TOXICITY, NATURAL AND INDUCED DEGRADATION OF CHLORPYRIFOS

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ABSTRACT

The increase in demand for agricultural products due to the growing population led to excessive inputs of pesticides in the agriculture field which resulted in contamination of the environmental segments of life i.e. air, water, and soil. Chlorpyrifos is one of the most extensively used broad-spectrum organophosphate insecticides. The usage and broad-spectrum applicability of chlorpyrifos lead to widespread contamination in the environment and serious damage to non-target organisms. Moreover, metabolites of chlorpyrifos i.e. chlorpyrifos-oxon and 3,5,6-trichloro-2-pyridinol are found to be more toxic than its parent compound. This review emphasizes on various toxic effects of chlorpyrifos and its metabolites on living organisms. The efforts put to develop the efficient methods for the degradation of the insecticide in soil and water i.e. photocatalytic, biodegradation, electrochemical and others have been discussed. Analytical techniques used for the study of degraded products and various intermediates formed during degradation under different conditions are summarized. It also includes the general pathway for the degradation of chlorpyrifos. The review will help in the development of tools for degradation and mineralization of organophosphate pesticides by knowing the mechanism of degradation and applicability of the developed process at a large scale.

Keywords: Chlorpyrifos, insecticide, degradation pathway, toxicity, intermediates.

INTRODUCTION

The issue of food security and to provide the food to an ever-increasing global population, the use of pesticides in agriculture has increased after World War II and different types of pesticides belonging to various groups had been developed. The occurrence of residues of these chemicals and their metabolites in every component of the environment, i.e. air, water and soil along with that in the crops, vegetables, and fruits due to their excessive use and emissions during their production poses serious threats to human and environmental health. [1] Pesticides may be neurotoxic, carcinogenic, immunotoxic, etc. and also affect hormonal growth and development. [2-5] Therefore, their removal from the environment is of utmost importance.

The pesticides are sold and used without certain restrictions in most of the developing countries. Although crop production increases on pesticides application as weeds, insects, fungi, rodents, etc are killed, but it affects human health when enter in living organisms through inhalation or consumption of contaminated food and water. [6-8]

Pesticides are classified in several ways, i.e. according to their occurrence in nature, their target, and their chemical structure, etc. The different classification of pesticides is summarized in Figure 1.

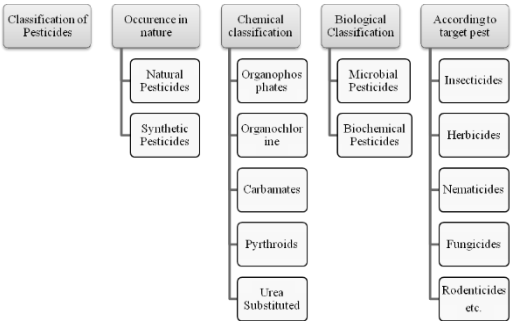

Figure 1. Classification of pesticides.

After the ban on organochlorine pesticides i.e. Dichlorodiphenyltrichloroethane, development of organophosphorus pesticides (OPs), fundamentally esters of phosphoric acids, came into enforced in 1940 due to their low persistence as compared to organochlorine pesticides and high killing efficiency. OPs like malathion, parathion, chlorpyrifos, diazinon, etc. widely used pesticides in agricultural fields, homes, etc., probably due to their low cost, low toxicity, and high effectiveness. OPs, when inhaled in small amounts are tolerable, but above the tolerance limit, it may be fatal. Such instances can occur in the countries where these pesticides are sold and used without certain precautions and regulations to an alarming extent.

The intentional or unintentional inhalation of such pesticides above a certain limit is toxic as they could inhibit the functioning of cholinesterase and causes neurotoxicity. OPs like tetrachlorvinphos and parathion are now recognized as carcinogenic under Group 2B and glyphosate, malathion and diazinon under Group 2A by International Agency for Research on Cancer. [9]

Chlorpyrifos [O,O-diethyl O-(3,5,6-trichloro-2-pyridinyl) thiophosphate] (CP), one of the most extensively used broad-spectrum OPs, is sold under various trade names like Dursban, Lorsban etc. It is used throughout the world to control a variety of chewing and sucking insects, flies, mosquitoes, and mites on a range of economically important crops, including cotton, wheat, rice, vegetables, citrus fruit, bananas, potatoes, coffee, cocoa, tea, etc. [10] It is also registered for use on lawns, ornamental plants, domestic dwellings as well as commercial establishments. [11] Chlorpyrifos can persist in soil with a half-life of 60-120 days, however, persistence is observed to be strongly dependant on pH, climate conditions and other factors of soil and it may range from two weeks to more than one year. [11-15] The persistence studies of B.K. Singh and co-workers [16,17] recognized the half-life of CP from 36-46 days in soil. The soil with slightly alkaline pH was reported to degrade CP in 90 days. The physical and chemical properties of CP are depicted in Table [a].

Table [a]. Physical/Chemical properties of CP.

Property	Value	Reference
Chemical Name	O,O-diethyl O-(3,5,6-trichloropyridin-2-yl) thiophosphate	
Molecular & Empirical formula	$C_9H_{11}Cl_3NO_3PS$	
Molecular weight	350.6 a.m.u.	
Trade names	Dursban®, Lorsban®, Empire 20, Equity, and Whitmire PT 270	[18]
Chemical Abstracts Service number	2921-88-2	[18]
United Nation number	2783	
Globally Harmonized System number	3	
Chemical number	59101	[18]
Physical State	Solid	
Colour	White	
Melting point	41- 42°C	
Vapour pressure	1.87×10^{-5} mm Hg at 20°C	
Odour	Mild Mercaptan	
Decomposition temperature	160°C	
Solubility in water	Less than 2 mg L^{-1} at 25°C	[11]
Log partition coefficient	4.82-5.11 (Octanol-water)	[142]
Acceptable Daily Intake	0.003 mg kg^{-1} d^{-1}	
Maximum Permissible	0.18 mg d^{-1}	
Intake		

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Evaluation of United State Environment Protection Agency and Food Quality Protection Act expresses risk to human health and 10X safety factor for children with excessive inhalation of CP. [18] Unfortunately, it shows significant harmful effects on aquatic animals and humans also, when it is present in the high amount by inhibiting the functioning of the enzyme acetylcholinesterase (AcHE) which in turn disrupts the transfer of the message from one neuron to another neuron which may prove to be fatal. [19-20]

Literature survey shows that there are reviews on toxicity, [21] food safety of pesticides, [22] bacterial degradation, [23,24] bioremediation of pesticides and petroleum hydrocarbons, [25,26] Photodegradation, [27,28] and pesticide formulations [29] which express the usage, toxic impacts, need and techniques of degradation of the various pesticides. Racke [11] in his review summarized the research information available at that time regarding the environmental fate of chlorpyrifos. To the best of our knowledge, there are no such efforts made on detailing the toxic impacts of CP on non-target organisms and the induced methods involved in the degradation of CP.

