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Study on Chemical Behavior of Pesticide Fungicide in Lake

Zhao Fan[a,b]

[a]Wuhan University of Technology, Wuhan 430070, China
[b]School of Chemistry and Environment, Henan University of Finance and Economics, Zhengzhou 450014, China
8040665@qq.com

Pesticide fungicides are widely used in agricultural production, these fungicides go into the lake through the rain or other means, having a greater impact on the lake environment. The environmental chemical behavior of pesticide fungicides in lakes includes photochemical degradation of pesticides, chemical degradation of water and toxicity of pesticides to aquatic organisms. In this work, the common triazolone was used as an example to study the chemical behavior of pesticide water environment. The effects of triazolone on photochemical degradation, the mechanism of water chemistry degradation and the effect on the toxicity of water were discussed. Rational use, evaluation of its environmental safety and ecological environment provides a scientific basis for repair.

1. Introduction

The effect of pesticide fungicides on the environment depends not only on the toxicity of the pesticide itself, but also on the chemical behavior of the pesticide fungicide after entering the environment (Arias-Estévez et al., 2008). Studying the chemical behavior of pesticide fungicides in water environment can provide scientific basis for the rational use of pesticide fungicides, prevent pesticide fungicides from polluting water bodies and endangering aquatic organisms (Sanchez-Cortes, 2001). In general, the greater the water solubility of the pesticide fungicide, the more stable the nature, the greater the probability of its use into the water after use, the higher the residual concentration in the water. In addition to the nature of pesticide fungicides (Buser et al., 2002), the acceptance of different water bodies also affect the degree of pesticide fungicide pollution. Residual pesticide fungicides in the surface water can undergo a series of physical and chemical processes such as volatilization, migration, photolysis, hydrolysis, aquatic metabolism, absorption, enrichment and adsorption by sediment in the waters. The pesticide fungicides entering the lake ecosystem can be bio-enriched through the food chain, and the ecological effects of pesticide fungicides on aquatic organisms are mostly related to their accumulation and transfer in organisms (Chiou et al., 1977).

Part of the pesticide fungicide in the lake water can be absorbed by the plankton or adsorbed by suspended particulate matter. After some of the suspended matter precipitates, it forms a substrate and becomes a bait for the low habitat. Phytoplankton is quick to absorb pesticide fungicides. The pesticide fungicides that enter the watershed water in the waters of the stratified waters are mainly absorbed by the phytoplankton in this water layer and are transferred down along the food chain, and finally accumulated in the fish, shrimp and shellfish in vivo (Fenik et al., 2011). According to the radioactive 14C experiments found that the content of minimal DDT, dieldrin and aldrin, it may reduce the phytoplankton photosynthetic capacity (Kahle et al., 2008). The study of the effects of pesticide fungicides on freshwater plants in most fresh water has shown that the population structure in freshwater ecosystems has changed, with the main populations being transformed from large daphnia to other small zooplankton such as Rot-ifers and Bosmina (Komárek et al., 2010). This suggests that pesticide fungicides promote the growth of small zooplankton, while inhibiting the growth of medium-sized zooplankton breeding. And the dominant population is large fleas, the whole system of the richness of the population is very low, when the pesticide fungicide change the population structure, greatly improving the diversity of the population. We through the triadimefon this common pesticide fungicide research, to explore the fungicide on the lake ecological environment (Gevao et al., 2000).

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2. Photochemical degradation of pesticide fungicides in lakes

After the application of pesticides, whether it is on the surface of plants, or into the soil, water and the atmosphere (González-Rodríguez et al., 2008), are subject to sunlight and photochemical degradation, light stability has become an important part of pesticide environmental safety evaluation. And according to the molecular absorption of light path, photolysis can be divided into direct photolysis and indirect photolysis (Sicbaldi et al., 1997).

2.1 Direct photochemical degradation

Direct photochemical solution refers to the pesticide fungicide molecules absorb the energy of the photon transition to stimulate the singlet reaction occurs after the reaction into the product, excited singlet state can also be generated by the channel between the excited triplet, excited triplet can occur split, dissociation, photoionization (Daly G L, 2007). The resulting particles and the surrounding medium react directly. Pesticide fungicide direct photochemical solution of the possible process is as shown in Figure 1 (Neumann et al., 2002):

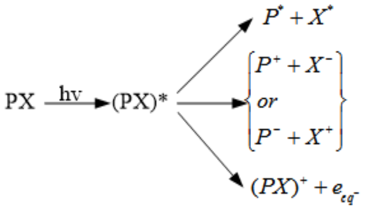

Figure 1: The process of direct photochemical hydrolysis.

