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# Environmental Fate of Temephos: Photodegradation Versus Hydrolysis

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## Abstract

The environmental fate of temephos a current-used pesticide was studied. It was subjected to photochemical degradation, acid and base driven hydrolysis to determine which process plays a more crucial role on its fate once released into the environment. Temephos is susceptible to direct photolysis as a result of its wavelength of maximum absorption ($\lambda \approx 390$nm). Hydrolysis was carried at pH 4, 7, 9 and 11 while photodegradation was carried out in the presence and absence of nitrate solution at ~30°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 $1.22\times 10^{-3}hr^{-1}$, $k_{pH7}$ $1.17\times 10^{-3}hr^{-1}$, $k_{pH9}$ $5.11\times10^{-3}hr^{-1}$ and $k_{pH11}$ $5.53 \times 10^{-3}hr^{-1}$ with corresponding half – lives of 568.03 hrs, 592.31 hrs, 135.62hrs and 125.3 hrs respectively. Temephos was found to be most stable in acidic medium with stability decreasing with increase in pH. There is a strong relationship between rate of degradation and the pH of the aqueous solution for acid and base driven hydrolysis of temephos. The photochemical degradation was also observed to follow first order rate kinetics with degradation rates of $1.25 \times 10^{-3}$ $hr^{-1}$ and half-life of 544.80 hrs for solutions without nitrate ion and $1.59 \times 10^{-2}$ $hr^{-1}$ with corresponding half-life of 43.54 hrs for solutions with nitrate ions. Photodegradation was observed to be faster in the presence of nitrate compared with those without nitrate ($k_{NO3^-} > k$). It can thus 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 temephos in aqueous systems. Implication for this study is relevant in understanding the fate of temephos once released into the environment with possible application in water/wastewater treatment.

**Keywords:** Temephos, photodegradation, Hydrolysis

## 1. Introduction

Organophosphorus (OP) pesticides are widely used in agriculture and 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

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present in remote locations like the Arctic (Gregor 1990; Chernyak et al., 1996; Macdonald et al., 2000; Grynkiewicz et al., 2001; Hermanson et al., 2005; Hoferkamp et al., 2010) in sediments OPs have however been detected in remote regions (Hermanson, Isaksson et al., 2005), in sediments and soil (Kjølholt 1985; Sujatha and Chacko 1991; Castilho et al., 2000; Sapozhnikova et al., 2004; Wang et al., 2005; Villaverde et al., 2008), in the atmosphere (Raina et al., 2010), and in crops and surface waters (Brunetto et al., 1992; Castilho, Fenzl et al., 2000; Gilliom et al., 2006). A recent study (Stout II et al., 2009) 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 understand the fate of such chemicals once released into the environment.

Temephos *(O,O,O',O' – tetramethyl O, O' – sulfanediylbis (1,4-phenylene) diphosphorothioate)* is a non-systemic organophosphorus pesticide, mainly used as a larvicide to control mosquitoes, midges and black fly larvae. It is the only remaining organophosphate pesticide used for larval mosquito control (USEPA, 2014). Like all organophosphorus pesticides, it elicits its toxicity by inhibiting the enzyme acetyl cholinesterase which is responsible for neural transmission (Smith, 1992). There also exists the risks of exposure to non – target organisms e.g. humans and other biota.

Temephos has found use in sites including domestic and non-domestic locations; highly polluted water bodies/areas, including moist areas, woodland pools, shallow ponds, edges of lakes, swamps, marshes, tidal waters, intertidal zones, catch basins, and tire piles.

Temephos is not very soluble in water and has a high octanol-water partition coefficient, helping it to adsorb on sediments and accumulate in living organisms in natural conditions. Temephos has a relatively high log $K_{ow}$ and, as would be expected, adsorbs to particles, sediment and the sides of containers (Edwards, 1974; Barnard et al., 1997; Altschuh et al., 1999; Carter, 2000). It is fat-soluble but very rapidly broken down.

There is only a minimal amount of information available about the fate and behaviour of temephos once released in the environment. Current evidence suggests that the compound has a low persistence in the environment. Weekly application of temephos at twice the normal application rates on pond water resulted in the rapid disappearance of the compound from the water and from the sediments (Smith, 1993). It appears to be rapidly degraded under field conditions (Lacorte et al., 1996). The primary means of degradation are sunlight and microbial action (USEPA, 2001).

