Fundamental effective technique for water treatment by using sonochemical and photocatalytic degradation of methylene blue in aqueous medium

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Abstract

Methylene blue (MB) is a carcinogenic contaminant known for its harmful effects on humans and marine life. This study focuses on the basics and variables of kinetic studies involved in the degradation of MB. It has been seen that TiO_2 and ZnO were used as adsorbents and photocatalysts under the effect of sonolysis in the absence and presence of H_2O_2. Fenton and photo-Fenton reactions under ultrasonic radiation were also used to investigate the degradation of MB dye. These methods successfully degraded the investigated dye by (89.2, 98.2, 87.8, 95.2, 64.5, 97.2, 87.5 and 98 % respectively). The most effective approach is photo-Fenton with ultrasound. The AOPs employed in this study can be used as an acceptable tool for degrading hazardous dyes into non-toxic end products.

Keywords: *Methylene blue, sonolysis, photo-Fenton, sonocatalytic, sono-photo-Fenton.*

1. Introduction

Colored effluents produced by various sectors, including textile, paper, printing, rubber, and plastic, can pose substantial environmental problems if discharged into the environment without treatment. Dyes are chemically stable, and because of their complex chemical structures, they can remain in the environment for long periods, causing turbidity and an unpleasant stench in water. Methylene blue (MB), a

Methylthioninium chloride dye, is a multi-core aromatic that causes acute toxic effects and major health problems including shortness of breath, chest discomfort, burning feeling, nausea, vomiting, and diarrhea.

Advanced oxidation processes (AOPs) are one of many strategies used to remove dyes from water and wastewater by potent oxidants such as H_2O_2, ozone, photocatalysts, UV radiation, and so on. The photocatalytic technique treats pollutants using renewable energy and has the potential to dramatically decrease highly dangerous molecules to less damaging compounds. As a result, it is a cost-effective, environmentally beneficial method. [1-7].

Several forms of AOPs are based on the production of •OH radicals via chemical, photochemical, sonochemical, or electrochemical processes. The generation of the hydroxyl free radical (•OH), a powerful non-selective chemical oxidant, is the basic assumption of advanced oxidation processes. Hydroxyl radicals are capable of destroying organic compounds that are not oxidized by conventional oxidants such as oxygen and chlorine [8].

Most of these processes combine a strong oxidizing agent, such as H_2O_2 and/or O_3, with a particular catalyst, such as transition metal ions, and solar or UV radiation [9]. Various AOPs are classed as homogenous use UV light to degrade substances or heterogeneous use of catalytic materials to generate the active species [10].

Photocatalytic degradation systems [11], photoelectrochemical processes, catalytic ozonation, and oxidizing agent activation are the most extensively researched heterogeneous AOPs. AOPs can also be classed according to how they employ external energy sources (for example, light, heat, microwave, or ultrasound).

Ultrasound is used for wastewater purification by producing •OH, HO_2•, and O• radicals [12]. The Sono Fenton procedure is also a useful method for degrading organic pollutants by increasing treatment efficiency through the generation of •OH radicals. The combination of homogeneous Fenton oxidation and ultrasonic radiation proved to be more effective than the sum of individual processes [13,14], particularly in the term of mineralization yield.

The current study aims to investigate the removal of Methylene Blue (MB) dye from an aqueous solution using sonochemical methods in the presence and

absence of H_2O_2 as an oxidizing agent. The sonocatalytic activity of the samples was assessed by degrading Methylene Blue (MB), a model azo dye. This study also attempted to investigate the influence of the presence of catalysts such as TiO_2 and ZnO on sonolysis under UV light and without UV.

2. Experimental

2.1. Instrumentation

All absorption measurements were made using a JASCO V-770 (Tokyo. Japan; UV-Vis) spectrophotometer with a scanning speed of 400-800 nm/min and a bandwidth of 0.2 nm and equipped with 10 mm matched quartz cells. An Adwa

Instrument Co. (ROMANIA) model AD11& AD12/digital pH meter was used to check the pH of the Methylene blue dye. Sonolysis effect using digital Ultrasonic Cleaner (MCS Instrument Co.) type CD-4830. Centrifuge (LC-04R, MCS Instrument Co.), UV-Lamp (UV-C G13 T8 20W, Philips Co.).

2.2. Reagents and Materials

Methylene blue dye was obtained from PIOCHEM Co, Egypt. The chemical formula for Methylene blue is $C_{16}H_{18}CIN_3S$, Molecular weight is 319.85 g/mol (Scheme 1). Its solubility in water is 100 g/L at 20^oC. It shows absorption spectra at 662 nm.
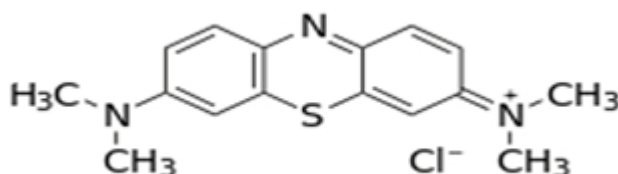
Scheme (1): Chemical structure of Methylene blue dye.

