J. Chem Soc. Nigeria, Vol. 44, No. 3, pp 582 -589 [2019]

ABIOTIC HYDROLYSIS OF AZINPHOS –METHYL AT VARYING pHs

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Received 12 April 2019; accepted 03 June 2019, published online 11 June 2019

ABSTRACT

The assessment and impact of the environmental fate of azinphos methyl (3(dimethoxyphosphinothioylsulfanylmethyl)-1,2,3-benzotriazin-4-one), a currently-used pesticide was studied. It was subjected to acid and base driven hydrolysis to determine which process plays a more crucial role on its fate once released into the environment. Hydrolysis of azinphos methyl was studied in solutions buffered to pH 4, 7, 9 and 11 with varying temperatures of 15 $^oC \pm 0.5\ ^oC$, 27± 0.5 ^oC and 37 ± 0.5 ^oC. The rate of degradation of azinphos- methyl was determined as a function of phosphate formation within the reaction solution. Results obtained indicated that both processes followed a pseudo-first order rate kinetics under the different temperatures. The rate constants for the hydrolysis experiments at 27± 0.5 ^oC were calculated to be kpH 4 as 1.49×10^{-2} hr^{-1}; kpH 7, 1.15×10^{-2} hr^{-1}; kpH 9, 1.54×10^{-2} hr^{-1} and kpH 11, 1.64×10^{-2} hr^{-1} with corresponding half – lives of 46.51 h, 60.26 h, 45 h and 42.26 h respectively. While, the rate constants and half-lives for the hydrolysis experiments at 15± 0.5 ^oC was pH 4 (1.9 x 10^{-2} hr^{-1}**;** 36.45 h), pH 7 (1.38 x 10^{-2} hr^{-1}; 50.22 h), pH 9 (1.24 x 10^{-2} hr^{-1}; 48.17 h), pH 11 (7.6 x 10^{-3} hr^{-1}; 91.18 h) and for conditions at 37± 0.5 ^oC had pH 4 (1.9 x 10^{-2} hr^{-1}; 36.28 h), pH 7 (1.25 X 10^{-2} hr^{-1}; 55.44 h), pH 9 (1.45 X 10^{-2} hr^{-1}; 47.783 h) and pH 11 (6.6 X 10^{-3} hr^{-1}; 105 h). This showed that temperature has an influence on the degradation of azinphos-methyl. The implication for this study is relevant in understanding the fate of azinphos-methyl once released into the environment with possible application in water/wastewater treatment.

Keywords: azinphos methyl, hydrolysis, buffered, degradation.

Introduction

As a result of increased agricultural activities, there has been an increased use in plant protection products (PPP) as well as other pests controlling chemicals of which pesticides have become important tools (1). This has led to an increase in the incidences of detection of such chemicals in continental and marine natural waters (2) with resultant environmental problems (3). Due to their chemical stability, resistance to biodegradation, they have the ability to penetrate and contaminate ground water (4-5). Although the benefits of pesticides cannot be overemphasized, their uses raises a number of environmental concerns such as potential toxicity to humans and other non-target organisms (6-8). Over 98% of sprayed insecticides and 95% of herbicides reach a destination other than their target species, including non-target species, air, water, bottom sediments, and food. About 25 million workers in developing countries may suffer mild pesticide poisoning yearly according to (9). Organophosphorus pesticides (OP) are widely used in agriculture and are among the most widely spread pollutants in the environment. They are present in environmental media, often well removed from the initial site of application. OP esters are very susceptible to hydrolysis, which is, therefore, their most common degradation pathway (10). Several studies and pathways on the photolysis and hydrolysis of organophosphorus pesticides have been reported (11-14). OPs exert their toxic action by inhibiting the enzyme acetylcholinesterase (AChE) not only in insects, but can also affect the nervous system of other non- target organisms as well as humans (15-16). Consequently, there is an urgent need to understand the fate of such chemicals once released into the environment.