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 (Draper and Crosby, 1983). 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 (Mikami et al., 1985; Lam et al., 2003; Zamy et al., 2004; Ukpebor and Halsall, 2012). Understanding the environmental fate of OPs is particularly useful since their genotoxic potentials of the OPs and their degradates have previously being established (Ukpebor et al., 2011).

Several studies on the photolysis and hydrolysis of organophosphorus pesticides had been reported (Mansour et al., 1983; Katagi, 1989; Durand et al., 1992), 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.

In this study, the physical degradation of temephos (acid and base driven hydrolysis; direct and indirect photochemical degradation) was investigated to ascertain which process is more effective for its removal in aqueous systems. The application of this research would be in environmental risk assessment as well as in water/wastewater treatment plants.

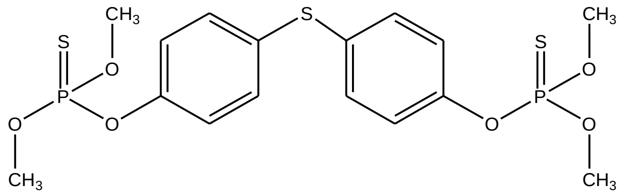

Figure 1: Chemical Structure of temephos *(O,O,O',O' – tetramethyl O, O' - sulfanediylbis(1,4-phenylene) diphosphorothioate)*; ( $C_{16}H_{20}O_6P_2S_3$ ); Mol. wt = 466.47gmol$^{-1}$; log $K_{OW}$ = 4.91 (25 °C); vapour pressure = $8 \times 10^{-6}$ Pa; Solubility = 30 µg/l. **(Source: WHO, 2005).**

## 2. Materials and Methods

**Chemicals:** Analytical Anhydrous potassium hydrogen 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 ($NaHPO_4$), temephos were purchased from Sigma Aldrich (UK). All solutions were prepared in distilled water unless otherwise stated. Buffers solutions of pH 4, 7, 9 and 11 were prepared using USEPA guidelines for buffer preparation (USEPA, 2008).

## Preparation of Reagents

### *Buffer solutions*

Buffer solutions were prepared according to standard procedures as set by USEPA (2008) 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.

The pH of the solutions prepared was checked using a pH meter (Mettler Toledo, UK) and the pH was adjusted if necessary using NaOH or HCl to the desired pH.

### *Ammonium molybdate solution*

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 make up to mark with distilled water.

### *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.

## Standard preparation

A seven – point calibration curve was developed with a concentration range of $1.0 \times 10^{-4}$ M to $5.0 \times 10^{-4}$ M.

## Hydrolysis experiment

Hydrolysis studies were carried out using set methods by USEPA (2008), 10 mg/L temephos was prepared in distilled into a 500 mL amber vessel (to exclude degradation due to photolysis) and transferred into a water bath and maintained at the set temperature (~25$^{o}$C

±0.5). 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 (Spectronic 21D). 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.

***Photolysis*:** 10 mg/L temephos 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.

### *Chemical kinetics*

The degradation can be described as a pseudo first order degradation curve with an expression

$$C_t = C_0\, e^{-kt.} \quad (1)$$

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

$$\ln \frac{C_0}{C_t} = -kt, \quad (2)$$

where $C_t$ is the concentration of the temephos 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:

$$k = \frac{0.693}{t_{1/2}}. \quad (3)$$

***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 temephos corresponding to the measured absorbance was read at each time intervals. The same procedure was done for all samples.

### *Statistical analysis*

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

## 3. Results and Discussion

The rate of hydrolysis of temephos buffered to pH 4, 7, 9 and 11 was found to follow pseudo first order degradation kinetics based on a nominal concentration of ~10 mg/L. Figure 2a shows the rate of hydrolysis of temephos as obtained for the different pH solutions. Temephos loss is described by a linear regression with the assumption that the initial temephos concentration at time 0 was 100%.

