



Ultrasound Assisted Sonochemical Decomposition of Methyl Orange in the Presence of H₂O₂ and CCl₄

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Authors' contributions

This work was carried out in collaboration among all authors. Authors JA, MA, MJH and MHU designed the study, performed the statistical analysis, wrote the protocol and wrote the first draft of the manuscript. Authors SMAR, SM, JA and MAAM managed the analyses of the study and also managed the literature searches. All authors read and approved the final manuscript.

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ABSTRACT

Methyl orange (MO) is an orange azoic dye; which has transition range from 3.1 to 4.4. Sonochemical decomposition of methyl orange in the presence of H₂O₂ and CCl₄ has given effective result to reclaim water from the effluents released by the industries. The aim of this research was to investigate the effective condition for the decomposition of MO in the presence or absence of additives. For this, 50 mg/L solution of MO was sonicated in the presence and absence of different additives. It was clearly confirmed that the rates of sonochemical decomposition of MO

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increased with increasing the concentration in both cases of H₂O₂ and CCl₄. The combination of advanced oxidation processes (AOPs) namely hydrogen per-oxide and carbon tetra-chloride with sonolysis harvests the decomposition of wide spectrum of organic contaminants. The combination of sonolysis with H₂O₂ and CCl₄ enhances the production of non-selective radicals to improve the decomposition process. The AOPs is technically feasible and also economic. Based on the results, it was suggested that the rate of MO decomposition can be effectively enhanced by the sonolysis of CCl₄ and also for H₂O₂. It was possible to include order- MO+200 μL H₂O₂ > MO+100 μL H₂O₂ > MO+20 μL H₂O₂ > MO; MO+200 μL CCl₄ > MO+100 μL CCl₄ > MO+20 μL CCl₄ > MO.

Keywords: Methyl orange; sonolysis; radical reaction.

1. INTRODUCTION

Energy, food and water are interconnected & within the nation, water is essential for all social and economic developments. In the oncoming years, worldwide crisis may arise for energy, food, and water [1]. The percentage of increasing in concentration of organic contaminants in surface water has been observed by the past two decades [2,3]. The removal of hazardous substances from industrial waste streams and the process of remediation of contaminants in groundwater, rock and soil is a major problem in the Asian countries [4]. As diseases spread through water which becomes unsuitable for usages in day to day life in human beings, for the usages of polluted water, water borne diseases spread throughout the world and in the awkward case, it causes the mortality of children [5,6].

Contamination of soil and groundwater from industrial waste streams is a serious health problem. Traditional techniques to remove contaminants from soil: including landfilling, air stripping/carbon adsorption, incineration, biological activity and chemical treatment. Incineration, adsorption and landfilling merely transfer the contaminant to another phase or location (i.e., a pollution shift) and produce a potentially dangerous and toxic secondary disposal requirement. To numerous environmental factors biodegradation is very sensitive, is slow, produces unpredictable results often, and is uneconomical for highly concentrated waste effluents. Current developments in environmental technologies involving chemical oxidation have the potential to treat all types of organic and inorganic contaminants (volatile, semi-volatile and non-volatile). Those processes, which all are oxygen based, are usually termed as advanced oxidation processes (AOPs).

An AOPs can define as the oxidation process that generally generates hydroxyl radicals in

sufficient quantity to affect water treatment. Complete mineralization can be entailed by the oxidative processes, implying that the final products of degradation reactions are carbon dioxide, short-chain organic acids, and inorganic ions, typically less toxic and favorable to biodegradation. The AOPs generally use a combination of oxidation agents (O₃, H₂O₂), irradiation (ultraviolet, ultrasound) and catalysts (TiO₂) as a means of generating the excited hydroxyl or hydroxyl radicals, which are more powerful oxidants than molecular O₃ or H₂O₂ [7-17].

