DEGRADATION OF DIISOPROPYL METHYLPHOSPHONATE IN AQUEOUS SOLUTIONS BY ULTRASONIC IRRADIATION COMBINED WITH OXIDATION PROCESS

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Abstract. The degradation of diisopropyl methylphosphonate (DIMP) in aqueous solutions was studied using ultrasound irradiation with a fixed frequency of 26.2 kHz, following the first-order kinetic model. The study's primary goal was to determine the influence of the following experimental parameters: the pH (at different values of 2, 7 and 10), the initial concentration of DIMP (at different concentrations: 7, 14, 30, 50, 80 mg/L), the processing time (at different periods: 15, 30, 45, 60, 80, 90 min), and the concentration of the additive CCl_4 (at different concentrations: 0.002, 0.004, 0.006, 0.008 mg/L). A DIMP removal efficiency of 98% from aqueous solution was obtained at pH 10 and 0.008 mg/L CCl_4, after an ultrasound irradiation time of 45 min, pointing out the influence of the above-mentioned experimental parameters on the DIMP degradation process.

Introduction

Organophosphorus compounds (OPCs) are organic molecules formed from phosphoric acid and its derivatives, which include at least one carbon-phosphorus bond. Pentavalent phosphorus-containing compounds are largely used for socioeconomic and ecological purposes. Organophosphorus refers to any toxic phosphorus-containing chemical compound [1]. Some examples of organophosphorus compounds are thiols, amides, or esters of phosphonic, phosphinic, phosphoric, or thiophosphoric acids with two extra phenoxy, cyanide, or thiocyanate side chains [2]. Arylated organophosphorus species offer a wide range of uses, such as pesticides, reagents involved in analytical and medicinal chemistry [3]. Many of these types of OPCs are inactive in their native form and must undergo biotransformation to become active. This biotransformation involves the oxidation of different functional groups, such as the sulfur group (*e.g.*, parathion and malathion), the thioether group (*e.g.*, disulfoton), the amide group (*e.g.*, schradan and dichrotophos), and the alkyl group (*e.g.*, triorthocresylphosphate) [4–11].

There are several ways of OPCs degradation, such as thermal decomposition, combustion, photolysis, and ultrasonic (US) irradiation [11–14]. An efficient way to study OPCs decomposition under laboratory conditions is by using diisopropyl methylphosphonate (DIMP) as a model system. Ultrasonic irradiation is a promising technique for pollutants elimination, along with chemical oxidation and biological degradation [15,16].

To the author's knowledge, no research has been previously done on the effectiveness of ultrasonic irradiation on DIMP degradation. Thus, the primary goal of the study was to determine the effect of the main process parameters on DIMP decomposition, such as pH value, treatment time, and concentrations of initial DIMP and carbon tetrachloride (CCl_4).

Experimental

Materials

The reagents used in this study: $C_7H_{17}O_3P$ diisopropyl methylphosphonate (DIMP) (Hubei Bluesky New Material INC, China), CCl_4 (Merck Co., Germany), NaOH (Loba chemie, Mumbai, India), and HCl (Thomas Baker, India), were of analytical grade. In all experimental tests, fresh distilled water was used.

The procedure of ultrasonic irradiation of DIMP samples

The primary equipment used for this study was a high-intensity ultrasonic system, consisting of an ultrasonic generator (controller), a titanium micro horn, and an ultrasonic transducer (Hielscher, UP200Ht, Germany). The experimental setup for the DIMP ultrasonic-assisted decomposition tests is depicted in Figure 1. DIMP solutions of increasing concentration (7, 14, 30, 50, 80 mg/L) at three pH levels (2, 7, and 10) were prepared, using a stirrer at a rotation of 300 rpm. Each concentration was prepared in a beaker of 1000 mL with distilled water and then transferred to a beaker of 250 mL. The solution pH was converted to acidic or basic, using HCl or NaOH respectively, and kept constant during the US-assisted treatment. Chemical treatment with CCl_4 was carried out using a chromatographic syringe for adding a controlled volume to the above prepared solutions. Irradiation processes were then initiated at a fixed frequency (26. 2 kHz) for six different treatment times (15, 30, 45, 60, 80, and 90 min). The temperature of the samples increased from initial value of 20°C up to 60°C during the irradiation process, while a temperature probe connected to a temperature controller stopped the excessive heating over 60°C by cooling with a water-jacketed vessel and switching off the USW Generator until the temperature decreased below the prescribed value.

