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## Ultrasonic Induced Decomposition of Methidathion Pesticide

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**Abstract:** A cost effective method of decomposition was developed for industrial effluents by using ultrasound in combination of H<sub>2</sub>O<sub>2</sub>. The process was optimized by studying the decomposition of methidathion pesticide at different frequencies, different ultrasonic wave amplitudes, pH and concentrations of the solutions. It was shown that the rate of sonochemical decomposition was directly linked to the OH<sup>•</sup> availability in the solution. The degradation was more efficient for the higher frequency because the rates of OH<sup>•</sup> formation in water saturated with air were more at higher frequency. It was observed that higher the ultrasonic frequency, higher was the energy consumption. This problem of higher energy consumption was resolved by increasing the concentration of H<sub>2</sub>O<sub>2</sub>. Ultrasound/H<sub>2</sub>O<sub>2</sub> process gave better decomposition than ultrasound alone. Decomposition of methidathion was effective with ultrasound at greater sound wave amplitude. When the pH was controlled below the p<sub>k</sub> value of methidathion, significantly better decomposition of methidathion resulted. The decomposition of methidathion appeared to follow first-order reaction kinetics. The reaction rate constant (k) was greater at smaller pH and there is an exponential relation between them.

**Key words:** Ultrasonic decomposition, sonochemical degradation, ultrasonic frequencies, organophosphorus compounds, pesticides, ultrasonic amplitudes, sonolysis with hydrogenperoxide

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### INTRODUCTION

Ultrasounds accelerate several reactions that lead to formation of novel compounds. Used alone or in conjunction with other technique (e.g., photochemistry, electrolysis (Hua and Thompson, 2000), oxidation), sonolysis can prove industrially useful and efficient technique.

Recent studies showed that hazardous organic compounds can also be degraded by the ultrasonic technique in the presence of catalysts, acids and non-oxidant gases (Sun *et al.*, 2007; Wang *et al.*, 2006; Hilla and Nava, 2005; Devinder *et al.*, 2004). The industrial organic effluents must be decontaminated before their discharge into aqueous ecosystems. The chemical effects of ultrasound are due to the high temperatures and pressures produced during violent collapse of cavitations bubbles (Hua and Thompson, 2000; Christen *et al.*, 1994; Farooq *et al.*, 2002). These collapsing micro bubbles become more efficient reactors when filled with dissolved gas (i.e., Ar) and solvent vapor (Farooq *et al.*, 2003). These collapsing bubbles act as micro reactors in which solvent vapors can be pyrolyzed, thus producing radicals that undergo further reactions. A thin shell of liquid

surrounding the collapsing micro bubbles experiences temperatures and pressures exceeding the critical temperatures and pressures of the liquid (these critical values are 374°C and 221 atm. for water). Thus, a supercritical fluid is formed in this region. The physical properties of the supercritical fluid differ from those of the bulk liquid. One of the most notable changes is the lowering of the dielectric constant of polar solvents such as water; which allows the accumulation of low polarity solutes at this interface. Thermolysis as well as radical abstraction reactions occurs in this region (Hua and Thompson, 2000). In water, implosion and fragmentation of the bubble, which collapses, are the center of high-energy phenomena; temperature, pressure and electric discharges giving rise to H<sub>2</sub>O sonolysis with production of radical species (OH<sup>•</sup>, H<sup>•</sup>, HOO<sup>•</sup>) and direct destruction of solute (Okouchi *et al.*, 1992; Mason, 1990; Koteonaru *et al.*, 1996).

Ultrasound is then a source of radicals, especially the hydroxyl radical (OH<sup>•</sup>). The hydroxyl radicals are very strong and nonspecific oxidizing species which escapes out of the bubble and react rapidly with compounds in solution (Koteonaru *et al.*, 1992; Christen and Anne, 1997). Sonolysis could prove industrially useful

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technique, especially if it were found to be efficient and economical to decontaminate industrial organic discharges before their input into aquatic ecosystems.

Methidathion is the organophosphorus pesticide and was chosen because it is difficult to degrade and high  $t_{1/2}$  under normal conditions of temperature and pressure if it is discharged in the water bodies. It is necessary to decrease its half life and convert it into biodegradable substance.

The objectives of the present study are;

- To determine the experimental conditions that increases the efficiency of decomposition of methidathion.
- To determine the kinetics of methidathion decomposition.

The following parameters are studied;

- Effect of ultrasonic double amplitude.
- Effect of  $H_2O_2$  addition.
- Effect of pH.
- Kinetics.
- Effect of ultrasonic frequency on decomposition.
- $OH^\bullet$  Production and methidathion decomposition.
- $^\bullet OH$  localization in an ultrasonic field.