Nitric acid and sodium hydroxide were used for adjusting pH values were of reagent-grade chemicals. Hydrogen peroxide (H_2O_2, 30%) was obtained from PIOCHEM Co., Egypt. Titanium dioxide and zinc oxide were percussed from PIOCHEM Co., Egypt. Ferrous sulfate heptahydrate ($FeSO_4.7H_2O$) was obtained from Alpha Chemika, India, Titanium dioxide (TiO_2) and zinc oxide (ZnO) were

percussed Piochem Co., Egypt and ADWIC Co., Egypt, respectively. All solutions were made using distilled water. All chemicals were AR grade and were utilized as received. Distilled water was used to create the working solution.

The stock solution, 500 mg of the dye was dissolved in one liter of distilled water. By properly diluting the stock, the

necessary dye concentrations were achieved. A glass beaker (500 mL capacity) was centered and fastened to the bottom of the ultrasonic device, and 250 mL of dye solution was added to it. At the start of the experiment, specific volumes of H_2O_2 (30%) and doses of solid $FeSO_4.7H_2O$ were introduced to the dye solution. Photolysis and photocatalysis tests were conducted by exposing the reaction medium to a UV lamp set 20 cm above the dye solution surface. Small amounts of dye solution were taken from the working solution and their absorptions were measured with a spectrophotometer at the optimum λmax=662. The removal efficiency (R%) was calculated by using Eq.1:

$$R\% = \frac{C_o - C_e}{C_o} \times 100 \qquad (1)$$

Where, C_o is the initial concentration of the dye (mg/L), C_e indicates the concentration of the dye solution (mg/L) at time t.

3. Results and Discussion

3.1. US system

During the sonolysis process in aqueous systems, reactive hydroxyl free radicals and hydrogen are generated as a result of the thermal dissociation of water vapor (Eq. 1) and the interactions of oxygen gas (Eqs. 2– 5) [15].

$$H_2O \rightarrow H^{\bullet} + {}^{\bullet}OH \qquad (1)$$
$$O_2 \rightarrow 2O \qquad (2)$$
$$H^{\bullet} + O_2 \rightarrow {}^{\bullet}OOH \qquad (3)$$
$$O + H_2O \rightarrow 2{}^{\bullet}OH \qquad (4)$$
$$H^{\bullet} + O_2 \rightarrow {}^{\bullet}OH + O \qquad (5)$$
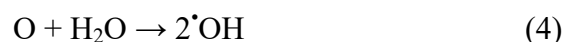
When sonolysis is performed in the presence of an organic species, a variety of chemical reactions are expected, depending on the solute's physical and chemical properties. A volatile and hydrophobic contaminant will most likely be pyrolyzed inside the generated bubbles of cavitation, whereas a nonvolatile and hydrophilic chemical could be oxidized by radicals in the interface or bulk solution [16-18].

Figure 2 shows the effect of ultrasonic degradation of MB dye at various pH settings using 2 g/L dye. The sonolysis process was monitored for 180 minutes, with the remaining dye concentration evaluated every 15 minutes. Figure 2 depicts the relationship between pH and the percentage of dye removed after 180 minutes. These findings suggest that increasing pH reduces the extent of MB breakdown. At equilibrium, a dye concentration drop of 81.46% was achieved in neutral solution, with the lowest removal percentage reported at pH 11. The degraded products can recombine to produce H_2O_2 and molecular hydrogen.
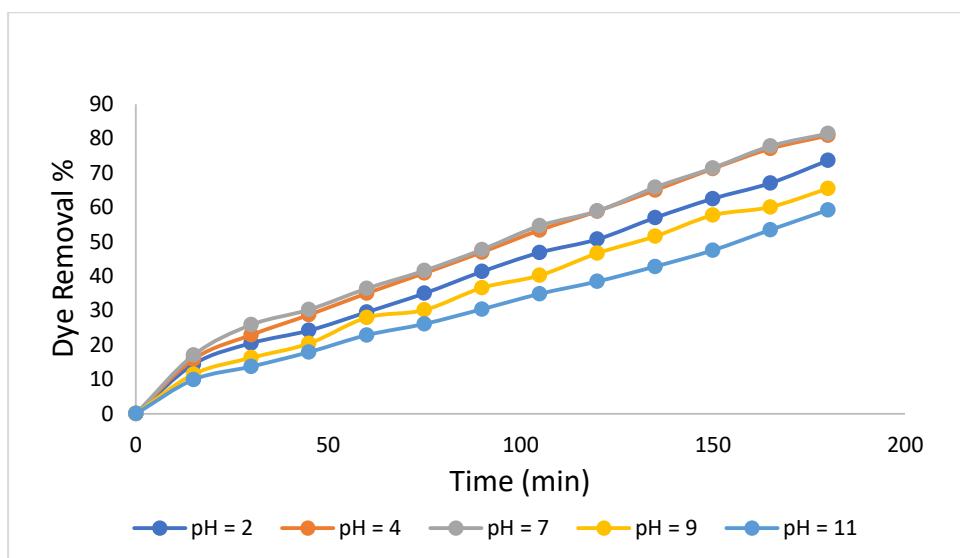
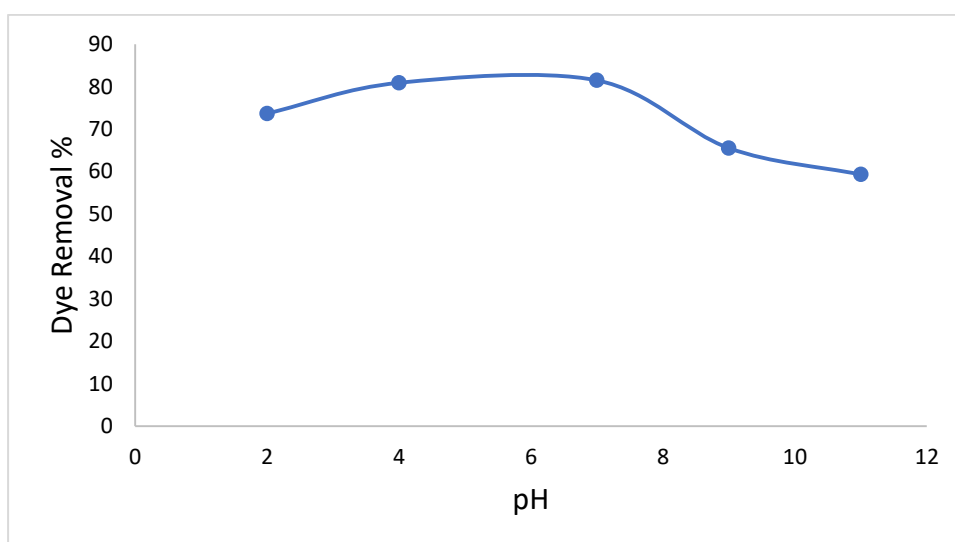**Fig. 2.** Effect of pH on the MB dye removal under US radiation.