The vessel was periodically opened, and all samples were evaluated by high-performance liquid cromatographic (HPLC) method. During the irradiation treatment, samples of the liquid mixture were withdrawn at pre-established times, in order to be analyzed by HPLC (SAYKAM, Germany).

The stationary phase of 5 mm particle size was contained in a C8 column with the following dimensions: 250 mm in length, and 4.6 mm internal diameter. The mobile phase for diisopropyl methylphosphonate is a 70:29:1 mixture of acetonitrile, water and H_3PO_4. HPLC was conducted at a flow rate of 0.7 mL/min. The UV detectors pointed out peaks at a wavelength of 210 nm. All samples were filtered using 0.2 μm syringe filter. Measurements were carefully done in triplicate, therefore the accuracy for the determined DIMP concentration is an average of measurements with standard deviation less than 10%.
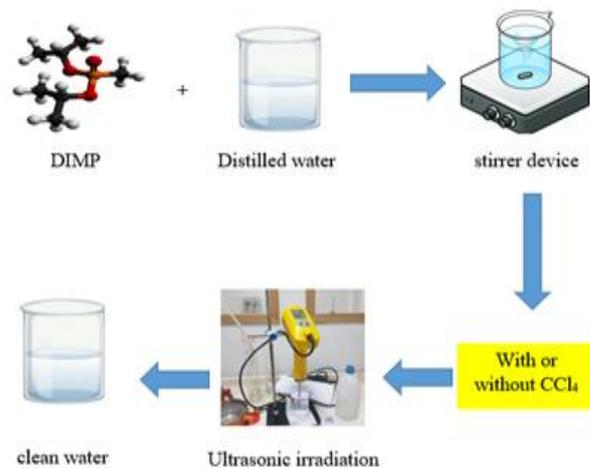
Figure 1. Brief graphical illustration of the experimental procedure of DIMP ultrasonic irradiation.

Kinetics study

Several kinetic studies on decomposition of organophosphorus wastewater pollutants were reported [17–19]. Those process follow a pseudo-first-order or pseudo-second-order kinetic law. In order to obtain the best removal rate in the frames of this study, the test was carried out at pH 10 and DIMP initial concentration of 80 mg/L was selected. The kinetic degradation of DIMP is governed by the first-order kinetic model, taking into consideration that the correlation coefficient (R^2) was closer to one (0.967) than that obtained when a second-order kinetic model was applied (0.762).

The first-order kinetic model in the linear form is given in Eq.(1).

$$ln\frac{C_o}{c} = kt \qquad (1)$$

where, C_o is the initial concentration (80 mg/L) of DIMP;

C is the concentration of DIMP after ultrasonic irradiation at different treatment times;

K is the first-order degradation rate constant, which can be derived from the line slope by plotting $ln\frac{C_o}{c} \, vs \, t$, as illustrated in Figure 2.
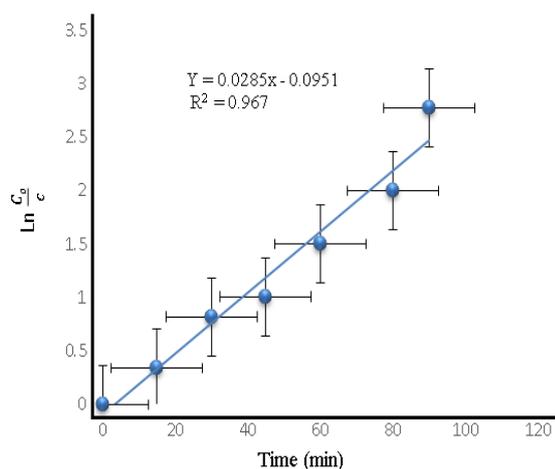
Figure 2. First-order kinetic model for DIMP concentration of 80 mg/L at pH 10.

