Sonochemical degradation of organophosphorus pesticide in dilute aqueous solutions

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Abstract: Ultrasonic irradiation was found to accelerate the rate of hydrolysis of omethoate in aqueous solution over the pH range of 2—12. Process parameters studied include pH, steady-state temperature, concentration, and the type of gases. Greater than 96% hydrolysis was observed in 30 minutes through this process and the rate of destruction increased with the help of more soluble and low thermal inert gas. So with Krypton, omethoate was found to undergo rapid destruction as compared with Argon. In the presence of ultrasound, the observed first-order rate of hydrolysis of omethoate is found to be independent of pH. The formation of transient supercritical water (SCW) appears to be an important factor in the acceleration of chemical reactions in the presence of ultrasound. A detailed chemical reaction mechanism for omethoate destruction in water was formulated. Experimental results and theoretical kinetic mechanism demonstrated that the most of the omethoate undergo destruction inside the cavitating holes. A very less effect of temperature on the degradation of omethoate within a temperature range of 20—70℃ proves that a small quantity of omethoate undergoes secondary destruction in the bulk liquid.

Keywords: sonochemical degradation; omethoate pesticide; sonolysis; role of inert gases

Introduction

The application of ultrasonic energy to problems associated with water pollution, especially in removing toxic and hazardous organic compounds from contaminated water have been focused in recent years. As the removal of these compounds is difficult and expensive, if very low concentration levels are required to achieve. For many years, the ultrasonic process has the advantage of completely destroying or converting the toxic organic compounds into simpler inorganic substances(Inez, 2000; Christian, 1996). The chemical effects of ultrasound are due to the phenomenon of acoustic cavitation. Sound is transmitted through any fluid as a wave consisting of alternating compression and rarefaction cycles. If the rarefaction wave is sufficiently powerful, it can develop a negative pressure large enough to overcome the intermolecular forces binding the fluid. As a result, the molecules are torn apart from each other and form tiny micro bubbles. These micro bubbles gradually grow during the compression/rarefaction cycles until they reach a critical size. Subsequent compression then causes the micro bubbles to collapse almost instantaneously, thereby releasing a large amount of energy. Temperatures of the order of 5000K have been experimentally obtained, and pressure of the order of 1000 atmospheres has been calculated(Kotnonarou, 1991). At 20 kHz and typical ultrasonic immersion horn intensities(10—100 W/cm^2), the radius of bubble prior to collapse can be estimated to be of the order of several hundred micrometers(400—500 μm). Time scale of bubble collapse is < 100 ns, and the time scale for the heat diffusion in the surrounding liquid is a few microseconds with a corresponding diffusion length of a few hundred nanometers (Okouchi, 1992; Anatassia, 1992).

The primary chemical reactions result, therefore from the transient state of these high pressure and temperatures, both during and immediately after the collapse of the micro bubbles(Mason, 1990). Solvent and solute vapors in the cavity undergo the direct thermal dissociation to yield CO_2 and H_2O, and radicals such as hydroxyl($^{\circ}OH$) and atomic hydrogen(H°). Some of these radicals may recombine to form new compounds. In the bulk liquid phase, secondary reactions between solute molecules and radicals generated in the cavities also take place. These two reaction schemes together are responsible for the chemical effect of ultrasound upon the solution(Lin, 1996; Vladimir, 1995). These changes favor substantial increase for rates of most chemical reactions such as hydrolysis and extraction and are useful for environmental applications such as destruction of hydrocarbons and phenols. Omethoate, an organophosphorus pesticide is expected to undergo thermal decomposition in the hot interfacial region of the collapsing cavitation bubbles

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and undergo hydrolysis via reaction with °OH radicals(Timothy, 1993; Peter, 1993).

Organophosphorus pesticides pollute water bodies by different means like pesticide production factories. Their effluents create sanitary and ecological hazards. So, it is necessary to find the conventional treatment method, which can hydrolyze the effluent completely and in minimum time, so that the effluent release in the water bodies should not be toxic to organisms.

Ultrasound has a broad range of industrial applications, its potential as a water and wastewater treatment alternative has not been explored extensively. So it is necessary to find effectiveness of hydrolysis of omethoate under ultrasonic conditions. There are two good reasons for using ultrasound for the destruction of organophosphorus pesticides including omethoate(Paul, 1996; Berlan, 1992): (1) During acoustic cavitation several hundred atmospheric pressure can be achieved easily with the help of ultrasonic technique, which is an easy method, while using commercially in the industry. (2) The application of supercritical water to wastewater treatment has been investigated for many years. One drawback of the large-scale application of SCW is the inherently aggressive nature of water in the supercritical state, which results in extensive corrosion of reaction vessels. Corrosion of the reaction chamber lessens the feasibility of this method. The treatment of hazardous compounds including organophosphorus pesticides with ultrasound could be a possible alternative to the treatment process in bulk supercritical water. Due to local confinement of high temperature and pressure as generated during acoustic cavitation, the bulk solution remain at ambient pressures and temperatures, thus avoiding extensive damage to the reaction vessel.