Recent advances in AOPs include environmental sonochemistry, which involves the application of ultrasound to induce in situ cavitation to destroy or accelerate the destruction of liquid-phase contaminants [18,19]. Some reactions involved in AOPs are found in Table 1 [20,21]. Cavitation is the nucleation, growth, and sudden collapse of gas or vapor-filled micro-bubbles formed from acoustical wave-induced compression or refraction in a body of liquid [19]. The number of reacted molecules per unit of ultrasonic energy is marked as the sonochemical efficiency value. For hazardous organic dye the degradation of methyl orange used as model in the presence of additives such as H₂O₂, CCl₄ was carried out. Because methyl orange (MO) is a pH indicator and due to its clear color change it is very often used in titrations. MO changes color at the pH of a mid-strength acid and is usually used in titrations for acids. Unlike a so called universal indicator, MO does not have a full spectrum of color change, but has a sharper end point. The structure of the MO can be observed in Fig. 1.

1.1 Fundamental Theory of Sonochemistry

The study of sonochemistry is concerned with understanding the effect of sonic waves and wave properties on chemical systems. The chemical effects of ultrasound do not come from

a direct interaction with molecular species. Studies have shown that no direct coupling of the acoustic field with chemical species on a molecular level can account for sonochemistry or sonoluminescence. Instead, sonochemistry arises from acoustic cavitation: the formation, growth, and implosive collapse of bubbles in a liquid. This is demonstrated in phenomena such as ultrasound, sonication, sonoluminescence, and sonic cavitation. The attractiveness of sonochemistry in environmental engineering seems to stem from three major facts.

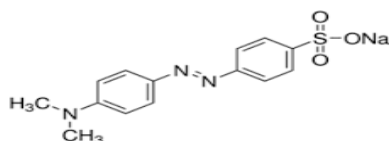


Fig. 1. Structure of methyl orange

Firstly, sonochemistry can cause real chemical changes to a solution without the necessity of adding any other compounds. Secondly, sonochemistry is often conducted at low or ambient temperatures and pressures; thus, no heating or pressurization is required. These two features simplify enormously the design and operation of reactors. Thirdly, in many cases, the peculiar nature of sonochemical reactions offers

alternative pathways, providing a faster or environmentally safer degradation of contaminants. Some sonochemical syntheses have also been successfully scaled up to plant size, providing convenient advantages such as lower operation costs and shorter times of operation compared to traditional techniques. The present challenge for sonochemists and acoustical physicists in the field of environmental remediation is to provide cost-effective sonochemical solutions to large-scale problems. Sonochemistry proceeds because the passing of acoustical waves of large amplitude, called finite amplitude waves, through solutions causes cavitation. Cavitation can be generated when large pressure differentials are applied in a flowing liquid (hydro dynamical cavitation), or by means of an electromechanical transducer, piezo electrical or magnetostrictive, in contact with the fluid (acoustical cavitation) according to Fig. 2.

The aim of this research was to investigate the effective condition for the decomposition of MO in the presence or absence of additives. In addition, was to make comparison the percentage of dye molecule degradation on ultrasound with and without additives such as H_2O_2 , CCl_4 at room temperature will be made.

Table 1. Some reactions involved in advanced oxidation processes

Sonolysis	$H_2O +))) \rightarrow \cdot OH + OH^-$ $H_2O +))) \rightarrow (1/2)H_2 + (1/2)H_2O_2$
Fenton reactions	$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + \cdot OH + OH^-$
Sonophotocatalysis (with H_2O_2)	$H_2O +))) \rightarrow \cdot OH + OH^-$
(a) Water sonolysis	$H_2O +))) \rightarrow (1/2)H_2 + (1/2)H_2O_2$
(b) Reaction of H_2O_2 with H atoms (formed from water sonolysis)	$H_2O_2 + H \cdot \rightarrow \cdot OH + H_2O$
(c) Photolytic dissociation of H_2O_2	$H_2O_2 + hu \rightarrow 2 \cdot OH$
(d) Reaction of H_2O_2 with superoxides (formed in the presence of TiO_2 and under UV radiation)	$H_2O_2 + O_2^{\cdot -} \rightarrow \cdot OH + OH^- + O_2$
(e) Reaction of H_2O_2 with electrons (conduction band electrons are generated from semi-conductor photocatalyst under UV irradiation).	$H_2O_2 + e^- \rightarrow \cdot OH + OH^-$ $O_3 + OH^- \rightarrow \cdot OH$ $UV + H_2O_2 + O_3$
Ozone + sonolysis	$H_2O +))) \rightarrow \cdot OH + OH^-$ $H_2O +))) \rightarrow (1/2) H_2 + (1/2)$ $H_2O_2 + O_3 +))) \rightarrow O_2(g) + O(^3P)(g)$ $O(^3P)(g) + H_2O(g) \rightarrow 2 \cdot OH$
Semiconductor photo-catalysis (TiO_2 -Semiconductor)	$TiO_2 + hu \rightarrow TiO_2^- + OH^-$ (or TiO_2^+) $TiO_2^- + O_2 + H^+ \rightarrow TiO_2 + H_2O + \cdot OH$ $TiO_2^- + 2H^+ \rightarrow TiO_2 + H_2$ $H^+ + H_2O \rightarrow \cdot OH + H^+$