The purpose of this study is to review the toxic effects of CP on environment and animal health i.e. non-target organisms. Various methods like bacterial degradation, ultrasonication, and photolytic degradation, photocatalytic degradation with TiO_2, ZnO and Ag, Au, Fe based nanoparticles (NPs), etc. developed for the degradation of the insecticide are also summarized here. Analytical techniques used for the study of degraded products and various intermediates formed during the degradation of CP are included to establish the general pathway for the degradation of CP under different conditions.

Toxic Effects of CP

According to one of the definitions of the insecticide, it is the substance that is poisonous and efficient to target organisms and is safe to non-target organisms and the environment. As CP is not selective in nature, therefore the poisonous nature of CP is not only restricted to target organisms, but it also shows paramount toxic effects on non-target organisms including humans, even at low concentrations. The insecticidal action of CP involves the inhibition in the functioning of AcHE and the insect undergoes decomposition and commences to decay slowly.

CP present in the environmental matrices undergoes oxidation and CP (P=S) is converted into CP (P=O) i.e. chlorpyrifos-oxon (CPO) which is found to be more toxic than CP itself. Oxidation of CP to CPO is enhanced by the presence of ·OH radicals in atmospheric conditions. [30] The structure of CP and CPO is shown in Figure 2(a) and 2(b).

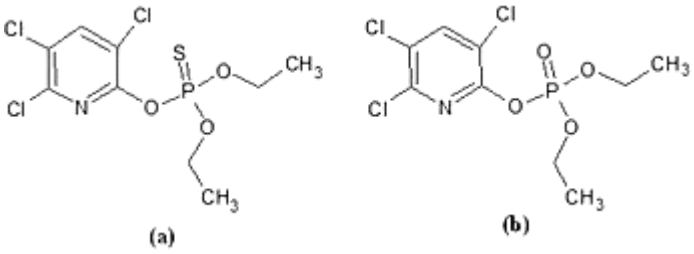

Figure 2. Structure of (a) Chlorpyrifos (b) Chlorpyrifos-oxon.

Chlorpyrifos is very harmful to various life forms even at a very low concentration and can kill aquatic animals. The toxic effects of CP at a low concentration has been confirmed through tests and studies performed on various animals.

The significant inhibition in the activity of enzyme AcHE with exposure at a low concentration of CP in combination with CPO is reported. [31] The study also reported that 3,5,6-trichloropyridinol (TCP) did not show significant inhibition in enzyme activity. The toxic effects of CP on zebrafish for short and long term exposure of different doses of CP (5µM and 2µM) had been observed by Canela et al. [32] The higher dose of CP produced greater variations in zebrafish muscles as compared to a lesser dose. However, no direct relation of time with toxicity was observed. The results obtained after continues observation on zebrafish muscle confirmed oxidative stress, disruption of neurotransmitter metabolism, and muscle exhaustion in zebrafish. Yen et al. [19] reported the inhibition of AcHE activity and a simultaneous decrease in locomotor activity in zebrafish at a low concentration of CP. Mccollister et al. [33] observed not only inhibition of AcHE but also in the activity of brain and plasma cholinesterase which might have been recovered with time. Similar recovery results were observed in studies of Drevenkar et al. [34] when erythrocyte AcHE and blood cholinesterase activities were measured in serum and urine of persons exposed with chlorpyrifos. The studies [35-37] reported significant inhibition by chlorpyrifos in plasma cholinesterase, butyrylcholinesterase and in gammarus pulex AcHE activity.

Various studies [38-40] on fish and mice are reported to prove significant oxidative stress on the exposure of CP. CP alone results in 2-deoxyribosenucleic acid (DNA) damage but presence of lipopolysaccharides along with CP enhances damage even at a low concentration, as found in fish Gasterosteus aculeeatus. [41] The variation in the concentration of insecticide delays the effect produced by insecticide on *Japanese medaka*. The introduction of a sublethal concentration of CP for a longer period and a lethal concentration for shorter period cause similar variation in social behavior. However, inhibition in blood cholinesterase activity was not observed with sublethal concentration. [42]

Significant inhibition and variations are observed on the behavior of rats even at the exposure of low concentration of CP. The variation in Ribose nucleic acid (RNA) concentration of rats in the brainstem was more prominent than in the forebrain. [43] Young animals are more sensitive as compared to adult animals with exposure to CP and a faster recovery was reported in young rats. [44] The neonatal rats are highly sensitive towards plasma and brain cholinesterase activity. [45,46] The concentration dependent inhibition in the normal movement of membrane bound organelles in the presence of CP at higher concentrations. [47] The studies [48-52] over rats give suitable evidence for the toxic nature of CP and reported the anxiety in rats during the pregnancy period, oxidative stress, anti-androgenic activity, and cholinesterase inhibition, and the changes in the functioning of brain cells.

CP shows disease toxicant interaction with mutant huntingtin. The mutant enhances the neurotoxicity induced by CP with the increase in the production of reactive oxygen species and nicotinamide adenine dinucleotide phosphate (NADPH) oxidase activity. The study recognized that CP-induced toxicity is enhanced via NADPH oxidase-mediated oxidative stress. [53] Dubey et al. [54] observed the effect of CP and fungicide propiconazole on barley (*Hordeum vulgare L. variety Karan-16*). CP showed more increase in the chromosomal aberrations and more reduction of the germination percentage as compared to propiconazole, which indicates a high ability of CP to cause genotoxicity on barley.

Fernandes et al. [55] studied the effect of different concentrations (0-0.08% w/v) of CP on the growth of green bean plants (*Phaseolus vulgaris*). Plants treated with a higher dose of CP resulted in the smaller size of leaves, and a reduction in the number of pods after 45 days of treatment. It could affect the yield of crops also. Along with induced oxidative stress, changes in lipid concentration, decrease in triacylglycerol content was observed and such changes could affect the nutritional value.

