Chapter 6
Pyrethroid-Degrading Microorganisms and Their Potential Application for the Bioremediation of Contaminated Environments

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Abstract Long-term and extensive application of synthetic pyrethroid (SP) insecticides indoor has resulted in a large increase in the number of people reported to have detected residues of pyrethroids and their major intermediate metabolite 3-phenoxybenzoic acid (3-PBA) in body fluids. The neurotoxicity and reproductive toxicity of pyrethroids to nontargets have attracted extensive attention. The microbial degradation of pyrethroids has been reported frequently in the past 30 years. In recent years, based on the development of biomolecular tools and materials science, the mode of action of microorganisms and their functional enzymes has been expanded. This chapter summarizes the pyrethroid degradation microorganisms that have been published in the past and proposes the metabolic pathways of pyrethroids. In addition, we also discussed the degradation mechanisms of pyrethroids based on the catalytic triad of the pyrethroid hydrolase.

Keywords Pyrethroids · Toxic effect · 3-Phenoxybenzoic acid · Bioremediation

6.1 Introduction

Pyrethroids are a synthetic organic compound similar in structure to natural pyrethrums extracted from *Chrysanthemum cinerariaefolium*. Their acid and alcohol parts are bound by ester bonds and usually contain 1–3 chiral centers. As a chiral compound, pyrethroids usually have 4–8 stereoisomers (Bhatt et al. 2020a). Different isomers exhibit different insecticidal activities and have enantioselective degradation characteristics during microbial metabolism (Garcia et al. 2017). Pyrethroids

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can be divided into two categories based on the presence or absence of cyano-group on the α-chiral carbon: type II pyrethroids with cyano-group and type I pyrethroids without cyano-group.

Allethrin is the first type I pyrethroid synthesized in the USA in 1949, which is to control domestic sanitary pests (Bhatt et al. 2020d). Compared with type II pyrethroids, pyrethroids of type I had structural diversity and were generally less toxic than type II due to the absence of cyano-group (Zhang et al. 2016). In addition to the cyano-group, pyrethroids have introduced halogens such as fluorine, chlorine, and bromine to increase insecticidal activity (Tang et al. 2018b; Zhan et al. 2018; Cycoń et al. 2014).

Pyrethroids have been used worldwide for more than 40 years since they were synthesized in the middle of the last century. With the increasing restrictions on organophosphorus and organochlorine pesticides by governments, the use of pyrethroids has increased year by year, from 25% of the world pesticide market in 2010 to more than 30% in 2018 (Zhai et al. 2012; Cycoń and Piotrowska-Seget 2016). A pyrethroid is a broad-spectrum insecticide with selective toxicity to Diptera, Hymenoptera, and mammals (Thatheyus and Gnana Selvam 2013). To improve the insecticidal activity and environmental stability of active ingredients, piperonyl butoxide and piperonyl sulfoxide were added to commercial pyrethroids (Thatheyus and Gnana Selvam 2013).

Pyrethroids are highly hydrophobic and will be adsorbed in sediment rapidly after entering the water body (Delgado-Moreno et al. 2011). Subsequently, some of them are utilized by indigenous microorganisms, and the other part enters the aquatic food web, which may eventually accumulate in the human body through biological amplification (Liu et al. 2012; Cycoń et al. 2017). A large number of results have confirmed that pyrethroids have high toxicity to aquatic organisms (Mendis et al. 2018; Mulla et al. 2017; He et al. 2008). Long-term exposure to pyrethroids can affect the quality of human semen (Ham et al. 2020). A series of environmental problems caused by the irrational use of pyrethroids has aroused public concern in recent years. At present, diverse methods have been developed to remove pyrethroids from the environment.

In this chapter, we are summarizing the previously isolated and characterized degrading microorganisms and introduce the metabolic pathways of common pyrethroids. In the last two decades, many researchers have reported pyrethroid hydrolases encoded by genes with open reading frames (ORF). We will discuss these functional enzymes and describe the metabolic mechanisms that catalyze the triad (Serine, Histidine, Aspartate) at the active site of the degrading enzyme.

6.2 Potential of Microbes in Pyrethroid Degradation

Pesticide-degrading microorganisms have become a scientific research hotspot and effective strategy to treat pesticide residues over 30 years of development due to their unique advantages. Microbes can catabolize the large-molecular heterologous

pollutants remaining in the environment into nontoxic or low-toxic inorganic small-molecule compounds in various ways (Huang et al. 2021; Lin et al. 2020; Mishra et al. 2020; Chen et al. 2012a). Generally, it is an effective way to use enrichment culture technology to screen functional microorganisms from soil, water, and activated sludge contaminated by pesticides (Zhang et al. 2021; Zhan et al. 2020; Lin et al. 2011). There are also reports that it is feasible to obtain degrading functional bacteria from resistant insects and fermented food (Cho et al. 2009). Type II pyrethroids are lethal to aquatic organisms which are often used as ship detergents to prevent the adhesion of marine organisms (Feng et al. 2009). Therefore, seawater has also been reported commonly as an important source of pyrethroid degrading microorganisms.

To date, a great number of studies have confirmed that bacteria and fungi can effectively degrade pyrethroid residues in water and soil (Table 6.1). There are also a few reports on yeast and algae (Pang et al. 2020). Microorganisms can use pyrethroids as the sole energy source or with the help of other nutrients to remove pyrethroids through co-metabolism (Zhao et al. 2019b). *Bacillus subtilis* 1D has been reported to hydrolyze 95% of cypermethrin within 15 days. And 700 bp esterase and 1200 bp laccase were extracted from strain 1D, which indicates that esterase and laccase are involved in the cypermethrin metabolism (Gangola et al. 2018). Wang et al. (2019) isolated a strain of *Photobacterium ganghwense* 6046 from seawater. This strain can grow with cyfluthrin as the sole carbon source and degrade 60% of cyfluthrin (100 $mg{\cdot}L^{-1}$) for 72 h (Wang et al. 2019). The intermediate products of cyfluthrin were identified, and the cyano-group was not found. It is speculated that cyano-groups may be metabolized by strain 6046 first. *Paracoccus acridae* SCU-M53 is an epiphytic bacterium isolated from locusts, which can metabolize 79.84% of cyhalothrin in 48 h (Tian et al. 2018).

Response surface methodology (RSM) is a common method to optimize microbial growth and degradation conditions. Based on the Box-Behnken design, Zhan et al. (2018) used RSM to optimize the degradation conditions of *Acinetobacter baumannii* ZH-14. Under the conditions of 30 °C and pH 7, permethrin with a concentration of 50 $mg{\cdot}L^{-1}$ was completely removed within 72 h. *Bacillus thuringiensis* ZS-19 obtained from activated sludge can completely eliminate 100 $mg{\cdot}L^{-1}$ cyhalothrin in 72 h and can continue to work effectively when the concentration is as high as 800 $mg{\cdot}L^{-1}$. In addition to cyhalothrin, strain ZS-19 can also efficiently metabolize fenpropathrin, deltamethrin, beta-cypermethrin, and cyfluthrin (Chen et al. 2015). Allethrin is the earliest synthesized pyrethroid, but reports on allethrin degradation bacteria are not common. *Acidomonas* sp. degraded 70% of allethrin at a concentration of 16 mM in MSM medium during 72 h and proposed a metabolic pathway (Paingankar et al. 2005). Recently, Bhatt et al. (2020b) manifested that *Sphingomonas trueperi* strain CW3 utilized allethrin as the sole source of energy and remove 93% of 100 $mg{\cdot}L^{-1}$ allethrin after 7 days. The optimal culture conditions are pH 7, temperature 30 °C, and inoculation amount of 0.1 g L^{-1}.