Results and discussion

In order to reach the aim of this work related to determining the effect of process parameters (pH, processing time, initial concentration, and CCl_4 concentrations) on the pollutant of DIMP, the main results are further graphically presented.

The results of HPLC analysis for DIMP degradation are shown in Figure 3(a,b). Figure 3(a) shows a decrease in DIMP concentration in the solution of 30 mg/L initial concentration after 30 min of treatment, due to ultrasonic irradiation and generation of hydroxyl radicals-rich species. Figure 3(b) shows a decrease in the concentration of DIMP in the solution of 80 mg/L initial concentration after 30 min, due to irradiation and the addition of the chemical oxidant CCl_4, which enhanced the decomposition process based on the generation of chlorine radicals.

Effect of pH on DIMP degradation

The influence of pH on the degradation of DIMP was investigated, and the experimental findings revealed that the optimal degree of degradation proceeded in alkaline solution (pH 10) followed by neutral (pH 7) and acidic (pH 2) ones, as shown in Figure 4. Because the hydroxyl radicals generation rate during sonochemical degradation is controlled by the solution's pH, higher pH solutions result in more radicals being recombined to create H_2O_2, which reduces the amount of radicals that may be used in the intended degradation reaction [20,21]. In addition, a high pH value may generate more free radical scavengers, which reduces the HO· concentration [22,23]. Degradation kinetics using sonochemistry at various pH levels is affected by the pollutant molecule's ionic or molecular state. The influence of pH on the

degradation rate is thus highly dependent on the pKa value of the ionizable organic pollutants. Since a pKa of 7.9 indicates a strong alkaline medium, the optimal environment for DIMP degradation was found in basic solutions, where the ionic form predominates, and bubbles cannot form. This ionic species is limited to the film area of the interface and reacts with the OH radicals [24].
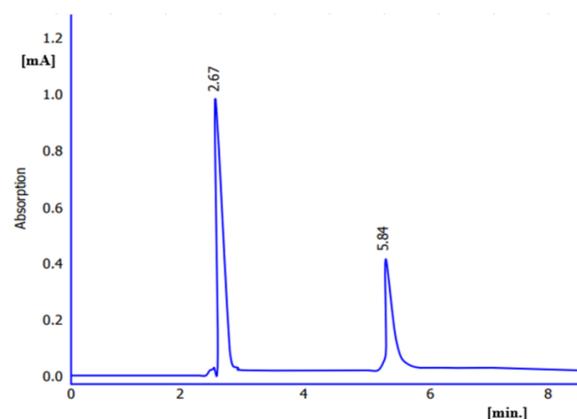
(a)
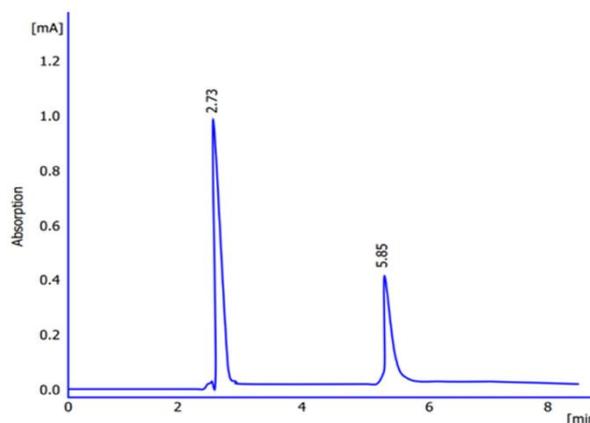
(b)

