are produced during the sonolysis of CCl<sub>4</sub>, and that these radicals or species would be useful for the breakdown of MB, despite some researchers' reports that CCl<sub>4</sub> could operate as a H atom scavenger [19]. According to earlier research [17, 36–39], the following responses ought to occur:



The radicals that develop containing chlorine ( $\text{Cl}$ ,  $\text{CCl}_3$ ,  $\text{CCl}_2$ ),  $\text{Cl}_2$ , etc., may accelerate the degradation of MB in an aqueous solution. According to Merouani et al. [13], the presence of  $200 \text{ mg L}^{-1}$  of  $\text{CCl}_4$  enhanced the sonochemical degradation rate of rhodamine B at 300 kHz by 21 times. According to Okitsu et al. [31], the addition of 100 ppm  $\text{CCl}_4$  enhanced the sonochemical breakdown rate of MO at 200 kHz by 41 times. The efficiency of  $\text{CCl}_4$  for MB degradation we have found in this study agrees with these results. From the above viewpoints, though  $\text{CCl}_4$  has high toxicity [40] it can be used as an additive.

### 3.3 Effect of $\text{H}_2\text{O}_2$ on the rate of degradation of MB

From the Fig. 5, it is evident that for 10 mg/L  $\text{H}_2\text{O}_2$  solution, the decomposition rate increases in presence of  $\text{H}_2\text{O}_2$ . It is clear from the data that the amount 20 and 200  $\mu\text{L}$  increased the rate of deterioration in comparison to pure MB but in presence of 100  $\mu\text{L}$  the degradation rate decreased. Fig. 5 demonstrates the graphical representation of the degradation of MB in presence of 20 mg/L  $\text{H}_2\text{O}_2$  solution. Here, it is noticeable from Fig 5 that lowest amount 20  $\mu\text{L}$  and 200  $\mu\text{L}$  of 20 mg/L  $\text{H}_2\text{O}_2$  solution added to the MB solution shows the highest degradation rate as compared with the amount 100  $\mu\text{L}$  of that  $\text{H}_2\text{O}_2$  solution.  $\text{H}_2\text{O}_2$  reaction mechanism for dye discoloration has been explained from the formation of free radicals as active species.



Research has indicated that the US/UV/ $\text{H}_2\text{O}_2$  approach is the most effective in degrading malachite green because it uses ultrasound to facilitate  $\text{H}_2\text{O}_2$  scission in addition to photolysis [41]. Another recent study demonstrated that the impact of adding hydrogen peroxide was examined by varying its concentration to 0.05, 0.10, and 0.15 M. The treatment with 0.10 M  $\text{H}_2\text{O}_2$  and 45 W was successful and energetically feasible, resulting in a 62.9% absorbance removal for the water assessed [42]. The amount of dissolved gas dropped and the amount of water vapor in the bubbles increased as the temperature of the aqueous solution rise [43], which led to a lower rate of OH radical production. As a result, when solution temperatures raise the rates of MB degradation decreased. The sonolysis of 4-chlorophenol in aqueous solution at 20 and 500 kHz as a function of solution temperature was reported by Jiang et al. [43]. They found

that, in the 10–40 °C range, the rates of H<sub>2</sub>O<sub>2</sub> production and 4-chlorophenol degradation increased with the rising of solution temperatures at 500 kHz but reduced with rising solution temperatures at 20 kHz. The sonolysis of bisphenol A in aqueous solution as a function of solution temperatures at 489 kHz was reported by Uddin et al. [44]. The outcome shown that as the temperature of the aqueous solution increased, the rates of degradation increased within the range of 10–40 °C. When compared to earlier studies, it is evident that a variety of applications for hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>) have been developed in the field of water treatment due to its relative safety and ease of use.

