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Research Progress of Microbial Degradation of Organophosphorus Pesticides

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ABSTRACT

In recent years, the extensive use of organophosphorus pesticides, especially the unreasonable use, has brought great safety risks to the environment. Organic phosphorus pollution has become a hotspot, and there are a large number of microorganisms in the soil and water body that can degrade organophosphorus pesticides. The extensive degradation performance of pesticides is applied to a variety of pollution remediation practices. This paper summarizes the current situation of organophosphorus pesticide use and pesticide residues, the species of organophosphorus pesticide degrading bacteria and its separation and screening and degradation of pesticide characteristics of the research progress.

KEYWORDS: organophosphorus pesticide; microbial degradation; pesticide residue; degrading bacteria

At present, China produces more than 200 kinds of pesticides, the annual output of nearly 10 million tons, of which organic phosphorus pesticide production accounts for about 80% of total output. Which as the main categories of pesticides in today's pesticides such as methamidophos, methyl parathion, parathion, methyl isofuran, monocrotophos, dimethoate, omethoate, phorate, phosphorus as the representative of the highly toxic, highly toxic pesticides, has been in the domestic mass production and extensive use [1]. Organophosphorus (Organophosphate, referred to as OPs) is a class of organophosphate compounds, it has high efficacy, variety of, wide range of control, low cost of choice of high, small injury in the environment, and other advantages [2] now widely used in the world, has a very important position. But its shortcomings are higher toxicity to humans and animals, often due to the use of safe custody, the occurrence of poisoning, and the loss of chemical pesticides and residues will lead to environmental pollution. In this paper, the existing types of organophosphorus pesticides, biodegradation technology and the existing results were systematically summarized and summarized, and reasonable suggestions for the further study of organophosphorus pesticide biodegradation were put forward.

As the scope of use of pesticides and the increasing number of pesticides and irrational use of pesticides, soil and other environmental pollution caused by pesticides, a large number of pesticide residues to people's health has brought great harm, the organophosphorus pesticide residues and Pesticide poisoning incidents are reported [3]. In addition, pesticide residues exceeded the certain obstacles to the export of agricultural products in China, but also affected the reputation of other related products and became an important means for setting up green trade barriers in some developed countries [4], affecting the sustainable development of the national economy. Even if the situation continues to worsen, it will threaten the sustainable development of mankind as a whole. The degradation of organophosphorus pesticides by soil microorganisms is an important means to control pesticide pollution. Microbial degradation of pesticides refers to the process of changing the structure of the active ingredients of pesticides under the action of microorganisms, leading to the process of chemical and physical properties change. By degrading them from macromolecular compounds into small molecule compounds, the degradation of water and carbon dioxide are harmless to the environment. Environmental factors and the chemical structure of the pesticide itself affect the degradation of pesticides by microorganisms. Therefore, it is necessary to understand the harmful effects of organophosphorus pesticides and their degradation processes and migration and transformation in the environment, and to find ways to degrade residual organophosphorus pesticides [5] and to remove their adverse effects on human life and to protect the environment. As the microbial degradation of pesticides with low cost, environmental impact is small, can minimize the concentration of pollutants and other advantages, so to strengthen the biodegradation of organophosphorus pesticides to address the environmental pollution of organic phosphorus pesticides, not only in today's relevant research areas of hot spots is also an urgent need to solve the current one of the problems.

1. The status of organophosphorus pesticides

1.1. 1Production and use of the status quo

China is a big agricultural country, but also a large country of pesticide production. The country has more than 2,000 pesticide production enterprises, producing about 200 kinds of pesticides. At present, the original drug production capacity of pesticides has reached more than 100 million tons, ranking second in the world, second only to the United States. According to the information, in 2005, China's total output of 1.09 million tons of pesticides, including organic phosphorus pesticide products accounted for 80% of the total. At present, there are 420 kinds of pesticide varieties produced in the world. Among them, 106 kinds of insecticides, 106 kinds of herbicides, 50 kinds of fungicides, and plant growth regulators and repellent are often used in more than 100 kinds. In China, the widely used organophosphorus pesticides have more than 30 kinds of [6], China's annual use of pesticides 80-100 million tons, ranking first in the world, commonly used pesticides have 150-160 [7]. Organophosphorus pesticide varieties are: (1) insecticides are trichlorfon, dichlorvos, dimethoate, omethoate, parathion, methyl parathion, methamidophos, monocrotophos, phoxim, water amine thiophosphate, phoxim, phoxim, phytophosphate, phytophosphate, phytophosphate, phorate, Herbicides are glyphosate, salted iron phosphorus; (3) fungicides are rice blast net, different rice blast net, methyl phosphorus, phosphorus phosphorus; (4) other such as ethephon, grams of phosphorus. With the development and progress of science and technology, to a certain extent, the demand for pesticides has been reduced, but the application of organophosphorus pesticides in agriculture still occupies an important position.