Azinphos methyl (AZM) is registered for use in the control of many insect pests on a wide variety of fruits, vegetables, nuts, and field crops, as well as on ornamentals, tobacco etc. (17). There is only a minimal amount of information available about the fate and behaviour of AZM once released in the environment. In this study, the physical degradation of Azinphos methyl (acid and base driven hydrolysis) was investigated to ascertain which process is more effective for its removal in aqueous systems.

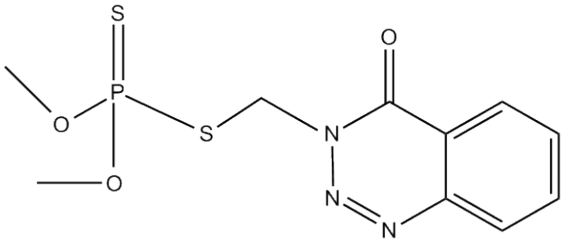

Figure 1: Chemical Structure of Azinphos-methyl,3-(dimethoxyphosphinothioylsulfanylmethyl)-1, 2,3-benzotriazin-4-one; ($C_{10}PN_3H_{12}S_2O_3$); Mol. wt. = 317.324 g/mol; vapor pressure = 8 x 10^{-9} mmHg. Density: 1.44 g/cm³ (9).

Materials and Methods

Chemicals: Azinphos methyl standard purchased from Sigma Aldrich (UK), analytical grade anhydrous potassium hydrogen phthalate ($C_8H_5KO_4$), ammonium molybdate ($(NH_4)_2MoO_4$), ascorbic acid ($C_6H_8O_6$) concentrated sulphuric acid (H_2SO_4), potassium dihydrogen phosphate (KH_2PO_4), borax ($Na_2B_4O_7 \cdot 10H_2O$), sodium bicarbonate ($NaHCO_3$), hydrochloric acid (HCl) and sodium hydroxide (NaOH). All solutions were prepared in distilled water.

Buffered solutions of pH 4, 7, 9 and 11 were employed for the hydrolysis experiment and to ensure a stable pH throughout the duration of the experiment. Individual buffer solutions were prepared to pH 4 (0.1 M potassium hydrogen phthalate and 0.1 M sodium hydroxide), pH 7 (0.1 M potassium dihydrogen phosphate and 0.1 M sodium hydroxide), pH 9 (0.025 M Borax and 0.1 M hydrochloric acid), pH 11 (0.05 M sodium bicarbonate and 0.1 M Sodium Hydroxide) according to standard procedures as set by (18). The pH of the solutions prepared were checked and corrected using a pH meter (Hanna Instruments, UK) and the pH was adjusted if necessary using NaOH or HCl to the desired pH.

Standard preparation

A five – point calibration curve was developed with a concentration range of 1.0 x 10^{-4} M to 5.0 x 10^{-4} M.

Hydrolysis experiment

Hydrolysis studies were carried out using set methods by (17), 10 mg/L AZM was prepared in distilled water and in the different buffer solutions and transferred into 250 mL amber glass vessels (to exclude degradation due to photolysis) and placed in a water bath and maintained at the set temperatures: 27 ± 0.5 ^{o}C, 15± 0.5 ^{o}C and 37 ± 0.5 ^{o}C. Triplicate samples were taken at different time intervals and absorbance readings were taken in a UV/Visible Spectrophotometer (LABTECH 722) for 7 days. 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 then added and the blue color was allowed to develop for about 15 minutes before reading. Phosphate formation was monitored as an indication of degradation of the OP (19).

Chemical kinetics

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

$$C_t = C_o\, e^{-kt} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (1)$$

$$\ln\frac{C_t}{C_o} = -kt \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (2)$$

$$\ln\,[C_t] = \ln\,[C_o] - kt \quad \ldots\ldots\ldots\ldots \quad (3)$$

Equation (3) has the form of the algebraic equation for a straight line $y = mx + c$

$y = \ln C_t,\ c = \ln[C_o],\ m = -k,\ x = t$

(Where Ct is the concentration of the AZM at time t; Co is its initial concentration and k is the rate constant. A plot of $\ln C_t/C_O$ against time will give a straight line graph with rate constant $(-k)$ 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:

$$t_{1/2} = \frac{0.693}{k} \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (4)$$