## MATERIALS AND METHODS

This study was conducted at COMSATS Institute of Information Technology in the Department of Environmental Sciences during 2006-2007.

The initial concentration of aqueous methidathion was prepared as  $200 \text{ mg L}^{-1}$ . The reaction was initiated on the addition of  $H_2O_2$ .

The concentrations of  $H_2O_2$  were 0, 100, 200 and  $500 \text{ mg L}^{-1}$ . The experiments were conducted with a sonicator (Microson XL-2020, Heat System Ltd., USA) operated at the frequency ranges from 20-100 kHz. The double amplitude at the tip of the standard horn (12.7 mm) was adjusted to 0, 72 and  $120 \mu\text{m}$ , corresponding to a power input 0, 125 and 160 W. The volume of solution was 1 L in a reaction flask. Oxygen was continuously purged into the flask to keep the dissolved oxygen at  $30\text{-}32 \text{ mg L}^{-1}$  so as to increase the  $H_2O_2$  produced. The temperature of the solution was kept constant at  $25^\circ\text{C}$  and the pH was controlled at 3, 5, 7, 9 and 11 with  $H_2SO_4$  and NaOH. The effect of different frequencies is determined by using Digital Ultrasonic Bath cleaner Model, Utech products, USA. On this bath, the desired frequency can easily be adjusted. The aqueous samples were withdrawn at regular intervals for analysis.

Different parameters in liquid were determined according to standard methods (Andrew *et al.*, 2005).

- Total Phosphorus (TP) was determined by persulphate digestion method followed by ascorbic acid method.
- Inorganic Phosphorus (IP) was determined by ascorbic acid (molybdenum blue) method.
- Organic Phosphorus (OP) was calculated by:

$$OP = TP - IP$$

The concentrations of  $H_2O_2$  were determined by titration with  $Na_2S_2O_3$  (Andrew *et al.*, 2005).

## RESULTS AND DISCUSSION

**Effect of ultrasonic double amplitude:** Typical variation of the aqueous concentration,  $C/C_0$  of methidathion. Where  $C_0$  is the initial concentration of methidathion and  $C$  is the concentration of methidathion at time  $t$ . The degradation of methidathion was more effective at greater amplitude of ultrasound. There was 5% degradation ratio with amplitude  $72 \mu\text{m}$  of ultrasound, but increased to 10% with ultrasonic amplitude  $120 \mu\text{m}$  (Fig. 1). Both were better than control (without sonication), which has only 2% degradation. In the literature no author assessed the effect of ultrasonic amplitude on the decomposition of hazardous materials. The sonicator (Micron XL 2020) of the type used in this research has a constant frequency output and the power of the ultrasound is set with the ultrasound amplitude. Greater ultrasound amplitude means greater energy supply so as to cause cavitation bubbles at a higher temperature. In relation to power our results resembled to those in which the reaction rate increased with greater ultrasonic power (Pandey *et al.*, 1980).  $H_2O_2$  generated in the ultrasonic process, measured by titration, indirectly caused the OH radical to be produced. However, the concentration was much small about  $120 \text{ mg L}^{-1}$ . Possibly the frequency is varied or the power supplied is insufficient. The limited  $H_2O_2$  generated might be the reason for the small degradation efficiency.

**Effect of  $H_2O_2$  addition:** Ultrasound alone poorly decomposes omethoate, so  $H_2O_2$  is added initially to enhance the ultrasonic process. This combination resulted in significant degradation efficiency. The concentration of  $H_2O_2$  increased the decomposition efficiency of omethoate. The more  $H_2O_2$  was added the greater the removal of omethoate (Fig. 2).

After reaction for 60 min, the improvement in methidathion decomposition with  $H_2O_2$  ( $500 \text{ mg L}^{-1}$ ) was as great as 57% over the control, i.e., without  $H_2O_2$ . The

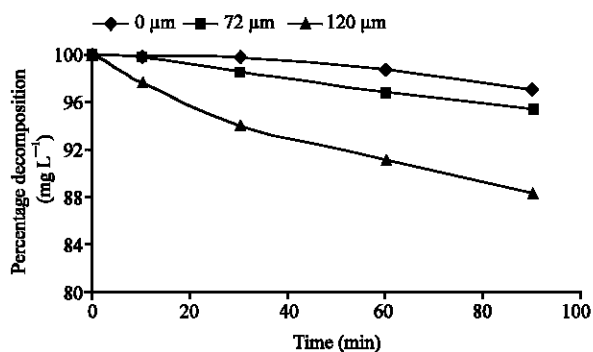


Fig. 1: The effect of variable ultrasonic waves amplitudes on the degradation of methidathion at 20 kHz