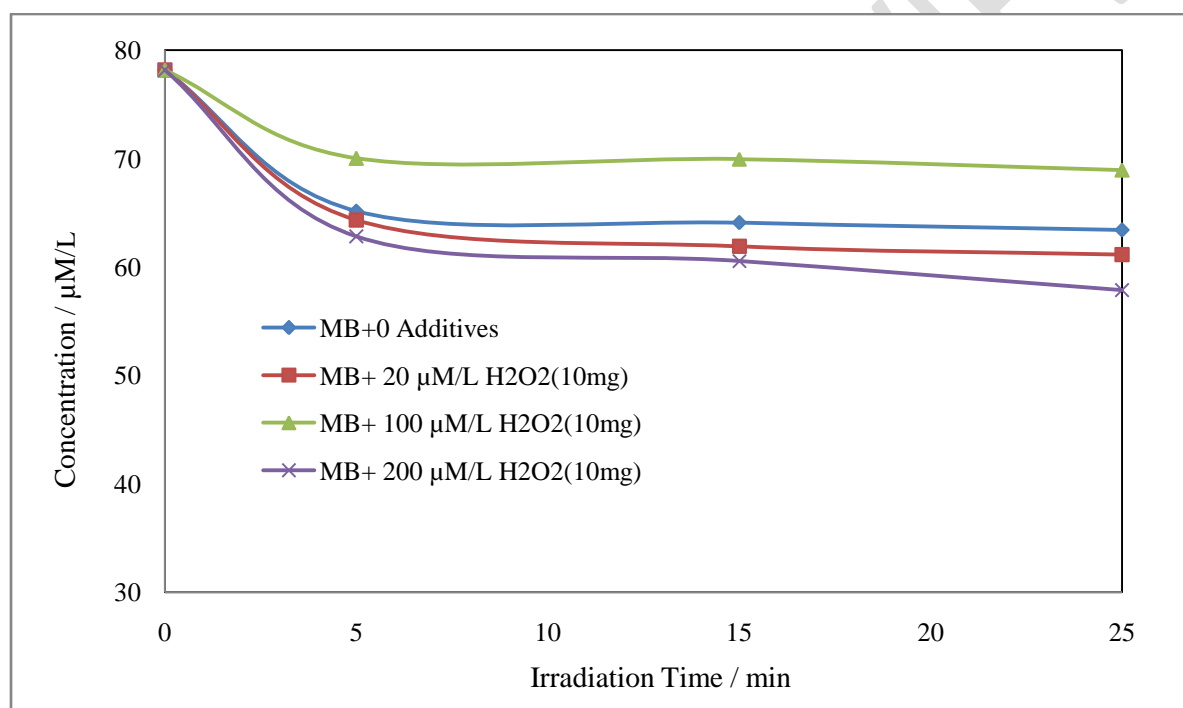


Fig. 5a: **Effect of H<sub>2</sub>O<sub>2</sub>(10mg) on the