Results and Discussion

Results of the various hydrolysis experiments are presented in Table 1. The rate of hydrolysis for solutions 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. All the plots of ln C_t/C_o versus time were found to be linear for all the pH studied (see Figure 2). AZM degraded significantly over the experimental period in all the buffered solutions with rate constants for the hydrolysis experiments at 27± 0.5 °C were calculated to be 1.49×10^{-2} hr^{-1} for kpH 4, kpH 7 1.15×10^{-2} hr^{-1}, kpH 9 1.54×10^{-2} hr^{-1} and kpH 11 1.64×10^{-2} hr^{-1} with corresponding half – lives of 46.51 h, 60.26 h, 45.00 h and 42.26 h respectively.

Degradation trends in buffered solutions at 27 ± 0.5 °C was found to in the order pH 11 > pH 9 > pH 4 > pH 7. This was found to be in agreement with (18)in the hydrolysis of temephos, an OP in which comparison of both acid and base driven processes, revealed that pH 11 was most effective for the degradation of temephos in aqueous systems. In their review (20) of the hydrolysis of organophosphates in the aquatic environment, data revealed that azinphos-methyl was less stable under basic than acidic conditions.

Table 1: Rate Constants (*k*) and Half-lives ($t_{1/2}$) for the different buffered solutions of Azinphos-methyl at 27± 0.5 °C, 15 ± 0.5 °C and 37 ± 0.5 °C

pH	***k*** **(hr^{-1})** **(27± 0.5 °C)**	**$t_{1/2}$ (h)** **(27± 0.5 °C)**	***k*** **(hr^{-1})** **(15 ± 0.5 °C)**	**$t_{1/2}$ (h)** **(15± 0.5 °C)**	***k*** **(hr^{-1})** **(37±0.5 °C)**	**$t_{1/2}$ (h)** **(37± 0.5 °C)**
4	$1.49 \times 10^{-2} \pm 0.02$	46.51 ± 0.95	$1.30 \text{ X } 10^{-3} \pm 0.008$	533.08 ± 0.06	$1.90 \text{ X } 10^{-2} \pm 0.06$	36.28 ± 0.07
7	$1.15\times 10^{-2} \pm 0.07$	60.26 ± 1.30	$2.24 \text{ X } 10^{-2} \pm 0.09$	30.94 ± 0.05	$1.37 \text{ X } 10^{-2} \pm 0.04$	55.44 ± 0.12
9	$1.54\times10^{-2} \pm 0.05$	45.00 ± 0.63	$6.9 \text{ X } 10^{-3} \pm 0.007$	100.44. ± 0.04	$1.45 \text{ X } 10^{-2} \pm 0.08$	47.78 ± 0.05
11	$1.64 \times 10^{-2} \pm 0.14$	42.26 ± 0.42	$2.58 \text{ X } 10^{-2} \pm 0.05$	26.86 ± 0.08	$6.60 \text{ X } 10^{-3} \pm 0.007$	105.00 ± 0.04