**Fig. 3.** MB dye removal at different pH values after 180 min of US radiation.

3.2. US/H_2O_2 and US/H_2O_2/UV systems

The combination of UV radiation and hydrogen peroxide (H_2O_2) has gained popularity as an AOP due to its capacity to produce hydroxyl radicals (•OH), which are particularly effective in pollutant destruction. Oxidative degradation by H_2O_2 has received a lot of a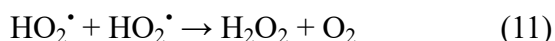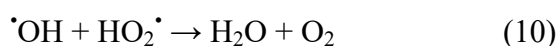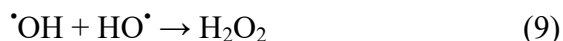ttention due to its low cost and non-toxicity. Many academics have looked into how this method works [19,20]. The primary reaction in such systems is given by the equation [21]:

$$H_2O_2 + h\upsilon \rightarrow 2\ ^{\bullet}OH \tag{6}$$

Radiation accelerates the generation of OH radicals from hydrogen peroxide molecules by the following reactions [22]:

$$H_2O_2 + {}^\bullet OH \rightarrow H_2O + HO_2{}^\bullet \qquad (7)$$

$$H_2O_2 + HO_2{}^\bullet \rightarrow H_2O + O_2 + {}^\bullet OH \qquad (8)$$
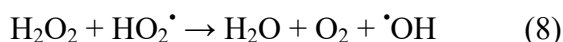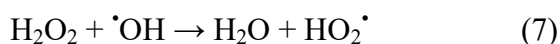
In some circumstances, radical recombination occurs, as follows [23]:

$${}^\bullet OH + HO^\bullet \rightarrow H_2O_2 \qquad (9)$$

$${}^\bullet OH + HO_2{}^\bullet \rightarrow H_2O + O_2 \qquad (10)$$

$$HO_2{}^\bullet + HO_2{}^\bullet \rightarrow H_2O_2 + O_2 \qquad (11)$$

Many factors influence the efficiency of the processes above, including the concentration of hydrogen peroxide, the source of UV radiation, and the physicochemical properties of the fluid involved in the oxidation process.

The ultrasonic technique is used to either accelerate or change chemical reactions.

When compared to other sources of AOPs, ultrasonic therapy is considered a green and environmentally benign procedure. Ultrasonic waves play a crucial function in the oxidative degradation process in the presence of H_2O_2, and their cavitation action can expedite the decomposition of H_2O_2 [24,25].