1   Experimental

Ultrasonic irradiation of aqueous solutions of omethoate, the organophosphorous pesticides were carried out with a vibra cell model VC-250 direct immersion ultrasonic horn(sonics and materials) operated at the frequency of 20 kHz with a constant power density of 50 W/cm^2. Reactions were conducted in a glass sonication cell. The horn titanium tip was immersed about 3 cm into the solution. The bottom of the glass reactor had a 1 cm indentation in the center for reflection of sound waves and for even distribution of cavitation bubbles in the solution. The reaction volume was 100 ml. The upper part of the cell is modified by the addition of gas dispersion and sampling tubes.

A number of experiments were done in the presence of Ar or Kr, which is dissolved in the solution of omethoate pesticide prior to experiment for 20 min at the flow rate of 15 ml/min. The cell is encased in a water jacket and is cooled with a circulating bath of water jacket set at 20 ℃. 5 ml aliquots are withdrawn through the sampling tube at variable time intervals. In order to determine the effect of pH on the rate of degradation, the pH of the solution was adjusted at 2, 3.5, 7, 8.5, 10 and 12 with the help of 2.5 mol/L H$_2$SO$_4$ or 5 mol/L NaOH.

2   Analytical methods

Different parameters in liquid were determined according to standard methods(Cum, 1992; Peter, 1992): (1) total phosphorus(TP) was determined by persulphate digestion method followed by ascorbic acid method; (2) inorganic phosphorus(IP) was determined by ascorbic acid(molybdenum blue) method and (3) organic phosphorus(OP) was calculated by: OP = TP – IP.

3   Results and discussion

Exposure of omethoate solutions in the presence of dissolved gas Kr results in a decrease of the [omethoate] in the solutions. Fig.1 shows the plot of [omethoate] versus sonication time at two initial [omethoate], greater than 96% removal efficiency is observed in the current experiment. Initial [omethoate] as high as 200 mg/L and 50 mg/L dropped to about 6.2 mg/L and 0.4 mg/L respectively after 30 minutes of irradiation. This enhanced rate of hydrolysis is considered due to two reasons. First is that during sonolysis, within the collapsing cavitation bubbles, the conditions of temperature and pressure exceeding the critical point of water. So there is supercritical water around the collapsing cavitation bubbles. Hydrolysis is accelerated in part, by a higher concentration of °OH at the hot bubbles interface, which result from the high ion product of water.

First-order plots of ln[C/C$_0$] versus sonication time for 50 and 200 mg/L initial concentrations are shown in Fig.2. The concentration of residual omethoate decreased exponentially with sonication time. The

ultrasonic degradation of [omethoate] apparently follow first-order kinetic within the current experimental concentration range. Sonication of solutions with [omethoate] = 50 mg/L resulted in degradation rates constants that were about twice as large as those observed in solutions with [omethoate] = 200 mg/L. The lower degradation rate constants at a higher initial concentration demonstrates that the cavitation sites approach saturation with increasing bulk solute concentrations.
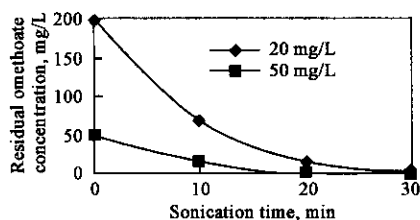

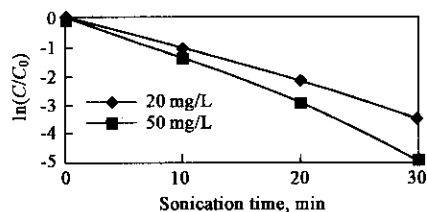Fig. 1   Effect of concentration on ultrasonic destruction of omethoate

Fig. 2   First order plot of ln (C/C_0) versus sonication time

Temperature control in the reaction vessel is an important factor in maintaining a high destruction rate of omethoate in the solution. In sonication, it has been reported that the attempt to increase the solvent temperature up to its boiling point is not useful, because the rarefaction cycle causes the water to boil as a result of the reduced pressure generated; consequently, any cavitation bubble formed will fill with water vapor almost instantaneously. This water vapor could reduce the extremes of temperature and pressure generated and thus decreases the direct destruction efficiency of the organics. On the other hand, operating the system at higher temperatures enhances the secondary reactions(Wang, 2000; Terese, 1994).