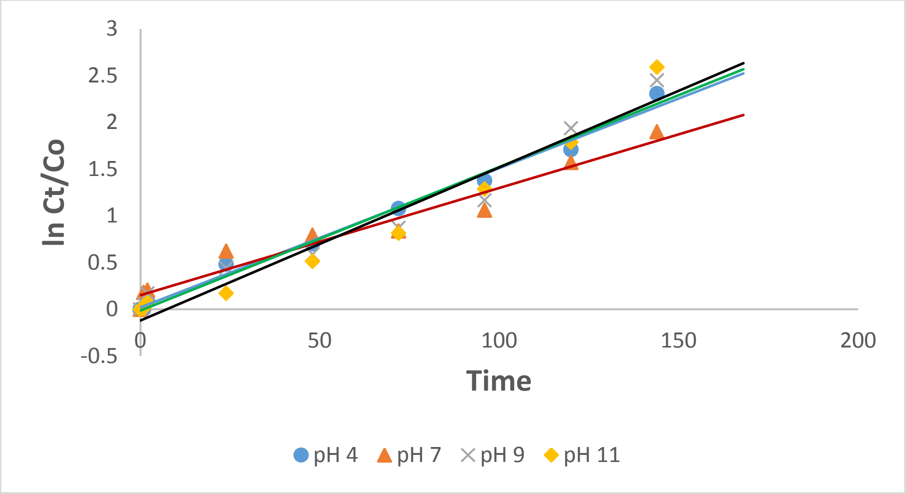

Figure 2: Kinetic data for the hydrolysis of azinphos methyl under the different pH conditions studied at 27± 0.5 ^{o}C.

Figure 3 shows the rate of hydrolysis of azinphos-methyl as obtained for the different pH solutions. Azinphos methyl loss is described by a linear regression with the concentrations normalized to 100%.

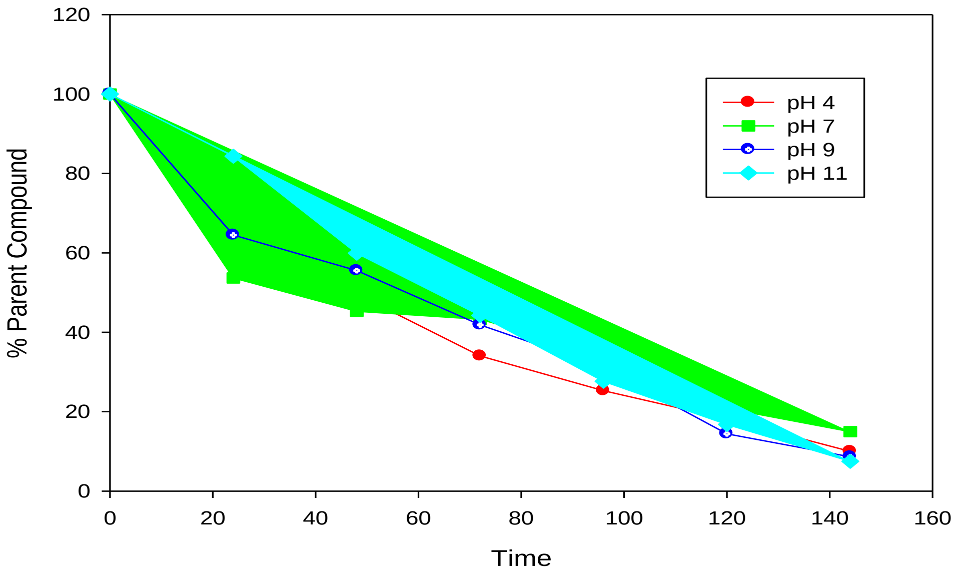

Figure 3: % degradation of azinphos methyl at pHs 4, 7, 9 and 11 at 27± 0.5 ^{o}C.

Results obtained from Figure 2 indicate the fastest degradation of AZM to be buffered solution of pH 11 with a rate of 1.64 × 10^{-2}hr^{-1}; and corresponding half-life of 42.26hr^{-1}. Fig 3 also shows that a significant degradation was observed for all the buffered solutions. However, there was an observed increase in rate with corresponding decrease in half – life as the pH increased from 7 to 11 respectively. The rates at 27± 0.5 ^{o}C were found to be in the order: kpH11

≥ kpH9 > kpH4 > kpH7 and this is in agreement with the pseudo-first-order hydrolysis rates of temephos at the same varied buffered solutions which give the same order: kpH11 > kpH9 > kpH4 ≥ kpH7 (14).

The temperatures were also varied at 15 ± 0.5 °C (Figure 5) and 37 °C± 0.5 °C (Figure 7) for AZM in the different buffered solutions to replicate various environmental temperatures. This was done in order to assess the impact/effect of changes in temperature on the abiotic hydrolysis of AZM. The rates were found to be in the order: kpH 11 > kpH 7 > kpH9 > kpH 4 at 15 ± 0.5 °C as shown below in Figure 4. Hence there was a significant loss of AZM in the solutions buffered at pH 11 and pH 7.