While earlier studies focused on the degradation kinetics of single strains, more studies now suggested that microbial consortia may exhibit higher degradation

Table 6.1 Pyrethroid-degrading microbes obtained from various sources

Pyrethroids	Microbial strains	Species	Results	References
β-Cypermethrin	*Pseudomonas aeruginosa* CH7	Bacteria	1. 25–900 mg/L *β*-cypermethrin is metabolized over 90% in MSM within 12 days 2. The optimal culture condition is 25–35 °C and pH 6–9, inoculation amount is 0.15 g/L	Zhang et al. (2011)
	Bacillus licheniformis B-1	Bacteria	1. 50% degradation observed in a liquid medium within 72 h 2. Degradation rate can be improved by adding surfactants Tween-80 and BRIj-35	Zhao et al. (2015)
	Aspergillus Niger YAT	Fungus	1. 54.83% degradation obtained with 50 $mg \cdot L^{-1}$ *β*-cypermethrin using strain YAT after 7 days	Deng et al. (2015)
	Brevibacillus parabrevis BCP-09	Bacteria	1. 75.87% of *β*-cypermethrin was removed by strain BCP-09 in 3 days 2. The optimal inoculation condition was pH 7.4, 38.9 °C	Tang et al. (2018a)
	Pseudomonas aeruginosa GF31	Bacteria	1. More than 80% of 50 mg/L *β*-cypermethrin was removed after 7 days 2. Supplementation of peptone significantly increased the degradation	Tang et al. (2015)
	Bacillus subtilis BSF01	Bacteria	1. 89.4% of 50 mg/L *β*-cypermethrin was eliminated after 7 days	Xiao et al. (2015)
	Ochrobactrum lupini DG-S-01	Bacteria	1. 90% of *β*-cypermethrin was degraded in MSM within 5 days and concentration was 50 mg/L	Chen et al. (2011a)
	Bacillus thuringiensis SG4	Bacteria	1. Approximately 80% *β*-cypermethrin (50 mg/L) was removed by strain SG4 after 15 days	Bhatt et al. (2020c)
	Bacillus sp. ISTDS2	Bacteria	1. *β*-cypermethrin with a concentration of 50 mg/L was complete catabolism in MSM within 8 days 2. Completely removed 100 mg/L beta-cypermethrin in soils after 30 days	Sundaram et al. (2013)
	Bacillus sp. SG2	Bacteria	1. 81.6% of *β*-cypermethrin (50 mg/L) were eliminated in MSM after 15 days	Pankaj et al. (2016)
	Bacillus subtilis 1D	Bacteria	1. 160 mg/L of *β*-cypermethrin was metabolized by 95% within 15 days	Gangola et al. (2018)

(continued)

Table 6.1 (continued)

Pyrethroids	Microbial strains	Species	Results	References
Fenvalerate	*Bacillus licheniformis* CY-012	Bacteria	1. When the culture was in the optimal condition at pH 7.48 and the initial concentration was 44 mg/L, about 80% fenvalerate was eliminated during 60 h	Tang et al. (2018b)
	Bacillus flexus XJU-4	Bacteria	1. Fenvalerate with a concentration of 2 mM was completely degraded within 6 days 2. Fenvalerate can be utilized as the sole source of carbon	Mulla et al. (2017)
	Stenotrophomonas sp. ZS-S-01	Bacteria	1. 100% removal of 50 mg/L fenvalerate was accomplished in 6 days 2. About 80% of fenvalerate was metabolized when concentration was 500 mg/L after 5 days	Chen et al. (2011c)
	Cladosporium sp. HU	Bacteria	1. More than 90% of fenvalerate with 100 mg/L was eliminated during 5 days	Chen et al. (2011d)
	Pseudomonas aeruginosa JQ-41	Bacteria	1. About 92.3% of fenpropathrin with an initial dose of 50 mg/L was degraded after 7 days	Song et al. (2015)
	Bacillus sp. DG-02	Bacteria	1. 93.3% degradation of fenpropathrin was achieved in a liquid medium within 72 h 2. Strain DG-02 can degrade a variety of pyrethroids	Chen et al. (2014)
Deltamethrin	*Bacillus cereus* Y1	Bacteria	1. About 99.4% deltamethrin was metabolized in MSM within 96 h 2. When deltamethrin in soils, the degradation rate is 74.9% after 24 days	Zhang et al. (2016)
	Streptomyces aureus HP-S-01	Bacteria	1. 100% initial dose of deltamethrin with a concentration of 300 mg/L was removed by strain HP-S-01 within 7 days 2. Deltamethrin can be used as a sole source of carbon	Chen et al. (2011b)
Cyhalothrin	*Bacillus thuringiensis* ZS-19	Bacteria	1. 100 mg/L of cyhalothrin was degraded completely in a minimal medium within 72 h	Chen et al. (2015)
	Paracoccus acridae SCU-M53	Bacteria	1. 79.84% of 75 mg/L cyhalothrin was degraded within 2 days, and the carried-out condition is 28 °C and 180 rpm	Tian et al. (2018)
	Cunninghamella elegans DSM1908	Fungus	1. Most of the 100 mg/L cyhalothrin is hydrolyzed within 120 h	Palmer-Brown et al. (2019)

(continued)

Table 6.1 (continued)

Pyrethroids	Microbial strains	Species	Results	References
	Aspergillus sp. CBMAI 1829	Fungus	1. 44.8% cyhalothrin was degraded when concentration was 100 mg/L in 14 days	Birolli et al. (2018)
Allethrin	*Sphingomonas trueperi* CW3	Bacteria	1. Approximately 93% allethrin (100 mg/L) was metabolized in the liquid medium after 7 days of incubation	Bhatt et al. (2020b)
	Fusarium proliferatum CF2	Fungus	1. Completely removal of allethrin (50 mg/L) was achieved after 5 days and used as a sole corban source	Bhatt et al. (2020d)
Permethrin	*Acinetobacter baumannii* ZH-14	Bacteria	1. Completely metabolism of chlorpyrifos with a concentration of 50 mg/L was achieved after 72 h 2. Permethrin can be utilized by strain ZH-14 for growth as a sole source of energy	Zhan et al. (2018)
Flucythrin	*Brevibacterium aureum* DG-12	Bacteria	1. About 88.6% of degradation was observed in 5 days	Chen et al. (2013a)
Cyphenothrin	*Staphylococcus succinus* HLJ-10	Bacteria	1. 92.8% cyphenthrin was metabolized in MSM within 7 days 2. Strain HLJ-10 can use cyphenthrin as the sole carbon source	Huang et al. (2020)
Phenothrin	*Pseudomonas fulva* P31	Bacteria	1. Strain P31 was able to completely degrade 100 mg/L phenothrin within 72 h 2. Phenothrin can be utilized as the sole carbon source by strain P31	Yang et al. (2018)

capabilities than single strains (Feng et al. 2020a, b). The previous results of Tang et al. (2020) showed that when the ratio of *Klebsiella pneumoniae* BPBA052 and *Acinetobacter Junii* LH-1-1 was 2.5:7.5, the dissipation of 75 mg·L^{-1} deltamethrin in 96 h was 94.25%. *Streptomyces aureus* HP-S-01 and *B. Cereus* ZH-3 can 100% metabolize cypermethrin (50 mg·L^{-1}) within 72 h (Chen et al. 2012b). A consortium composed of four beta-cypermethrin-degrading bacteria, which was *Streptomyces* sp. GXZQ4, *Enterobacter* sp. GXZQ6, *Streptomyces* sp. GXZQ7, and *Pseudomonas* sp. GXZQ13, was obtained by enrichment culture and high-throughput sequencing. The consortium's degradation rate of beta-cypermethrin (100 mg·L^{-1}) was up to 89.84% after 96 h (Qi and Wei 2017).

Among the published pyrethroid degrading bacteria, only a few strains can degrade pyrethroid 100% in a short time. Pyrethroids are similar in structure,

which means that the same strain may degrade many different pyrethroid pesticides (Bhatt et al. 2020f). The essence of microbial metabolism is an enzymatic reaction, in which complex macromolecular compounds are gradually broken down under the action of various enzymes (Feng et al. 2020a; Zhang et al. 2020; Bhatt et al. 2021a). 3-Phenoxybenzoic acid is the main intermediate metabolite of most pyrethroids. 3-PBA has high water solubility and antibacterial properties, which is one of the reasons limiting the further metabolism of pyrethroids (Zhao et al. 2019a). It is a new attempt to solve the toxicity of 3-phenoxybenzoic acid (3-PBA) through co-culture. Two strains of *Aspergillus oryzae* M-4 and *B. licheniformis* B-1 were combined by Zhao et al. (2016). After 72 h of cocultivation, 100 $mg \cdot L^{-1}$ β-cypermethrin was removed by 78.85%. The toxic intermediate product 3-PBA formed by the hydrolysis of β-cypermethrin with *B. licheniformis* B-1 was effectively utilized by *A. oryzae* M-4, the gallic acid produced by the metabolism of beta-cypermethrin with *A. oryzae* M-4 was effectively degraded by *B. licheniformis* B-1.