Figure 3. HPLC analysis for DIMP degradation: 30 mg/L at pH 2 and 30 min with ultrasonic irradiation (a); 80 mg/L at pH 10 and 30 min with 0.006 mg/L of CCl_4 (b).
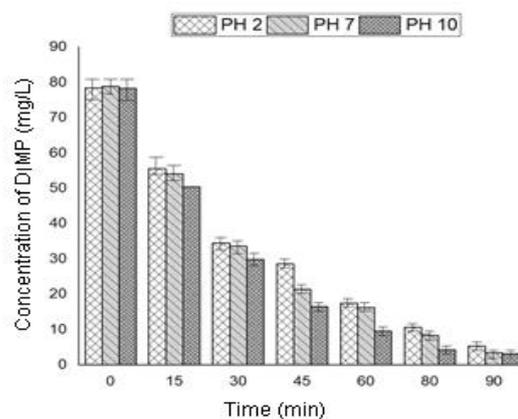
Figure 4. Time evolution of DIMP degradation in a solution of 80 mg/L initial concentration, at different pH values.
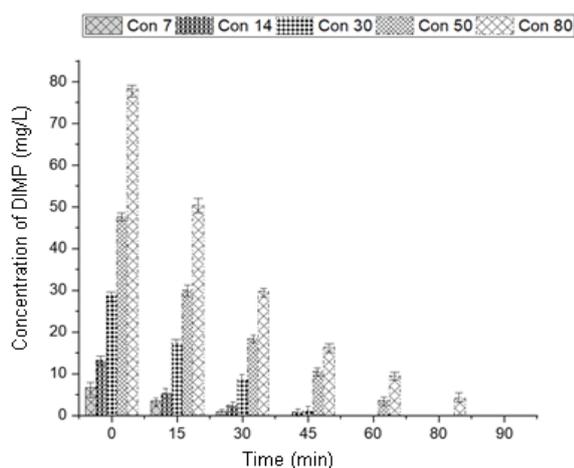
Figure 5. Time evolution of DIMP degradation at different initial concentrations, at pH 10.
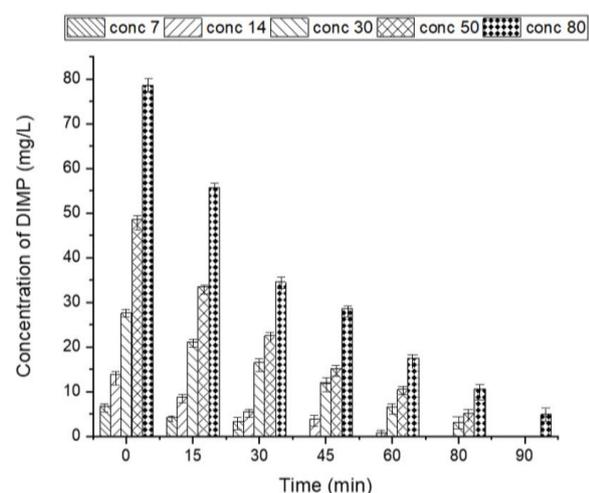
Figure 6. Time evolution of DIMP degradation at different initial concentrations, at pH 2.
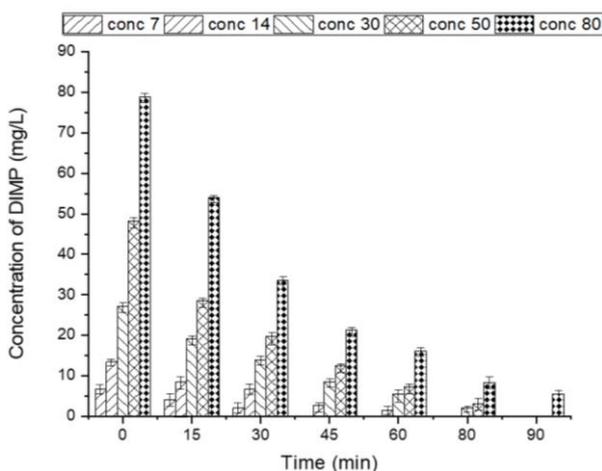
Figure 7. Time evolution of DIMP degradation at different initial concentrations, at pH 7.

Effect of DIMP initial concentration on their degradation

The initial concentration can affect the efficiency of US-assisted degradation, as the degradation efficiency increases as the concentration lowers. The DIMP degradation rate was affected by rising its initial concentration. This is because in bulk solution hydroxyl radicals were produced, which reacted with molecules during ultrasonic decomposition to form H_2O_2 [25].