degradation of MB**

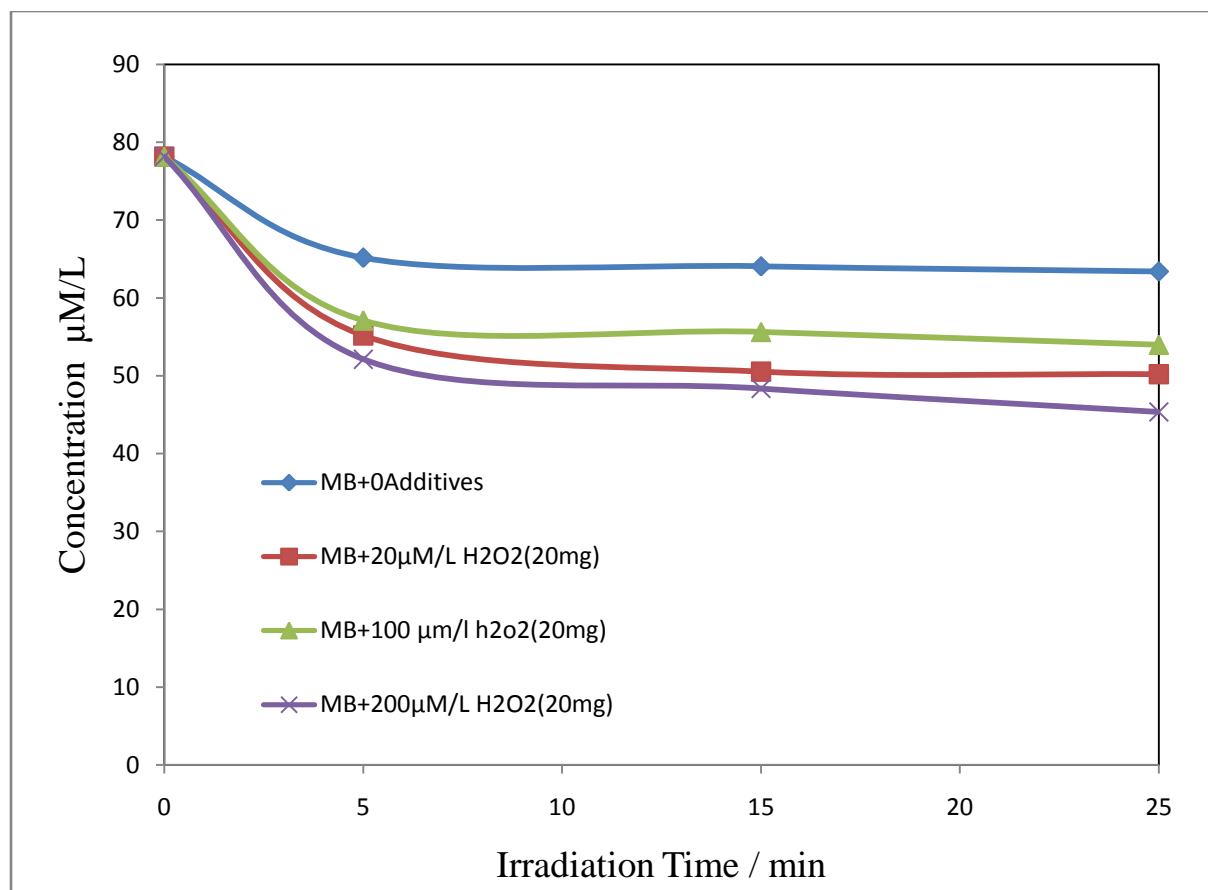
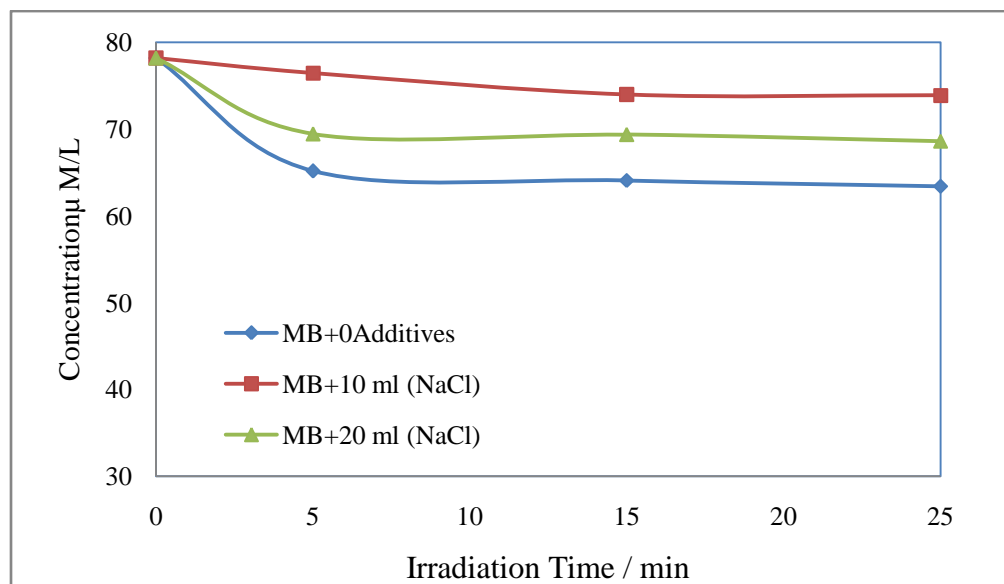