6.3 Genes and Enzymes Involved in Pyrethroid Metabolism

Carboxylesterase is a very important class of pyrethroid hydrolases. It is a subtype of esterase and had classified in subtype 3.1.1 by the International Union of Biochemistry (Bhatt et al. 2021b). Carboxylesterase/lipase is divided into eight families (I–VIII). Group I esterases are true lipases, while group II–VIII esterases are carboxylesterase (Zhan et al. 2020). Carboxylesterase is the most studied enzyme among pyrethroid hydrolases. It is widely found in resistant insects, mammals, and microbial cells. It can hydrolyze a variety of organic compounds containing esters, such as carbamate and pyrethroid, and produce nontoxic acids and alcohols (Liu et al. 2017). The active site of esterase contains serine residues, which are located in the conserved pentapeptide motif (Gly-X-Ser-X-Gly) (Diegelmann et al. 2015).

Many pyrethroid degradation genes, such as *pye3*, *pytY*, *estA*, *pytZ*, *pytH*, *est3385*, *mes1*, and *sys410*, have been cloned and identified (Wang et al. 2009; Li et al. 2008; Ruan et al. 2013; Luo et al. 2018). Phylogenetic analysis indicated that Est3385 derived from *Rhodopseudomonas palustris* PSB-S belong to the esterase group I, Sys410 belongs to esterase V family, and the pyrethroid carboxylesterase PytY encoded by *pytY* gene is a member of esterase VI families (Luo et al. 2018; Ruan et al. 2013; Fan et al. 2012). Most pyrethroid hydrolase activities have been reported to require no cofactor, but the presence of some metal ions can severely inhibit enzyme activity. The pyrethroid hydrolase extracted from *A. niger* ZD11 has a pI value of 5.4 and a molecular weight (MW) of 56 kDa; a pyrethroid esterase, Pye3, with an open reading frame (ORF) of 819 bp and an MW of about 31 kDa, was obtained from the soil by using metagenomics tools; and the esterase EstP with an ORF of 1914 bp was extracted from *Klebsiella* sp. strain ZD112 cells. These three enzymes can be strongly inhibited by Hg^{2+} and Ag^{+} (Wu et al. 2006; Li et al. 2008; Liang et al. 2005).

Due to the similarity in the structure of pyrethroid pesticides, most pyrethroid functional enzymes show broad-spectrum substrate specificity to pyrethroids. Pyrethroid hydrolytic esterase (EstP) was isolated from *Klebsiella* sp. ZD112 and encoded by gene *estP*, has an ORF of 1914 bp. The molecular weight of EstP is about 73 kDa, which contains 637 amino acid residues (Wu et al. 2006). No similarity was found with the reported nucleotide sequences of esterase/lipase family members by multiple sequence alignment. The purified EstP has a broad spectrum of substrate utilization. The K_m and k_{cat} values of EstP hydrolyzing *trans*- and *cis*-permethrin indicated that EstP hydrolyzes pyrethroids more efficiently than carboxylesterases obtained from insect-resistant insects and mammals.

The ORF of the pyrethroid hydrolytic gene *est 3385* contains 963 nucleotides, and the optimum pH and temperature are 6.0 and 35 °C, respectively (Luo et al. 2018). The enzyme can metabolize a variety of pyrethroid pesticides, and fenpropathrin is the best substrate. The enzyme degradation kinetics indicated that the V_{max} and K_m values of hydrolyzed fenpropathrin were 0.918 ± 0.025 U/microg and 0.734 ± 0.013 mmol/L, respectively. The *pytH* cloned from *Sphingobium* sp. strain JZ-1 encodes the carboxylesterase PytH. In addition to hydrolyzing a variety of pyrethroids, PytH can also convert short-chain fatty acids (Wang et al. 2009). Studies have shown that transferring the carboxylesterase encoding gene *pytH* into *Pseudomonas putida* KT2440 can completely hydrolyze 0.2 mM permethrin, fenpropathrin, and cypermethrin within 48 h (Zuo et al. 2015).

Previous results showed that there is enantioselective degradation of pyrethroid hydrolase. The pyrethroid hydrolase extracted from the *A. Niger* ZD11 was able to detoxification various pyrethroids, but compared with *cis*-permethrin, the substrate utilization of *trans*-permethrin was higher (Liang et al. 2005). A pyrethroid hydrolase esterase gene *pytY* containing 897 bp ORF was isolated from *Ochrobactrum Anthropi* YZ-1 by Ruan et al. (2013). PytY can hydrolyze different pyrethroids, but it showed the highest hydrolysis activity with *lambda*-cyhalothrin as the substrate. The kinetic constants of *V*max and *K*m were 56.33 nmol/min and 2.34 mmol/L, respectively.

The *beta*-cypermethrin-degrading monooxygenase CMO was first identified by Chen et al. (2013b) from environmental microorganisms. The natural enzyme showed that the CMO has a pI of 5.4 and an MW of 41 kDa. The enzyme exerted the greatest activity against *beta*-cypermethrin at 30 °C and pH 7.5. Fe^{2+} can significantly enhance the activity of CMO, while Cu^{2+}, Al^{3+}, and Ag^{+} have a strong inhibitory effect on CMO activity. Most of the pyrethroid hydrolases are extracted from the cells of organisms. It has been proved that it is feasible to extract pyrethroid metabolizing enzymes from extracellular regions. A functional enzyme was isolated from *Pseudomonas aeruginosa* strain GF31 cells. The molecular weight of the enzyme was 53.7 kDa, and the pI value was 7.67. The ORF contained a 1611 bp DNA fragment, encoding 536 amino acids. Through phylogenetic analysis, it was highly similar to aminopeptidases (Tang et al. 2017).

6.4 Catalytic Mechanisms of Pyrethroids

Pyrethroid hydrolases are members of the α/β superfamily. Most of the active site amino acids of carboxylesterase have conservative sites, with the active site amino acids contain a catalytic triad composed of nucleophiles, basic groups, and acidic groups (Bhatt et al. 2020a). Hydrolase folds into a complex three-dimensional structure in space, and the different residues of the catalytic triad (Ser-His-Asp) come together during the folding process. The triad is hidden in the enzyme protein molecule, and the serine residue at the active site is masked by the alpha helix. Through the folding of enzyme protein, the catalytic triad of carboxylesterase activity site is combined with a pyrethroid.

Aspartate and histidine combine with two hydrogen bonds to increase the *pKa* value (acidity coefficient) of the triad and activate the nucleophile serine. After the hydroxyl molecule of the serine is activated by catalytic histidine/aspartate, the latter obtains electrons from the hydroxyl molecule of the nucleophile. The active site of pyrethroid hydrolases contains serine residues, which is situated in the common pentapeptide sequence Gly-X-Ser-X-Gly of esterases. It acts as a nucleophile to attack the carbonyl group of pyrethroids through hydroxyl (OH), then releases alcohols, and produces a covalent intermediate of acylation (Bhatt et al. 2019). The basic group (His) and the acidic group (Asp) obtain hydrogen ions from the OH of serine, and the carbonyl group's nucleophilic attack of pyrethroid is performed by hydroxyl anion generated from serine. These two processes are carried out simultaneously.