1.2. Pesticide residues

Pesticide residue refers to pesticide residues in the use of organisms, agricultural and sideline products and the environment of pesticides, toxic metabolites, degradation products and impurities in general. Pesticide residues are an inevitable phenomenon after the application of pesticides, but if the maximum residue limit, it will have a negative impact on humans and animals or through the food chain on the ecosystem caused by biological poisoning. According to Cornell University, the world's annual use of more than 400 million tons of pesticides, the actual performance of only 1%, the remaining 99% are scattered in the soil, air and water [8]. The pesticides in the environment circulate under various environmental factors under meteorological conditions and biological effects, resulting in the redistribution of pesticides in the environment and the proliferation of their pesticides, resulting in global atmospheric, water (surface water, groundwater), soil and biology the body contains pesticides and their residues. The invention and use of pesticides undoubtedly greatly increase the yield of crops, but with the development of science and technology and people's living standards, pesticide residues on the environment and human health caused by the negative impact of increasingly exposed. The development of rapid, sensitive, reliable and practical environment of pesticide residues in the analysis of technology and research methods of pesticide degradation is undoubtedly the control of pesticide residues, the protection of the ecological environment and human health an effective means.

2. Study on Pesticide Degradation Bacteria

2.1. The main microbial flora of organophosphorus pesticides

Table 1 Part of the pesticide degrading bacteria and their degradation of pesticide species [11-12]

Microbial species Pesticide name
Pseudomonas, methamphetamine, malathion, phthalocyanine, phorate, dichlorvos, parathion, methyl parathion, phoxim, fenitroth, dimethoate
Bacillus thiophosphate, parathion, methyl parathion, methamidophos, dichlorvos, dimethoate, fenitrothion
Festival bacteria is malathion, two throat agriculture
Flavobacterium parathion, methyl parathion, malathion, two throat, poisonous cicadas, methamidophos
Alkaline is parathion, methyl parathion,
Pseudomonas aeruginosa is parathion, poisonous cicadas
Brevibacterium parathion, methyl parathion
Polymorphic bacteria are malathion, parathion
Thiobacillus is phorate
Acinetobacter maleic acid, methyl parathion, triazophos, parathion, dichlorvos
Aspergillus
Antipyret, bromothiophosphate, Diptera phosphorus, methamidophos, dimethoate, parathion, malathion, omethoate
Penicillium Insect Pest, Parathion, Trichlorfon
Rhizopus is also insects phosphorus, bromothiophosphate

Trichoderma is dichlorvos, parathion, malathion	
Fusarium is an enemy	
Yeast is methamidophos	
Small green algae phorate, parathion	

Soil microbes include bacteria, fungi, actinomycetes and algae, all of which are degraded in soil and agricultural products. At present, there are two kinds of bacteria and fungi [9]. Bacteria are dominated by microbial biodegradation due to their biochemical adaptability and susceptibility to mutant bacteria [10]. The organophosphorus pesticide residues present in the environment. In addition to partial physical degradation and chemical degradation, most of the microbial degradation or transformation occurs through the role of toxic pesticides into non-toxic or low toxicity of other compounds. Some of the microbes that degrade pesticides from nature, including bacteria, fungi and actinomycetes (see Table 1).

As can be seen from Table 1, some of the same bacteria can simultaneously degrade several pesticides [13], such as pseudomonas can degrade most organophosphorus pesticides, including parathion, methamidophos, Dichlorvos, dimethoate, dimethoate, etc .; some bacteria are only a specific degradation of the role of pesticides, such as thiophanate has a degradation of phorate; some show the degradation of inert, such as Arthrobacter and Escherichia coli; do not directly degrade pesticides, but through the total metabolism to complete the degradation process.