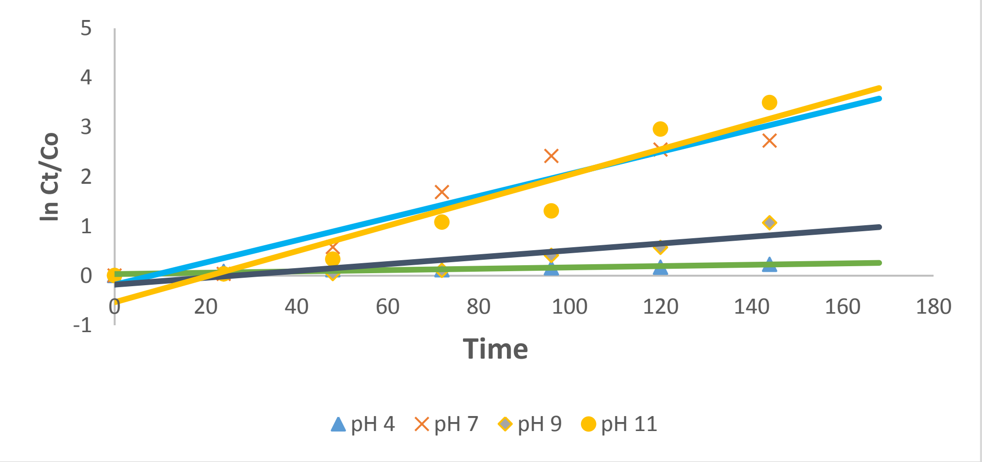

Figure 4: Kinetic data for the hydrolysis of azinphos methyl under the different pH conditions studied at 15± 0.5 °C

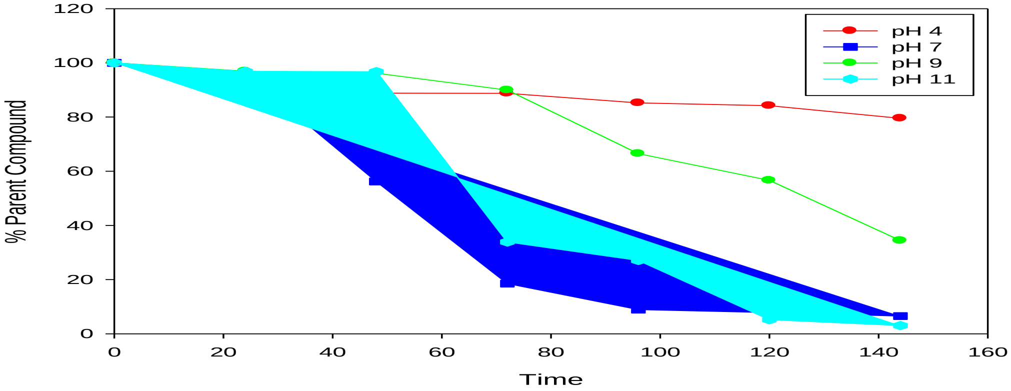

Figure 5: % degradation curve for azinphos methyl hydrolysis experiment at 15± 0.5 °C

For the hydrolysis experiment carried out under extreme conditions of 37 ± 0.5 °C, the rate of reaction followed a different order: pH 4 > pH 9 > pH 7 > pH 11. Therefore, showing that under hot conditions in acidic medium of buffered solution pH 4, measurable rates of hydrolysis were apparent for AZM indicating that temperature plays a role in AZM transformation as shown in Table 1 and Figure 7.