The carbon atom of the ester bond of pyrethroid is attacked by serine (nucleophile) and forces the oxygen atom of the ester bond to accept electrons, forming a tetrahedral intermediate. Restoration of the intermediate carbonyl leads to the transfer of histidine protons to the carbon atoms of pyrethroids adjacent to the α-chiral carbons. Subsequently, water molecules replace serine as a nucleophile to supply a proton to histidine, and the remaining OH attacks the carbonyl carbon atom to form a complex intermediate (Bhatt et al. 2020a). Furthermore, the serine in the enzyme regains protons from the basic group histidine, which further hydrolyzes the complex intermediate into nontoxic acids and alcohols. The specific metabolic process is shown in Fig. 6.1.

6.5 Metabolic Pathways of Pyrethroid Biodegradation

The main intermediate metabolites detected in pyrethroids during microbial metabolism are 3-phenoxybenzyl alcohol, 3-phenoxyebenzoic acid (3-PBA), and 3-phenoxybenzaldehyde. The metabolite α-hydroxy-3-phenoxybenzeneacetonitrile is a unique intermediate product of pyrethroid II due to the absence of cyanogen in I pyrethroid (Guo et al. 2021; Bhatt et al. 2021c). Under alkaline conditions, pyrethroids are easily hydrolyzed into cyclopropane-containing acid and α-hyroxy-3-

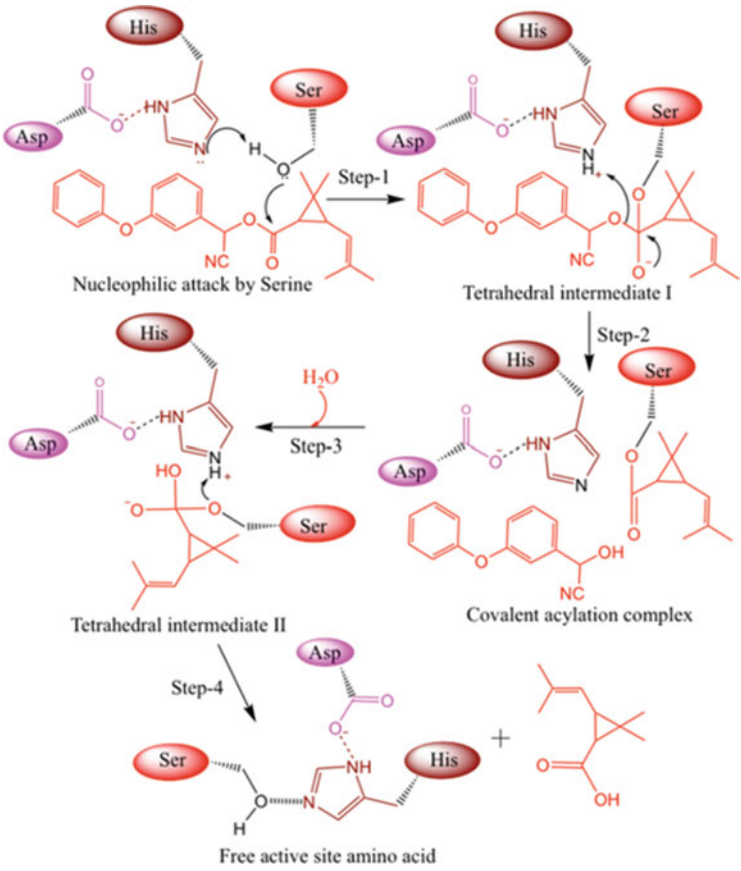

Fig. 6.1 Catalytic mechanisms of pyrethroids

phenoxybenzeneacetonitrile, and then quickly converted into 3-phenoxybenzaldehyde (Chen et al. 2011a). In the presence of dehydrogenase, 3-phenoxybenzaldehyde is further oxidized to 3-PBA (Deng et al. 2015). 3-PBA is an endocrine disruptor which stables in the environment, has higher water solubility than the parent compound, and is frequently detected in human urine. When monitoring the residues of pyrethroids, 3-PBA is often used as a detection indicator (Hongsibsong et al. 2019).

Most of the time, microorganisms follow the same metabolic pattern and metabolize the parent pesticide into 3-PBA (Chen et al. 2012d). *Staphylococcus succinus* HLJ-10 converts *D*-cyphenothrin through the cleavage of ester bonds and diaryl bonds. 3-PBA, 3-phenoxybenzaldehyde, and α-hyroxy-3-phenoxybenzeneacetonitrile were detected in this process (Huang et al. 2020); *B. licheniformis* B-1, *A. niger* YAT, *B. subtilis* BSF01, and *Brevibacillus parabrevis* BCP-09 have been reported to have similar metabolic steps on beta-cypermethrin (Tang et al. 2018a; Deng et al. 2015; Xiao et al. 2015). However, after the formation

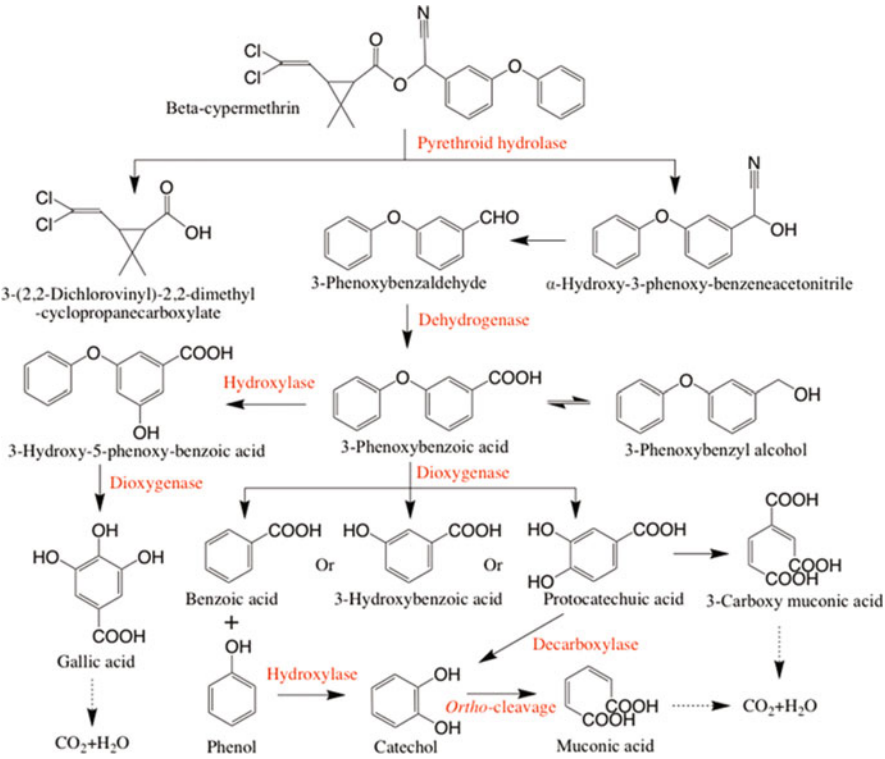

Fig. 6.2 Microbial degradation pathways of pyrethroids

of 3-PBA, different strains hydrolyze 3-PBA in completely different ways (Fig. 6.2). Under the catalysis of dioxygenase, 3-PBA may have a variety of downstream metabolic mechanisms. *Bacillus licheniformis* CY-012 can hydrolyze 3-PBA into benzoic acid and phenol (Tang et al. 2018b). Subsequently, phenol is hydrolyzed to catechol by hydrolase, and benzoic acid is further generated into 3-hydroxybenzoate. Another approach is performed by *A. niger YAT*; 3-PBA was hydrolyzed into protocatechuic acid and phenol (Deng et al. 2015). Protocatechuic acid undergoes aromatic ring cleavage with the assistance of dioxygenase to form 3-carboxy-muconic acid.

3-Phenoxybenzoic acid is one of the most studied pyrethroid intermediates. An interesting phenomenon was observed by Zhu et al. (2016) that 3-phenoxybenzyl alcohol and 3-PBA can be converted to each other, but will soon be hydrolyzed further. In addition, *Candida pelliculosa* ZS-02 and *A. oryzae* M-4 revealed another possibility of transforming 3-PBA into 3,5-dimethoxyphenyl or gallic acid (Chen et al. 2012a). After the formation of phenol into catechol, dioxygenase played an important catalytic role in the further decomposition of the aromatic ring to muconic acid (Zhao et al. 2019a). Ultimately, it is mineralized into nontoxic water molecules and carbon dioxide.