2.2. Overview of domestic research

Pesticide pollution is becoming increasingly serious, China's scientific workers since the 1940s began to study, after the mid-60s. This field is active and has become a hot topic in environmental pollution control. In recent years has made great progress in research, mainly in: (1) many organophosphorus pesticide microbial degradation strains (including fungi, bacteria, etc.) have been separated and identified, such as Wang Yongjie, who separated from the sludge Degradation rate of dimethoate (degradation rate of 43.6%, P <0.05) was higher than that of the control group (P <0.05) L00 mg / L), but did not degrade methamidophos; (2) has been reported to the organophosphorus pesticide degradation pathway, oxidation, reduction, hydrolysis, condensation, isomerization, methylation and demethylation, etc., its essence is enzymatic reaction; (3) Organophosphorus pesticide degrading enzymes, hydrolyzing enzymes of parathion are cloned from the parathion-degrading enzyme gene and the Pseudomonas sp. Of the degraded strain of Huangfeng 1, which has been screened, and the enzyme Characteristics of the study, has been reported with the degradation of the enzymes related to oxygenase, dehydrogenase, azo reductase and hydrolase, etc., and carried out the degradation of bacteria to reduce enzyme localization research. With the development of modern molecular biology, bioinformatics means to clone the degrading enzyme gene into a convenient way; (4) Construction of highly efficient pesticide-degrading genetic engineering bacteria In recent years, with the development of genetic engineering and molecular biology, the researchers have used gene recombination technology or protoplast fusion technology to construct the gene expressing the enzyme which degrades the pesticide efficiently , To obtain engineering bacteria, to improve the degradation of specific protein or enzyme expression level, thereby improving the degradation efficiency, expand the degradable bacteria degradation spectrum and improve the strain adaptability to the environment [14]. By understanding the distribution of microorganisms in the degradation of organophosphorus pesticides in ecosystems, mastering the microbial degradation of organophosphorus pesticides, and exploring the organophosphorus pesticide degrading enzymes and their genetic characteristics of microorganisms will help to predict and control the organic Phosphorus pesticide pollution dynamics, at the same time for the construction of genetic engineering degradation bacteria, innovation and environmental monitoring technology to provide new tools. However, both domestic and foreign studies have reported that both the production and application of microbial degrading bacteria and fungicides that promote both crop growth and pesticide degradation have been reported.

2.3. Enrichment and separation of organophosphorus pesticide degrading bacteria

Sources of organophosphorus pesticide-degrading bacteria

(1) Separation of organophosphorus pesticide degrading bacteria

Mainly from the soil, water or sludge pollution environment such as direct separation of screening or enrichment culture obtained. The enrichment and culture methods of the degrading bacteria are: liquid enrichment culture method, soil circulation method and continuous flow culture method. Chemostat as a continuous culture is an effective method to target the pesticide as a culture medium to limit the growth of the substrate, under the effect of changing the choice of pressure can be screened to degrade the target pesticide microbial strains or induced Degrading ability of mutant strains.

In most cases, it is directly separated from the environment contaminated by the target pesticide, which is based on the natural enrichment of pesticide-degrading bacteria in some special environments (ie, long-term contamination of the target pesticide or long-term pollution of the pesticide produced by the target pesticide) Common in the soil, combined with artificial pressure selection, often will accelerate the separation of degrading bacteria.

(2) Man-made access to organophosphorus pesticide pathogens

The presence of organic phosphorus pesticide degrading bacteria due to the impact of external environmental factors, their ability to solve their own very limited, or cannot fundamentally solve the problem of organophosphorus pesticide pollution and agricultural pesticide exceeded the standard, and thus directly isolated from the natural degradation of bacteria, as a study of organophosphorus pesticide microbial degradation of the basic way, according to the actual needs of the production of society, must be obtained on the transformation of the degradation of bacteria. One is to modify the organophosphorus pesticide degrading bacteria, which will degrade the different strains of different organophosphorus pesticides for gene recombination and protoplast fusion. The degradation ability of the original degraded bacteria is low, the target is single and the growth conditions are harsh and other biological properties, access to new degradation of engineering bacteria. The second is the use of different species of organophosphorus pesticide degradation and metabolic capacity of the different creative transformation. The third is the use of chemical mutagens or other mutagenesis methods to obtain new degrading bacteria Liu Yuhuan et al. [15]

3. Study on Microbial Degradation of Pesticides

3.1. Factors Influencing Microbial Degradation of Organophosphorus Pesticides

Environmental factors, pesticide species and their chemical structure and the types of microorganisms, metabolic mechanisms and metabolic types affect the degradation of pesticides by microorganisms.

