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PHOTODEGRADATION AND HYDROLYSIS OF CHLORPYRIFOS IN AQUEOUS SYSTEMS

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ABSTRACT

Hydrolysis and photodegradation of chlorpyrifos a widely used organophosphorus pesticide was studied. Hydrolysis is a dominant process for pesticide loss in the environment. Chlorpyrifos by virtue of its wavelength of maximum absorption is susceptible to direct photolysis. Degradation via hydrolysis was studied at pHs 4, 7, 9 and 11 while photodegradation was carried out in the presence and absence of nitrate solution at ~30^{o}C for a period of seven days. The rate of degradation was determined for both conditions as a function of the phosphate formation within the reaction solution. Results obtained indicated that both processes were found to follow a first order rate kinetics with rate constants for the hydrolysis experiments to be k_{pH4} as 1.54× $10^{-3}hr^{-1}$, k_{pH7} 4.63× $10^{-3}hr^{-1}$, k_{pH9} 9.21×$10^{-3}hr^{-1}$ and k_{pH11} 2.56 × $10^{-2}hr^{-1}$ with corresponding half – lives of 449.52 hrs, 149.76 hrs, 75.36 hrs and 27.12 hrs respectively. Chlorpyrifos was found to be most stable in acidic medium with stability decreasing with increase in pH. The photochemical degradation was also observed to follow first order rate kinetics with degradation rates of 7.08 x 10^{-4} hr^{-1} and half-life of 978.35 hrs for solutions without nitrate ion and 1.25 x 10^{-2} hr^{-1} with corresponding half-life of 55.44 hrs for solutions with nitrate ions. Photodegradation was observed to be faster in the presence of nitrate compared with those without nitrate ($k_{NO_3^-} > k$). It can be concluded that the presence of nitrate ions acts as a photo-sensitizer towards the degradation rate of organophosphorus pesticide studied thus accelerating the process. Comparison of both processes revealed that pH 11 was most effective for the degradation of chlorpyrifos in aqueous systems. Implication for this study is relevant in understanding the fate of chlorpyrifos once released into the environment with possible application in water/wastewater treatment.

Keywords: *Chlorpyrifos, photodegradation, Hydrolysis, organophosphorus pesticide, nitrate ion*

1. INTRODUCTION

Organophosphorus (OP) pesticides are esters and thioesters of phosphoric acid and are widely used for agricultural, industrial and domestic purposes throughout the world [1]. They are indispensable in modern agriculture and rank among the most widely used in the United States and are used extensively worldwide [2]. OPs are used as alternative to their more persistent organochlorines counterpart; however there is growing concern about their longevity in the environment because of increased cases of detection in various environmental compartments.

They are present in environmental media, often well removed from the initial site of application with evidence that some of these chemicals can undergo long range transport and have been observed to be present in remote locations like the Arctic [3-8]. Residues of these chemicals have been detected in sediments and soil [9-14], atmosphere [15], and in crops and surface waters [9, 16, 17]. A recent study [18] in homes in the US detected chlorpyrifos and diazinon in 78% and 35% respectively, of the samples collected, raising more concern about their fate and human exposure. Consequently, there is an urgent need to better understand their degradation processes once released.

Chlorpyrifos *(O,O, -diethyl O-[3, 5, 6- trichloropyridyl] -phosphorothioate)* (Figure 1) is a non-systemic organophosphorus pesticide, commonly used for

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household and agricultural purposes until its ban for household use in 2000 [19]. Despite its restriction, chlorpyrifos is still one of the most widely used insecticide in agriculture with an estimated 8 – 10 million kg applied in the US [2, 20]. The crops with the most intense chlorpyrifos use are cotton, corns, almonds and fruit trees (e.g. oranges and apples). Like all organophosphorus pesticides, it elicits its toxicity by inhibiting the enzyme acetyl cholinesterase which is responsible for neural transmission [21]. There also exists the risks of exposure to non – target organisms e.g. humans and other biota. OPs fate in the environment is affected by transport, chemical, and biological processes, the rate of which are largely unknown. Direct and indirect photochemical processes are the methods involved in the photo-degradation of pesticides in aquatic environment [22]. Direct absorption of sunlight by the pollutants is accompanied by chemical reactions in a process called direct photolysis, while the indirect photolysis is sometimes initiated through light absorption by natural substances. Direct photolysis plays a key role in the degradation of some pollutants in the aquatic environment [23].