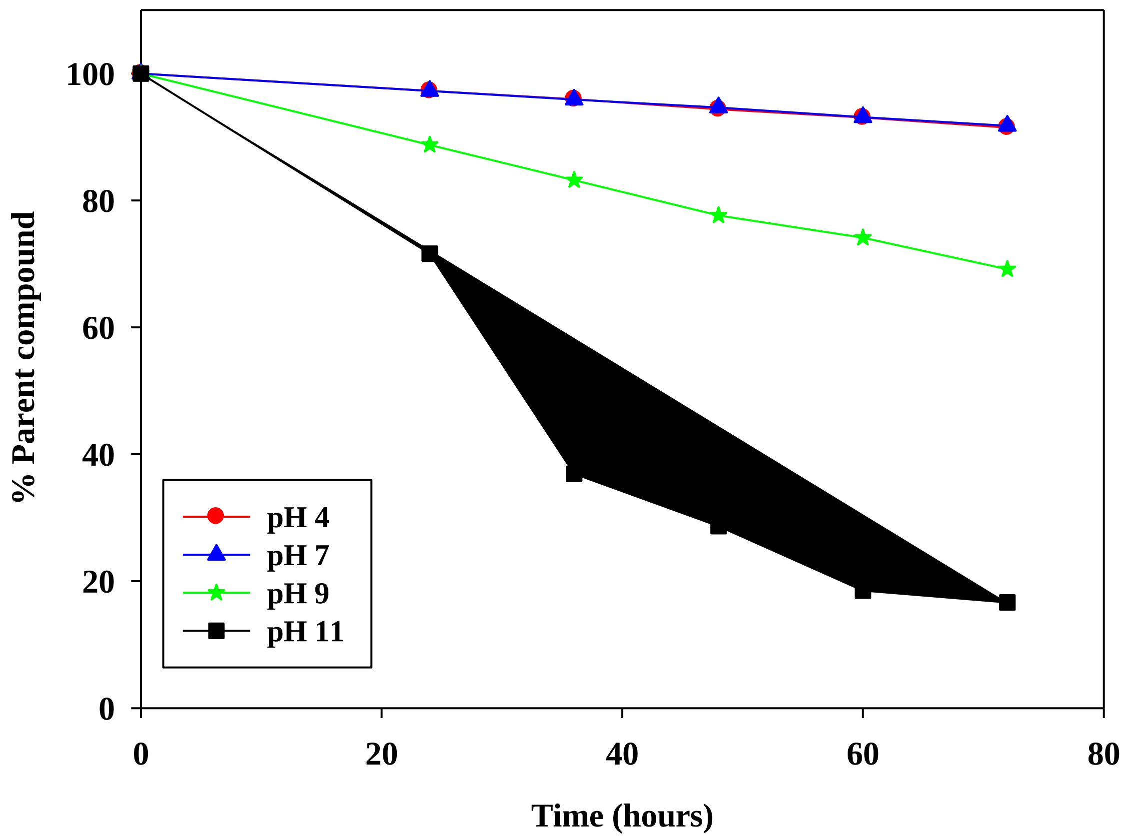

Figure 2a: Hydrolysis of temephos at pHs 4, 7, 9 and 11 kept in a thermostated water bath at ~30°C.

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. 2b). The hydrolysis rate of temephos (Fig. 2a) indicates the relative stability of temephos at pHs 4 ($k_{pH4}$ = 1.22 x $10^{-3}$ $hr^{-1}$; half life 568.03 hr) and 7 ($k_{pH7}$ = 1.17 x $10^{-3}$ $hr^{-1}$; half – life 592.31 hr) indicative of neutral and acidic solutions. However, there appears to be a more drastic increase in rate with corresponding decrease in half – life as the pH increased further from 7 to 11. The rates were found to be in the order: $k_{pH4} \geq k_{pH7} < k_{pH9} < k_{pH11}$.