From the above studies it can be concluded that CP is harmful to humans and animals and due to its neurotoxic nature, it is supposed to be health hazardous for all living organisms. [56-58] However, Zhang et al. [59] reported that if chlorpyrifos is present below the maximum residual limit, then it does not produce any harmful effects and it shows useful applications at specific conditions. The toxic nature of chlorpyrifos increases in the presence of pesticides like chlorothalonil. [14] Besides showing such harmful effects, chlorpyrifos also inhibits the progress of the brain, affects the cell shape and growth of cell organelles, and inhibits carboxylsterase activity of the soil, catalase and dehydrogenase activity in the soil. [60-63]

Apart from above toxic affects the high concentration of CP inhibited the growth and amount of *chlorophyll a*. [64] The inhibitory effects on reproduction and survival of springtail folsomia candida also give evidence for the toxicity of CP. [65] Various studies on the toxic effects of CP in different organisms are summarized in Table [b].

Table [b]. Toxic effects of CP.

Sr. No.	System	Concentration of CP	Comments on toxicity	Reference
1.	Zebrafish	300 nM	Inhibited AcHE and locomoter activity	[14]
2.	Human	-	Blood Cholinesterase activity effected	[34]
3.	Zebrafish	100-300 µg L^{-1}	Developmental toxicity, Oxidative stress, Neurotoxicity, locomoter activity	[38]
4.	Mice lacking glutamate cysteine ligase	-	Oxidative stress and cytotoxicity	[39]
5.	Three spined stickleback (*Gasterosteus aculeeatus*)	1.75, 0.88, 0.35, 0.18, 0 µg L^{-1}	Lipopolysaccharides enhanced DNA damage	[41]
6.	Japanese medaka (Oryziaslatipes)	0.12 mg L^{-1} (lethal) 0.012 mg L^{-1} (sub- lethal)	Decrease in Social behavior in 12 days with sub-lethal concentration was similar in 4 days with lethal	[42]
7.	Rats	1 mg kg^{-1} (days 1-4) and 5 mg kg^{-1} (days 11-14)	Effected RNA Concentration and showed delayed neurotoxicity	[43]
8.	Rats	Young rats, 15 mg kg^{-1} Adult rats, 80 mg kg^{-1}	Behavioral changes and Brain and Blood ChE inhibition. Young animals are more sensitive than adult.	[44]
9.	Rats	-	Body weight Reduction and cholinesterase inhibition in neo-natal rat is more sensitive	[46]
10.	Rats	0.1 nM - 10 µM	Higher doses inhibited the movement of blood circulation in axons	[47]
11.	Offspring rats	0.1-10 mg kg^{-1} d^{-1}	Even low concentration of CP causes anxiety in rats during pregnancy	[48]
12.	Wistar Rats	10 mg kg^{-1}	Changes in spleen weight, Thymus Atrophy, Splenomegaly and Oxidative stress	[49]
13.	Rats	2-250 mg kg^{-1}	Anti-androgenic activity	[50]
14.	Rats	0.4-40 mg kg^{-1} (CPO)	Cholinesterase inhibition	[51]
15.	Neonatal Rats	1 mg kg^{-1} d^{-1}	Permanent changes in brain cell	[52]
16.	Green Algae (*Ankistrodesmusgracilis*)	9.37 – 150 mg L^{-1}	Inhibited the growth and cell shape of cell organelles at high concentration	[61]
17.	Soil	10 mg kg^{-1}	Inhibition of carboxylesterase activity	[62]
18.	Soil	4.8 & 24 kg ha^{-1}	Strong inhibition of hydrolases and oxidoreductases	[63]
19.	Freshwater Microalgaes *Chlorella pyrenoidosa and Merismopediasp*	0-100 mg L^{-1}	Inhibited the growth, and content of *Chlorophyll a* at high concentration	[143]
20.	Mice	0.28-8.96 mg kg^{-1}	DNA damage	[144]

The toxic effects of CP are not only observed in target organisms but the effects are also seen in non-target organisms including humans and animals. Moreover, due to properties of CP i.e. low water solubility and soil sorption, intensive and repetition applications in agriculture crops may result in the accumulation of its residue. Consequently, the increased residue of the insecticide in the soil interferes with the functional properties of beneficial soil microbes i.e. plant growth-promoting microbes (PGPM), which play a crucial role in enhancing plant growth and improving soil fertility. [66] CP also suppressed nodulation in chickpea and specific rhizobial counts in the crop rhizosphere. [67]

So it is necessary to degrade CP from the environment. Some of the major methods used so far for the degradation of CP and the techniques used for the analysis of residual CP and its degraded products were discussed in this paper.

Degradation of CP

The above studies reveal the toxic impact of CP and its potential to produce harmful effects on non-target organisms, even serious damage to human health and other organisms in the environment. There is a need to degrade the CP/CP residues from the environment. The degraded products of chlorpyrifos should be non-toxic or less toxic than chlorpyrifos itself. However, Chlorpyrifos-oxon, which is a major metabolite of chlorpyrifos, is much more toxic than chlorpyrifos itself. [68] So an analysis of degraded products is also important. Various methods and techniques are used for the degradation of CP and degraded products/intermediates of CP under different conditions. Such studies along with possible degradation products of CP are summarized below.

Natural degradation

Chlorpyrifos in the environment undergoes adsorption, hydrolysis, oxidation or photolysis. The photolytic experiment involves direct treatment of CP in sunlight or ultraviolet (UV) light from water or soil. The photolysis of CP from soil solutions in acidic and alkaline medium at different temperatures in UV and sunlight is reported. Alkaline conditions (pH 8) caused higher degradation than acidic conditions (pH 6). The degradation rate was higher at high temperature (40^oC) than at low temperature (22^oC). Moreover, the study was extended to check the influence of various metal ions. The presence of 0.01M Ca^{2+} and K^+ enhanced solar degradation, however, 0.1M Mg^{2+} and PO_4^{3-} enhanced UV degradation. [69]

CPO and TCP are major metabolites of CP during its photolysis under UV radiation. These metabolites are more water-soluble than CP itself and thus show greater field mobility. [70] The photolysis of CP also confirmed that soil with higher organic matter enhances the rate constant during photolysis. In this study medium pressure, Hg Lamp was used for photolysis and it was found to be more effective than xenon lamp or low-pressure Hg Lamp. TCP was observed to be formed as a major metabolite. [71] Identical intermediate was identified during photolysis with Xe arc lamp. [72]

The rapid degradation of the pesticide in the presence of NOx forms various multi oxygenated products and most of the products retained their pyridine ring. The degradation of CP under atmospheric conditions indicates the formation of CPO on oxidation in the presence of ·OH radicals. It is reported that the atmospheric lifetime of CP (2 hrs) is less than CPO (11 hrs). [30,73]

Biodegradation

Biodegradation involves the breakdown of large and complex substances to small and simple molecules, which are less toxic or non-toxic than their respective parent substances, with the help of microorganisms like fungi, bacteria, etc. A wide range of pesticides, present in the environment, are slowly degraded by microorganisms. As this process is economical and efficient, so, continued efforts are being done to increase the degradation ability of microorganisms. Several microorganisms are isolated for the degradation of CP. The use of microorganisms for degradation of CP in soil and water is an efficient method. During degradation, two major intermediates TCP and diethylphosphate (DEP) are detected, their structures are shown in Figure 3.