Several studies on the photolysis and hydrolysis of organophosphorus pesticides had been reported [24-26], and a few studies have studied photo-transformation of chlorpyrifos [27-30]. However, these studies were carried out under simulated light conditions and the light intensities not as strong as to what is prevalent in Africa in general and Nigeria in particular.

This objective of this study was to investigate the photodegradation of chlorpyrifos under sunlight in Benin City, Southern Nigeria and compare it with the half lives for the hydrolysis of chlorpyrifos to ascertain which process is more effective for its removal in aqueous systems. The application of this research would be in risk assessment as well as in water/wastewater treatment plants.

2. MATERIALS AND METHOD

2.1 Chemicals

Analytical Anhydrous potassium hydrogen phosphate phthalate ($C_8H_5KO_4$), Ascorbic Acid, concentrated sulphuric acid (H_2SO_4), hydrochloric acid (HCl), sodium hydroxide (NaOH), potassium nitrate (KNO_3), ammonium molybdate [$(NH_4)_2MoO_4$], sodium hydrogen orthophosphate ($NaHPO_4$), chlorpyrifos were purchased from Sigma Aldrich (UK), All solutions were prepared in distilled water unless otherwise stated. Buffers solutions to pH 4, 7, 9 and 11 were prepared using USEPA guidelines for buffer preparation [32].

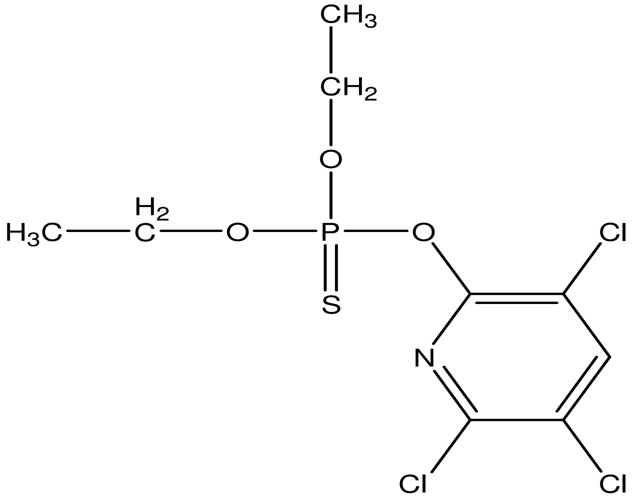

Figure 1: Chemical Structure of chlorpyrifos (O,O, -diethyl O-[3, 5, 6- trichloropyridyl] -phosphorothioate); Mol. wt = 350.59gmol^{-1}; log K_{OW} = 4.96 (25 °C); vapour pressure = 2.50 mPa; Solubility = 1.39mg L^{-1}. (Source: [31])

2.2 Preparation of Reagents

2.2.1 Buffer solutions: Buffer solutions were prepared according to standard procedures as set by USEPA [32] as shown below:

pH 4: 50 ml of 0.1M potassium hydroxide phthalate was added to 0.1 ml of 0.1 M sodium hydroxide (NaOH) and the volume adjusted to 100 ml with distilled water.

pH 7: 50 ml of 0.1 M potassium dihydrogen phosphate was added to 29 ml of 0.1 M NaOH and made up to the 100 ml mark using distilled water.

pH 9: 50 ml of 0.025 M borax ($Na_2B_4O_7$) was added to 4.6 ml of 0.1 M hydrochloric acid (HCl) and made up to mark with distilled water

pH 11: 50 ml of 0.05 M sodium bicarbonate was added to 22.6 ml of 0.1 M NaOH and the volume adjusted to 100 ml with distilled water.

2.2.2 Ammonium molybdate solution: A 250 ml of concentrated sulphuric acid was added to 500 ml of distilled water in a beaker placed in a cool water bath. 25 g of ammonium molybdate was then added and stirred until fully dissolved; it was then made up to mark with distilled water.

2.2.3 Ascorbic acid: 25 g of ascorbic powder was weighed and dissolved in water. The solution was transferred into a 100 ml flask and diluted to the mark with distilled water.

2.3 Standard preparation

A seven – point calibration curve was developed with a concentration range of 1 µg/ ml to 20 µg/ml for the effective determination of phosphate in water.