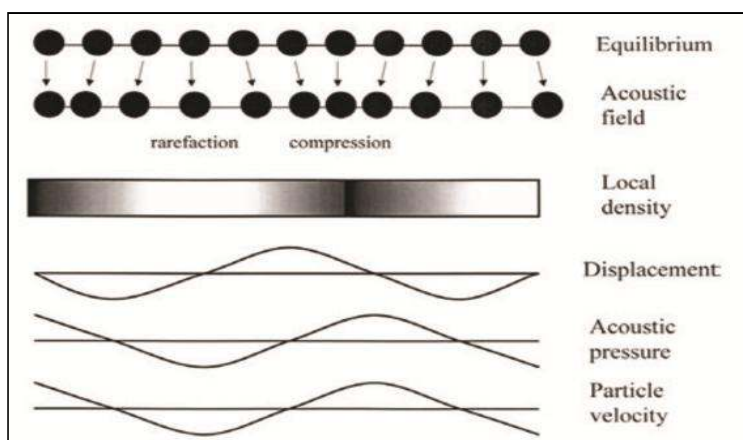


Fig. 2. Propagation of a one-dimensional ultrasound wave
[C.E. Brennen, et al. *Journal of fluid mechanics*, 355 (1998) 255-283]

2. EXPERIMENTAL METHODOLOGY

Hydrogen peroxide, methyl orange and carbon tetrachloride were purchased from Merck KGaA 64271 Damstadt, Germany. All the chemicals were reagent grade and used as received. An ultrasonicator model soniclean 250HT, 50-60 Hz was used to decompose dye molecule in aqueous medium. The schematic diagram of the experimental setup to shown in the Fig. 3. A conical flask with a total volume of 100 mL of 50 mg/L sample solution was used for ultrasonic irradiation under air at room temperature around 24°C. The sonicated solution was extracting every (0, 3, 7 and 10 min) by a glass syringe (1 mL) without exposing the sample to air. The glass vessel was flat bottomed and was mounted at a constant position (4.0 mm from the oscillator). The sonicated solutions were analysed by a UV-Vis spectrophotometer (Shimadzu UV-1650).

2.1 Calorimetrically Measurement of Temperature Change with Sonication Time

A technique for quantitatively evaluating an ultrasonic reaction field has been investigated. Ultrasonic power is one of the important factors for sonochemistry. Calorimetry is one of the most frequently used methods for measuring the actual ultrasonic power input for a solution. Equation (1) gives the calculated ultrasonic output power (P).

$$P = (dT/dt) C_p M \quad (1)$$

Where,

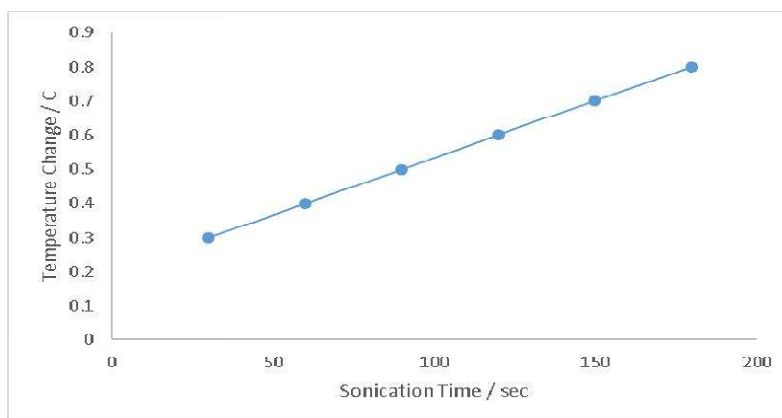
C_p is heat capacity of water (4.178 kJ/mole)
 M is mass of water (100 gm)
 dT is temperature of the sample solution (°C)
 dt is ultrasonic irradiation time/s.