Figure 5 illustrates the time evolution of DIMP concentration at different initial concentrations at pH 10 and reveals that a percent degradation rate of up to 98% occurred at a concentration of 7 mg/L in 45 min, whereas at a concentration of 80 mg/L, the degradation rate was of only 78%, which demonstrates the effect of low concentrations on the degradation processes: at lower DIMP concentration, the degradation rate was higher than at high concentration. The same results were obtained for pH 2 and 7, as shown in Figures 6 and 7.

Effect of ultrasonic treatment time on DIMP degradation

Experimental data confirm that the sonochemical degradation of DIMPS depends on the treatment/irradiation time duration. Longer exposure time results in more hydroxyl radicals being produced, as seen in Figures 5-7. Degradation of organophosphorus compounds has been studied extensively, and the obtained results are in agreement with literature data. It was reported that during the sonolysis treatment of azinphos-methyl over a period of 60 min, showed that the removal effectiveness of azinphos-methyl improved rapidly in the first 20 min, but dropped considerably between 20 and 60 min. Sonolysis's ability to remove pesticides did not change in terms of yield [26].

Effect of CCl_4 addition on DIMP degradation

The influence of CCl_4 concentration (0.002, 0.004, 0.006, 0.008 mg/L) on the degradation of DIMP in solution of 80 mg/L initial concentration was examined throughout time periods ranging from 15 to 80 min. This demonstrates that a complete elimination of 0.008 mg/L CCl_4 was achieved in a short period of time. Figure 8 and Table 1 illustrate the percentage degradation rate of DIMP over time, at different CCl_4 concentrations.

Table 1

Degradation efficiency/rate of DIMP at 80 mg/L initial concentration and pH 10, at various CCl_4 concentrations.

Time	CCl_4 Concentration (mg/L)			
(min)	0.002	0.004	0.006	0.008
15	32%	39%	51%	52%
30	66%	77%	81%	85%
45	83%	90%	94%	98%
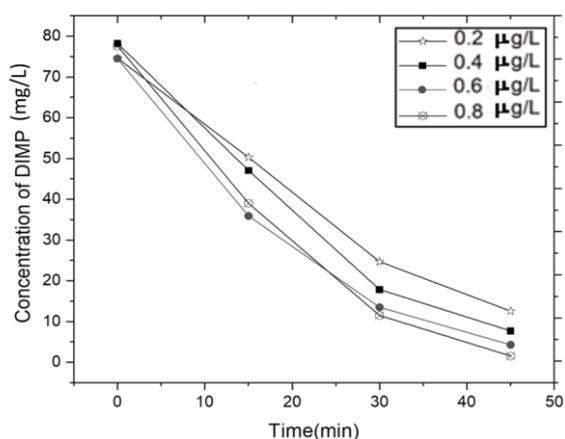
Figure 8. Degradation of 80 mg/L DIMP solution and 10 pH at different CCl₄ concentrations over 45 min treatment.

As a result of the creation of additional oxidizing species in the system, during ultrasonic treatment, the addition of carbon tetrachloride can accelerate the rate of pollutant elimination. Due to its hydrophobic nature, CCl$_4$ is easily sucked into cavitation bubbles, where it undergoes a cleavage, leading to the dissociation of CCl$_4$ molecules and the formation of highly reactive chlorine radicals [27].

The formation of chlorine radicals will result in a sequence of recombination reactions that produce highly oxidizing species inside the system [18,28]. The formation of chlorine radicals leads to the recombination of strong oxidizing types in the system, as shown in Eqs.(2-9) [28].

$$CCl_4 + USW \rightarrow \cdot CCl_3 + Cl \tag{2}$$

$$CCl_4 + USW \rightarrow : CCl_2 + Cl_2 \tag{3}$$

$$\cdot CCl_3 + USW \rightarrow : CCl_2 + \cdot Cl \tag{4}$$

$$CCl_3 + CCl_3 \rightarrow CCl_4 + : CCl_2 \tag{5}$$

$$CCl_3 + CCl_3 \rightarrow C_2Cl_6 \tag{6}$$

$$CCl_2 + : CCl_2 \rightarrow C_2Cl_4 \tag{7}$$

$$Cl + Cl \rightarrow Cl_2 \tag{8}$$

$$Cl_2 + H_2O \rightarrow HClO + HCl \tag{9}$$
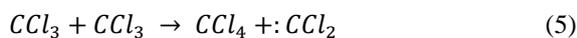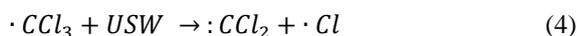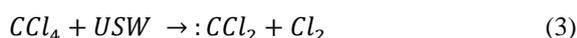
where, USW - ultrasonic waves.