2.4 Hydrolysis experiment

Hydrolysis studies were carried out using set methods by USEPA [32], 10 mg/l chlorpyrifos was prepared in distilled water into a 500 ml amber vessel (to exclude degradation due to photolysis) and transferred into a water bath and maintained at the set temperature. There was no need to shake the reaction vessel continuously as previous studies had reported that continuous vigorous stirring has only a minimal effect on hydrolysis rate [1, 33]

For the buffer solutions, freshly prepared buffers were used in place of distilled water to prepare the solutions. Triplicate samples were taken at different time intervals and absorbance readings were taken in a UV Spectrophotometer. 3 ml of sample was taken from the experimental vessel and transferred into a 10 ml volumetric flask, 2 ml of ammonium molybdate solution was then added and shaken vigorously. 1 ml of the ascorbic solution was added and the blue colour was allowed to develop for ~10 minutes before reading. Phosphate formation was monitored as an indication of degradation of the OP.

***2.4.1 Photolysis*:** A 1 mg/l chlorpyrifos was prepared and exposed to direct sunlight in the presence (0.1mg/l) and absence of potassium nitrate over a period of seven days. Dark samples were kept in amber vials covered with tin foil to account for loss through other processes.

2.4.2 Chemical kinetics: The degradation can be described as a pseudo first order degradation curve with an expression:

$$C_t = C_0\, e^{-kt} \tag{1}$$

Taking the natural logarithm of both sides equation (1) becomes

$$\ln\frac{C_0}{C_t} = -kt \tag{2}$$

where C_t is the concentration of the chlorpyrifos at time t; C_0 is its initial concentration and k is the rate constant. A plot of ln C_0/C_t against time will give a straight line graph with rate (k) calculated from slope.

The half-life corresponds to the time at which the pesticide concentration is equal to half of its initial concentration given by the equation below:

$$k = \frac{0.693}{t_{1/2}} \tag{3}$$

***2.4.3 Spectrophotometric Analysis of Sample*:** Analysis for the amount of parent compound remaining was performed by employing spectrophotometer. 3 ml aliquot of the samples was added to 2 ml of ammonium molybdate. 1 ml of the freshly prepared ascorbic acid solution was then added and the solution shaken. This produced a blue colour which was due to the formation of molybdenum blue. The intensity of the blue colour corresponds to phosphate concentration after the hydrolysis reaction was being minimized or quenched. The absorbance of the blue solution was measured with a spectrophotometer at 660 nm against a blank consisting of 2 ml ammonium molybdate, 1 ml ascorbic acid and 1 ml de-ionized water. From the prepared calibration curve, concentration of chlorpyrifos corresponding to the measured absorbance was read at each time intervals. The same procedure was done for all samples.

2.5 Statistical analysis:

Data obtained were analyzed using Microsoft Excel, SigmaPlot® and SigmaStat

3. RESULTS AND DISCUSSION

The chemical hydrolysis of chlorpyrifos in solutions buffered to pHs 4, 7, 9 and 11 at 30°C was studied. Figure 2 shows the rate of hydrolysis of chlorpyrifos as obtained for the different pH solutions. Chlorpyrifos loss is described by a linear regression with the assumption that the initial chlorpyrifos concentration at time 0 was 100%. A plot of the logarithm of the concentration as a function of the reaction time gave a straight line graph indicative of a pseudo first order degradation kinetics based on a nominal concentration of ~1 mg/l (see Figure 3).

All the plots of ln (C_t/C_0) (C_0 is the reactant concentration at t = 0, C is the reactant concentration at various times) versus time were found to be linear for all the pH studied (see Fig. 3). The hydrolysis rate of chlorpyrifos (Fig. 2) revealed its relative stability of at pH 4 ($k_{pH4} = 1.54 \times 10^{-3}$ hr^{-1}; half life 449.52 hr) the stability was then observed to decrease with increasing pH thus pH 7 ($k_{pH7} = 4.63 \times 10^{-3}$ hr^{-1}; half – life 149.76 hr), pH 9 ($k_{pH9} = 9.21 \times 10^{-3}$ hr^{-1}; half – life 75.63 hr) and pH 11 ($k_{pH11} = 2.56 \times 10^{-2}$ hr^{-1}; half – life 27.12 hr) . The rates were found to be in the order:

$k_{pH4} < k_{pH7} < k_{pH9} < k_{pH11}$ showing that chlorpyrifos is more susceptible to alkaline – driven hydrolysis.