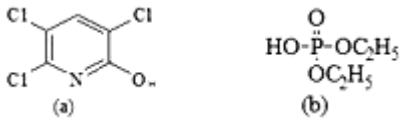

Figure 3. Structure of (a) TCP and (b) DEP.

These metabolites are further degraded into simpler organic and inorganic substances. The review on degradation ability of *pseudomonas species* for chlorpyrifos suggests that these species have the highest capacity to degrade chlorpyrifos and its metabolites TCP and DEP to nontoxic compounds like CO_2, H_2O etc. and out of various *pseudomonas species, p. putida MAS-1* is reported to be more efficient. [74] The various microorganisms which have shown high efficacy in biodegradation are listed in Table [c].

Table [c]. Various microorganisms used for bacterial degradation of CP.

Sr. No.	Microorganism	Concentration of CP	%age degradation	Degradation time	Optimum temperature	Optimum pH	Reference
1	*Pseudomonas (Iso 1) sp*	500 mg L^{-1}	>90 %	-	37°C	7.5	[75]
2	*Pseudomonas putida*	50 mg L^{-1}	>97 %	3 h	25°C	3	[76]
3	*B. safensis strain FO-36b^T*	400 mg L^{-1}	62-89 %	14 d (maximum degradation)	25°C	-	[78]
4	*B. subtilis subsp. inaquosorum strain KCTC13429^T*	400 mg L^{-1}	39 - 89 %	14 d (maximum degradation)	25°C	-	[78]
5	*B. cereus strain ATCC14579^T*	400 mg L^{-1}	38-87 %	14 d (maximum degradation)	25°C	-	[78]
6	*Bacillus subtilis Strain, Y242*	150 mg L^{-1}	95.12 %	48 h	-	8	[79]
7	*Bacillus pumilus strain C2A1 in MSM*	100-1000 mg L^{-1}	73 - 89 %	2 d -2 weeks	37°C (exp performed)	8.5 (for 50 mg L^{-1})	[81]
8	*Alcaligenes faecalis Strain DSP 3*	500 mg L^{-1}	>90 %	10 d	30°C	8	[82]
9	*Brucella melitensis M19*	50 mg L^{-1}	87%	30 d	-	-	[84]
10	*Bacillus subtilis, M119*	50 mg L^{-1}	85%	30 d	-	-	[84]
11	*Bacillus cereus, D113*	50 mg L^{-1}	-	20 d	-	-	[84]
12	*Klebsiella Species, Q1a/Q2a*	50 mg L^{-1}	77 % - 81 %	20 d	-	-	[84]
13	*Serratia marcescens, Q2b*	50 mg L^{-1}	80%	20 d	-	-	[84]
14	*Paeroginosa, Q2c*	50 mg L^{-1}	84%	20 d	-	-	[84]
15	*P. Fluorescence, P*	50 mg L^{-1}	89%	30 d	-	-	[84]
16	*Acremonium sp. strain (GFRC-1)*	300 mg L^{-1}	83.9 %	20 d	30°C	-	[85]
17	*Enterobacter strain B-14*	25 mg L^{-1}	Complete degradation	2 d	35°C	5.5-7.6	[86]
18	*Paracoccus sp.*	50 mg L^{-1}	100%	4 d	35°C	8	[87]
19	*Actinobacteria*	50 mg L^{-1}	92%	24 h	-	-	[88]
20	*Cupriavidus sp. DT-1,*	100 mg L^{-1}	>90 %	14 h (Liquid) 30 d (Soil)	30°C	7	[89]
21	*Cyperus alternifolius plant and Fe biochar*	380.3 ± 2.1 µg L^{-1}	>99 %	50 d (maximum degradation)	-	-	[92]
22	*Cladosporium cladosporioides Hu-01*	50 mg L^{-1}	>90 %	5 d	40°C	6.5	[93]
23	*Sphigomonas sp. strain Dsp-2*	100 mg kg^{-1}	98.7 %	7 d	-	8.7	[94]
24	*Mesorhizobium sp. HN3*	400 mg L^{-1}	Complete degradation	10	37°C	7	[97]
25	*Ochrobactrum sp. JAS2*	300 mg L^{-1}	Complete degradation	4 d	30°C	-	[99]

The *pseudomonas (Iso 1) sp*. has degraded more than 90% for high initial concentration of CP (500 mg L^{-1}) in bioreactors packed with polyurethane foam at pH 7.5 and temperature 37°C. [75] The *pseudomonas putida MB 285 cells* degraded 95% of CP (50 mg L^{-1}) is observed in 3 hrs only. A wide range of temperature and pH were investigated during degradation, temperature 25°C and pH 3 was found to be optimum. [76]

Pseudomonas Sp. has shown a high tendency for degradation of CP; however, other bacterial strains like *bacillus and agrobacterium sp*. have also been reported to produce comparable degradation efficiency. [77] The degradation capacity of three bacterial strains i.e. *bacillus safensis strain FO-36bT, bacillus subtilis subsp. inaquosorum strain KCTC13429T,* and *bacillus cereus strain ATCC14579T* was investigated in pesticide polluted soil of sudan. *B. Safensis* showed maximum degradation percentage (62-89%) for CP. TCP, a major metabolite of CP, was identified during degradation with *b. Safensis* only, whereas other bacterial strains did not show the formation of such intermediates after 14 days of incubation at 25°C in a mineral salt medium. [78]

Bacillus subtilis Y242 has shown the potential to utilize CP (150 mg L^{-1}) as a carbon source under alkaline medium. Lower concentration of CP (50 mg L^{-1})

was degraded completely after 24 hrs but a higher concentration of CP (150 mg L^{-1}) was degraded up to 95.12% even after 48 hrs. [79] *Bacillus cereus MCAS 02* degraded 89% of CP (50 mg L^{-1}) under optimum conditions pH 7.5, shaking speed 90 rpm, temperature 32°C and yeast extract concentration 2.5 g L^{-1} was observed. [80]