Fig. 3. Schematic diagram of the experimental set-up

Table 2. Measurement of temperature change during sonication

Observation	Sonication time (sec)	Initial temperature (°C)	Final temperature (°C)	Temperature change (°C)	Actual power (Watt)
1	30	24.7	25.0	0.3	4.180
2	60	25.0	25.4	0.4	2.787
3	90	25.4	25.9	0.5	2.322
4	120	25.9	26.5	0.6	2.090
5	150	26.5	27.2	0.7	1.951
6	180	27.2	28	0.8	1.858

**Fig. 4. The change of temperature with increasing sonication time**

3. RESULTS AND DISCUSSION

3.1 Sonochemical Decomposition of Methyl Orange

Sonication experiments were conducted with Methyl Orange solutions to study the decomposition of 50 mg/L dye solution at room temperature. Fig. 5 represents the effect of sonolytic decomposition of MO in aqueous solution.

As it can be seen from Fig. 5, the concentration of MO decreased gradually as the sonication time increased. So, it can be said that, MO degrades gradually with the increase in sonication time. When no sonication occurred the concentration of MO was 0.153 mM. After sonicating for 5, 10 and 15min, the concentration decreased gradually. Also, the rate constant was obtained 0.003.

3.1.1 Sonochemical decomposition of methyl orange in presence of different concentration of H₂O₂

One of the most popular advanced oxidation processes (AOPs) methods for decomposition of

organic compounds is the oxidation with H₂O₂. In the presence of H₂O₂ is a key parameter for dye decomposition in AOPs technique, depending on its concentration and nature of reductants H₂O₂ increase the formation rate of hydroxyl radicals in two ways. Firstly, the reduction of H₂O₂ at the conduction band would produce hydroxyl radicals. Secondly, the self-decomposition as a result of ultrasound irradiation would also produce hydroxyl radicals. Generally, the decolorization rate of dye increases as the H₂O₂ concentration increases until an optimal concentration is achieved [22]. Recently, ultrasound irradiation was described as a possible generation of highly active [•]OH, HOO[•] and H[•] radicals [23]. However, at high concentration, H₂O₂ can also become a scavenger of valence bond holes and [•]OH radicals causing less dye to be degraded. The effect of ultrasonic irradiation combined with H₂O₂ is observed only when free radical attack is the controlling mechanism. In order to investigate the effect induced from the addition of different concentration of H₂O₂, the sonolytic degradation of 100 mL of MO solution was performed. The concentration of H₂O₂ used are 20 μL, 100 μL, and 200 μL of H₂O₂ solution. These results are illustrated in Fig. 6.

3.1.2 Comparison of sonochemical decomposition of Methyl Orange (MO) with and without different concentrations of H₂O₂

In the presence of ultrasound, the decomposition of MO without H₂O₂ increased. But when H₂O₂ added to the solution of MO, it enhances the rate of decomposition of MO. The higher the concentration H₂O₂, the rate of decomposition of MO also increases Fig. 7.

According to this Fig. 7 shows the increase in the concentration of H₂O₂, increasing the rate of decomposition of MO and follows the trend of

sequences below; MO + 200 μL H₂O₂ > MO + 100 μL H₂O₂ > MO + 20 μL H₂O₂ > MO. Sonochemical decomposition of MO in the presence of different concentrations of H₂O₂ are MO + 20 μL H₂O₂ is 0.005, MO + 100 μL H₂O₂ is 0.016 and MO + 200 μL H₂O₂ is 0.021 Fig. 7.