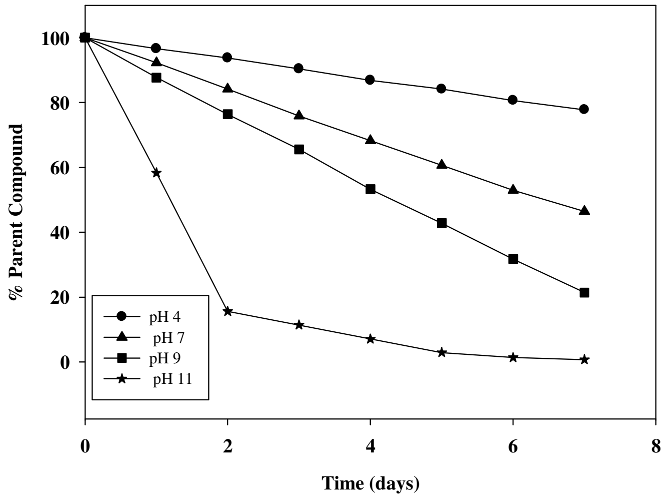

Figure 2: Hydrolysis of chlorpyrifos at pHs 4, 7, 9 and 11 kept in a thermostated water bath at ~30°C

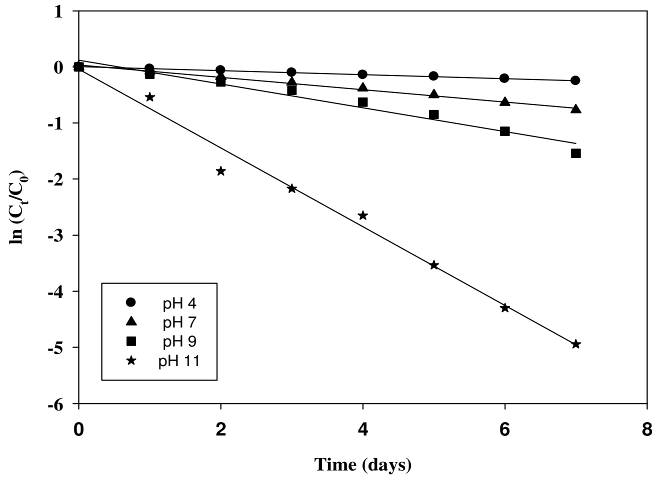

Figure 3: Kinetic data for the hydrolysis of chlorpyrifos under the different pH conditions studied.

Chlorpyrifos was found to degrade significantly over the experimental period in solution buffered to pHs 7, 9 and 11 but not so significantly at pH 4 (Fig. 2). A possible explanation for this was due to the fact that OH^- groups react readily with the chlorpyrifos molecules and break the molecules into two parts; an evidence for alkaline-driven (OH^-) hydrolysis. The rate constants were found to be reproducible with a relative error less than 2.5%. It is difficult to compare half lives values obtained here with literature as half lives values reported for chlorpyrifos has been found to vary from a few hours up to 210 days [31].

Chlorpyrifos possess three ester bonds that are candidates for hydrolytic cleavage; two tertiary alkyl ester bonds and one phosphate ester (pyridyl) bond [1]. Proposed hydrolysis pathway via alkaline driven hydrolysis would involve a cleavage of the P-O ester bond in the thiophosphoric ester with the formation of 3,5,6 – trichloropyridinol (TCP) and diethyl thiophosphate (DETP) as the main metabolites (Fig. 4). The phosphorus atom is electron deficient and nucleophilic attack is the first step in the hydrolytic reaction [34]

For the photodegradation experiment, chlorpyrifos was chosen as a model chemical because it absorbs strongly in the UV region (>290nm) and thus is susceptible to direct photolysis. Comparison was also done to assess if it is susceptible to photosensitized/ indirect photolysis as a result of the presence of certain species (nitrate ion) that could further enhance its degradation. Figure 5 shows degradation of chlorpyrifos in different aqueous systems. The decay rate of chlorpyrifos in a nitrate solution (k_{NO3^-}) was calculated to be 1.25×10^{-2} hr^{-1} with a corresponding half life of 55.44 hrs. However, in solutions without the nitrate ion, chlorpyrifos was found to have a degradation rate (k) of 7.08×10^{-4} hr^{-1} with corresponding half life of 978.35 hrs. Thus the light induced degradation of chlorpyrifos was observed to be significantly higher in solutions with nitrate ions present when compared with solutions of chlorpyrifos in distilled water (Fig. 5). There was no observed significant degradation in the control experiment indicating photolysis as the main pathway of degradation.