The effect of organophosphorus pesticide type and chemical structure on biodegradation

(P = O), such as methamidophos, omethoate, and dichlorvos. The other is the two types of pesticides, which are divided into two types: one is phosphorus through the double bond and oxygen (P = S), such as parathion, methyl parathion, phoxim, water amine thiophosphate, and chlorpyrifos.

(2) The chemical structure of the impact of pesticide groups and molecular structure to determine its degradation in the microbial environment behavior. The chemical structure of pesticides determines its solubility, molecular arrangement and spatial structure, chemical functional groups, molecular attraction and exclusion and other characteristics, and thus affect the pesticide can be microbial intake. Many of the broad-spectrum degraders, which are currently isolated from nature, have a degrading effect on the same pesticide because these pesticides have the same or similar structure. Pesticide chemical structure contained in the halogen, nitrogen, hydrogen and other atoms will reduce the biodegradability of organic matter, the more the number of such groups, the worse biodegradability. And the presence of hydroxyl groups and carboxyl groups favors biodegradability. The chemical structure of the pesticide determines the rate at which it is degraded by microorganisms. For aromatic compounds, the more the number of substituted chlorine on the benzene ring is, the more difficult it is to degrade, and the type of substitution on the benzene ring is most difficult to degrade. Therefore, the biodegradation of 2,4,5-T is more difficult than that of 2,4-D More [16]. Other physical and chemical properties of pesticides, such as water solubility, adsorption, etc. also affect the degradation of microorganisms.

Impact of environmental factors

Environmental factors such as soil pH, temperature, water content, dissolved oxygen, salinity, organic matter content, viscosity and climatic conditions affect the degradation of pesticides by microorganisms. Among them, the soil pH value on the degradation of relatively large, not only affect the activity of microbial degrading enzymes, but also affect the chemical degradation of pesticides. Brajesh et al. (2000) studied the effect of pH on the degradation of phenanthroline and chlorpyrifos at pH 4.7-6.7 (acid), and the half-life of chlorpyrifos degradation decreased from 256 d to 35 d. However, 7.7-8.4 (alkaline), the half-life decreased to 16 days, while the phenanthroline-degrading bacteria were the fastest at pH 6.7-6.8 [17]. Wang Jun et al. studied the degradation of microorganisms at 75% FC (soil water content) and 120% FC at 30% FC [18], which may be due to the relative activity of soil microbes under high FC Higher. Temperature affects the enzyme reaction kinetics, microbial growth rate and so on. Some nutrient elements, especially growth factors, must be ingested from environmental organic matter, which plays a vital role in the life and degradation of microbes. In general, the optimum conditions for microbial degradation under laboratory conditions are: temperature 28-35 ° C, pH 6.8-7.5, and other suitable conditions.

3.2. Biodegradation mechanism

When organophosphorus pesticides enter the soil environment, can be physical degradation, chemical degradation and microbial degradation. Physical degradation and chemical degradation mainly include photoreaction, thermal reaction, redox reaction, electrochemical reaction, microbial degradation mainly includes a variety of enzymatic reactions [19]. Compared with the physical and chemical degradation methods, microbial degradation has the characteristics of mild reaction conditions, fast reaction and strong reaction.

A large number of studies have shown that there are two main types of microbial degradation of pesticides: one is the direct effect of degrading bacteria on pesticides, which is mainly a series of enzymatic hydrolysis [20], the use of microorganisms and their degradation the enzyme degrades the residual organophosphorus pesticides in the environment. Hilda et al. (1999) found that many strains of Pseudomonus, Bacillus and Rhizobium genus have potent functions for the degradation of phosphorus, and are believed to play an important role in the degradation of organophosphorus pesticides [21]. In general, the microbial itself contains the degradation of the pesticide enzyme gene, or itself, although the enzyme gene, but by the introduction or the choice of environmental pressure, gene mutation, resulting in a new degrading enzyme system, often said pesticide microorganisms Degradation belongs to this class. The coding sequence of the organophosphorus-degrading enzyme gene from Flavobacterium sp. and Pseudomonas sp. were also confirmed to be identical [22-23]. When the biodegradation of pesticides is caused by intracellular enzymes [24], whether it is symbiotic or a single microbial degradation of pesticides are mostly in the enzyme under the conditions of participation. Microorganisms have the enzymatic reaction directly on the organophosphorus pesticide in the way of oxidation, dehydrogenation, reduction, hydrolysis and other types of reactions [25].