3.1.3 Sonochemical decomposition of methyl orange in presence of different concentration of CCl₄

In order to investigate the effects induced from the addition of different concentration of CCl₄, the sonolytic decomposition of 100mL of MO solution was performed. Here the concentration of CCl₄

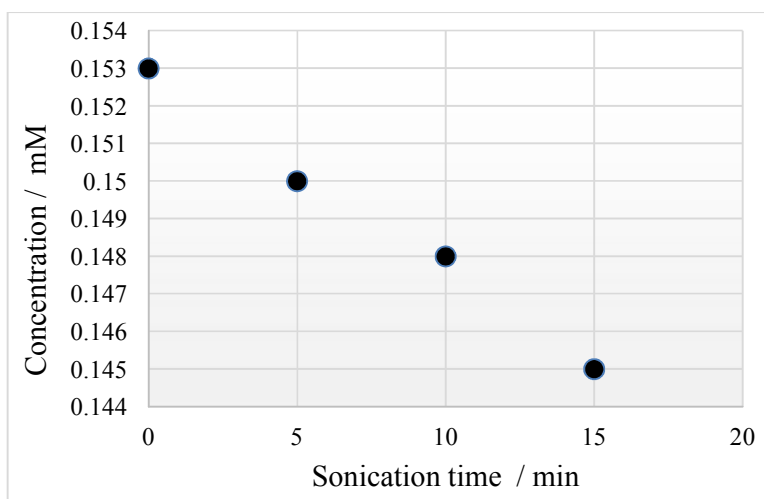


Fig. 5. Sonochemical decomposition of methyl orange in the absence of additives

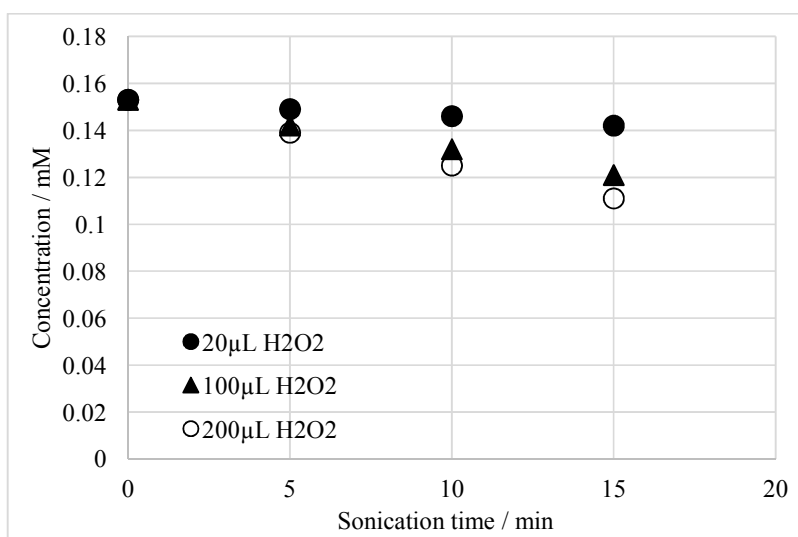


Fig. 6. Sonochemical decomposition of methyl orange in the presence of different concentrations of H₂O₂

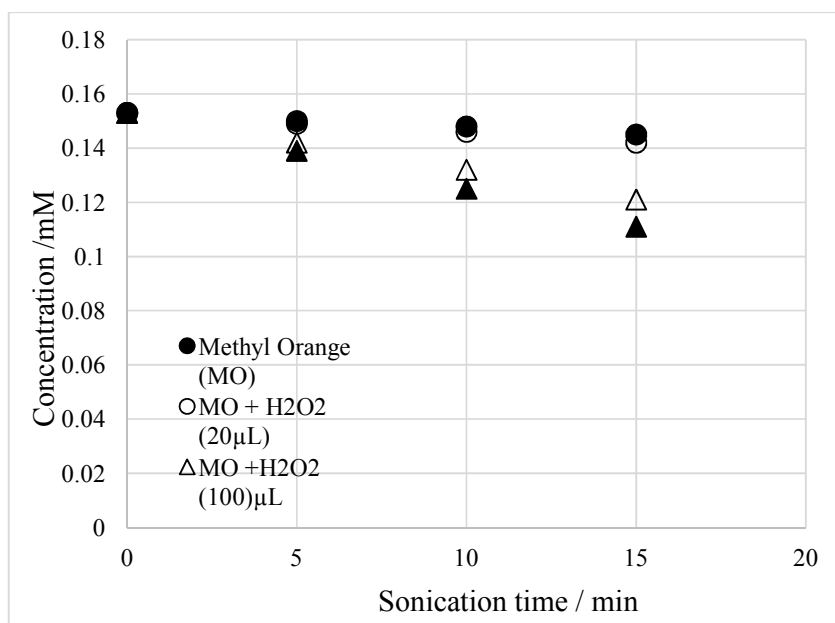


Fig. 7. Comparison of sonochemical decomposition of MO with and without different concentrations of H₂O₂