Until now, there are few reports on the biodegradation pathway of type I pyrethroids. In recent years, microbial degrading strains which can efficiently degrade permethrin, bifenthrin, d-cypermethrin, and permethrin have been screened from different sources, and their metabolic pathways have been demonstrated. Bhatt et al. (2020b) first hydrolyzed the ester bond of permethrin by *S. trueperi* CW3 to produce chrysanthemic acid and alcohol 2-(1,4,4-trimethyl-cy-clohex-2-enyl) ethanol. Then, the alcohol was oxidized to 1,4,4-trimethylcyclohex-2-ethylene carboxylic acid, which was further transformed into chrysanthemyl alcohol. Under the metabolism of *Acinetobacter baumannii* ZH-14, permethrin first formed 2,2-dimethyl-3-(2,2-dichlorovinyl) cyclopropanecarboxylic acid and 3-phenoxybenzenemethane, and then transformed into 3-phenyl benzaldehyde by redox. Finally, 3-Phenoxybenzaldehyde converted to 1,2-benzenedicarboxylic acid with the diaryl cleavage (Zhan et al. 2018).

6.6 Bioremediation of Pyrethroid-Contaminated Environments

The large-scale application of pyrethroids has caused ecological pollution of soil, sediments, and surface water, as well as serious indoor residues (Yoshida 2009; Chen et al. 2012c). After applying pyrethroids in the environment, as long as a small part of the active ingredients reach the target organism, most of them remain on the surface of plants and soil (Bhatt et al. 2020e; Huang et al. 2019). Most of the pyrethroid residues that contact the surface of plants and soil will be degraded by solar radiation. A small proportion of pyrethroids are utilized by indigenous microorganisms as a carbon source for growth. However, there are reports that the presence of deltamethrin can interfere with indigenous microbial communities (Braganca et al. 2019).

The long-term residues of pyrethroids in the soil force indigenous microorganisms to induce the expression of pyrethroid-related metabolic genes, thereby accelerating the metabolism of pyrethroid residues in contaminated environments. In addition to their own enzyme activities, soil temperature, pH, initial pyrethroid concentration, soil water content, and organic matter content also affect the soil bioremediation process by pyrethroid-degrading microbes (Bhatt et al. 2021d; Mishra et al. 2021). Zhang et al. (2016) collected a *B. cereus* strain Y1 from soil contaminated with deltamethrin, which can metabolize 74.9% of deltamethrin within 24 days. *Bacillus* sp. ISTDS2 was isolated from the marble mining area and was observed to use beta-cypermethrin as the sole source of nitrogen and carbon for growth (Sundaram et al. 2013). The β-cypermethrin with a concentration of 100 mg/L is thoroughly hydrolyzed by strain ISTDS2 in the field after 30 days. Recently, Bhatt et al. (2020c) obtained a *B. thuringiensis* SG4 from farmland. The experimental results suggested that 83.3% of 100 mg/L cypermethrin was removed from soil after 15 days of incubation.

6.7 Conclusions and Future Perspectives

Microbial degradation of pesticides in the environment faces many different problems. The metabolic activity of purified strain in soil has been the focus of previous research. Studies have shown that some microorganisms will give priority to the use of nutrients in soil media, leading to a decrease in the utilization of pyrethroids. The biodegradative efficiency of hydrophobic pyrethroids by microorganisms is related to the bioavailability of cells to pesticide molecules. The degradation rate of pyrethroids can be improved by adding appropriate surfactants Tween-80 and BRIj-35. The transformed pyrethroids pose another challenge to the environment. Pyrethroids metabolites are more water-soluble and have biological toxicity than the original pyrethroids. In the past 30 years, although a variety of microorganisms have been screened out and have the ability to hydrolyze pyrethroids. However, only a few strains can metabolize 3-PBA and pyrethroids simultaneously.

In order to solve these problems, many governance schemes have been proposed in recent years. Microorganisms that can utilize different substrates were combined to form consortia, which often exhibits a higher biodegradation effect than a single strain. Most microorganisms in nature cannot be obtained directly. Metagenomics provides a powerful tool for obtaining novel microbial enzyme resources. At present, the main pyrethroid degrading enzymes reported are carboxylesterase, monooxygenase, CYP, and laccase. However, not all enzymes have all the characteristics of high stability, high productivity, and high enzyme activity, which is essential for practical field application. Random mutagenesis, as another powerful tool, can enhance the catalytic activity and stability of enzymes through molecular modification, providing the possibility to obtain more potential enzymes.

Based on multidisciplinary results, many studies on immobilized degradation strains have been reported. Using calcium alginate in the form of microcapsules can immobilize a single purified strain or a multi-strain consortium. Compared with free cells, the immobilized strain has a higher substrate utilization rate. By regulating the flow rate, the number of repetitions of fixed strains can also be prolonged. With the development of materials science, many kinds of substrates for fixing cells have been developed, showing different advantages. In addition to immobilizing living cells, the immobilization of degrading enzymes has also been reported. Most of these experiments are currently in the laboratory research stage, and there are still many studies that need to be further carried out before the real large-scale application.

References

Bhatt P, Huang Y, Zhan H, Chen S (2019) Insight into microbial applications for the biodegradation of pyrethroid insecticides. Front Microbiol 10:1778. https://doi.org/10.3389/fmicb.2019.01778

Bhatt P, Bhatt K, Huang Y, Lin Z, Chen S (2020a) Esterase is a powerful tool for the biodegradation of pyrethroid insecticides. Chemosphere 244:125507. https://doi.org/10.1016/j.chemosphere.2019.125507

Bhatt P, Huang Y, Rene ER, Kumar AJ, Chen S (2020b) Mechanism of allethrin biodegradation by a newly isolated *Sphingomonas trueperi* strain CW3 from wastewater sludge. Bioresour Technol 305:123074. https://doi.org/10.1016/j.biortech.2020.123074

Bhatt P, Huang Y, Zhang W, Sharma A, Chen S (2020c) Enhanced cypermethrin degradation kinetics and metabolic pathway in *Bacillus thuringiensis* strain SG4. Microorganisms 8:223. https://doi.org/10.3390/microorganisms8020223

Bhatt P, Zhang W, Lin Z, Pang S, Huang Y, Chen S (2020d) Biodegradation of allethrin by a novel fungus *Fusarium proliferatum* strain CF2, isolated from contaminated soils. Microorganisms 8:593. https://doi.org/10.3390/microorganisms8040593

Bhatt P, Bhatt K, Sharma A, Zhang W, Mishra S, Chen S (2020e) Biotechnological basis of microbial consortia for the removal of pesticides from the environment. Crit Rev Biotechnol. https://doi.org/10.1080/07388551.2020.1853032

Bhatt P, Rene ER, Kumar AJ, Zhang W, Chen S (2020f) Binding interaction of allethrin with esterase: bioremediation potential and mechanism. Bioresour Technol 315:123845. https://doi.org/10.1016/j.biortech.2020.123845

Bhatt P, Gangola S, Bhandari G, Zhang W, Maithani D, Mishra S, Chen S (2021a) New insights into the degradation of synthetic pollutants in contaminated environments. Chemosphere 262:128827. https://doi.org/10.1016/j.chemosphere.2020.128827

Bhatt P, Zhou X, Huang Y, Zhang W, Chen S (2021b) Characterization of the role of esterases in the biodegradation of organophosphate, carbamate, and pyrethroid pesticides. J Hazard Mater 406:125026. https://doi.org/10.1016/j.jhazmat.2020.125026

Bhatt P, Bhandari G, Bhatt K, Maithani D, Mishra S, Gangola S, Bhatt R, Huang Y, Chen S (2021c) Plasmid-mediated catabolism for the removal of xenobiotics from the environment. J Hazard Mater 420:126618. https://doi.org/10.1016/j.jhazmat.2021.126618