The effect of UV radiation on the degradation of MB dye by H_2O_2 under the impact of ultrasonic radiation is shown in Fig. 4, at an initial dye concentration 500 mg/L and 40 mM H_2O_2. As indicated in the figure, approximately 64.5% of the dye was eliminated after 180 minutes of treatment, with the percentage increasing significantly to 97.2% under UV.
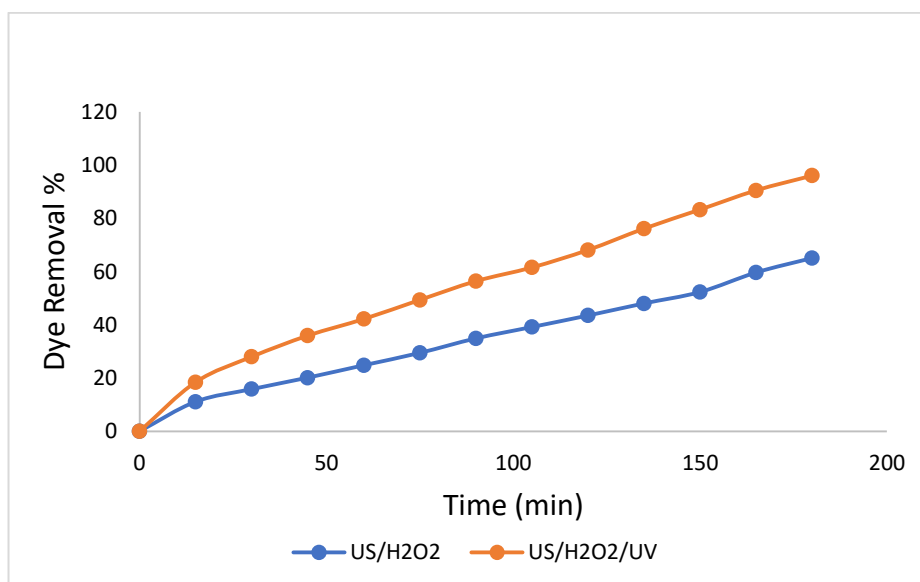

Fig. 4. Sonication of MB dye in H_2O_2 solution in the presence and absence of UV radiation. [MB = 500 mg/L, H_2O_2 = 40 mM].

3.3.   US/catalyst   and   US/catalyst/UV systems

The combination of catalysts and ultrasonication results in a heterogeneous sonocatalytic process that significantly boosts the degradation efficiency of organic contaminants. Because of their increased surface area, the sonocatalysts boosted mass transfer efficiency. In addition, they increase the quantity of cavitation bubbles by functioning as nucleation sites. [26-28]. The presence of catalysts enhances the degradation rate of organic pollutants [29].

To evaluate their catalytic activity, the catalytic degradation efficiencies of two distinct metal oxides, TiO_2 and ZnO, were measured and compared using ultrasound. TiO_2 has a higher degrading efficiency than ZnO, as seen in Figs. 5 and 6. The dye degrades 89.8% in the presence of TiO_2, compared to 87.8% in the presence of ZnO, when exposed to ultrasonic radiation. This could be due to the dye particles' weaker adsorption on ZnO particles compared to TiO_2 particles.

As seen in the figures, the presence of UV radiation marginally increases the breakdown rate of MB dye by both catalysts. This finding could be attributable to the high efficiency of the ultrasonic effect in comparison to photocatalysis. To investigate the influence of catalyst dose on degradation efficiency, varying amounts of TiO_2 or ZnO were added to the dye solution (40 mM) during the ultrasonication process, either in the absence or presence of UV radiation. Figures 7 and 8 show the relationship between TiO_2 removal percentage and ZnO catalyst dosages, respectively. The results show that the optimal dose of TiO_2 is 0.1 g/L, while the optimal dose of ZnO is 0.2 g/L for both sono catalysis and sono photocatalysis processes.
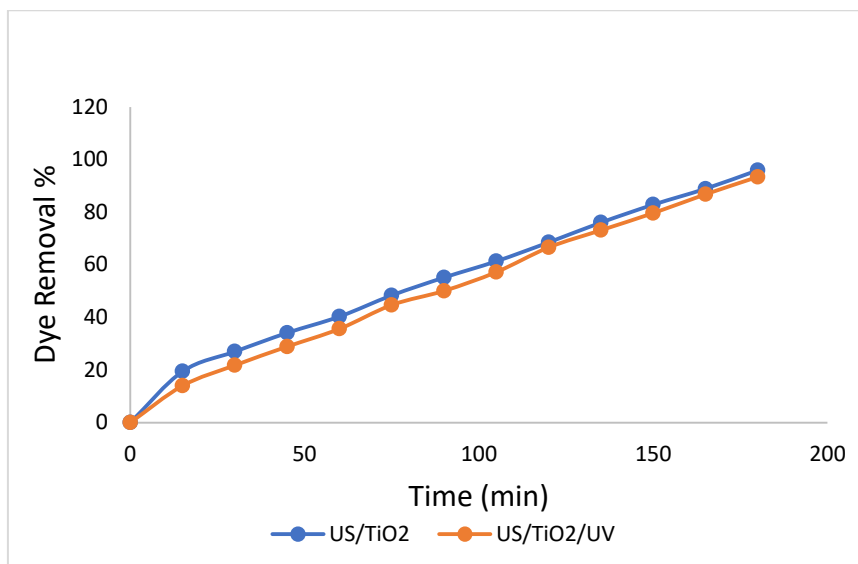
Fig. 5. Effect of TiO$_2$ during sonolysis of MB dye solution in the presence and absence of UV radiation.
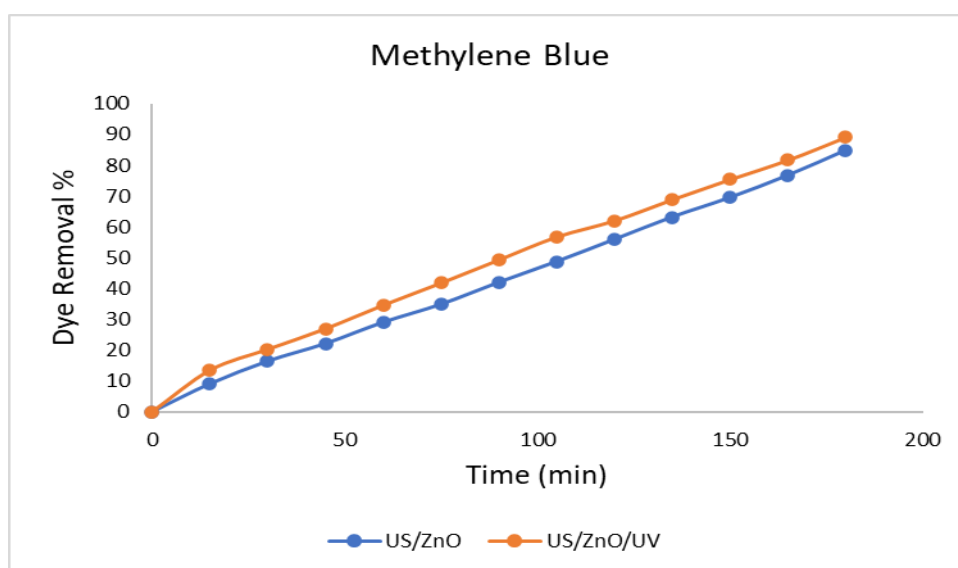