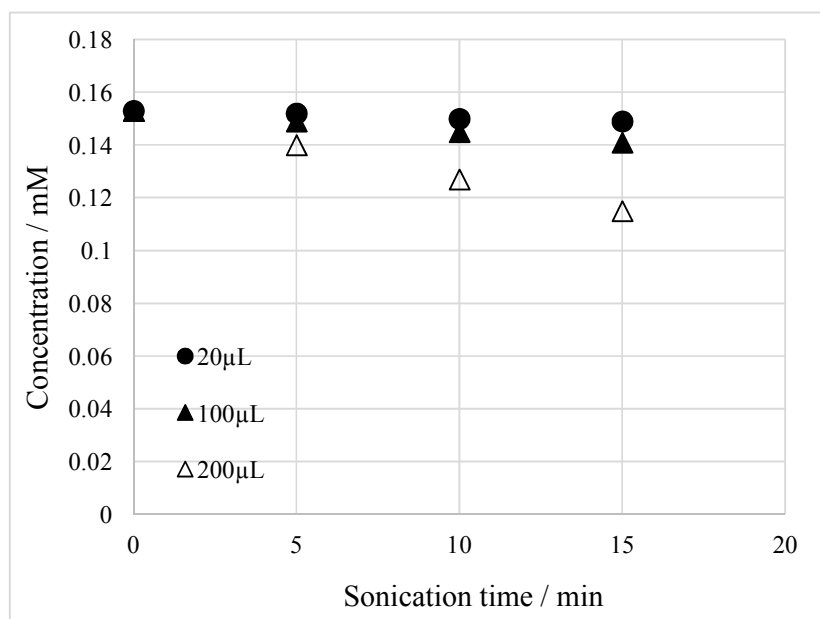


Fig. 8. Sonochemical decomposition of methyl orange in the presence of different concentrations of CCl₄

used are 20 µL, 100 µL and 200 µL respectively. These results are illustrated in Fig. 8.

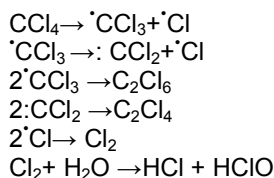
The rate of dye decomposition increases with the increasing of concentration of CCl₄. Recently, it has been reported that the analysis for the rate of the sonochemical decomposition of organic

compounds in water can be colorimetrically performed to understand the sonochemical efficiency, where the rate of the sonochemical decomposition is suggested to be reasonably correspondent to the yield of H₂O₂. For examples, porphyrins [24] are so far used for the model compounds. These methods would be

convenient for the analysis of the sonochemical efficiency under an ultrasonic irradiation condition. Our results suggested that the sonochemical decomposition of MO in the presence of CCl_4 would be useful to evaluate the sonochemical efficiency, because the rate of the MO decomposition can be effectively enhanced by the sonolysis of CCl_4 .

3.1.4 Comparison of decomposition of Methyl Orange (MO) with and without different concentration of CCl_4

In this study, it was found that the rate of the MO decomposition could be enhanced by the addition of CCl_4 . This reason could be qualitatively explained by the sonochemical decomposition of CCl_4 to form various types of active species, which can react with MO molecules. It has been reported that the sonolysis of CCl_4 in water occurs as seen in Equations below [25, 26]:



In the presence of ultrasound, the decomposition of MO without CCl_4 increased. But when CCl_4 added to the solution of MO, it enhances the rate of decomposition of MO. The higher the concentration CCl_4 , the rate of decomposition of