Bhatt P, Joshi T, Bhatt K, Zhang W, Huang Y, Chen S (2021d) Binding interaction of glyphosate with glyphosate oxidoreductase and C–P lyase: molecular docking and molecular dynamics simulation studies. J Hazard Mater 409:124927. https://doi.org/10.1016/j.jhazmat.2020.124927

Birolli, W.G., Vacondio, B., Alvarenga, N., Seleghim, M.H.R., and Porto, A.L.M. (2018). Enantioselective biodegradation of the pyrethroid (+/−)-lambda-cyhalothrin by marine-derived fungi. *Chemosphere* 197, 651–660. doi: https://doi.org/10.1016/j.Chemosphere.2018.01.054

Braganca I, Mucha AP, Tomasino MP, Santos F, Lemos PC, Delerue-Matos C, Domingues VF (2019) Deltamethrin impact in a cabbage planted soil: degradation and effect on microbial community structure. Chemosphere 220:1179–1186. https://doi.org/10.1016/j.chemosphere.2019.01.004

Chen S, Hu M, Liu J, Zhong G, Yang L, Rizwan-ul-Haq M, Han H (2011a) Biodegradation of beta-cypermethrin and 3-phenoxybenzoic acid by a novel *Ochrobactrum lupini* DG-S-01. J Hazard Mater 187:433–440. https://doi.org/10.1016/j.jhazmat.2011.01.049

Chen S, Lai K, Li Y, Hu M, Zhang Y, Zeng Y (2011b) Biodegradation of deltamethrin and its hydrolysis product 3-phenoxybenzaldehyde by a newly isolated *Streptomyces aureus* strain HP-S-01. Appl Microbiol Biotechnol 90:1471–1483. https://doi.org/10.1007/s00253-011-3136-3

Chen S, Yang L, Hu M, Liu J (2011c) Biodegradation of fenvalerate and 3-phenoxybenzoic acid by a novel *Stenotrophomonas* sp. strain ZS-S-01 and its use in bioremediation of contaminated soils. Appl Microbiol Biotechnol 90:755–767. https://doi.org/10.1007/s00253-010-3035-z

Chen S, Hu Q, Hu M, Luo J, Weng Q, Lai K (2011d) Isolation and characterization of a fungus able to degrade pyrethroids and 3-phenoxybenzaldehyde. Bioresour Technol 102:8110–8116. https://doi.org/10.1016/j.biortech.2011.06.055

Chen S, Luo J, Hu M, Geng P, Zhang Y (2012a) Microbial detoxification of bifenthrin by a novel yeast and its potential for contaminated soils treatment. PLoS One 7:e30862. https://doi.org/10.1371/journal.pone.0030862

Chen S, Luo J, Hu M, Lai K, Geng P, Huang H (2012b) Enhancement of cypermethrin degradation by a coculture of *Bacillus cereus* ZH-3 and Streptomyces aureus HP-S-01. Bioresour Technol 110:97–104. https://doi.org/10.1016/j.biortech.2012.01.106

Chen S, Geng P, Xiao Y, Hu M (2012c) Bioremediation of beta-cypermethrin and 3-phenoxybenzaldehyde contaminated soils using *Streptomyces aureus* HP-S-01. Appl Microbiol Biotechnol 94:505–515. https://doi.org/10.1007/s00253-011-3640-5

Chen S, Hu W, Xiao Y, Deng Y, Jia J, Hu M, Zhou Z (2012d) Degradation of 3-phenoxybenzoic acid by a *Bacillus* sp. PLoS One 7:e50456. https://doi.org/10.1371/journal.pone.0050456

Chen S, Dong YH, Chang C, Deng Y, Zhang XF, Zhong G, Song H, Hu M, Zhang LH (2013a) Characterization of a novel cyfluthrin-degrading bacterial strain *Brevibacterium aureum* and its biochemical degradation pathway. Bioresour Technol 132:16–23. https://doi.org/10.1016/j.biortech.2013.01.002

Chen S, Lin Q, Xiao Y, Deng Y, Chang C, Zhong G, Hu M, Zhang LH (2013b) Monooxygenase, a novel beta-cypermethrin degrading enzyme from *Streptomyces* sp. PLoS One 8:e75450. https://doi.org/10.1371/journal.pone.0075450

Chen S, Chang C, Deng Y, An S, Dong YH, Zhou J, Hu M, Zhong G, Zhang LH (2014) Fenpropathrin biodegradation pathway in *Bacillus* sp. DG-02 and its potential for bioremediation of pyrethroid-contaminated soils. J Agric Food Chem 62:2147–2157. https://doi.org/10.1021/jf404908j

Chen S, Deng Y, Chang C, Lee J, Cheng Y, Cui Z, Zhou J, He F, Hu M, Zhang LH (2015) Pathway and kinetics of cyhalothrin biodegradation by *Bacillus thuringiensis* strain ZS-19. Sci Rep 5:8784. https://doi.org/10.1038/srep08784

Cho KM, Math RK, Islam SM, Lim WJ, Hong SY, Kim JM, Yun MG, Cho JJ, Yun HD (2009) Biodegradation of chlorpyrifos by lactic acid bacteria during kimchi fermentation. J Agric Food Chem 57:1882–1889. https://doi.org/10.1021/jf803649z

Cycoń M, Piotrowska-Seget Z (2016) Pyrethroid-degrading microorganisms and their potential for the bioremediation of contaminated soils: a review. Front Microbiol 7:1463. https://doi.org/10.3389/fmicb.2016.01463

Cycoń M, Zmijowska A, Piotrowska-Seget Z (2014) Enhancement of deltamethrin degradation by soil bioaugmentation with two different strains of Serratia marcescens. Int J Environ Sci Technol 11:1305–1316. https://doi.org/10.1007/s13762-013-0322-0

Cycoń M, Mrozik A, Piotrowska-Seget Z (2017) Bioaugmentation as a strategy for the remediation of pesticide-polluted soil: a review. Chemosphere 171:52–71. https://doi.org/10.1016/j.chemosphere.2016.12.129

Delgado-Moreno L, Lin K, Veiga-Nascimento R, Gan J (2011) Occurrence and toxicity of three classes of insecticides in water and sediment in two Southern California coastal watersheds. J Agric Food Chem 59:9448–9456. https://doi.org/10.1021/jf202049s

Deng W, Lin D, Yao K, Yuan H, Wang Z, Li J, Zou L, Han X, Zhou K, He L, Hu X, Liu S (2015) Characterization of a novel beta-cypermethrin-degrading *Aspergillus niger* YAT strain and the biochemical degradation pathway of beta-cypermethrin. Appl Microbiol Biotechnol 99:8187–8198. https://doi.org/10.1007/s00253-015-6690-2

Diegelmann C, Weber J, Heinzel-Wieland R, Kemme M (2015) Characterization of a cypermethrin-degrading *Methylobacterium* sp. strain A-1 and molecular cloning of its carboxylesterase gene. J Basic Microb 55:1245–1254. https://doi.org/10.1002/jobm.201500186

Fan XJ, Liu XL, Huang R, Liu YH (2012) Identification and characterization of a novel thermostable pyrethroid-hydrolyzing enzyme isolated through metagenomic approach. Microb Cell Factories 11:33. https://doi.org/10.1186/1475-2859-11-33

Feng D, Ke C, Li S, Lu C, Guo F (2009) Pyrethroids as promising marine antifoulants: laboratory and field studies. Mar Biotechnol (NY) 11:153–160. https://doi.org/10.1007/s10126-008-9130-9

Feng Y, Huang Y, Zhan H, Bhatt P, Chen S (2020a) An overview of strobilurin fungicide degradation:current status and future perspective. Front Microbiol 11:389. https://doi.org/10.3389/fmicb.2020.00389

Feng Y, Zhang W, Pang S, Lin Z, Zhang Y, Huang Y, Bhatt P, Chen S (2020b) Kinetics and new mechanism of azoxystrobin biodegradation by an *Ochrobactrum anthropi* strain SH14. Microorganisms 8:625. https://doi.org/10.3390/microorganisms8050625