In 1954 Gunther first observed insecticide P, P-DDT was sprayed into the field in the summer due to natural light degradation and soon lost its efficacy (Singh N, 2002). In 1946, Wichmann and Lindquist studied the photolysis product of DDT and its disappearance of insecticidal activity by using 253nm ultraviolet light and solar light source respectively. Later, many researchers used sunlight, ultraviolet light, xenon lamp, mercury lamp and other different sources of pesticides in different media (organic solvents, aqueous solution, soil surface, etc.) in the direct photolysis carried out extensive research: 300W low pressure mercury lamp, the photolysis of Pterosporin in aqueous solution was the first order reaction kinetics, the photolysis half-life was 6.81H, and the photodegradation of cyanuricillin in aqueous solution and petroleum ether solution showed secondary reaction kinetics The half-life of the solution was 13.7 min and 9.4 min, respectively (Iwakuma et al., 1993).

2.2 Indirect photochemical degradation

Indirect photochemical degradation refers to the excretion of photons in certain substances in the environment excited state and then induced pesticide molecules to stimulate the product. Indirect photochemical degradation includes photodegradation and photocatalytic degradation (Bollen et al., 1961). Photodegradation refers to the presence of some natural substances in the environment can be excited by solar energy, and then the energy transfer to the pesticide molecules to the process of degradation. Photocatalytic degradation refers to natural substances such as semiconductor powders TiO. After the sun radiation to produce free radicals, pure oxygen and other intermediates, pesticide molecules and then react with these intermediates process. Photocatalytic degradation is actually a special case of sensitized photolysis. Pesticide light sensitive reaction path is as shown in Figure 2

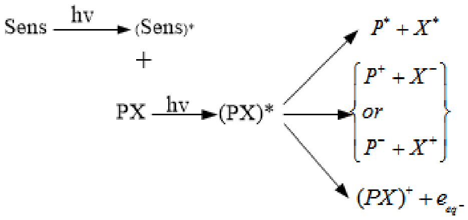

Figure 2: The process of indirect photochemical hydrolysis

Some of the substances which are widely present in natural water, such as humus, hydrogen peroxide, metal ions and salts, have an important effect on the photochemical degradation of pesticides. In the photochemical degradation of pesticides commonly used photosensitizers are: acetone, benzophenone, nucleus yellow cable, hydrogen peroxide, methylene blue, acetophenone, TiO2,Anthraquinone, rotenone and some aromatic amines and so on. It is reported that with 254nm UV lamp as the light source, the aqueous solution of fulvic acid on the herbicide atrazine photolysis has a quenching effect; acetone and H2O2 on the fast kill barnyard has a great impact on high pressure mercury lamp In the presence of 1 mg/L acetone and H2O2, the photosynthetic rate of the barley was increased by 56.54% and 41.04%, respectively. After 30 min irradiation, the results showed that the humic acid on the carbamate, organic phosphorus, pyrethroid Esterification, triazole and sulfonylurea pesticides under high pressure mercury lamp. The results show that the photolysis can improve the photodegradation rate and sensitize the photolysis reaction. In addition, some pesticides themselves have a photosensitizer or a light quencher of the characteristics, can accelerate or delay the rate of other pesticide molecules photolysis. Through the solid phase and the liquid phase of the photolysis found that grams of mites and tyrosive mites between each other there is a significant light or light quenching effect, the sun, grams of mites against Pa mite spirit of 176.53% The results showed that the photodegradation effect of methyl parathion, chlorpyrifos and dimethoate on the photolysis of nicotine, pyrethrin and cypermethrin in aqueous solution was studied. Pyridazine and thiophosphate, carbendazim on three kinds of pyrethroid insecticides in three different light sources have a photodegradation effect, and carbofuran three pyrethroid insecticides in the sun and high pressure mercury Light has a light quenching effect (Tremolada, 2004).

3. Hydrochemical Degradation of Pesticide Fungicide in Lake Environment

Chemical degradation of pesticide fungicides is a chemical reaction process, pesticide molecules (RX) interact with water molecules, pesticide molecules leaving the group X fracture, and water covalent to form new groups. Pesticide hydrolysis will change its molecular structure and toxicity, the hydrolysis of the general formula (González-Rodríguez et al., 2008; Daly et al., 2007):

$$RX + H_2O \rightarrow ROH + HX \tag{1}$$

In many pesticide molecules there are chemical structures which can be hydrolyzed, such as esters, amides, nitriles, ethers and acid chlorides. After the hydrolysis of the above structure, always formed a polarized degradation of the product, the result is often the pesticide to lose its original biological activity.