The other is through the activities of microorganisms to change the chemical or physical environment and indirectly play a role in the degradation of organophosphorus pesticides. Common ways are mineralization, co-metabolism and intergeneric synergistic metabolism [26]: (1) mineralization: refers to the microbial directly to the organic phosphorus pesticide as a growth matrix, its complete decomposition into inorganic; (2) co-metabolism [27] role refers to the micro-organisms in its available carbon source, the original cannot use the material can also be catabolic; (3) interspecific synergistic metabolism: refers to the same environment in a number of microbial joint metabolism of certain organophosphorus pesticides.

3.3. Microbial degradation of organophosphorus pesticide metabolic types

Currently screened organophosphorus pesticide degradation of highly effective bacteria mainly bacteria, fungi and algae. Different microbes have a significant difference in their ability to dissolve phosphorus. There are three main ways for microbial degradation of organophosphorus pesticides [28]:

(1) Microorganisms directly to organic phosphorus pesticides as a growth matrix, in the process of catabolism of the organic matter to obtain the energy required for life activities and raw materials required for their own renewal.

(2) Co-metabolism: refers to the microbial in its available carbon source, the original cannot use the material can also be catabolic phenomenon. Co-metabolism was first proposed by Leadbetter and Foster, who found that methanogens were able to oxidize ethane but could not use it as a growth matrix [29].

(3) Interspecific synergistic metabolism: refers to the same environment in a number of microbial joint metabolism of certain organophosphorus pesticides. In-depth study of co-metabolism and synergistic metabolism can provide new ideas for the biodegradation of organophosphorus pesticides that are more difficult to degrade [30].

In addition, from the nutritional type of microbes, some microbes to a certain pesticide for its growth of the only carbon source, nitrogen source or energy, and some by metabolic degradation of pesticides. In addition, some micro-organisms do not get from the pesticide nutrition or energy, but the development of the detoxification to protect their own survival, known as detoxification metabolism [31].

3.4. Application of Microbial Degradation of Pesticides

In recent years, with the clarification of microbial degradation of pesticide mechanism and the rise of molecular biology, more and more scientific research workers to study the direction of pesticide microbial degradation of the applied research.

Since the pollution of the pesticide to the environment is not only due to its residue in the use of farmland, a large part of the pollution is in the production and transportation of pesticides have occurred, such as pesticide wastewater discharge is a major source of pollution, the environment caused serious pollution and harm. Most pesticide plants use microbial degradation to treat wastewater. At present, several commonly used methods are active sludge method, biofilm method, oxidation pond method, anaerobic wastewater treatment and aerobic biological treatment method [32]. However, these conventional methods have some shortcomings cannot be overcome, such as activated sludge method prone to sludge expansion phenomenon, easy to produce secondary pollution. To overcome these shortcomings, researchers turn their attention to new directions, such as immobilized microbial technology, biological remediation technology, genetic engineering bacteria are the current research hot spots.

4. Conclusions

So far, despite the high efficiency, low toxicity, low residue, easy to degrade the development and development of new chemical pesticides has made great progress, but agricultural products, soil and rivers and lakes in the large number of chemical pesticides residues, as well as new chemical pesticides new pollution is still unavoidable. Biological pesticides with high efficiency and environmental pollution and other characteristics of small, but the biological pesticides in the short term are still impossible to replace chemical pesticides. With the improvement of people's living standard, the awareness of organophosphorus pesticide residues and the urgent requirement of green food, the research on the degradation of organophosphorus pesticide microbes has been paid much attention. The screening, culture and enzyme preparation of highly effective bacteria Production and the development of modern molecular biotechnology and genetic engineering technology, microbial degradation of organophosphorus pesticide research has been greatly developed. At present, microbial degradation of organophosphorus pesticides are mainly concentrated in methamidophos and dimethoate but there are still some organophosphorus pesticides cannot be degraded by microorganisms, so the accumulation of these non-biological substances in the environment and solve the treatment of organophosphorus pesticides Long cycle, slow effect and other issues is the difficult task of future research. It is believed that the strains with high degradation characteristics can be separated and screened by multi-channel and multi-method. The characteristics of microbial degradation of pesticides can be studied deeply, and the highly efficient genetic engineering bacteria and genetic engineering bacteria can be used to comprehensively control the environmental pollution of pesticides and microbial degradation of organophosphorus pesticides showing attractive application prospects.

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