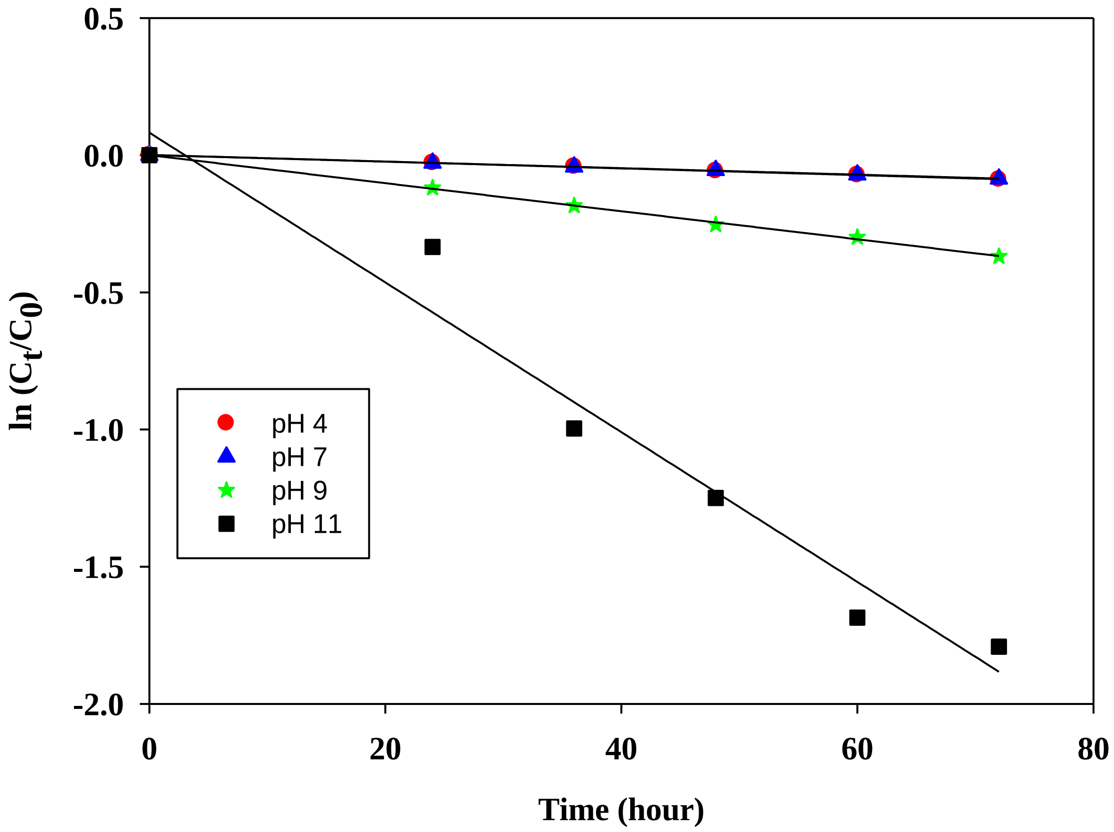

Figure 2b: Kinetic data for the hydrolysis of temephos under the different pH conditions studied.

This showed that temephos did not degrade significantly over the experimental period in solution buffered to pH *4* and 7 but was significant at higher pH of 9 and 11. A possible explanation for this was due to the fact that $OH^-$ groups react readily with the temephos molecules and break the molecules into two parts; an evidence for alkaline-driven ($OH^-$) hydrolysis and in agreement with pseudo first order hydrolysis rates derived by Mazieski *et al;* (1992) at these higher. The rate constants were found to be reproducible with a relative error less than 3%. Comparison of the half lives values with those reported in literature (Lacorte et al., 1995) showed a variance from the results obtained here, this could be due to the different environmental matrices (estuarine water) utilized.

Proposed hydrolysis pathway via alkaline driven hydrolysis would involve a cleavage of the P-O ester bond with the formation of dimethyl phosphoric acid (DMP). The phosphorus atom is electron deficient and nucleophilic attack is the first step in the hydrolytic reaction (Pearson and Songstadt, 1967)