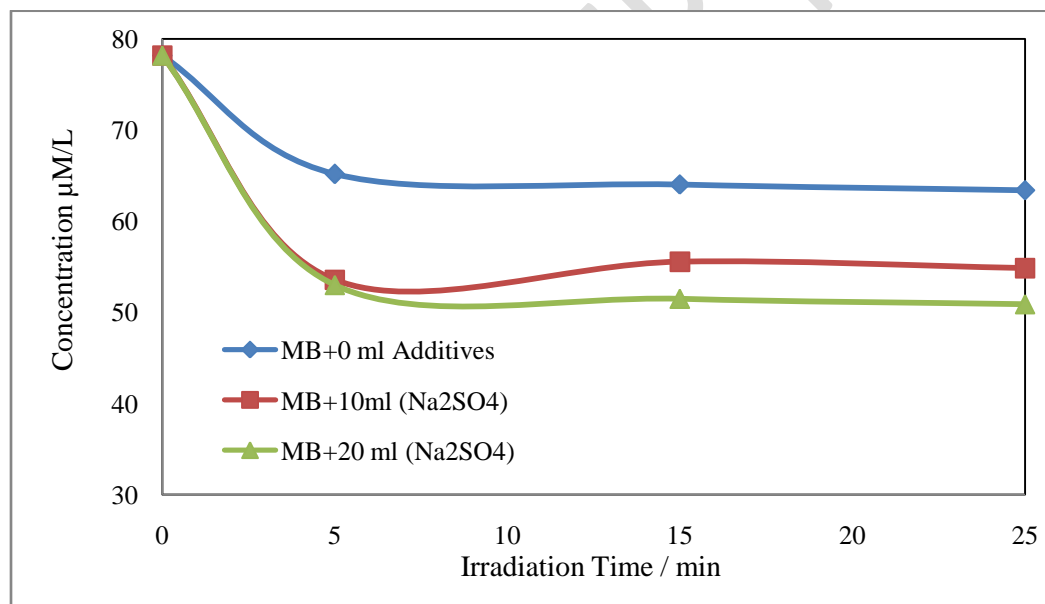
Fig. 5b: Effect of H<sub>2</sub>O<sub>2</sub>(20mg) on the degradation of MB

**3. 4Effect of NaCl and Na<sub>2</sub>SO<sub>4</sub> on the degradation of MB:** NaCl and Na<sub>2</sub>SO<sub>4</sub> were added in amounts of 10ml each to the MB solution in order to find the effects of the addition of inorganic salts on dye degradation. Figure 6 and Figure 7 shows the experimental result. It is seen in the figure, the addition of Na<sub>2</sub>SO<sub>4</sub> improved the degradation of MB, but the addition of NaCl caused it to decrease. Previous studies have shown that various synthetic dye solutions with a number of mixtures of Na<sub>2</sub>SO<sub>4</sub> and NaCl, Na<sub>2</sub>SO<sub>4</sub> influenced the decolorization efficiency more modestly than NaCl. Higher concentration of Na<sub>2</sub>SO<sub>4</sub> did not hinder the decolorization process and even improved the effectiveness of reactive intense red K-2BP in dye solutions with the similar salt or Na<sup>+</sup> concentration [45]. Additionally, the deterioration rate accelerated due to the elevated salt concentration. Following comparison, it can be said that Na<sub>2</sub>SO<sub>4</sub> is superior to NaCl in terms of MB degradation. Sonochemical degradation in absence and presence of Na<sub>2</sub>SO<sub>4</sub> or NaCl for 4-chlorophenol, phenol, catechol, and resorcinol under Ar was published by Uddin et al. in 2016

(Uddin et al., 2016)[46]. The rate of phenolic compound breakdown followed a pseudo-first order rate constant [47].