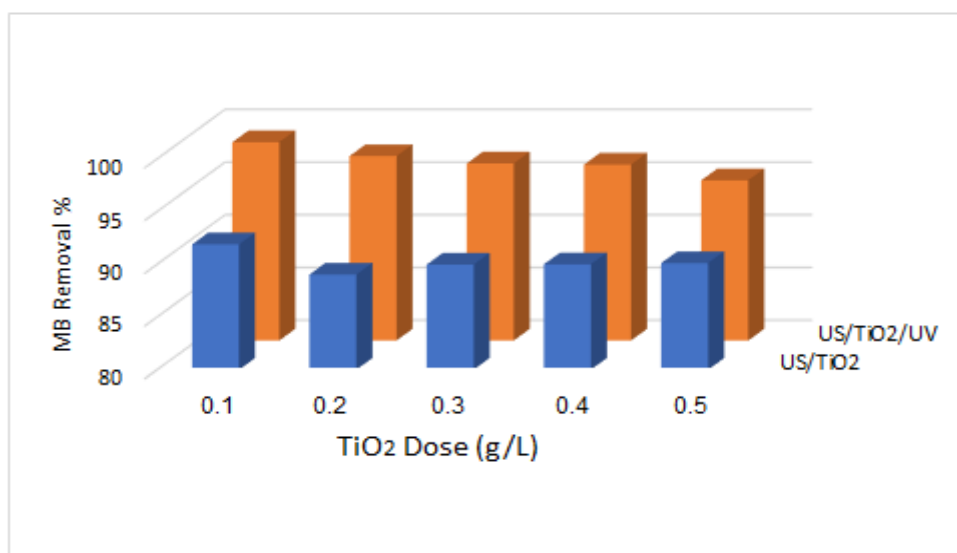**Fig. 6.** Effect of ZnO during sonolysis of MB dye solution in the presence and absence of UV radiation.

Fig. 7. Effect of TiO_2 dose on MB removal under sono-catalysis and sono-photocatalysis processes.
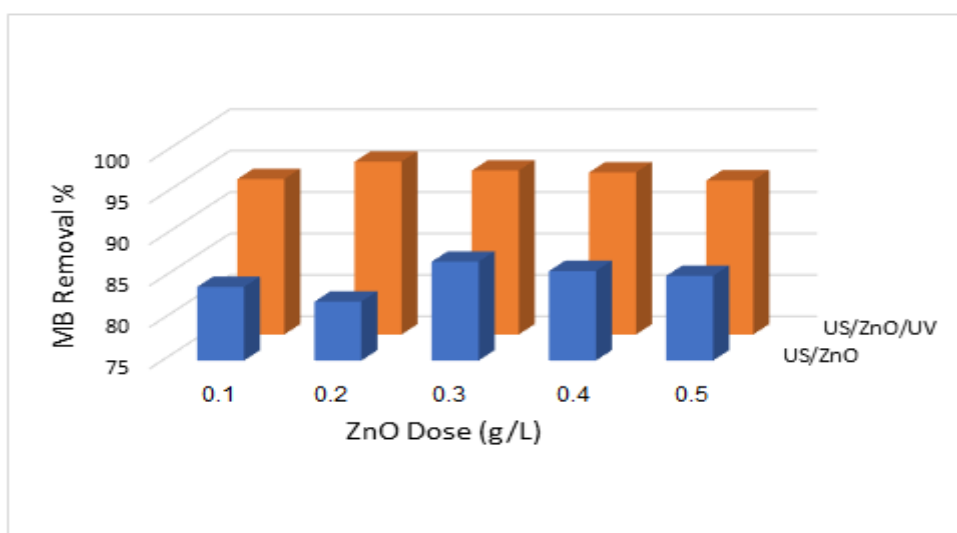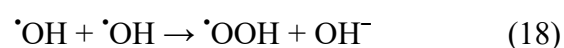

Fig. 8. Effect of ZnO dose on MB removal under sono-catalysis and sono-photocatalysis processes.