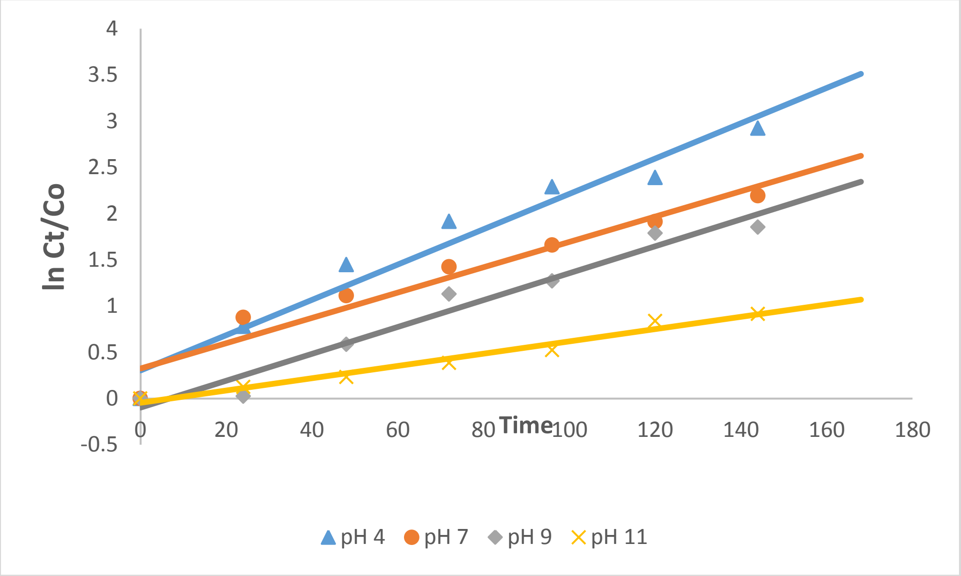

Figure 6: Kinetic data for the hydrolysis of azinphos methyl under the different pHs studied at 37± 0.5 °C

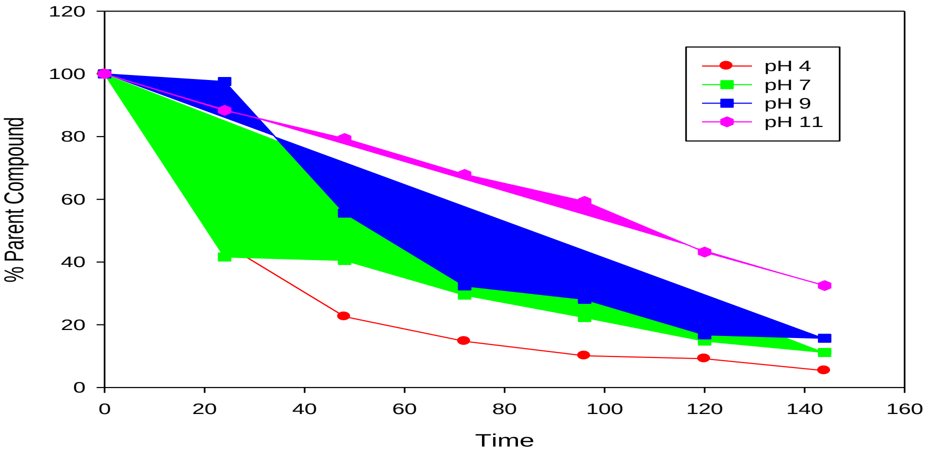

Figure 7: % degradation of AZM at different pHs at 37 ± 0.5 °C

Effect of Varying Temperatures on the Rate of Hydrolysis

The effect of varying temperature on the rate of hydrolysis was also monitored. One of the factors that affect the rate of a chemical reaction is temperature. Chemical reactions typically occur faster at higher temperatures. This wasn’t the case for AZM because it was prepared in different buffered solutions which was to mimic the different soil environments. However, the optimum temperature for the most significant loss of AZM for each of the solutions buffered to pH 4 - 9 was recorded as follows: 37 ^{o}C was the optimum temperature for solutions buffered to pH 4 while 15 ^{o}C, 27 ^{o}C and 15 ^{o}C were the optimum temperature for pH 7, pH 9 and pH 11 respectively.

The proposed hydrolysis pathway via alkaline driven hydrolysis would involve a cleavage of the P-O ester bond with the formation of degradation products to be identified as bis (methylbenzazimide) sulphide, benzazimide, anthranilic acid and trace amount of azinphos – methyl oxygen (21). In one study, azinphos methyl was very stable in water below pH 10.0. Above pH 11.0, it was rapidly hydrolyzed to anthranilic acid, benzamide, and other metabolites as shown in mechanism of reaction in Figure 8 (22).