The hydrolysis rate of the pesticide fungicide under certain temperature conditions can be expressed as follows:

$$-\frac{dA}{dt} = K \bullet C_A \bullet C_{OH^-} (or\, C_{H_3O^+}) \tag{2}$$

Where C_A is the concentration of pesticide; C_{OH^-} and C_{H3O^+} are the concentration of hydroxide ions and hydrogen ion in the reaction medium respectively; K is the secondary reaction rate constant. The hydrolysis reaction of pesticide fungicide in water is secondary. However, when the concentration of the reactants is low and the concentration of hydroxide ions remains constant in buffer or ambient water, then equation (2) can be expressed as:

$$-\frac{dA}{dt} = k \bullet C_A \tag{3}$$

According to the formula (3), it can be considered that the hydrolysis reaction of the pesticide in the buffer condition F is in accordance with the kinetic reaction, and k is the first order reaction rate constant. (3) to get the following formula:

$$C_t = C_0 \bullet \exp(-kt) \tag{4}$$

3.1 Effect of pH on Chemical Degradation of Water

The results showed that the hydrolysis rate of the four pesticides at different pH conditions was different, and the effect of pH on the hydrolysis rate of different pesticide varieties was different: The methylamine is stable under neutral and alkaline conditions, while pyrimidine is less stable under neutral conditions than in acidic conditions. It has also been shown that sulfonylurea compounds are hydrolyzed in acidic pH solutions and are relatively stable under neutral conditions: it has been reported that the results of the hydrolysis of aldicarb and its metabolites in aqueous media at pH 6, When the pH of the medium increased from 7 to 8, the hydrolysis rate constant increased by 4~10 times and the half-life was correspondingly shortened. The hydrolysis of imidacloprid found that imidacloprid was in acidic and neutral condition. The hydrolysis is slow or does not occur, but it is susceptible to OH^- attack under alkaline conditions, and the nucleophilic substitution reaction occurs, and the hydrolysis mechanism of the insect is predicted (Singh et al., 2002; Iwakuma et al., 1993; Nemet et al., 2017).

3.2 Effect of Temperature on Chemical Degradation of Water

According to the relationship between temperature and reaction rate, that is, Arrenhinus (Arnieus) formula:

$$Ink = -E / RT + InA \tag{5}$$

where, E is reaction activation energy (J/mol); R is gas constant (8.314J/mol.K); T is absolute temperature(K); A is a constant; k is the reaction rate constant.

It can be seen from the formula, the temperature can increase the hydrolysis rate of pesticides, but the extent of pesticide varieties and media pH conditions vary. In the acidic condition (pH5), the increase of the temperature can greatly accelerate the hydrolysis rate. Under alkaline condition (pH 9), the hydrolysis rate increases with the temperature and the phenomenon is not obvious. The hydrolysis rate of methyl isofuran is affected by temperature, which is significantly lower under alkaline conditions than in acidic conditions. The results show that the hydrolysis effect of sulfonylurea herbicides shows a significant temperature effect and can be described by the first order kinetic equation. In the case of chlorosulfonated dragon, Based on the literature, the activation energy of the sulfonylurea compounds was 83-135kJ / mol.

4. Experimental results and discussion

The photochemical degradation of triazolone in three organic solvents was designed to reveal the difference of photodegradation of triazolone in organic solvents and three different polarities in two kinds of light sources to investigate the photostability of triunone. The experimental results are shown in Figure 3 and Figure 4.

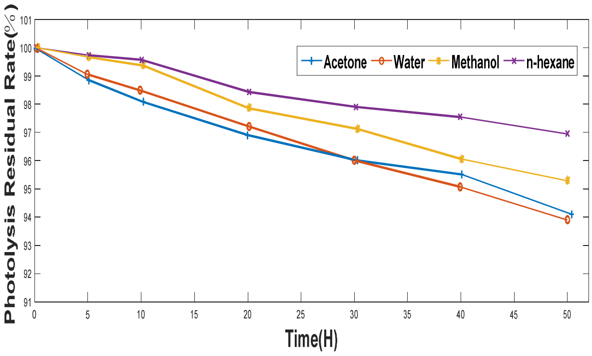

Figure 3: Photolysis Residual Rate of Three Different Organic Solvents in Sunlight

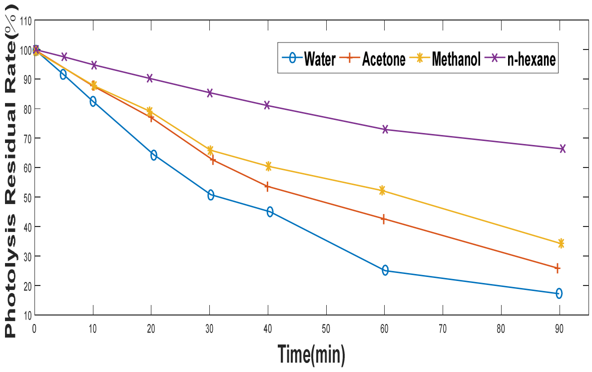

Figure 4: Photolysis Residual Rate of Three Different Organic Solvents in 300W mercury lamp