Effect of steady-state temperature on omethoate destruction efficiency is shown in Fig.3. There is very less effect on the degradation of omethoate within a temperature range of 20—70℃. It means that the hydrolysis of omethoate, mostly occur inside the cavities and the temperature inside the cavities is independent on the surrounding temperature.
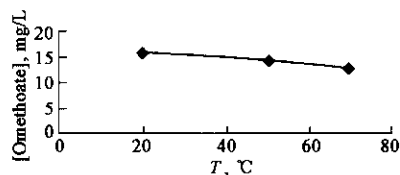

Fig. 3   Effect of steady state temperature on omethoate degradation
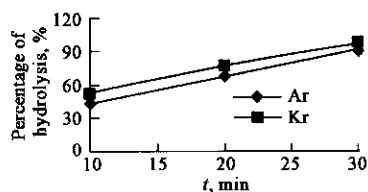

Fig. 4   Effect of gas type on the percentage hydrolysis

The rate of hydrolysis has increased in the presence of Kr as compared to Ar. In the presence of Kr the rate is 96 ± 2.7% and is 92 ± 2.5% in the presence of Ar after 30 minutes of irradiation(Fig. 4). Thermal conductivities of the dissolved gases have been inversely correlated to sonoluminescence intensity as well as with variable rates of free-radical formation during sonolysis. A low thermal conductivity favors high collapse temperatures because the heat of collapse will dissipate less quickly from the cavitation site. Highly soluble gases should result in the formation of large number of cavitation nuclei and more extensive bubble collapse since gases with high solubility is more readily force back into the aqueous phase. On the basis of this, it is concluded that krypton yields higher rate of degradation as compare to Ar. Physical properties of Ar and Kr are given in Table 1.

It is studied that changes in pH of the solution do not have considerable effect on the rate of hydrolysis. This pH

Table 1   Physical properties of selected gases used during sonolysis

Gas	Polytropic index, k	Thermal conductivity λ, mW/mK	Solubility in water, m^3/m^3
Kr	1.66	17.1	0.0594
Ar	1.66	30.6	0.032

independency is consistence with the tendency for water in a dense supercritical state to have a higher ion activity product relative to normal phase water; a higher value for k_w should result in a higher concentration of both OH^- and H^+ for a given set of conditions. There is a pronounced effect in the decrease in the pH of the solution after 120 min. This decrease in pH of the solution can arise from the process involving the formation of inorganic phosphate and nitrate.

4   Mechanism and model development

Considering the major plausible elementary reactions of water and organics, the developed systematic chemical mechanism is presented in Table 2. The reactions are initiated by the dissociation of water molecules in the collapsing cavitation holes(the hot spot; Eq.(1)). Atomic hydrogen($H°$) and hydroxyl ($°OH$) are formed through this reaction. These two radicals recombine to form water or hydrogen molecules (H_2), or they react with oxygen molecules(O_2) to yield hydroperoxide(HO_2) or hydrogen peroxide(H_2O_2; Eqs.(2—6)). These radicals further react with the H_2O_2 produced in these reactions to form hydrogen molecules(H_2), water or other radicals(Eqs.(7—10)).

In the presence of dissolved nitrogen, nitrogen molecules(N_2) decompose in the collapsing cavitation holes(Eq.(11)) to form atomic nitrogen(N). Following a series of reactions, N then react with the OH radicals produced from the dissociation of water and related reactions to yield nitrate and nitrite(Eqs.(12—15)). Atomic nitrogen also reacts with $H°$ and O_2 molecules to regenerate N_2 and H_2 molecules and to produce nitric oxide(NO) and O_2 radicals(Eqs.(16—18)).

Oxygen molecules dissolved in the water also decompose in the cavitation holes(Eq.(19)) to produce atomic oxygen(O) and compete with H in Eq.(2), leading to the formation of hydroxyl radicals(Eq.(20)). Atomic oxygen then reacts with H_2 molecules, H_2O_2 and HO_2 to form O_2 molecules and other radicals, such as $H°$ and $°OH$(Eqs.(21—23)). The target contaminant, omethoate, present in water is either directly decompose in the cavities(Eq.(28)) or reacted by radicals(Eqs.(24—27)).