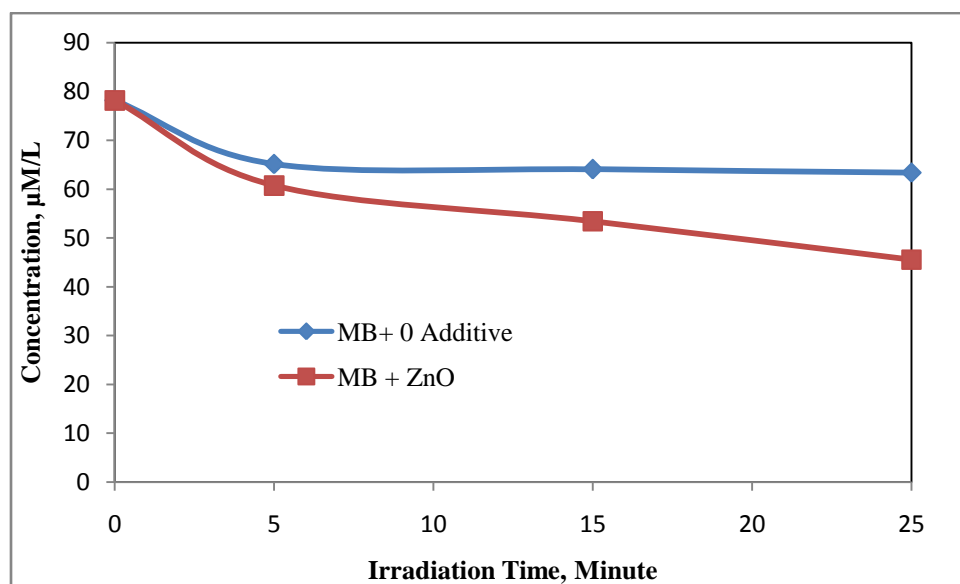
**Fig. 6: Effect of NaCl on the degradation of MB**



**Fig. 7: Effect of Na<sub>2</sub>SO<sub>4</sub> on the degradation of MB**

**3.5 Effect of ZnO nanoparticle on MB degradation:**Figure 8 shows the degradation rate of Methylene blue with ZnO nanoparticle. The degradation of Methylene blue is significantly increased with the increasing of sonication time. Maedeh Asgharian et al. observed the maximum degradation of MB in presence of rGO/ZnO/Cu compound at 25 mg photocatalyst dosage

[48]. Presence of ZnO nanoparticle is also showed second highest degradation of MB in this study.



**Fig. 8: Effect of ZnO on the degradation of MB**

#### 4. Conclusions

The sonochemical degradation rate of MB was studied with several parameters, such as pH, addition of  $\text{CCl}_4$ ,  $\text{H}_2\text{O}_2$ , NaCl,  $\text{Na}_2\text{SO}_4$  and ZnO nanoparticle. The degradation of MB increased under acidic pH condition. 400  $\mu\text{M/L}$  doses of  $\text{CCl}_4$  is more efficient to degrade the MB compared to 200 and 600  $\mu\text{M/L}$  doses. It is thought that the degradation of  $\text{CCl}_4$  created chlorine species and radicals, which accelerated the destruction of MB. The decomposition rate is also higher in presence of  $\text{H}_2\text{O}_2$  compared to the pure MB and 200  $\mu\text{M/L}$  doses of 20mg/L  $\text{H}_2\text{O}_2$  shows the highest degradation rate than the other used doses of  $\text{H}_2\text{O}_2$  in this study. On the other hand inorganic salt like NaCl and  $\text{Na}_2\text{SO}_4$  facilitate the deterioration of MB. The degradation power of  $\text{Na}_2\text{SO}_4$  is higher than the NaCl. Use of ZnO nanoparticle improved the degradation rate significantly. The results showed that the MB degradation rate increases as the order of  $\text{H}_2\text{O}_2 > \text{ZnO} > \text{CCl}_4 > \text{Na}_2\text{SO}_4 > \text{NaCl}$ . Therefore, all these additives and catalysts are suitable for ultrasonic degradation of methylene blue in aqueous medium.

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