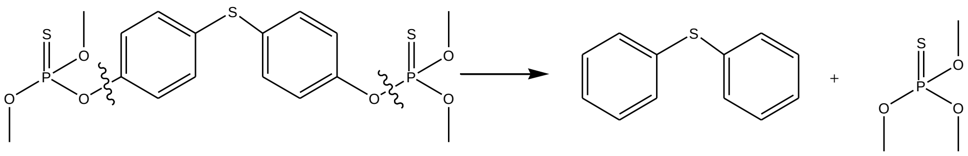

**Figure 2c:** Proposed hydrolysis pathway for temephos

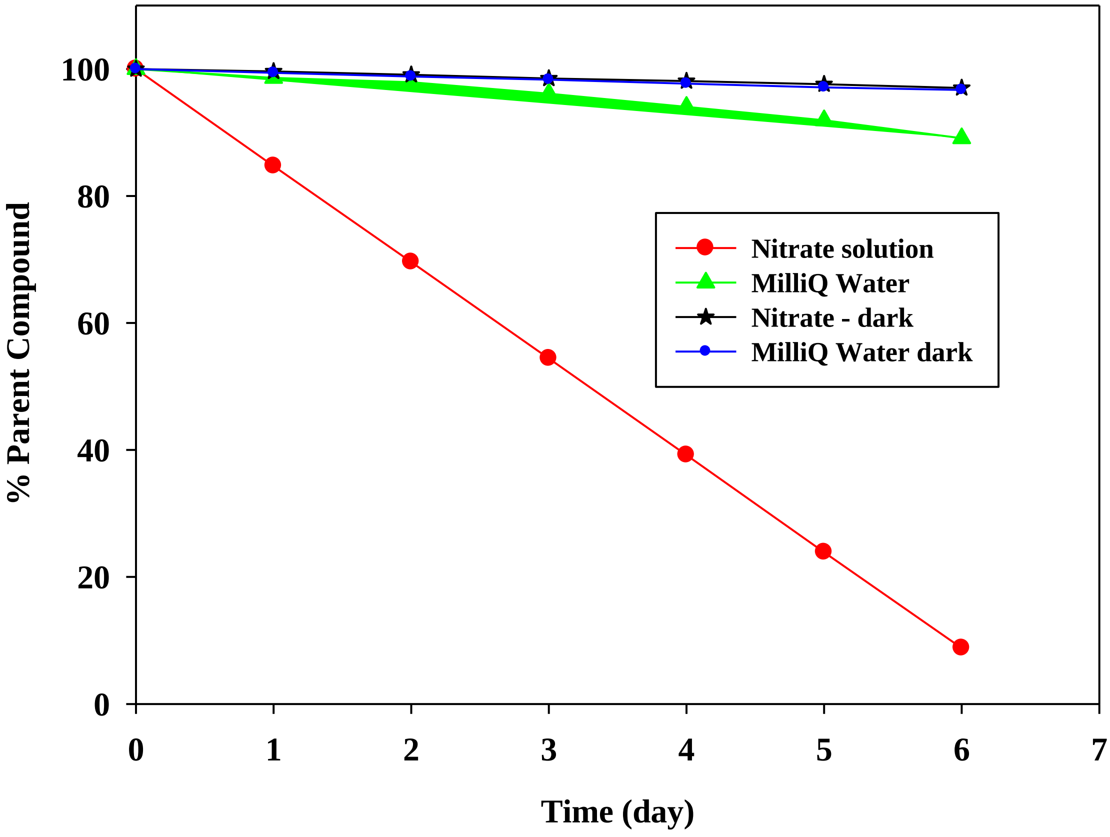

Figure 3**:** Photodegradation of temephos in solutions with and without nitrate at ~ 30ºC.

For the photodegradation experiment, temephos 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. The decay rate of temephos in a nitrate solution ($k_{NO_3^-}$) was calculated to be 1.59 x $10^{-2}$ $hr^{-1}$ with a corresponding half life of 43.54 hrs. However, in solutions without the nitrate ion, temephos was found to have a degradation rate (k) of 1.25 x $10^{-3}$ $hr^{-1}$ with corresponding half life of 544.80 hrs.

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

Comparison of both physico – chemical process for the degradation of temephos in aqueous solution revealed that hydrolysis at elevated pH (pH 11) was the most important process for pesticide loss in aqueous systems. This findings are similar to what Racke (1992) observed for hydrolysis of organophosphorus pesticides in aqueous systems.

## 4. Conclusion

Temephos was found to undergo direct photodegradation albeit slowly when compared with solutions with possible photosensitizers (nitrate ions). Thus the presence of nitrate ion in polluted water and tidal zones where temephos are applied would significantly enhance its breakdown. Degradation of temephos in aqueous medium through hydrolytic processes is largely dependent on the pH of the medium with significantly decay observed at elevated pH. The results are particularly relevant for water/wastewater treatment application. This research is also relevant to Nigeria where no attention is given to the fate of these chemicals in the environment.

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