Gangola S, Sharma A, Bhatt P, Khati P, Chaudhary P (2018) Presence of esterase and laccase in *Bacillus subtilis* facilitates biodegradation and detoxification of cypermethrin. Sci Rep 8:12755. https://doi.org/10.1038/s41598-018-31082-5

Garcia MA, Menendez-Lopez N, Boltes K, Castro-Puyana M, Marina ML (2017) A capillary micellar electrokinetic chromatography method for the stereoselective quantitation of bioallethrin in biotic and abiotic samples. J Chromatogr A 1510:108–116. https://doi.org/10.1016/j.chroma.2017.06.056

Guo Y, Huang Y, Pang S, Zhou T, Lin Z, Yu H, Zhang G, Bhatt P, Chen S (2021) Novel mechanism and kinetics of tetramethrin degradation using an indigenous *Gordonia cholesterolivorans* A16. Int J Mol Sci 22:9242. https://doi.org/10.3390/ijms22179242

Ham J, You S, Lim W, Song G (2020) Bifenthrin impairs the functions of Leydig and Sertoli cells in mice via mitochondrion-endoplasmic reticulum dysregulation. Environ Pollut 266:115174. https://doi.org/10.1016/j.envpol.2020.115174

He LM, Troiano J, Wang A, Goh K (2008) Environmental chemistry, ecotoxicity, and fate of lambda-cyhalothrin. Rev Environ Contam Toxicol 195:71–91. https://doi.org/10.1007/978-0-387-77030-7_3

Hongsibsong S, Prapamontol T, Dong JX, Bever CS, Xu ZL, Gee SJ, Hammock BD (2019) Exposure of consumers and farmers to organophosphate and synthetic pyrethroid insecticides in Northern Thailand. J Consum Prot Food Saf 14:17–23. https://doi.org/10.1007/s00003-019-01207-7

Huang Y, Zhan H, Bhatt P, Chen S (2019) Paraquat degradation from contaminated environments: current achievements and perspectives. Front Microbiol 10:1754. https://doi.org/10.3389/fmicb.2019.01754

Huang Y, Lin Z, Zhang W, Pang S, Bhatt P, Rene ER, Kumar AJ, Chen S (2020) New insights into the microbial degradation of D-cyphenothrin in contaminated water/soil environments. Microorganisms 8:473. https://doi.org/10.3390/microorganisms8040473

Huang Y, Zhang W, Pang S, Chen J, Bhatt P, Mishra S, Chen S (2021) Insights into the microbial degradation and catalytic mechanisms of chlorpyrifos. Environ Res 194:110660. https://doi.org/10.1016/j.envres.2020.110660

Li G, Wang K, Liu YH (2008) Molecular cloning and characterization of a novel pyrethroid-hydrolyzing esterase originating from the metagenome. Microb Cell Factories 7:38. https://doi.org/10.1186/1475-2859-7-38

Liang WQ, Wang ZY, Li H, Wu PC, Hu JM, Luo N, Cao LX, Liu YH (2005) Purification and characterization of a novel pyrethroid hydrolase from Aspergillus niger ZD11. J Agric Food Chem 53:7415–7420. https://doi.org/10.1021/jf051460k

Lin QS, Chen SH, Hu MY, Rizwan-ul-Haq M, Yang L, Li H (2011) Biodegradation of cypermethrin by a newly isolated actinomycetes HU-S-01 from wastewater sludge. Int J Environ Sci Technol 8:45–56. https://doi.org/10.1007/BF03326194

Lin Z, Pang S, Zhang W, Mishra S, Bhatt P, Chen S (2020) Degradation of acephate and its intermediate methamidophos: mechanisms and biochemical pathways. Front Microbiol 11:2045. https://doi.org/10.3389/fmicb.2020.02045

Liu X, Zhan Y, Luo Y, Zhang M, Geng S, Xu J (2012) Almond organophosphate and pyrethroid use in the San Joaquin Valley and their associated environmental risk. J Soils Sediments 12:1066–1078. https://doi.org/10.1007/s11368-012-0519-8

Liu X, Liang M, Liu Y, Fan X (2017) Directed evolution and secretory expression of a pyrethroid-hydrolyzing esterase with enhanced catalytic activity and thermostability. Microb Cell Factories 16:81. https://doi.org/10.1186/s12934-017-0698-5

Luo X, Zhang D, Zhou X, Du J, Zhang S, Liu Y (2018) Cloning and characterization of a pyrethroid pesticide decomposing esterase gene, Est3385, from *Rhodopseudomonas palustris* PSB-S. Sci Rep 8:7384. https://doi.org/10.1038/s41598-018-25734-9

Mendis JC, Tennakoon TK, Jayasinghe CD (2018) Zebrafish embryo toxicity of a binary mixture of pyrethroid insecticides: D-tetramethrin and cyphenothrin. J Toxicol 2018:4182694. https://doi.org/10.1155/2018/4182694

Mishra S, Zhang W, Lin Z, Pang S, Huang Y, Bhatt P, Chen S (2020) Carbofuran toxicity and its microbial degradation in contaminated environments. Chemosphere 259:127419. https://doi.org/10.1016/j.chemosphere.2020.127419

Mishra S, Pang S, Zhang W, Lin Z, Bhatt P, Chen S (2021) Insights into the microbial degradation and biochemical mechanisms of carbamates. Chemosphere 279:130500. https://doi.org/10.1016/j.chemosphere.2021.130500

Mulla SI, Ameen F, Tallur PN, Bharagava RN, Bangeppagari M, Eqani S, Bagewadi ZK, Mahadevan GD, Yu CP, Ninnekar HZ (2017) Aerobic degradation of fenvalerate by a gram-positive bacterium, *Bacillus flexus* strain XJU-4. 3 Biotech 7:320. https://doi.org/10.1007/s13205-017-0957-5

Paingankar M, Jain M, Deobagkar D (2005) Biodegradation of allethrin, a pyrethroid insecticide, by an *Acidomonas* sp. Biotechnol Lett 27:1909–1913. https://doi.org/10.1007/s10529-005-3902-3

Palmer-Brown W, de Melo Souza PL, Murphy CD (2019) Cyhalothrin biodegradation in *Cunninghamella elegans*. Environ Sci Pollut Res Int 26:1414–1421. https://doi.org/10.1007/s11356-018-3689-0

Pang S, Lin Z, Zhang W, Mishra S, Bhatt P, Chen S (2020) Insights into the microbial degradation and biochemical mechanisms of neonicotinoids. Front Microbiol 11:868. https://doi.org/10.3389/fmicb.2020.00868

Pankaj SA, Gangola S, Khati P, Kumar G, Srivastava A (2016) Novel pathway of cypermethrin biodegradation in a *Bacillus* sp. strain SG2 isolated from cypermethrin-contaminated agriculture field. 3 Biotech 6:372. https://doi.org/10.1007/s13205-016-0372-3

Qi Z, Wei Z (2017) Microbial flora analysis for the degradation of beta-cypermethrin. Environ Sci Pollut R 24:6554–6562. https://doi.org/10.1007/s11356-017-8370-5

Ruan Z, Zhai Y, Song J, Shi Y, Li K, Zhao B, Yan Y (2013) Molecular cloning and characterization of a newly isolated pyrethroid-degrading esterase gene from a genomic library of *Ochrobactrum anthropi* YZ-1. PLoS One 8:e77329. https://doi.org/10.1371/journal.pone.0077329

Song HH, Zhou ZR, Liu YX, Deng S, Xu H (2015) Kinetics and mechanism of fenpropathrin biodegradation by a newly isolated *Pseudomonas aeruginosa* sp. strain JQ-41. Curr Microbiol 71:326–332. https://doi.org/10.1007/s00284-015-0852-4

Sundaram S, Das MT, Thakur IS (2013) Biodegradation of cypermethrin by *Bacillus* sp. in soil microcosm and in-vitro toxicity evaluation on human cell line. Int Biodeterior Biodegradation 77:39–44. https://doi.org/10.1016/j.ibiod.2012.11.008