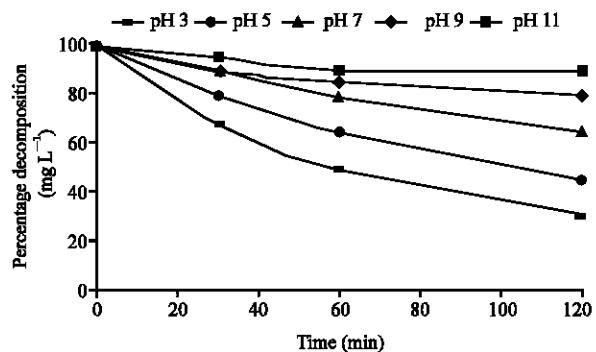


Fig. 3: Effect of pH on the ultrasound/H<sub>2</sub>O<sub>2</sub> process at amplitude 120 μm and H<sub>2</sub>O<sub>2</sub> (200 mg L<sup>-1</sup>)

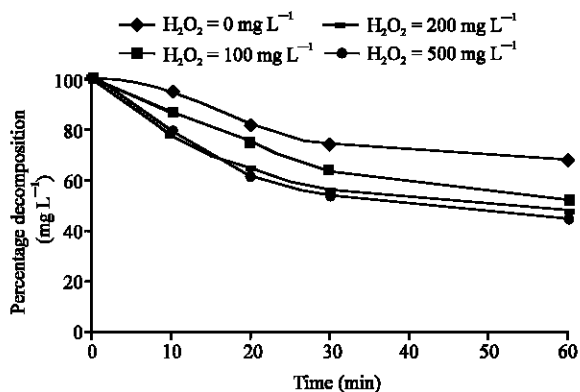


Fig. 2: Effect of dose of H<sub>2</sub>O<sub>2</sub> on the decomposition of methidathion

results revealed that there were more OH radicals generated on addition of H<sub>2</sub>O<sub>2</sub>, which was effective for degradation. However there was no significance difference between concentrations 200 and 500 mg L<sup>-1</sup> of H<sub>2</sub>O<sub>2</sub>, with regard to decomposition of methidathion (45 and 48%). Possibly the concentration of OH radicals was saturated; further H<sub>2</sub>O<sub>2</sub> failed to increase the OH radicals, so was useless to reaction. Thus a significant dosage of H<sub>2</sub>O<sub>2</sub> was found to be 200 mg L<sup>-1</sup> according to this experiment.

**Effect of pH:** The effect of pH on the decomposition of methidathion vs. time (Fig. 3), which indicates that a smaller pH value is more effective.

The decomposition of methidathion attained 99% at pH 3, 85% at pH 5 and 62% at pH 7. For samples controlled at pH 9 and 11, the extents of methidathion decomposition were only 22 and 15%. The obvious variation among them arises because the pK<sub>a</sub> value of methidathion is 8.49 at 25°C, but in a molecular form. The fraction in the molecular state of methidathion was larger

when the pH was smaller. The methidathion ions cannot vaporize into the cavitation bubbles; they can react only outside the bubble film with OH radicals cleaved from water. However, in the molecular state methidathion can vaporize into cavitation bubbles and react both inside by thermal cleavage and outside with OH radicals as an oxidation reaction (Hua and Thompson, 2000). Hence the smaller pH (especially less than the pK<sub>a</sub>) was effective for decomposition. There might exist other reasons such as that OH radical can easily contact with molecular omethoate. The state of methidathion had a large influence on the degradation efficiency of the ultrasound/H<sub>2</sub>O<sub>2</sub> process.

**Kinetics:** In analyzing the experimental results, decomposition of methidathion appeared to follow first-order kinetics. The predicted decomposition of methidathion is compared with the observed data (Fig. 3) for various pHs. The squared correlation coefficients, R<sup>2</sup>, of the model exceeded 0.9 at various pHs. The rate of coefficients increased with decreased pH. We also used logarithmic regression with rate coefficients and pH and obtained a close relationship (Fig. 4). The relationship between pH and k is:

$$k = 0.0422 \exp(-0.476(\text{pH}))$$

**Effect of ultrasonic frequency on decomposition:** Exposure of methidathion solution of different concentrations to ultrasound at 20 and 100 kHz shows a higher rate of decomposition for the higher frequency (Fig. 5).