Bacillus strain C2A1 [81] and *alcaligenes faecalis* [82] had been prospered to degrade CP under alkaline medium. *Bacillus Strain C2A1* has shown 89% degradation of high concentration of CP (1000 mg L^{-1}) in a liquid medium within 15 days under alkaline medium at 37°C temperature. *Bacillus pumilus strain C2A1* [83] had shown a higher potential to degrade CP and its metabolite TCP when bacterial strain is inoculated with plant ryegrass. Plant bacteria partnership enhanced degradation of CP (50 mg kg^{-1}) to 97.5% whereas with alone plant and alone ryegrass only 89% and 76% degradation was achieved after 45 days of incubation, respectively. CP (50 mg kg^{-1}) has been degraded 75-87% with *pseudomonas fluorescence, brucella melitensis, bacillus subtilis, bacillus cereus, klebsiella species, serratia marcescens* and *pseudomonas aeroginosa* as consortium. However, *p. aeroginosa* showed 92% degradation when applied individually. [84]

The fungal degradation of CP (300 mg L^{-1}) with *acremonium sp. strain (GFRC-1)* in soil enriched with carbon and nitrogen. Nearly, 84% degradation is achieved in 20 days. [85] The *enterobacter strain B-14* utilized CP as a sole source of carbon and phosphorus. The degradation was complete in nearly 2 days at temperature 35°C in mineral salt medium inoculated with nitrogen. The addition of glucose and succinate delayed the degradation process. However, no significant effect of pH was observed. [86] The studies also demonstrate the formation of intermediates DEP and TCP.

Nearly complete degradation of CP (50 mg L^{-1}) with *paracoccus species* under slightly alkaline medium, i.e. pH 8 and temperature 35°C. [87] Similarly, *actinobacteria strains* have also been found useful for this purpose where proximately 90% degradation is reported after 24 hrs. [88]

The *cupriavidus sp. DT-1* had shown the potential to degrade CP and TCP in both liquid and soil medium using them as a sole source of carbon. CP (100 mg L^{-1}) along with its metabolite TCP is found to be completely degraded by *strain DT-1* in the liquid medium after only 14 hrs under neutral pH and 30°C temperature. The strain has also shown more than 90% degradation of CP in the soil after 30 days. [89] Bacterial *strain stenotrophomonas sp. G1 species* degraded 63% of CP (50 mg L^{-1}) at temperature 40°C. This strain not only degraded CP but also other OP's like methyl parathion, diazinon, phoxim, profenofos and triazaphos, parathion, methyl paraoxon effectively under similar conditions. [90]

The plant *cyperus alternifolius* and Fe-impregnated biochar have been reported to enhance the degradation of CP. [91,92] Studies of Gao et al. [93] reported more than 90% of CP (50 mg L^{-1}) degraded in 5 days with *cladosporium cladosporioides Hu-1*. The enzyme has shown maximum hydrolase activity at pH 6.5 and temperature 40°C. The activity of the enzyme was examined in the presence of metal ions like Hg^{2+}, Fe^{3+}, Zn^{2+}, Cu^{2+}, Mn^{2+}, and Mg^{2+}. The strong inhibition of activity was observed with Hg^{2+} and Fe^{3+}, while other metal ions showed only 5-10% inhibition.

The *sphingomonas sp. strain Dsp-2* rapidly degraded CP in alkaline medium. CP (100 mg kg^{-1}) was degraded up to 98.7% in soil with pH 8.7. However, only 58.1% degradation was achieved in soil with pH 4.8 and 90% degradation was achieved in the neutral medium after first 7 days. In cell culture, CP (100 mg L^{-1}) was degraded completely in 24 hrs only, but its metabolite TCP was degraded only upto 30 mg L^{-1} after 48 hrs of treatment at 30°C. [94]

CP has a high potential for adsorption in the soil as compared to triagophos and TCP also in the paddy field of China. It indicates lesser partitioning of CP in water as compared to soil. This study was extended to observe the degradation capacity of bacterial strain *diaphorobacter sp. GS-1*. Complete degradation of CP was obtained after 21 days of inoculation in soil. [95] The adsorption of CP in soil has a direct relation with soil organic matter. [96] The study also reveals that the adsorption of CP was high at lower pH.

Complete degradation of high concentration of CP (400 mg L^{-1}) is with bacterial strain *mesorhizobium sp. HN3* in 10 days. Among the wide range of pH and temperature conditions, maximum degradation was observed at pH 7 and temperature 37°C. Under similar conditions of pH and temperature, CP (100 mg L^{-1}) was degraded only in 5 days. [97] The bacterial strain *sphingobacterium sp. JAS3* had shown the ability to degrade CP (300 mg L^{-1}) and TCP also within 5 days of incubation. [98] Whereas, the bacterial strain *ochrobactrum sp. JAS2* degraded CP (300 mg L^{-1}) and TCP in an aqueous medium within 4 days of incubation. TCP was also completely degraded in both soil and aqueous medium. However, degradation in soil without enriched by nutrients was slower than soil enriched with nutrients. [99] Akbar et al. [100] observed 78.6% and 84.4% degradation of CP (100 mg L^{-1}) with two bacterial strains *ochrobactrum sp. FCp1* and *achromobacter xylosoxidans JCp4* respectively in a liquid medium within 10 days and more than 93% degradation of CP (200 mg kg^{-1}) in sterilized and non-sterilized soil after 42 days. Degradation is found to be enhanced in unsterilized soil.

The above studies reveal that CP is effectively degraded with the help of various microbes and degradation can be enhanced with certain bacterias which can utilize CP as a sole source of carbon or phosphorous under optimum pH and temperature. One of the drawbacks of extensive use of the insecticide is the loss of beneficial microbial diversity. [101] Therefore, research on the effect of pesticides on microbial community dynamics should not be neglected to have background information. [102]

Hence genome sequence of the PGPM, which have tolerance or degradation ability towards organophosphate insecticide and promotes seed germination of vegetable even under insecticide stress should be known. Recently, several studies have indicated that native PGPM consortium enhances plant growth in the presence of residual OP insecticide and also has the capability to remediate pesticide-contaminated soils. [101,103-105]

A recent study on Brinjal, Tomato, and Okra vegetables reported that excessive application of CP on vegetables can be harmful. The study also reported that the presence of organophosphate degrading *opdA* and *opd* genes in strain *bacillus licheniformis* (BHUJP-P3) and *bacillus cereus* (BHUJP-P4), degrade 53 and 90% CP of (50 mg kg^{-1}), respectively in 3 days only and can decrease its toxic effects on seed germination. The presence of such genes can enhance vegetable production and soil fertility also. [106] A gene (*ophB*) from the bacterial strain *pseudomonas sp. BF1-3* was cloned into *escherichia coli DH5α* and it was able to degrade 97% of CP (100 mg L^{-1}) and 86% of TCP in 9 days of incubation. [107]

Photocatalytic degradation

The biodegradation of CP is achieved efficiently with a good percentage, but the process mostly takes a long time for degradation and also it is not a cost-effective treatment. The degradation with nanoparticles is an alternative to such traditional methods. Nanoparticles have a very small size between 1-100 nm, [108] which leads to an increase in surface area to volume ratio and favors enhanced degradation. [109] Many studies [7,110-114] explained the consequential role played by metal NPs like Fe, Au, Ag, TiO_2, ZnO etc. in the degradation of CP.