The degradation of chlorpyrifos without a nitrate salt was found to proceeds via a first order reaction while degradation of chlorpyrifos in the presence of a nitrate salt was observed to proceed via a pseudo first order reaction.

Comparison of the two pathways of degradation revealed that hydrolysis at elevated pH (pH 11) was the most important process for chlorpyrifos loss in aqueous systems. This findings are similar to what Racke [35] observed for hydrolysis of organophosphorus pesticides in aqueous systems.

4. CONCLUSIONS

Chlorpyrifos was found to undergo direct photodegradation relatively slowly compared with solutions with possible photosensitizers (nitrate ions). Nitrate ion presence in polluted water and tidal zones where chlorpyrifos have been applied would significantly enhance its breakdown. Chlorpyrifos hydrolysis in aqueous medium is dependent on the pH of the medium with significantly decay observed at elevated pHs. These results are particularly relevant for water/wastewater treatment application.

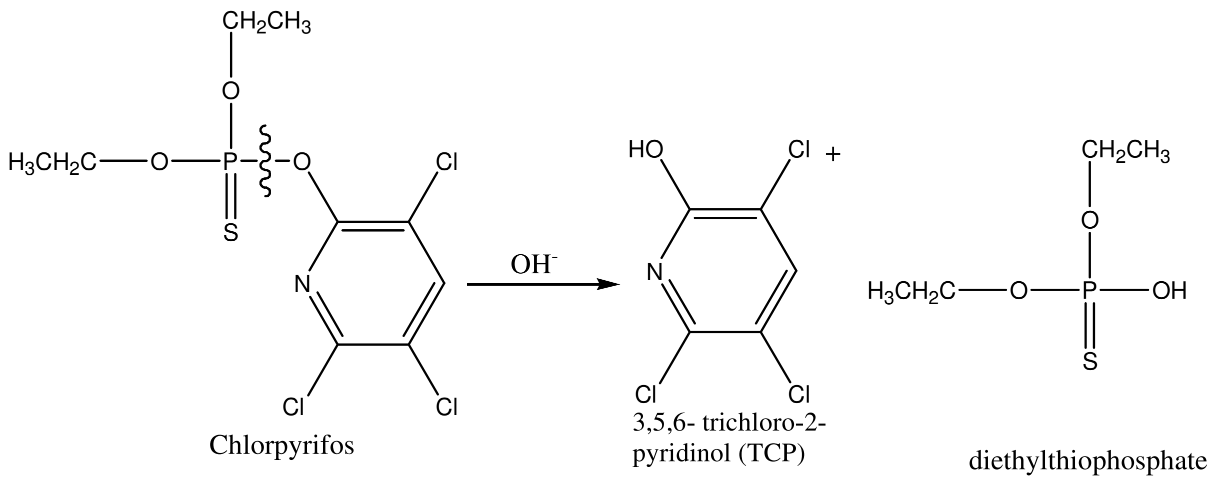

Figure 4: Proposed hydrolysis pathway for chlorpyrifos

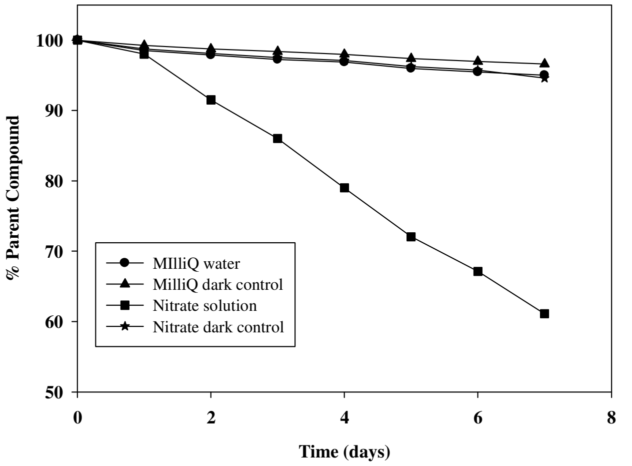

Figure 5: Photodegradation of chlorpyrifos in solutions with and without nitrate at ~ 30°C

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