Other oxidizing species attack the organic component in the bulk phase or at the gas-liquid interface, in addition to the hydroxyl radicals created by the sonolysis of water vapor in the cavitation bubble. This coordinated assault in the presence of CCl$_4$ dramatically speeds up the degradation of contaminants. It is also crucial to remember that the addition of CCl$_4$ can impact the system's final toxicity levels if the additive is not properly used during the treatment process.

If the amount of CCl$_4$ is in excess in comparison with the optimal amount, the formation of vaporous cavitation bubbles takes place due to the volatile additive, leading to the decreasing of energy during the bubble implosion and finally to the decreasing of oxidants production [28].

The obtained results of this study pointed out once again the enhancing treatment efficiency of the organic refractory pollutants from wastewater, using the combining ultrasonic irradiation with other wastewater treatment process [15], even when the ultrasonic irradiation could act independently with enough good treatment efficiency.

Conclusions

This study investigated and clarified the degradation of DIMP in aqueous solutions under ultrasonic irradiation, by means of the effect of different influence factors on DIMP decomposition, including initial concentration, pH, treatment time, CCl$_4$ concentrations, at a constant intensity of the irradiator. The highest degradation was observed at pH 10, compared with pH 2 and respectively pH 7, which values changed during experiments. The pH of the solution has a major role in the generation of hydroxyl radicals through the collision of solution molecules with each other. In particular, the pH of the solution (pH>7) played an essential impact on the effectiveness of degradation, particularly when different amounts of CCl$_4$ were utilized as a DIMP breakdown catalyst.

The most favourable experimental conditions for DIMP decomposition in the presence of CCl$_4$ were 0.008 mg/L CCl$_4$ and 45 min of ultrasonic treatment time when a quasi-complete degradation of 98% was recorded. Sonolysis of water vapour in the cavitation bubble results in the production of hydroxyl radicals, which then attack the organic substance from both liquid and gas-liquid phases. The additional chlorine radicals oxidizing species participate in this attack. The first-order kinetics model can be used to describe the degradation kinetics of DIMP in aqueous solution.

author, which is a master student from Chemical Engineering Department, University of Technology, Bagdad, Iraq. The samples were analyzed at Environment and Water Research Unit, Iraqi Ministry of Science and Technology. The authors are grateful to their universities/institutions, for the support in the frame of inter-institutional collaboration agreement, which allow the issue of this common publication.

References

1. Mukherjee, S.; Gupta, R.D. Organophosphorus nerve agents: types, toxicity, and treatments. Journal of Toxicology, 2020, 2020, pp. 1–16. DOI: https://doi.org/10.1155/2020/3007984

2. Kumar, S.; Kaushik, G.; Dar, M.A.; Nimesh, S.; López-Chuken, U.J.; Villarreal-Chiu, J.F. Microbial degradation of organophosphate pesticides: A review. Pedosphere, 2018, 28(2), pp. 190–208. DOI: https://doi.org/10.1016/S1002-0160(18)60017-7

3. Chen, J.; Fan, R.; Liu, Z.J. Reactions of organophosphorus compounds with arynes: reactivity and mechanism. Advanced Synthesis & Catalyst, 2021, 363(3), pp. 657–667. DOI: https://doi.org/10.1002/adsc.202001237

4. Jokanovi, M. Biotransformation of organophosphorus compounds. Toxicology, 2001, 166(3), pp. 139–160. DOI: https://doi.org/10.1016/S0300-483X(01)00463-2

5. Gupta, R.C. Eds. Toxicology of organophosphate & Carbamate Compounds. Academic Press, 2006, pp. 5–24. DOI: https://doi.org/10.1016/B978-012088523-7/50003-X

6. Senyurt, E.I.; Schoenitz, M.; Dreizin, E.L. Rapid destruction of sarin surrogates by gas phase reactions with focus on diisopropyl methylphosphonate (DIMP). Defence Technology, 2021, 17(3), pp. 703–714. DOI: https://doi.org/10.1016/j.dt.2020.06.008

7. Zegers, E.J.P.; Fisher, E.M. Gas-phase pyrolysis of diisopropyl methylphosphonate. Combustion and Flame, 1998, 115(1–2), pp. 230–240. DOI: https://doi.org/10.1016/S0010-2180(98)00003-0

8. Wilson, C.; Cooper, N.J.; Briggs, M.E.; Cooper, A.I. ; Adams, D.J. Investigating the breakdown of the nerve agent simulant methyl paraoxon and chemical warfare agents GB and VX using nitrogen containing bases. Organic & Biomolecular Chemistry, 2018, 16(47), pp. 9285–9291. DOI: https://doi.org/10.1039/c8ob02475h

9. Chauhan, S.; D'Cruz, R.; Faruqi, S.; Singh, K.K.; Varma, S.; Singh, M.; Karthik, V. Chemical warfare agents. Environmental Toxicology and Pharmacology, 2008, 26(2), pp. 113–122. DOI: https://doi.org/10.1016/j.etap.2008.03.003

10. Battin-Leclerc, F.; Baronnet, F.; Paternotte, G.; Leclerc, J.P.; Gourhan, R. Thermal decomposition of bis(2-chloroethyl) sulphide and bis(2-chloroethyl) ether between 300 and 500°C. Journal of Analytical and Applied Pyrolysis, 2000, 55(2), pp. 203–216. DOI: https://doi.org/10.1016/S0165-2370(99)00098-4

11. Korobeinichev, O.P.; Ilyin, S.B.; Bolshova, T.A.; Shvartsberg, V.M.; Chernov, A.A. The chemistry of the destruction of organophosphorus compounds in flames - III: The destruction of DMMP and TMP in a flame of hydrogen and oxygen. Combustion and Flame, 2000, 121(4), pp. 593–609. DOI: https://doi.org/10.1016/S0010-2180(99)00171-6

12. Korobeinichev, O.P.; Chernov, A.A.; Bolshova, A. The chemistry of the destruction of organophosphorus compounds in flames-IV: Destruction of DIMP in a flame of H_2 +O_2 +Ar. Combustion and Flame, 2000, 123(3), pp. 412–420. DOI: https://doi.org/10.1016/S0010-2180(00)00141-3

13. Blacker, N.C.; Findlay, P.H.; Sherrington, D.C. Synthesis of CuII-complexed polymers and use as catalysts in the hydrolytic decontamination of sarin nerve agent. Polymers for Advanced Technologies, 2001, 12(3–4), pp. 183–196. DOI: https://doi.org/10.1002/pat.133

14. Cao, Y.; Hui, X.; Elmahdy, A.; Maibach, H. *In vitro* human skin permeation and decontamination of diisopropyl methylphosphonate (DIMP) using dermal decontamination gel (DDGel) and reactive skin decontamination lotion (RSDL) at different timepoints. Toxicology Letters, 2018, 299(2), pp. 118–123. DOI: https://doi.org/10.1016/j.toxlet.2018.09.013

15. Raschitor, A.; Fernandez-Marchante, C.M.; Cretescu, I.; Cañizares, P.; Rodrigo, M.A. Sono-electrocoagulation of wastewater polluted with Rhodamine 6G. Separation and Purification Technology, 2014, 135(15), pp. 110–116. DOI: https://doi.org/10.1016/j.seppur.2014.08.003

16. Dehghani, M.H.; Jahed, Gh.; Vaezi, F. Evaluation of USR technology on the destruction of HPC organisms. Pakistan Journal of Biological Sciences, 2006, 9(11), pp. 2127–2131. DOI: https://doi.org/10.3923/pjbs.2006.2127.2131

17. Matouq, M.A.; Al-Anber, Z.A.; Tagawa, T.; Aljbour, S.; Al-Shannag, M. Degradation of dissolved diazinon pesticide in water using the high frequency of ultrasound wave. Ultrasonics Sonochemistry, 2008, 15(5), pp. 869–874. DOI: https://doi.org/10.1155/2020/3007984

18. Nawała, J.; Jóźwik, P.; Popiel, S. Thermal and catalytic methods used for destruction of chemical warfare agents. International Journal of Environmental Science and Technology, 2019, 16(7), pp. 3899–3912. DOI: https://doi.org/10.1007/s13762-019-02370-y

19. Yao, J.J.; Gao, N.Y.; Li, C.; Li, L.; Xu, B. Mechanism and kinetics of parathion degradation under ultrasonic irradiation. Journal of Hazardous Materials, 2010, 175(1–3), pp. 138–145. DOI: https://doi.org/10.1016/j.jhazmat.2009.09.140

20. Bagal, M.V.; Gogate, P.R. Sonochemical degradation of alachlor in the presence of process

intensifying additives. Separation and Purification Technology, 2012, 90(2), pp. 92–100.
DOI: https://doi.org/10.1016/j.seppur.2012.02.019

21. Raut-Jadhav, S.; Saharan, V.K.; Pinjari, D.V.; Saini, D.R.; Sonawane, S.H.; Pandit, A.B. Intensification of degradation of imidacloprid in aqueous solutions by combination of hydrodynamic cavitation with various advanced oxidation processes (AOPs). Journal of Environmental Chemical Engineering, 2013, 1(4), pp. 850–857. DOI: https://doi.org/10.1016/j.jece.2013.07.029

22. Raut-Jadhav, S.; Pinjari, D.V.; Saini, D.R.; Sonawane, S.H.; Pandit, A.B. Intensification of degradation of methomyl (carbamate group pesticide) by using the combination of ultrasonic cavitation and process intensifying additives. Ultrasonics Sonochemistry, 2016, 31(3), pp. 135–142. DOI: https://doi.org/10.1016/j.ultsonch.2015.12.015

23. Golash, N.; Gogate, P.R. Degradation of dichlorvos containing wastewaters using sonochemical reactors. Ultrasonics Sonochemistry, 2012, 19(5), pp. 1051–1060. DOI: https://doi.org/10.1016/j.ultsonch.2012.02.011

24. Wu, C.; Liu, X.; Wei, D.; Fan, J.; Wang, L. Photosonochemical degradation of phenol in water. Water Research, 2001, 35(16), pp. 3927–3933. DOI: https://doi.org/10.1016/S0043-1354(01)00133-6

25. González-García, J.; Sáez, V.; Tudela, I.; Díez-Garcia, M.I.; Esclapez, M.D.; Louisnard, O. Sonochemical treatment of water polluted by chlorinated organocompounds. A review. Water, 2010, 2(1), pp. 28–74.
DOI: https://doi.org/10.3390/w2010028

26. Agarwal, S.; Tyagi, I.; Gupta, V.K.; Dehghani, M.H.; Bagheri, A.; Yetilmezsoy, K.; Amrane, A.; Heibati, B.: Rodriguez-Couto, S. Degradation of azinphos-methyl and chlorpyrifos from aqueous solutions by ultrasound treatment. Journal of Molecular Liquids, 2016, 221, pp. 1237–1242.
DOI: https://doi.org/10.1016/j.molliq.2016.04.076

27. Merouani, S.; Hamdaoui, O.; Saoudi, F.; Chiha, M. Sonochemical degradation of Rhodamine B in aqueous phase: Effects of additives. Chemical Engineering Journal, 158(3), pp. 550–557.
DOI: https://doi.org/10.1016/j.cej.2010.01.048

28. Pirsaheb, M.; Moradi, N. Sonochemical degradation of pesticides in aqueous solution: Investigation on the influence of operating parameters and degradation pathway-a systematic review. RSC Advanced, 2020, 10(13), pp. 7396–7423.
DOI: https://doi.org/10.1039/c9ra11025a