The advantage of polyurethane foam and cellulose acetate membrane along with NPs has been reported to achieve expeditious mineralization of CP. A piece of 20 cm x 25 cm polyurethane foam incorporated with silver NPs achieved complete mineralization of CP (3 mg L^{-1}) in 180 min. Silver NPs with cellulose acetate membrane achieved complete mineralization of CP (2 mg L^{-1}) in nearly 120 min using 500 mg of catalyst. The use of silver and gold NPs may lead to better percentage removal [110]. The efficiency of silver NPs for consummate degradation of CP from water has been reported. The degradation efficiency has been found to increase over the surface of activated alumina. [111]

99% of CP had been degraded with iron NPs over chitosan with help of carbodiimide laccase. [112] Iron NPs are convenient for the degradation as far as cost is a matter of concern but, if their aggregation takes place then their efficiency gets reduced. [115]

Silica NPs coated with molecularly imprinted polymers had shown potential for the detection and degradation of CP from the complex matrices. In their study, 25 nm thick layers coated with the vinyl group over SiO_2 NPs show good binding capacity and provide efficient degradation, but the excess of vinyl groups decreased the binding efficiency. [116]

Degradation of organophosphate pesticides with heterogeneous photocatalysts is proposed to be a highly attractive and cost-effective technique. The modification of photocatalysts results in the utilization of visible light as an

energy source. [117] Photocatalysts like TiO_2 and ZnO have shown great efficiency for the degradation of pesticides. Photocatalysts have a high potential to degrade complex organic substances. The excitation of electrons from the valence band to conduction band leads to the formation of electron-hole pair combinations which in turn generates $^{\cdot}OH$ and $O_2^{\cdot-}$ radicals. Due to very high oxidizing power these radicals have high potential to degrade pesticide adsorbed on the surface of a photocatalyst to simple organic and inorganic substances.

ZnO over support of a cellulose acetate membrane have shown higher degradation of 5 ppm CP in 60 min under UV radiations than ZnO alone. [114] TiO_2 had shown a higher tendency to degrade aqueous suspensions of CP (10 - 30 mg L^{-1}) in sunlight than ZnO nanoparticles. TiO_2 achieved complete degradation within 100 min whereas ZnO was unable to achieve complete degradation. The study also observed that degradation was enhanced in an acidic medium. [118] Under UV radiations TiO_2 had shown nearly 90% degradation of CP in 25 min of irradiation whereas only 80% degradation was achieved with ZnO. The optimum concentration of catalyst 0.15 g L^{-1} and pH 9 were observed. [119]

The presence of H_2O_2 had shown a marked effect on the degradation of CP. The results verified that there is an enhancement in the activity of TiO_2 under UV light with the presence of H_2O_2 [120,121]. The effect of various anions and other parameters like temperature, pH, H_2O_2, etc., during the degradation of CP under UV radiations, is reported. Temperature and pH did not show any significant effect on degradation. The addition of H_2O_2 provides enhanced degradation under alkaline medium in UV light. The addition of H_2O_2 enhanced the degradation and 1.5 g L^{-1} amount of H_2O_2 was observed to be optimum, however, the presence of other ions like chloride, nitrate, sulfate, and bicarbonate anions does not show any significant impact on degradation efficiency. [122]

It is also reported that an excessive concentration of H_2O_2 might decrease the performance because H_2O_2 produces water molecules by reacting with hydroxyl radicals that might lead to some other reactions. [123] Murillo et al. [12] reported more than 90% degradation of CP in sunlight with a 1g L^{-1} dose of TiO_2. However, better results were obtained when 0.02M H_2O_2 was used in the reaction mixture. Only 10 mg L^{-1} catalyst dose along with H_2O_2 provided better results than alone 1 g L^{-1} catalyst dose. [124]

Most of the studies recognized higher degradation of CP under acidic medium. [124,125] Sivagami et al. [125] also reported 80-90% degradation of CP with varying amounts of TiO_2 (0.5-2 g L^{-1}) and concentration of CP (5-50 mg L^{-1}) under acidic conditions.

Doping of TiO_2 with V^{5+}, Mo^{6+}, and Th^{4+} has also shown remarkable degradation potential for CP under solar light. Among these doped photocatalysts Th^{4+} (0.06 % TiO_2) has shown maximum activity in solar light. But, in UV light undoped TiO_2 had shown high activity than doped photocatalyst. [126]

Photocatalytic degradation of CP with Co-Fe nanocomposites has been observed to be cheap, eco-friendly and reusable. [127] The low cost of TiO_2 makes its utilization convenient at an immensely large scale. [128] The various photocatalysts used for the degradation of CP and their efficiencies are summarized in Table [d].

Table [d]. Degradation of CP with nanoparticles.

Sr. No.	Nanoparticle	Support material/ Membrane	Light Source	Concentration of CP	Optimal conditions	Comments	Maximum degradation time	Reference
1.	Silver NP	Poly Urethane Foam	-	3 ppm	-	Complete removal	180 min	[7]
2.	Silver NP	Cellulose acetate Membrane	-	2 mg L^{-1}	-	100 % removal	nearly 120 min with 500 mg L^{-1} Ag NPs	[110]
3.	Silver NP	Alumina	UV	1 ppm	-	Complete removal	10 h	[111]
4.	Gold NP	Citrate	UV	2 ppm	-	Complete removal	4 h	[111]
5.	Magnetic iron NPs	Laccase immobilization on chitosan coated NP	-	500 mg L^{-1}	pH =7, temperature 60°C	99%	12 h	[112]
6.	TiO_2	-	UV lamp (16 W)	2-10 mg L^{-1}	pH = 5, TiO_2 (100 mg / 100 mL)	97.6-98.6 %	60 min	[113]
7.	ZnO	Cellulose acetate mixed polymeric membrane	UV lamp (11 W)	5 mg L^{-1}	-	-	60 min	[114]
8.	TiO_2 and ZnO	-	Sun light	10-30 mg L^{-1}	ZnO = 0.25 g L^{-1} TiO_2 = 0.75 g L^{-1} pH(ZnO) = 6.4 pH(TiO_2) = 4.2	100 % for TiO_2	120 min	[118]
9.	TiO_2 and ZnO	-	UV	6 mg L^{-1}	pH= 9 catalyst dose = 0.15 g L^{-1}	80 % for ZnO 90 % for TiO_2	25 min	[119]
10.	TiO_2	-	UV(365nm) / H_2O_2 (100mg/L)	400 mg L^{-1} (100 CP, 50 cypermethrin, 250 chlorothalonil)	pH= 6, TiO_2= 1.5 g L^{-1}	Complete removal	30 min (total irradiation time 300 min)	[120]
11.	TiO_2		UV/H_2O_2	50-150 mg L^{-1}	H_2O_2=1.5 gL^{-1}			[122]
12.	TiO_2	-	Sun light / 0.02 M H_2O_2	30 mg L^{-1}	TiO_2 = 10 mg L^{-1}	Nearly 90 %	20 min	[124]
13.	TiO_2	-	UV	5-25 mg L^{-1}	pH < 7 TiO_2=1 g L^{-1}	80-90 %	-	[125]
14.	Co-Fe-TiO_2 nano composite	Reduced graphene oxide nanocomposite	UV lamp (400 W)	5 mg L^{-1}	pH= 5.8	-	60 min	[127]
15.	TiO_2	-	UV lamp (9 W)	5-25 mg L^{-1}	no significant effect of pH TiO_2=1 g L^{-1}	84-94 % degradation	4-5 h	[140]
16.	Cd, Te Quantum Dots	Alumina	-	-	-	Complete removal	-	[145]
17.	TiO_2	-	UV (27-30 W m^{-2})	2 mg L^{-1}	pH= 6.5 TiO_2=4 g L^{-1}	94%	8 hrs	[149]

Other methods used for degradation of CP

Besides biodegradation and photocatalytic degradation, other efficacious methods such as electrochemical, hydrolytic, ultrasonic methods, etc. have been developed for the degradation of CP, which shows good efficacy for degradation of CP. Liu et al. [129] observed the hydrolytic degradation of CP from various river water of the Chesapeake Bay region gives TCP as a major product. The %age recovery of CP and TCP varies from 103-116%. The study also shows that along with pH, the presence of dissolved metals like copper additionally affects the degradation process.

The enzymatic hydrolysis of CP had been prosperously achieved by *paraoxonase*. Hydrolysis was quick in the presence of chloride ions, however, the presence of EDTA, phenylacetate inhibited the hydrolysis. The solvent also has a consequential effect as the hydrolysis was found to be enhanced in the presence of methanol instead of acetone. [130]

Electrochemical methods had also been effective for the purpose. [131,132] The mineralization of CP with graphite carbon as the cathode and Nb/PbO_2 as anode showed more than 70% COD removal at an ambient temperature of 60°C and with a current density of 50 mA cm^{-2} within 10 hrs. The utilization of boron-doped diamond as anode had led to proximately 99% COD removal with relatively lower current density (20 mA cm^{-2}) within 6 hrs only. So, the use of the boron-doped diamond had shown better efficiency for the mineralization of CP.

The ultrasonic irradiation reported the formation of two metabolites TCP and CPO during degradation. The parameters like pH, temperature and electric power were also monitored and degradation was found to vary with variations of the parameters. The maximum degradation (85 %) was observed at pH 7 at electric power 900 W and 25°C temperature. [133] The degradation of CP increases with an increase in electric power and ultrasound frequency. However, no significant effect with variation in pH was observed. [134]

Low doses of oxytetracyclene (OTC) enhance the mineralization of CP. [135] The degradation of CP in pure water and sludge utilizing activated carbon and micelle clay complexes demonstrated that ultra filtration-hollow fiber column |was unable to abstract CP, but the mixing of activated carbon or micelle clay complexes filtration resulted in the efficient removal of CP. Experimental results showed that the use of octadecyltrimethylammonium bromide (ODTMA) complexes degraded CP up to 90% in 180 min of contact time. [8]

Treatment with microencapsulated CP in the soil gives virtually complete abstraction of CP with an initial concentration of 5 and 20 mg kg^{-1}. However, this dissipation was observed to be slower than emulsifiable CP treated soil, but side effects on soil microbes were less than emulsifiable CP. [64] The plant e*lodea densa* had the competency to absorb the CP from water. The experiments reported that plant material *elodea densa* could adsorb CP in a fortnight to dissipate CP. [136]

Utilizing oxidizing agents like hydrogen peroxide, potassium permanganate, etc. in high concentration for removal of pesticides from nectarines led to the formation of CPO that is more toxic than its parent compound. The formation of toxic by-products was confirmed by Gas Chromatography-Mass spectroscopy (GC-MS) technique, however, the use of simple washing technique with the addition of ethanol, glycerol, and sodium lauryl sulphate (SLS) was found to be efficacious for removal of CP. [137]

Gamma radiations had shown the potential to degrade aqueous solutions of low concentration of CP (5 mg L^{-1}). In the presence of sunlight CP (20 mg L^{-1}) is degraded up to 33.5% and 47.15% after 10 days. [138] Such common methods studied for the degradation of CP are summarized in Table [e].

Table [e]. Other methods used for degradation of CP.

Sr. No.	Method	Surface / Light source	Concentration of CP	Degradation %age	Optimal conditions/ factors	Reference
1	Micelle clay complex and advanced treatment technology	Activated carbon / micelle clay complex (ODTMA)	100 mg/L	90%	Total contact time 180min, optimal contact time 30±5 min, pH 6.58 and temperature 25°C	[8]
2	Atmospheric degradation	Solar radiations	Injection with pressure $2*10^5$ mm Hg	95% degradation	Presence of [NO_x], [OH^0] enhance degradation	[30]
3	Microencapsulated CP	-	5 and 20 mg CP kg^{-1}	-	Disappearance of CP after 120 d	[64]
4	Hydrolytic degradation	-	20 µg L^{-1}	-	pH, dissolved metals show significant effect	[129]
5	Hydrolytic degradation	Human serum plasma paraoxonase / arylesterase	-	-	Presence of chloride ions	[130]
6	Electrochemical	Anode, Nb/PbO_2 Cathode, graphite carbon	COD=115- 450 mg L^{-1}	COD removal 76 %	Current density 50 mA cm^{-2}, temperature 70°C, time 10 h	[131]
7	Electrochemical	Anode, boron doped diamond Cathode, graphite carbon	COD, 115- 450 mg L^{-1}	COD removal> 99 %	Current density 20 mA cm^{-2} and temperature 70°C, time 6 h, pH=2	[132]
8	Ultrasonic irradiations	Electric Power 900 W	1.4 mg L^{-1}	85% mineralization	Temperature 25°C, pH= 7, electric power 900 W, time 60 min	[133]
9	Ultrasound	Electric power 500 W	1 mg L^{-1}	98.96 %	pH= 9, frequency 130 kHz, contact time 20 min, electric power 500 W	[134]
10	Effect of OTC on biomixture	-	50 mg kg^{-1}	-	Low doses of OTC (1-10 mg kg^{-1}) increased mineralization of CP	[135]
11	Aquatic Macrophyte	Elodea densa	-	-	Tendency to accumulate CP from water in 2 weeks	[136]
12	Washing process	SLS, Ethanol	-	50%	Hydrophobic nature of SLS makes it effective	[139]

The analysis of intermediates formed during the degradation of CP is necessary to confirm the toxicity of degraded products. The formation of intermediates under biodegradation, photocatalytic degradation, etc., and the residual concentration of CP are traced with techniques [113,120,139,140] like UV spectroscopy, GC, Liquid Chromatography-Mass Spectroscopy (LC-MS), and High Performance Liquid Chromatography (HPLC).

The quantitative determination of CP along with dimethoate, fenthion, diazinon simultaneously in human blood has been prosperously achieved. [141] Some common and efficient techniques used so far for analysis of such degraded products are listed in Table [f].

Table [f]. Techniques used for analysis of CP and its degraded products

Sr. No.	Technique for analysis of CP/ degraded products of CP	Degradation method	Reference
1	HPLC, Quantitative determination of CP/TCP	Biodegradation	[81]
2	GC-Flame Ionization Detector, Degradation of CP/TCP	Biodegradation	[82]
3	TCP analysis, HPLC	Biodegradation	[88]
4	GC-MS	Photocatalytic	[112]
5	UV spectroscopy	Photocatalytic	[113]
6	GC-MS	Photocatalytic	[120]
7	LC-MS	Photocatalytic	[127]
8	GC-MS analysis	Ultrasonic	[133]
9	TCP analysis, HPLC and UV spectrometry	Photocatalyst	[139]
10	Liquid chromatography–tandem mass spectrometry	--	[141]
11	GC-Nitrogen Phosphorus Detector	--	[146]
12	LC-MS	--	[147]
13	Liquid–Liquid extraction and subsequent normal phase solid-phase extraction	--	[148]

General Pathway of Degradation

To the best of our knowledge, this is the first review that deals exclusively with the degradation of CP. The degradation of CP with natural methods, biodegradation, and photocatalytic systems have been reviewed above. The results obtained by various techniques like HPLC, [87,139] GC-MS have shown the formation of two major intermediates TCP and DEP during the degradation of CP.

However, the degradation of CP occurs through the formation of CPO in which P=S moiety of CP is replaced by P=O in presence of some oxidizing agents like H_2O_2. [137] The studies show the formation of CPO before TCP and DEP, however, at the cessation of the process, no traces of these intermediates are observed as they can be degraded into simpler inorganic ions. Most of the studies provide evidence that the pyridine ring of CP remains intact during the degradation. The CP is found to form multi-oxygenated products under atmospheric conditions. Biodegradation of CP may provide the precursors of the Krebs cycle. The formation of TCP in almost all pathways indicates the retention of the pyridine ring. TCP is a major metabolite of CP and under all photolytic and photocatalytic pathways, it is observed to undergo ring cleavage to form smaller organic and inorganic molecules. The products formed during various degradation methods are shown in Figure 4.

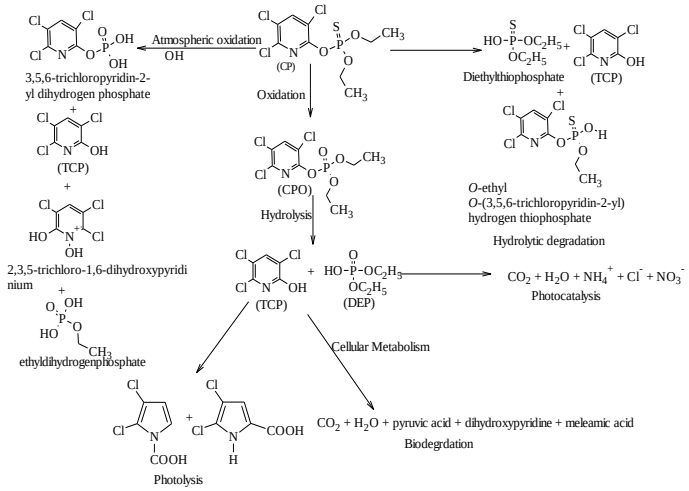

Figure 4. General pathway for degradation of CP with different methods.

CONCLUSION

The studies on chlorpyrifos recognize the toxic effects on various living organisms including humans. The inhalation of chlorpyrifos above the maximum residue limit causes neurotoxicity and even death in some cases. Therefore, its degradation is necessary for the safety of organisms and the environment. For this purpose, studies are reviewed in this paper and it is concluded that the various degradation methods like natural degradation, biodegradation, photocatalytic degradation, electrochemical degradation etc. have their own advantages and disadvantages. However, biodegradation is a promising technique for complete mineralization, but it takes a long time for treatment. Moreover, for the biological degradation, it is important to know molecular characterization and genome sequence of insecticide-degrading micro-organisms to better understand the mechanism of insecticide degradation at the gene level so that plant growth-promoting microbes can be developed which can act even under insecticide stress. This will help in designing new alternative and efficient tools for the bioremediation of contaminated sites. Photocatalytic degradation has also shown great efficiency for the insecticide-degradation but the future will be towards the practical applicability and develop the commercial designs. Another future approach is to investigate the effectiveness of hybrid technologies in combination with other existing technologies for the treatment of insecticides like CP contaminated wastewater. Indeed, the combination of such methods for e.g., the combination of photocatalytic degradation and biodegradation by understanding the mechanism of both the processes may give better results.

Table [g]. List of Abbreviations.

Abbreviation Title	Abbreviation Name
AcHE	Acetylcholinesterase
CP	Chlorpyrifos
CPO	Chlorpyrifos oxon
DNA	2-deoxyribosenucleic acid
DEP	Diethylphosphate
GC-MS	Gas Chromatography-Mass Spectroscopy
HPLC	High Performance Mass Spectroscopy
LC-MS	Liquid Chromatography-Mass Spectroscopy
NPs	Nanoparticles
NADPH	Nicotinamide Adenine Dinucleotide Phosphate
ODTMA	Octadecyltrimethylammonium bromide
OP	Organophosphate
OTC	Oxytetracyclene
PGPM	Plant Growth Promoting Microbes
RNA	Ribose nucleic acid
SLS	Sodium Lauryl Sulphate
TCP	3,5,6-trichloropyridinol

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