Tang AX, Wang BW, Liu YY, Li QY, Tong ZF, Wei YJ (2015) Biodegradation and extracellular enzymatic activities of *Pseudomonas aeruginosa* strain GF31 on beta-cypermethrin. Environ Sci Pollut R 22:13049–13057. https://doi.org/10.1007/s11356-015-4545-0

Tang AX, Liu H, Liu YY, Li QY, Qing YM (2017) Purification and characterization of a novel beta-cypermethrin-degrading aminopeptidase from *Pseudomonas aeruginosa* GF31. J Agric Food Chem 65:9412–9418. https://doi.org/10.1021/acs.jafc.7b03288

Tang J, Liu B, Chen TT, Yao K, Zeng L, Zeng CY, Zhang Q (2018a) Screening of a beta-cypermethrin-degrading bacterial strain *Brevibacillus parabrevis* BCP-09 and its biochemical degradation pathway. Biodegradation 29:525–541. https://doi.org/10.1007/s10532-018-9850-0

Tang J, Liu B, Shi Y, Zeng CY, Chen TT, Zeng L, Zhang Q (2018b) Isolation, identification, and fenvalerate-degrading potential of *bacillus licheniformis* CY-012. Biotechnol Biotec Eq 32:574–582. https://doi.org/10.1080/13102818.2018.1438210

Tang J, Hu Q, Lei D, Wu M, Zeng C, Zhang Q (2020) Characterization of deltamethrin degradation and metabolic pathway by co-culture of *Acinetobacter junii* LH-1-1 and *Klebsiella pneumoniae* BPBA052. AMB Express 10:106. https://doi.org/10.1186/s13568-020-01043-1

Thatheyus AJ, Gnana Selvam AD (2013) Synthetic pyrethroids: toxicity and biodegradation. *Appl Ecol environ Sci* 1:33–36. https://doi.org/10.12691/aees-1-3-2

Tian JW, Long XF, Zhang S, Qin QM, Gan LZ, Tian YQ (2018) Screening cyhalothrin degradation strains from locust epiphytic bacteria and studying *Paracoccus acridae* SCU-M53 cyhalothrin degradation process. Environ Sci Pollut R 25:11505–11515. https://doi.org/10.1007/s11356-018-1410-y

Wang BZ, Guo P, Hang BJ, Li L, He J, Li SP (2009) Cloning of a novel pyrethroid-hydrolyzing carboxylesterase gene from *Sphingobium* sp. strain JZ-1 and characterization of the gene product. Appl Environ Microbiol 75:5496–5500. https://doi.org/10.1128/AEM.01298-09

Wang T, Hu C, Zhang R, Sun A, Li D, Shi X (2019) Mechanism study of cyfluthrin biodegradation by *Photobacterium ganghwense* with comparative metabolomics. Appl Microbiol Biotechnol 103:473–488. https://doi.org/10.1007/s00253-018-9458-7

Wu PC, Liu YH, Wang ZY, Zhang XY, Li H, Liang WQ, Luo N, Hu JM, Lu JQ, Luan TG, Cao LX (2006) Molecular cloning, purification, and biochemical characterization of a novel pyrethroid-hydrolyzing esterase from *Klebsiella* sp. strain ZD112. J Agric Food Chem 54:836–842. https://doi.org/10.1021/jf052691u

Xiao Y, Chen SH, Gao YQ, Hu W, Hu MY, Zhong GH (2015) Isolation of a novel beta-cypermethrin degrading strain *Bacillus subtilis* BSF01 and its biodegradation pathway. Appl Microbiol Biotechnol 99:2849–2859. https://doi.org/10.1007/s00253-014-6164-y

Yang J, Feng Y, Zhan H, Liu J, Yang F, Zhang K, Zhang L, Chen S (2018) Characterization of a pyrethroid-degrading *Pseudomonas fulva* strain P31 and biochemical degradation pathway of D-phenothrin. Front Microbiol 9:1003. https://doi.org/10.3389/fmicb.2018.01003

Yoshida T (2009) Simultaneous determination of 18 pyrethroids in indoor air by gas chromatography/mass spectrometry. J Chromatogr A 1216:5069–5076

Zhai Y, Li K, Song J, Shi Y, Yan Y (2012) Molecular cloning, purification and biochemical characterization of a novel pyrethroid-hydrolyzing carboxylesterase gene from *Ochrobactrum anthropi* YZ-1. J Hazard Mater 221-222:206–212. https://doi.org/10.1016/j.jhazmat.2012.04.031

Zhan H, Wang H, Liao L, Feng Y, Fan X, Zhang L, Chen S (2018) Kinetics and novel degradation pathway of permethrin in *Acinetobacter baumannii* ZH-14. Front Microbiol 9:98. https://doi.org/10.3389/fmicb.2018.00098

Zhan H, Huang Y, Lin Z, Bhatt P, Chen S (2020) New insights into the microbial degradation and catalytic mechanism of synthetic pyrethroids. Environ Res 182:109138. https://doi.org/10.1016/j.envres.2020.109138

Zhang C, Wang S, Yan Y (2011) Isomerization and biodegradation of beta-cypermethrin by *Pseudomonas aeruginosa* CH7 with biosurfactant production. Bioresour Technol 102:7139–7146. https://doi.org/10.1016/j.biortech.2011.03.086

Zhang H, Zhang Y, Hou Z, Wang X, Wang J, Lu Z, Zhao X, Sun F, Pan H (2016) Biodegradation potential of deltamethrin by the *Bacillus cereus* strain Y1 in both culture and contaminated soil. Int Biodeterior Biodegradation 106:53–59. https://doi.org/10.1016/j.ibiod.2015.10.005

Zhang W, Lin Z, Pang S, Bhatt P, Chen S (2020) Insights into the biodegradation of lindane (γ-hexachlorocyclohexane) using a microbial system. Front Microbiol 11:522. https://doi.org/10.3389/fmicb.2020.00522

Zhang WP, Pang S, Lin Z, Mishra S, Bhatt P, Chen S (2021) Biotransformation of perfluoroalkyl acid precursors from various environmental systems: advances and perspectives. Environ Pollut 268:115908. https://doi.org/10.1016/j.envpol.2020.115908

Zhao JY, Chi YL, Liu FF, Jia DY, Yao K (2015) Effects of two surfactants and beta-cyclodextrin on beta-cypermethrin degradation by *Bacillus licheniformis* B-1. J Agr Food Chem 63:10729–10735. https://doi.org/10.1021/acs.jafc.5b04485

Zhao JY, Chi YL, Xu YC, Jia DY, Yao K (2016) Co-metabolic degradation of beta-cypermethrin and 3-phenoxybenzoic acid by co-culture of *Bacillus licheniformis* B-1 and *Aspergillus oryzae* M-4. PLoS One 11:e166796. https://doi.org/10.1371/journal.pone.0166796

Zhao J, Jia D, Chi Y, Yao K (2019a) Co-metabolic enzymes and pathways of 3-phenoxybenzoic acid degradation by *Aspergillus oryzae* M-4. Ecotoxicol Environ Saf 189:109953. https://doi.org/10.1016/j.ecoenv.2019.109953

Zhao J, Jia D, Du J, Chi Y, Yao K (2019b) Substrate regulation on co-metabolic degradation of beta-cypermethrin by *Bacillus licheniformis* B-1. AMB Express 9:83. https://doi.org/10.1186/s13568-019-0808-3

Zhu YT, Li JL, Yao K, Zhao N, Zhou K, Hu XJ, Zou LK, Han XF, Liu AP, Liu SL (2016) Degradation of 3-phenoxybenzoic acid by a filamentous fungus *Aspergillus oryzae* M-4 strain with self-protection transformation. Appl Microbiol Biotechnol 100:9773–9786. https://doi.org/10.1007/s00253-016-7847-3

Zuo ZQ, Gong T, Che Y, Liu RH, Xu P, Jiang H, Qiao CL, Song CJ, Yang C (2015) Engineering *Pseudomonas putida* KT2440 for simultaneous degradation of organophosphates and pyrethroids and its application in bioremediation of soil. Biodegradation 26:223–233. https://doi.org/10.1007/s10532-015-9729-2