MO also increases. Based on the obtained results, it was suggested that the enhancement effect was dependent on the ultrasonic irradiation condition. This would be due to that the cavitation phenomenon induced by ultrasonic irradiation is sensitively affected by the experimental conditions such as ultrasound frequency and power, volume of solution, etc. For example, a change in the ultrasound frequency may affect one or many of the following factors [24,26,27]: (1) the temperature and pressure inside the collapsing cavitation bubbles,(2) the number and distribution of bubbles,(3) the size and lifetime of bubbles,(4) the dynamics and symmetry (shape) of the bubble collapse,(5) the effect of organic additive on bubble temperature,(6) the effect of intermediates and products, etc. It is quite difficult to quantify the individual effects of these factors, since they are interdependent and it is almost impossible to control one factor without affecting the others. In addition, the rate of the decomposition would be affected by the geometrical placement of the instrumental components such as the shape of the reaction cell, the volume of the sample solution, the size of the used ultrasonic oscillator, etc. According to, increase in concentration of CCl_4 , the increasing rate of decomposition of MO can be written as (Fig. 9): $\text{MO} + 200 \mu\text{L CCl}_4 > \text{MO} + 100 \mu\text{L CCl}_4 > \text{MO} + 20 \mu\text{L CCl}_4 > \text{MO}$. In addition, sonochemical decomposition of MO in the presence of different concentrations of CCl_4 are $\text{MO} + 20 \mu\text{L CCl}_4$ is 0.002, $\text{MO} + 100 \mu\text{L CCl}_4$ is 0.005 and $\text{MO} + 200 \mu\text{L CCl}_4$ is 0.019 Fig. 9.

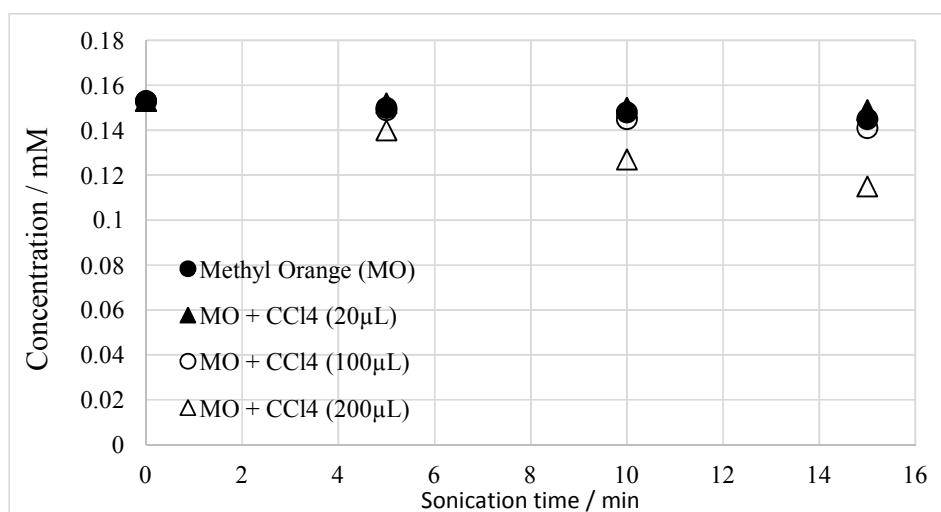


Fig. 9. Comparison of sonochemical decomposition of MO with and without different concentrations of CCl_4

4. CONCLUSION

Sonochemical decomposition of methyl orange (MO) was studied in the absence and presence of different concentrations of H₂O₂ and CCl₄. MO molecule can be effectively removed from water by sonolysis. This study exhibits that the sonochemical decomposition occurs mainly through reactions with hydroxyl and chloride radicals. It was found that the initial decomposition of MO molecule increased. But by the addition of CCl₄ and also for H₂O₂, the rates of sonochemical decomposition of MO were enhanced. This process is technically feasible & also economic. Eventually reached to a conclusion. According to, increase in concentration of CCl₄, the increasing rate of decomposition of MO can be written as: MO + 200 µL CCl₄ > MO + 100 µL CCl₄ > MO + 20 µL CCl₄ > MO. Similarly for H₂O₂ the increasing rate of decomposition of MO can be written as: MO + 200 µL H₂O₂ > MO + 100 µL H₂O₂ > MO + 20 µL H₂O₂ > MO.

COMPETING INTERESTS

Authors have declared that no competing interests exist.

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