3.4. US/Fenton and US/Fenton/UV systems
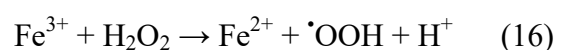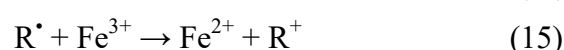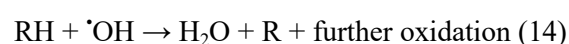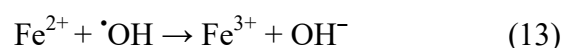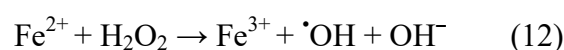
The Fenton oxidation reaction removes hazardous organic contaminants from industrial effluent. It involves the reaction of Fenton's reagent (iron salt in Fe^{2+} form) with hydrogen peroxide to produce the hydroxyl radical. The power of Fenton's process is based on the strong oxidizing capacity of the hydroxyl radicals [30], and the action is continued in the presence of the organic pollutant as illustrated [31]:

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + {}^{\bullet}OH + OH^- \qquad (12)$$

$$Fe^{2+} + {}^{\bullet}OH \rightarrow Fe^{3+} + OH^- \qquad (13)$$

$$RH + {}^{\bullet}OH \rightarrow H_2O + R + \text{further oxidation} \quad (14)$$

$$R^{\bullet} + Fe^{3+} \rightarrow Fe^{2+} + R^+ \qquad (15)$$

$$Fe^{3+} + H_2O_2 \rightarrow Fe^{2+} + {}^{\bullet}OOH + H^+ \qquad (16)$$

$${}^{\bullet}OH + H_2O_2 \rightarrow {}^{\bullet}OOH + H_2O \qquad (17)$$

$${}^{\bullet}OH + {}^{\bullet}OH \rightarrow {}^{\bullet}OOH + OH^- \qquad (18)$$
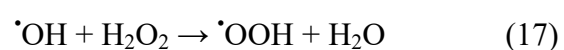
To investigate the influence of Fe(II) dose on dye removal efficiency, different doses of ferrous ion (10-50 mg/L) were added to the dye solution (500 mg/L) in the presence of a set volume of H2O2 (1 mL) using US radiation. Figure 9 shows that as the ferrous ion content grew, so did the clearance percentage. This result supports the role of Fe(II) ions as a catalyst for increasing the generation of •OH radicals. The maximum dye removal was observed at 50 mg Fe(II) with 1 mL of H_2O_2.

The same studies were performed with UV radiation to determine its influence on dye removal. As illustrated in Fig. 10, the removal of MB dye increased with increasing iron content, but the extent of removal was more than in the absence of UV radiation. Figure 11 was created to compare these results and identify differences in dye removal effectiveness in both cases.
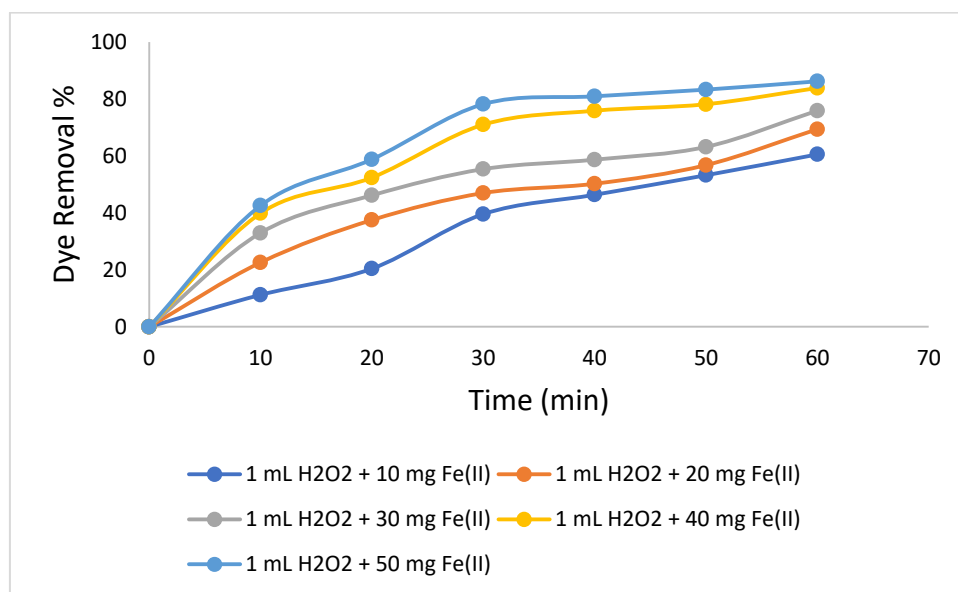