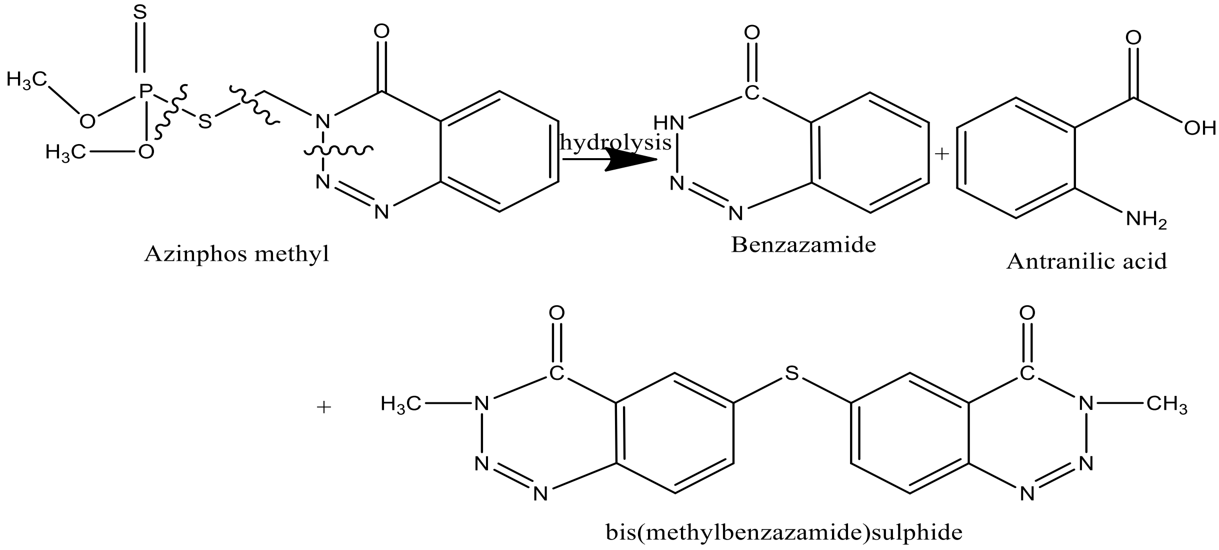

Figure 8: Postulated degradation products of azinphos- methyl

Conclusion

The degradation of AZM in the presence of different buffered solutions of pH 4, pH 7, pH 9 and pH 11 was investigated. Degradation of azinphos-methyl via hydrolysis (in aqueous medium) is dependent on the pH of the medium and to an extent, also dependent on temperature. A significant degradation was observed at solutions buffered at pH 11 under temperatures of 27± 0.5 ^{o}C but under extreme conditions of 37± 0.5 ^{o}C, significant decay was observed at lower buffered solutions of pH 4. The kinetics (rates of the reaction, half-lives and activation energies) of all degradation processes was also determined and were all found to be pseudo first order kinetics. Comparison of both acid and base driven hydrolysis processes, revealed that hydrolysis at elevated pH 11 was the most important process for pesticide loss in aqueous systems under temperature conditions of 15± 0.5 ^{o}C and 27± 0.5 ^{o}C. This finding is similar to what (23) observed in the hydrolysis of AZM, whereby chemical hydrolysis was probably important only in alkaline waters. These results will be particularly relevant for water/wastewater treatment application. Thus, this research is relevant to Nigeria where little or no attention is given to the fate of these chemicals in the environment.

References

1. S. Wu, D. Li, J. Wang, Y. Zhao, S. Dong and X. Wang (2017), Gold nanoparticles dissolution based colorimetric method for highly sensitive detection of organophosphate pesticides. *Sens. Actuators B Chem.* 238: 427–433.
2. R. Grover and A.J. Cessna (1991) (Eds.), Environmental Chemistry of herbicides, CRC Press, Boca Raton, FL.

3. S.D. