

# Effective Methods for the Chemical Degradation of Organophosphate Pesticides

Ramin Karimian\*

Chemical Injuries Research Center, Systems Biology and Poisonings Institute, Baqiyatallah University of Medical Sciences, Tehran, Iran

\* Corresponding author: Ramin Karimian, karimian.r@gmail.com

Article Received: 10 September 2024 Revised: 21 October 2024 Accepted: 11 November 2024 ePublished: 10 December 2024

## Abstract

Organophosphate pesticides are extensively employed in agriculture due to their efficiency in controlling pest populations. However, their persistence in the environment and toxic effects on non-target organisms pose serious ecological and health challenges. This study provides a comprehensive evaluation of chemical degradation strategies for these compounds. The review focuses on the structural characteristics of organophosphates that influence their reactivity, highlighting hydrolysis as a key pathway for initial detoxification. Oxidation processes including photocatalysis reactions, are explored for their potential to achieve complete mineralization. By examining the efficiency, scalability, and environmental impact of these methods, this work aims to identify sustainable approaches for mitigating the adverse effects of organophosphate pesticides and enhancing chemical safety in agricultural practices.

**Keywords:** Organophosphate, pesticide, chemical method, Degradation.

## 1. Introduction

Since the mid-20th century, conventional agricultural practices have struggled to meet the growing demands of a rapidly increasing global population. This challenge has led to the widespread adoption of pesticides as a means to enhance crop yields and ensure food security. However, the active ingredients in many pesticides are inherently toxic and environmentally persistent, with half-lives that can extend over several years [1-4]. Pesticides infiltrate ecosystems via air and water pathways [5-8], accumulating within food chains and posing significant risks to biodiversity and human health [9]. Consequently, the development of technologies for the effective degradation of residual pesticides is critical to mitigating these impacts. Rather than imposing restrictions on pesticide usage, a more pragmatic approach involves advancing methods to degrade residual pesticides, thereby fostering environmental restoration and promoting sustainability [10-11]. Pesticides vary widely in their objectives, efficacy, and chemical composition, necessitating tailored degradation strategies under different environmental conditions. Among the most prominent pesticide classes are organophosphate pesticides (OPs), synthetic

compounds extensively utilized in agriculture for pest management. OPs are esters, amides, or thiol derivatives of phosphoric, phosphonic, phosphorothioic, or phosphonothioic acids, characterized by a central phosphorus atom double-bonded to either oxygen or sulfur and single-bonded to two alkoxy groups (commonly methoxy or ethoxy) alongside a leaving group. Frequently employed OPs include parathion, malathion, chlorpyrifos, diazinon, dichlorvos, phosmet, and azinphos-methyl. OPs account for approximately 75% of insecticides used in agriculture globally, with over 100 million pounds applied annually [12]. Despite representing only 10% of total pesticide use in certain regions, these compounds are applied to more than 65% of insecticide-treated crops. Their extensive use underscores the pressing need for advanced degradation methods to address their environmental persistence and toxicity effectively.

## 2. Chemical and Physical properties

The chemical structure of organophosphate pesticides (OPs) is a critical determinant of their reactivity, stability, and toxicity. At the core of these compounds lies the phosphate moiety, typically substituted with O,O-dialkyl groups, which forms ester

bonds with organic substituents. These ester bonds are prone to hydrolysis, a key degradation pathway for OPs in environmental systems. A defining feature of OPs is the presence of a phosphoryl group (P=O) or its sulfur analog, the thiophosphoryl group (P=S). Compounds containing the latter, such as malathion, are categorized as organothiophosphates but are often grouped with OPs due to their analogous biological activities. The diverse physical and chemical properties of OPs influence their environmental behavior and toxicity potential. Most OPs exhibit low water solubility and high oil-water partition coefficients (log K<sub>ow</sub>), reflecting their lipophilic nature. This characteristic facilitates their penetration through biological membranes and accumulation in lipid-rich tissues. Vapor pressures among OPs vary, with the majority demonstrating low volatility under ambient conditions, except for dichlorvos, which is significantly more volatile. These properties influence their potential for atmospheric dispersion and inhalation exposure. The stability of OPs is highly dependent on environmental pH. Many OPs are stable in slightly acidic to neutral conditions, as exemplified by parathion, which remains stable at pH levels below 7.5. Hydrolysis represents a primary degradation mechanism, converting OPs into water-soluble products that are generally less toxic at practical concentrations [13]. However, hydrolysis rates vary widely among different OP compounds; for instance, dichlorvos degrades within hours under neutral pH, whereas parathion can persist for several weeks [14]. In acidic soils (pH 4–5), these half-lives are further extended. Furthermore, the hydrophobicity of OPs spans a broad spectrum, with log K<sub>ow</sub> values ranging from -0.98 to 10.6, influencing their potential for bioaccumulation in aquatic ecosystems and environmental persistence [15]. Understanding the chemical structure and intrinsic properties of organophosphate pesticides is fundamental for evaluating their environmental impact, toxicity, and potential risks to ecosystems and human health. Additionally, this knowledge underpins the development of targeted degradation strategies, addressing the challenges posed by the persistence, mobility, and bioavailability of OPs in diverse environmental contexts.

### 3. Chemical Degradation Methods

In chemical degradation methods, pesticides are typically organic compounds containing specific functional groups that can undergo various chemical transformations. Incineration is a common yet crude method for the disposal of residual pesticides in

wastewater. At high temperatures (around 1000 degrees Celsius) and in the presence of adequate oxygen, non-volatile pesticides like methomyl can be broken down effectively [16-17]. However, this process also leads to the release of organic compounds and carbon dioxide when volatile pesticides are incinerated, resulting in significant environmental impacts. Incineration is not regarded as a suitable method for comprehensive pesticide degradation due to these adverse effects. Nevertheless, it can still serve as a cost-effective approach for wastewater treatment within the pesticide manufacturing industry.

#### 3-1- Hydrolysis Mechanisms for Organophosphate Degradation

Hydrolysis is a pivotal process in the degradation of organophosphate pesticides, serving as an effective method for their breakdown under various environmental conditions. This process involves the cleavage of chemical bonds through the addition of water molecules, resulting in the formation of less toxic byproducts. The hydrolysis of organophosphates can proceed via different mechanisms, each with its own specific characteristics and efficiency.

#### 3-2- Alkaline hydrolysis

Alkaline hydrolysis represents a powerful method for the decomposition of organophosphate pesticides. In this process, hydroxide ions act as nucleophiles in a bimolecular nucleophilic substitution reaction. The alkaline hydrolysis mechanism can follow two distinct pathways depending on the orientation of the attacking nucleophile. In one pathway, the reaction progresses through a multi-step process characterized by the formation of a pentavalent intermediate. Alternatively, a one-step mechanism can occur, involving a single transition state. The efficiency of alkaline hydrolysis is influenced by factors such as the pH of the solution and the specific structure of the organophosphate compound. Research indicates that alkaline hydrolysis can significantly accelerate the degradation process compared to natural degradation methods. For instance, studies have shown that a crude cell extract from a mixed bacterial culture can hydrolyze parathion at a rate approximately 2,450 times faster than the chemical hydrolysis using 0.1 N sodium hydroxide at 40°C. This version is more concise, uses specific scientific terms appropriately, and provides context on the efficiency and impact of alkaline hydrolysis in the degradation of organophosphate pesticides [13].

### 3-3- Acid-catalyzed hydrolysis

While alkaline hydrolysis is a well-studied method for the degradation of organophosphate pesticides, acid-catalyzed hydrolysis also plays a significant role in their breakdown. This mechanism becomes particularly relevant in acidic soil environments or during certain industrial applications. The rate of acid-catalyzed hydrolysis can vary widely depending on the specific organophosphate compound and the pH of the surrounding medium. Acid-catalyzed hydrolysis typically involves the protonation of the phosphoryl oxygen, which increases the susceptibility of the phosphorus center to nucleophilic attack. This process can be further facilitated by the presence of certain metal ions or clay minerals in the soil, which can act as catalysts, thereby accelerating the hydrolysis rate.

### 3-4- Enzymatic hydrolysis

Enzymatic hydrolysis serves as one of the most effective and environmentally sustainable approaches for the degradation of organophosphate pesticides. A variety of enzymes, such as organophosphorus hydrolase (OPH), methyl parathion hydrolase (MPH), and organophosphorus acid anhydrolase (OPAA), have shown notable catalytic activity against these compounds. Among these, phosphotriesterase (PTE), belonging to the amidohydrolase superfamily, has been extensively investigated for its proficiency in hydrolyzing a diverse array of organophosphate substrates. PTE displays exceptional catalytic efficiency, with its hydrolysis of paraoxon nearing the diffusion limit in a solvent [14].

The mechanism of enzymatic hydrolysis generally occurs in two stages. The initial stage involves a nucleophilic attack by a hydroxide ion on the phosphorus atom, which leads to the formation of a pentacoordinated phosphorus intermediate. The subsequent stage entails the cleavage of the bond between the phosphorus atom and the oxygen of the leaving group, culminating in the formation of an enzyme-product complex [15]. The catalytic performance of these enzymes is affected by several factors, including pH, temperature, and the presence of organic solvents. Notably, the optimum pH for the enzymatic hydrolysis of eight commonly used organophosphate pesticides ranges from 8.5 to 9.5, with less than 50% of maximal activity observed at pH 7.0 [13].

Enzymatic hydrolysis presents numerous advantages for the degradation of organophosphate pesticides. These enzymes demonstrate the capability

to rapidly hydrolyze nerve agents while being environmentally benign, non-flammable, and non-corrosive. Furthermore, they can be safely and easily disposed of, positioning them as promising candidates for decontamination efforts [14]. In summary, various hydrolysis mechanisms, including alkaline, acid-catalyzed, and enzymatic processes offer effective strategies for the chemical degradation of organophosphate pesticides. A comprehensive understanding of these mechanisms is essential for devising approaches to reduce the environmental impact and toxicity of these commonly used agricultural chemicals, ultimately enhancing chemical safety and promoting environmental protection.

### 3-5- Oxidation Processes

Oxidation processes (OPs) have emerged as highly effective technologies for the degradation of organophosphate pesticides in aquatic environments. These processes operate by generating highly reactive hydroxyl radicals ( $\text{OH}^\bullet$ ), which can rapidly and non-selectively oxidize organic molecules, facilitating their breakdown. OPs have garnered considerable attention for their capability to degrade stubborn organic pollutants, including pesticides, pharmaceuticals, and organic solvents. In these processes, transition metals commonly act as catalysts, while compounds such as hydrogen peroxide are utilized along with ultraviolet radiation to produce radicals [16-17].

### 3-6- Ozonation

Ozonation has emerged as an effective method for the removal of pesticide residues from various matrices, including fruits and vegetables. Ozone ( $\text{O}_3$ ) as a powerful oxidizing agent is highly effective against a broad spectrum of microorganisms and organic pollutants. The use of ozonated water has shown promise as a technique for eliminating pesticide residues from agricultural products. Research indicates that ozonation can achieve pesticide removal efficiencies ranging from 40% to 99%, depending on the specific pesticide and matrix involved [14, 18]. The effectiveness of ozonation in pesticide degradation can be attributed to several factors:

1. *Generation of hydroxyl radicals:* Ozone decomposes in water to produce hydroxyl radicals, which are highly effective in breaking down organic molecules, including pesticide residues.
2. *Direct oxidation:* Ozone can directly oxidize pesticide molecules, facilitating their degradation.

3. *Physicochemical properties*: The efficiency of pesticide removal through ozonation is influenced by physicochemical factors such as the pesticide's solubility, molecular weight, and stability.

### 3-7- Photocatalysis

Photocatalysis has garnered significant attention as an effective and environmentally friendly approach for the degradation of organophosphate pesticides. This process utilizes semiconductor photocatalysts, typically titanium dioxide (TiO<sub>2</sub>), in conjunction with UV or visible light irradiation. The photocatalytic process generates highly reactive species, such as hydroxyl radicals, which can effectively break down pesticide molecules. To enhance photocatalytic activity, researchers have investigated the development of heterojunctions by combining different semiconductors. For example, the combination of  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> and MgO has shown promising results in the photocatalytic degradation of organophosphate pesticides. These composite materials facilitate improved charge separation and increased light absorption, leading to enhanced catalytic performance [19-21].

### 4. Conclusion

The investigation of chemical degradation methods for organophosphate pesticides reveals promising strategies to address environmental contamination and health risks. Hydrolysis mechanisms, including alkaline, acid-catalyzed, and enzymatic processes, have been shown to effectively break down these harmful compounds. Additionally, oxidation reactions such as ozonation and photocatalysis demonstrate significant potential for pesticide degradation in various environmental contexts. These findings carry important implications for agricultural practices and environmental protection initiatives. By advancing our understanding and implementation of these degradation methods, we can mitigate the impact of organophosphate pesticides on ecosystems and human health. This research paves the way for the development of more sustainable pest control strategies and enhanced remediation techniques, ultimately contributing to a safer and cleaner environment.

### Acknowledgment

Author gratefully acknowledges support of this work by Chemical Injuries Research Center, Systems Biology and Poisonings Institute, Baqiyatallah University of Medical Sciences, Tehran, Iran.

### References

1. Concha C, Manzano CA. Priority pesticides in Chile: Predicting their environmental distribution, bioaccumulation, and transport potential. *Integrated Environ Assess Manag* 2022;00:1–8. <https://doi.org/10.1002/ieam.4680>.
2. Coperchini F, Awwad O, Rotondi, M, Santini F, Imbriani M. Thyroid disruption by perfluorooctane sulfonate (PFOS) and perfluorooctanoate (PFOA). *J Endocrinol Invest* 2017;40:105–121. <https://doi.org/10.1007/s40618-016-0572-z>.
3. Yu J, Xia Y, Tian X, Zhang R, Bian Z. Endocrine disrupting compounds (EDCs) in source water, finished water, and tap water from drinking water treatment plants and its human risk assessment in Chengdu Plain, China. *Human and Ecological Risk Assessment: An International Journal* 2022;8:862-877. <https://doi.org/10.1080/10807039.2022.2105195>.
4. Pitzer EM, Williams MT, Vorhees CV. Effects of pyrethroids on brain development and behavior: deltamethrin. *Neurotoxicol Teratol* 2021;87:106983. <https://doi.org/10.1016/j.ntt.2021.106983>.
5. Bhattacharyya S, Poi R, Mandal S, Baskey M, Hazra DK, Saha S, et al. Method development, validation, monitoring, seasonal effect and risk assessment of multiclass multi pesticide residues in surface and ground water of new alluvial zone in eastern India. *Environ Sci Pollut Res* 2022;29:17174–87. <https://doi.org/10.1007/s11356-021-16959-9>.
6. Gunier RB, Raanan R, Castorina R, Holland NT, Harley KG, Balmes JR, et al. Residential proximity to agricultural fumigant use and respiratory health in 7- year old children. *Environ Res* 2018;164:93–9. <https://doi.org/10.1016/j.envres.2018.02.022>.
7. Bhandari G, Atreya K, Scheepers PTJ, Geissen V. Concentration and distribution of pesticide residues in soil: Non-dietary human health risk assessment. *Chemosphere* 2020;253:126594. <https://doi.org/10.1016/j.chemosphere.2020.126594>.
8. Darrin AT, Kolpin DW, Michelle LH, Kimberlee KB, John DV, William FR. Prevalence of neonicotinoids and sulfoxaflo in alluvial aquifers in a high corn and soybean producing region of the Midwestern United States. *Science of The Total Environment* 2021;782:146762. <https://doi.org/10.1016/j.scitotenv.2021.146762>.
9. Mali H, Shah CD, Raghunandan BH, Prajapati AS, Patel DH, Trivedi U, et al. Organophosphate pesticides an emerging environmental contaminant: pollution, toxicity, bioremediation progress, and remaining challenges. *J Environ Sci* 2023; 127:234–50. <https://doi.org/10.1016/j.jes.2022.04.023>.
10. Bolan S, Padhye LP, Mulligan CN, Alonso ER, Saint -Fort R, Jasemizad T, et al. Surfactant-enhanced mobilization of persistent organic pollutants: potential for soil and sediment remediation and unintended consequences. *J Hazard Mater* 2023;443:130189. <https://doi.org/10.1016/j.jhazmat.2022.130189>.
11. Bokade P, Gaur VK, Tripathi V, Bobate S, Manickam N, Bajaj A. Bacterial remediation of pesticide polluted soils: exploring the feasibility of site restoration. *J Hazard Mater* 2023;441:129906. <https://doi.org/10.1016/j.jhazmat.2022.129906>.
12. Ruomeng B, Meihao O, Siru Z, Shichen G, Yixian Z, Junhong C, Ruijie M, Yuan L, Gezhi X, Xingyu C, Shiyi Z, Aihui, Z, Baishan F. Degradation strategies of pesticide residue: From chemicals to synthetic biology. *Synthetic and Systems Biotechnology* 2023;8(2):302–313. <https://doi.org/10.1016/j.synbio.2023.03.005>

13. Yaxin L, Shuai G, Langjie Y, Jianhua L, Chunsheng L, Da Ch, Fang M, Letcher R, Guanyong S. Organophosphate (OP) diesters and a review of sources, chemical properties, environmental occurrence, adverse effects, and future directions. *Environment International* 2021;155, 106691. <https://doi.org/10.1016/j.envint.2021.106691>.
14. Jyoti K, Madhu Kh, Shailendra K. A treatise on Organophosphate pesticide pollution: Current strategies and advancements in their environmental degradation and elimination. *Ecotoxicology and Environmental Safety* 2021;207:111483. <https://doi.org/10.1016/j.ecoenv.2020.111483>.
15. Monique C, Joyce SFDA, Samir FdAC, Jacqueline RSS, Arlan SG, Tanos CCF, Kamil K, Humberto RB. Biodegradation of Organophosphorus Compounds Predicted by Enzymatic Process Using Molecular Modelling and Observed in Soil Samples Through Analytical Techniques and Microbiological Analysis: Comparison. *Molecules* 2020;25(1),58; <https://doi.org/10.3390/molecules25010058>.
16. Li XH, Xu H, Liu FM, Peng QR, Chen F, Guo YY. Utilizing Plackett-Burman design and response surface analysis to optimize ultrasonic cleaning of pesticide residues from rape. *J Sci Food Agric*. 2022;102:2061–2069. doi: 10.1002/jsfa.11545.
17. Wang H, Meng Z, Liu F, Zhou L and Lu H, Characterization of boscalid-induced oxidative stress and neurodevelopmental toxicity in zebrafish embryos. *Chemosphere* 2020;238:e124753. <https://doi.org/10.1016/j.chemosphere.2019.124753>.
18. Mehmet AO, Jean-Jacques A. Advanced Oxidation Processes in Water/Wastewater Treatment: Principles and Applications. A Review. *Critical Reviews in Environmental Science and Technology*. 2014;2:2577-2641. <https://doi.org/10.1080/10643389.2013.829765>.
19. Fouad K, Bassyouni M, Alalm MG, Saleh MY. Recent developments in recalcitrant organic pollutants degradation using immobilized photocatalysts. *Appl Phys A: Mater Sci Process*. 2021;127:612. <https://doi.org/10.1007/s00339-021-04724-1>.
20. Sharma T, Kaur M, Sobti A, Rajor A, Toor AP. Sequential microbial-photocatalytic degradation of imidacloprid. *Environ Eng Res*. 2020;25:597–604. <https://doi.org/10.4491/eer.2019.150>.
21. Suryaman D, Hasegawa K, Kagaya S. Combined biological and photocatalytic treatment for the mineralisation of phenol in water. *Chemosphere*. 2006;65:2502–2506. <https://doi.org/10.1016/j.chemosphere.2006.07.059>.