On the basis of chemical reaction mechanism proposed above, the primary pathway appears to be the thermal dissociation in the collapsing cavitation holes, such as those represented in Eqs.(1), (11), (19) and (28). The high temperature and pressure created during cavitation provide the activation energy required for the bond cleavage. Water, nitrogen, oxygen, and omethoate molecules decompose in these cavities to directly form the radicals. These radicals then either react with each other to form new molecules and radicals or diffuse into the bulk liquid to serve as reactants. The secondary reactions seem to be in the bulk-liquid phase, where omethoate and other molecules are reacted by those radicals, which are generated in the cavities (Nick, 1994). Therefore to better clarify these reactions, the whole system can be divided into two major areas:

(1) The collapsing cavitation holes in which molecule vapors may reach critical conditions of temperature and pressure and decompose. These reactions follow first order rate constant

Table 2   Proposed chemical kinetic mechanism

Water dissociation:	In the presence of oxygen
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1. $H_2O \longrightarrow H° + °OH$	19. $O_2 + \cdots\cdots \longrightarrow 2O$
2. $H° + H° \longrightarrow H_2$	20. $H° + O_2 \longrightarrow °OH + O$
3. $H° + O_2 \longrightarrow HO_2$	21. $O + H_2 \longrightarrow °OH + H°$
4. $HO_2 + HO_2 \longrightarrow H_2O_2 + O_2$	22. $O + HO_2 \longrightarrow °OH + O_2$
5. $°OH + °OH \longrightarrow H_2O_2$	23. $O + H_2O_2 \longrightarrow °OH + HO_2$
6. $H° + °OH \longrightarrow H_2O$	In the presence of omethoate
7. $H° + H_2O_2 \longrightarrow °OH + H_2O$	24. Pesticides + $°OH \longrightarrow$ products
8. $H° + H_2O_2 \longrightarrow H_2 + HO_2$	25. Pesticides + $O \longrightarrow$ products
9. $°OH + H_2O_2 \longrightarrow HO_2 + H_2O$	26. Pesticides + $H° \longrightarrow$ products
10. $°OH + H_2 \longrightarrow H° + H_2O$	27. Pesticides + $HO_2 \longrightarrow$ products
In the presence of nitrogen	28. Pesticides + $\cdots\cdots \longrightarrow$ products
......	
11. $N_2 + \cdots\cdots \longrightarrow 2N$	
12. $N + °OH \longrightarrow NO + H°$	
13. $NO + °OH \longrightarrow HNO_2$	
14. $NO + °OH \longrightarrow NO_2 + H°$	
15. $2NO_2 + H_2O_2 \longrightarrow HNO_2 + HNO_3$	
16. $H° + N \longrightarrow NH$	
17. $NH + NH \longrightarrow N_2 + H_2$	
18. $N + O_2 \longrightarrow NO + O$	

(Fig, 2; Eq. (28)).

The rate law for such reactions is written as: $V = k_{obs}$ [omethoate] $= -$ d[omethoate]/dt.

Where, $k_{obs} = k_{H_2O} + k_{OH}^-$ [OH$^-$] + k$_H^+$ [H$^+$].

(2) The bulk-liquid phase under normal operating temperatures and pressures, in which molecules are reacted by radicals to form new products and the rate constant appears to be second order rate of reaction, in which the destruction of omethoate can be represented by the following equation (Eqs. (24)—(27)):

$-$ d[omethoate]/d$t = k$[OH][omethoate] $+ k$[H][omethoate] $+ k$[HO$_2$][omethoate] $+ k$[O]] [omethoate].

By considering Fig. 2 and Table 1, it is concluded that the omethoate undergo two kinds of reactions i.e., the direct destruction inside the cavitations are dominant, which follow first order rate of reaction and undergo secondary reactions in the bulk liquid which follow second order rate of reaction. It has been reported that at low concentration, the destruction of organic compounds follow first order but at high concentrations this is a second order reaction.

5   Conclusions

Ultrasonic irradiation process is a promising and effective process for the destruction of omethoate in water. More than 98% rate of hydrolysis is achieved through this process. The major reactions are the destruction inside the cavitation bubbles because the rate of reaction increases by subjecting more soluble and low thermal conductive gas that results the increase of temperature inside the collapsing bubble. The rate of hydrolysis is almost unaffected by increasing the temperature of the bulk liquid. This shows that a few secondary reactions of omethoate take place in the solution. Decreasing the concentration increases the rate of hydrolysis, so this ultrasonic irradiation is a valuable tool to hydrolyze those solutions, which contain low concentration of organics. pH value of the irradiation solution is found to have a little effect upon the omethoate destruction. This is an advantage over other methods where the adjustment of pH is a problem, so solution having any pH can result efficient hydrolysis.

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