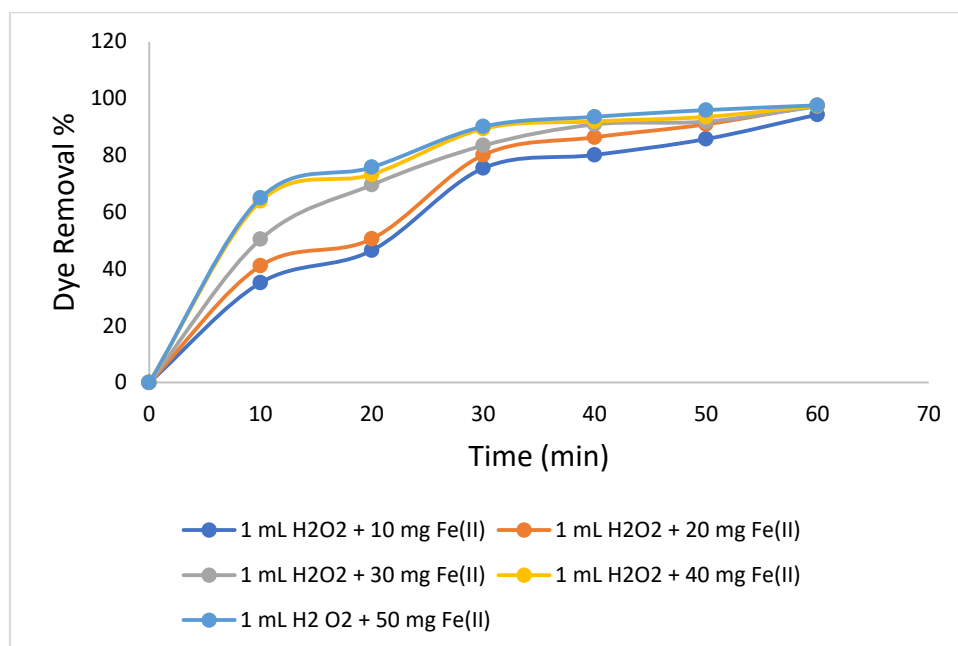**Fig. 9.** Effect of Fe(II) on MB removal at constant amount of H_2O_2 using sono-Fenton reaction.

Fig. 10. Effect of Fe(II) on MB removal at constant amount of H_2O_2 using sono-Photo Fenton reaction.
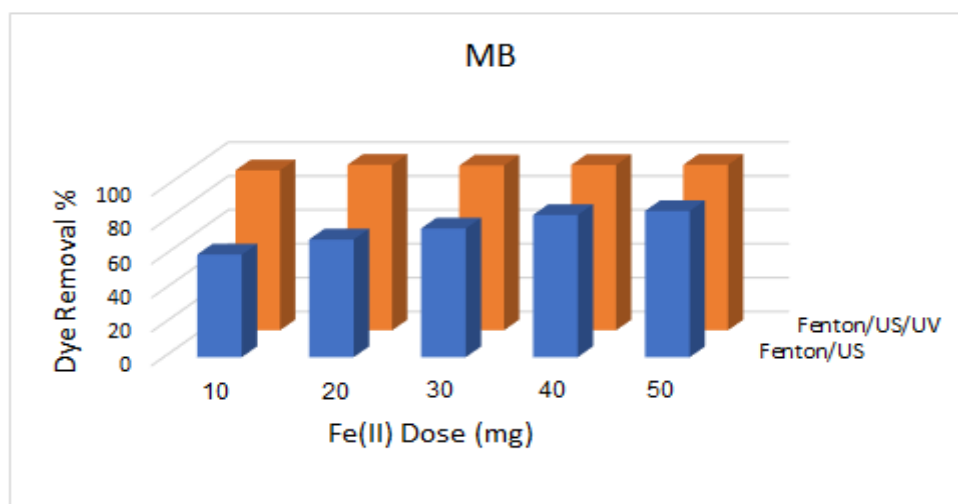