It can be seen that the photodegradation behavior of triazolone in two organic sources shows that triazolone is difficult to undergo direct photolysis in sunlight, which is related to the absorption potential of triazolone in organic solvent. The absorbance of triadimefon in pure water is significantly higher than that of other solvents, and there is a wide and strong absorption band at 240-290 nm. Acetone decreases with increasing wavelength between 230-250 hm, but between 250 and 280 nm and there was a tendency to increase the absorbance with wavelength. There was a strong absorption peak around 290 hm, while that of methanol and n-hexane increased at 230 nm or more with the increase of wavelength and increased to about 300 nm. The photolysis of triazolone in pure water and three organic solvents is difficult to occur due to the fact that the shortest wavelength of sunlight is 28613 nm and the wavelength below 28613 nm is almost completely absorbed by the ozone layer in the atmosphere. While the short-wave light (230nm-280nm) in the high-pressure mercury lamp spectrum can be absorbed by triadimefon, so that its photolysis is more likely to occur. The order of photodegradation of triazolone in pure water and three organic solvents is pure water> acetone> fermentative> n-hexane, which is obviously related to the absorption of shortwave ultraviolet light with pure water and three organic solvents. In addition, studies have shown that acetone is a triplet sensitizer, it can through the energy transfer mechanism to promote organic photolysis. This also explains why the triazolone photolysis in the acetone is faster than the other two organic solvents.

The chemical degradation efficiency of triazolone at two temperatures and three pH conditions is shown in Table 1.

Table 1: Hydrolysis of tradimefon at different temperature and pH values

pH	Temperature	Hydrolysis kinetic equation	Hydrolysis rate constant	Half-life	Correlation coefficient	Activation energy
	T(° C)	$C_t=C_t \bullet e^{-kt}$	$K(d^{-1})$	$T_{t/2}(d^{-1})$	R^2	E(kJ/mol)
6	25	$C_t=9.9486^{-0.0502t}$	0.0502	13.81	0.9919	85.65
	50	$C_t=9.9475^{-0.7296t}$	0.7296	0.95	0.9937	
7	25	$C_t=9.9227^{-0.1213t}$	0.1213	5.71	0.9888	79.53
	50	$C_t=9.9303^{-1.4561t}$	1.4561	0.48	0.9998	
8	25	$C_t=9.9185^{-0.3266t}$	0.3266	2.12	0.9651	74.7
	50	$C_t=10.457^{3372t}$	3.372	0.21	0.9952	

It can be seen from the data in the above table that the rate of hydrolysis is significantly accelerated as the temperature of the reaction system increases, but the degree of increase of different pH conditions is not the same. The reaction rate was 14.5 times higher than that of the acidic condition (pH 6), and the half-life decreased from 13.81d (25° C) to 0.95d (50° C), while the reaction rate of neutral condition (pH7) increased by 11.9 times, and the reaction rate for alkaline conditions (pH 8) was only 10.1 times.

5. Conclusion

In this work, triazolone was used as an example to study the chemical behavior of pesticide fungicide in lake environment. Under the sunlight, triadimefon can be more stable in organic solvent and aqueous solution, indicating that it is difficult to produce direct degradation. The degradation rate of tri-ketone in organic solvent is related to acetone> methanol> "F-hexane, which is related to the absorption of short-wave ultraviolet light in three organic solvents. The rate of photolysis in pure water is pure water> well water > River water> pond water, a variety of water contained in the solubility of organic and inorganic substances is different from the difference caused by triazolone photolysis of the main reasons. Triadimefon in the acidic solution of high stability, not easy to hydrolysis, but in alkaline water hydrolysis faster. Judging from the rate of neutral hydrolysis, triazolone in the natural environment is easy to disappear by hydrolysis, the residence time is short, the higher the acidity of the natural water body, the longer the time required for the self-purification of the triethoate, which is more serious in the acid rain of the area is particularly noticeable. The photochemical degradation and water chemistry degradation of water environment were discussed, and the influence factors of two kinds of degradation were found. This provides the basis for the processing of pesticide fungicides, scientific and rational use and pollution control, but also for the further evaluation of pesticide fungicide on the surface water pollution and pesticide waste water treatment laid the foundation, with a positive guiding value.

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