The rates of degradation have been determined when the proportion of degraded methidathion does not surpass 46% at 20 kHz (Fig. 2). This could be attributed to the competition between methidathion

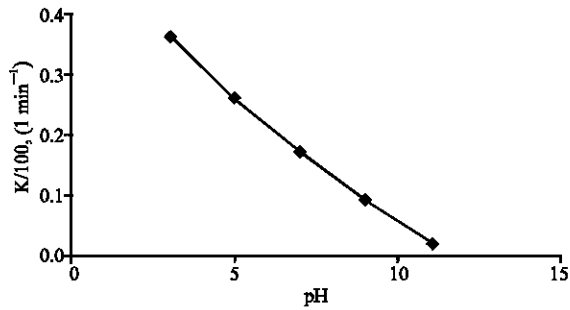


Fig. 4: Relationship between pH and k on the ultrasound/H<sub>2</sub>O<sub>2</sub> process

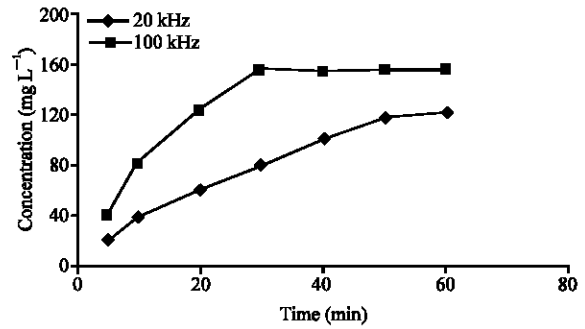


Fig. 6: Concentration of H<sub>2</sub>O<sub>2</sub> produced as a function of insonation time in aerated water

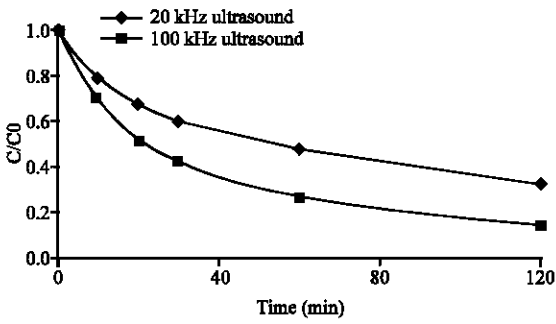


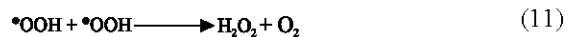
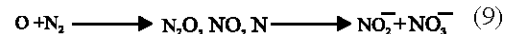
Fig. 5: Effect of ultrasonic frequency on the decomposition of methidathion

and products of the reaction. However at 100 kHz, the degradation has increased to more than 74% in the same period of time.

**OH<sup>•</sup> production and methidathion decomposition:** The physical phenomena leading to sonochemical effects in water are complex and not fully elucidated. Nevertheless, whatever the theoretical model describing the origin of the molecular activation (thermal and/or electrical), the place where the molecules are brought to an excited state and dissociate is the interior of the bubble of cavitation, which is filled with gas and vapor. In the cleavage of water saturated with air, the first step appears to be the cleavage of water and the dioxygen molecule (Misik *et al.*, 1995).



Inside the bubble or in the liquid shell surrounding the cavity, these radicals can combine in various ways or react with gases and vapor present, leading to the detection in the medium of HNO<sub>3</sub>, HNO<sub>2</sub> and H<sub>2</sub>O<sub>2</sub>.



The main fraction of the H<sub>2</sub>O<sub>2</sub> formed during water sonolysis seem to come from the OH<sup>•</sup> and <sup>•</sup>OOH radicals, which combine in the bubble or in the layer surrounding the bubble of cavitations in the absence of substrate (Okouchi *et al.*, 1992) (reactions 10, 11). The amount of H<sub>2</sub>O<sub>2</sub> produced at each of the two frequencies was determined (Fig. 6). The concentration of hydrogen peroxide increases linearly vs. time and the rate of formation were found higher at 100 kHz than at 20 kHz. With these results in hand H<sub>2</sub>O<sub>2</sub> production was examined in the presence of various concentrations of methidathion at 100 kHz. There is a close relationship between methidathion degradation and H<sub>2</sub>O<sub>2</sub> production (Fig. 7). The hydrogen peroxide yield decreases when the methidathion concentration increases. There is always H<sub>2</sub>O<sub>2</sub> formation, this may be due to the fact that part of the hydrogen peroxide originates through reaction 11 is consumed by methidathion added.