Fig. 11. Fenton Reagent [1 mL H_2O_2/Fe(II)], MB = 500 mg/L

In another series of studies, increased H_2O_2 concentration resulted in increased dye removal (Fig. 12). These investigations were repeated with UV and illustrated in Fig. 13. As shown, increasing H_2O_2 level at a constant Fe(II) dose reduces dye clearance. Figure 14 depicts a comparison of the Fenton and photo-Fenton reactions under sonolysis. These results suggest that an optimal Fe(II)/H_2O_2 ratio is essential for maximal dye elimination. It was also observed that the use of UV light results in a significant increase in MB dye elimination.
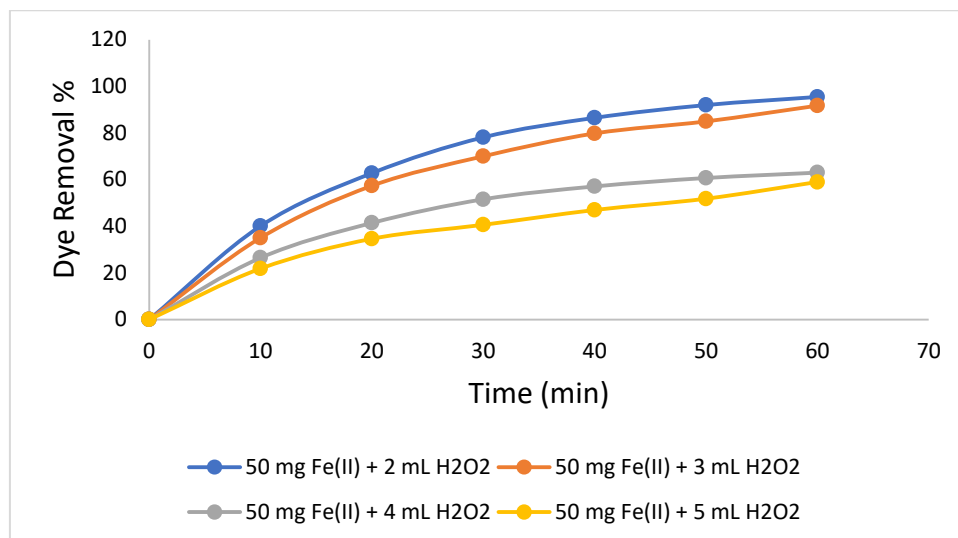
Fig. 12. Effect of H_2O_2 concentration at constant Fe(II) dose on MB dye removal under the effect of US.
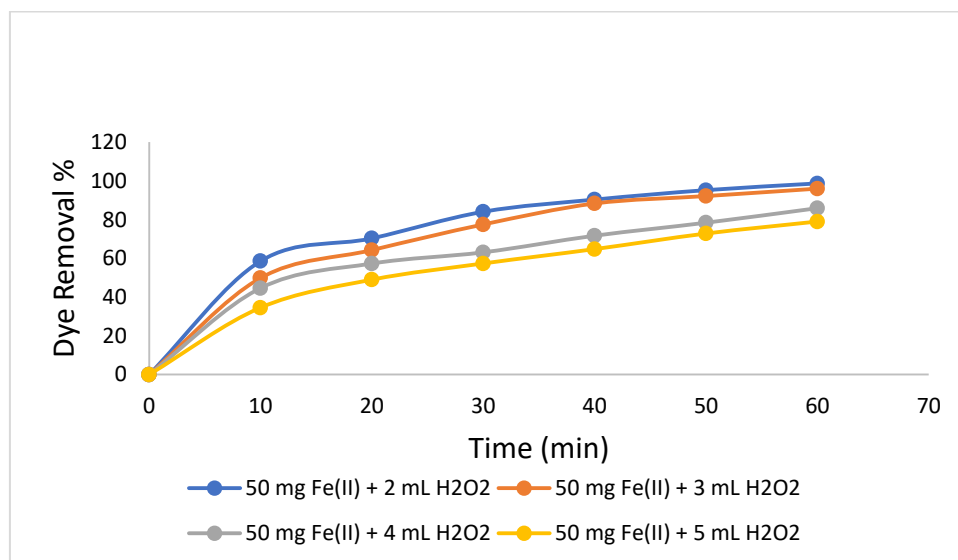

Fig. 13. Effect of H_2O_2 concentration at constant Fe(II) dose on MB dye removal under the effect of US and UV.
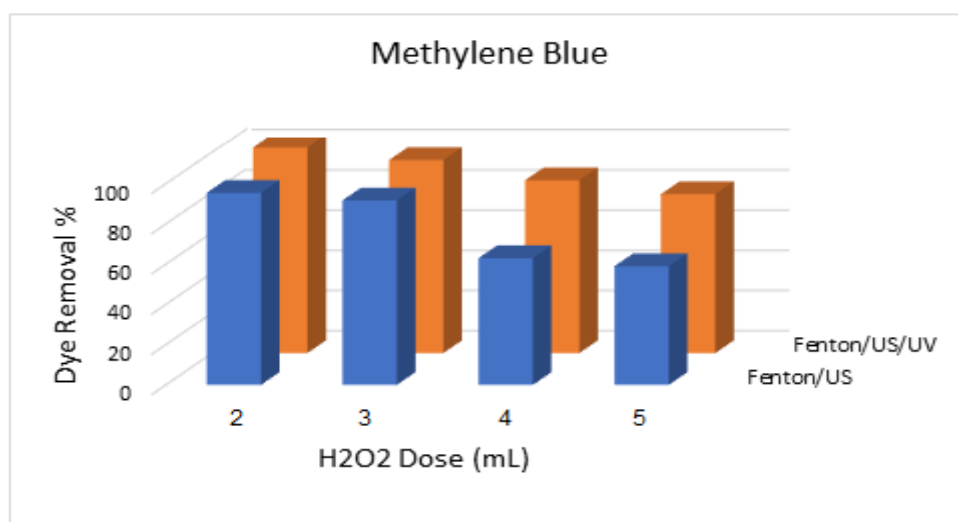
Fig. 14. Comparison between the effects of H_2O_2 dose in Fenton reaction by the effect of US and US/UV radiation.

4. Conclusion

In this study, various AOP processes for MB degradation are being praised as an effective approach for resolving the issue of the presence of hazardous dyes (i.e. MB) in the aquatic environment. These techniques include ultrasonic (US) radiation, US/H_2O_2, $US/TiO_2/H_2O_2$, $US/ZnO/H_2O_2$, US/Fenton, and US/Fenton/UV. The Sono-Photo-Fenton reaction demonstrated a rapid breakdown rate of the MB dye. The results revealed that the dye had been entirely oxidized and decomposed into CO_2 and H_2O. A successful full degradation process for methylene blue using Sono-photo-Fenton's reaction has been proposed.

5. References

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