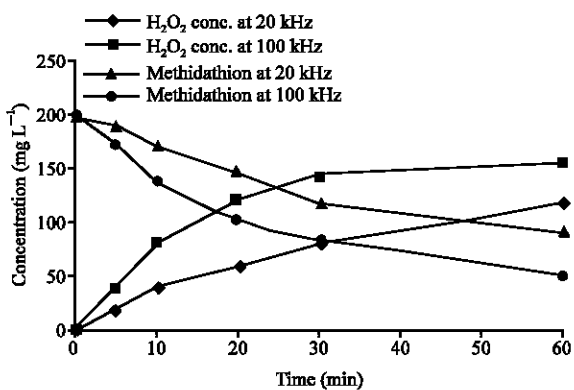
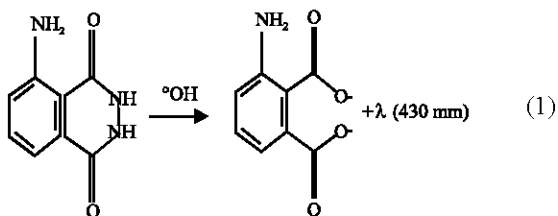


Fig. 7: Methidathion degradation and rate of hydrogen per oxide formation at different frequencies

The sonochemical methidathion degradation which proceeds more rapidly at high than at low frequency can be related to a better release of OH<sup>•</sup> in the solution in the former case. The basis of this discrepancy is not yet well understood, but there must be some differences between the behavior of a 20 kHz and a 100 kHz bubble. The more important cavitation effects occur when the frequency of the ultrasonic wave is equal to the resonance frequency of bubble. The duration of collapse is shorter at 100 kHz than at 20 kHz. In such conditions, at high frequency, OH<sup>•</sup> radicals could be ejected more efficiently in the solution before they have time to combine in the bubble of cavitation (Christen and Anne, 1997).

**•OH localization in an ultrasonic field:** There are several reports in the literature, which demonstrate that the sonochemical yields are related to the configuration of the reactor. For instance, iodide oxidation and carbon tetrachloride degradation were reported to proceed faster when a standing wave system is created in the column of liquid above the emitting surface (Sun *et al.*, 2007; Hua and Thompson, 2000). The difference between high and low-frequency ultrasonic field was also observed. The high-frequency wave generates a directive acoustic beam which induces convection currents and foundation effects at the surface of the liquid.



The acoustic field spread at low frequency, it was then important to determine where the site of the

sonochemical reaction in the 20 and 100 kHz reactors were located. Since the OH<sup>•</sup> radical is the reagent involved in the sonochemical methidathion degradation, the place where it is produced was studied with the help of sonochemically induced luminescence of luminol. In basic medium, luminol reacts with hydroxyl radicals, giving aminophalate anion and a blue fluorescence (Eq. 1) (Koteonrou *et al.*, 1996).

The two very different patterns are observed with this method for the two frequencies (Koteonrou *et al.*, 1996). In the two cases, the surface of the solution is heavily disturbed, which prevents the standing waves in the medium. At 20 kHz the luminescence is located near the surface of the transducer. At 100 kHz, most of the fluorescence originates from a wider volume close to the surface of the liquid, without any light near the surface of the emitter. It can be noted that modifications on the height of the liquid do not change the location of the luminescence zone or the yield of methidathion degradation.

## CONCLUSIONS

Ultrasound/H<sub>2</sub>O<sub>2</sub> process gave better decomposition than ultrasound alone, although the decomposition of methidathion was effective with ultrasound at greater amplitude. When the pH was controlled below the pK<sub>a</sub> value of omethoate, significantly better decomposition resulted than for greater pH. The decomposition of methidathion at 200 mg L<sup>-1</sup> was 88% at about amplitude 120 μm with H<sub>2</sub>O<sub>2</sub> and at pH 3, after reaction for 90 min. The decomposition of methidathion appeared to follow first-order reaction kinetics. The reaction rate constant (k) was greater at smaller pH and there is an exponential relation between them. The experimental data of this work demonstrated that the ultrasonic frequency has an important effect on the yield of the sonochemical degradation of methidathion. Because of the phenomenon, it appears difficult to provide a complete interpretation of the experimental data. For economic consideration and from a fundamental point of view, studies of frequency effects seem to be of interest.

## Significant findings of the research

- Ultrasound/ H<sub>2</sub>O<sub>2</sub> process gave better decomposition than ultrasound alone.
- When the pH was controlled below the pK<sub>a</sub> value of omethoate, significantly better decomposition resulted than for greater pH.
- The decomposition of methidathion appeared to follow first-order reaction kinetics.

- The experimental data of this work demonstrated that the ultrasonic frequency has an important effect on the yield of the sonochemical degradation of methidathion.

This research has the capacity to launch it in industries as a treatment technique for effluent treatment.

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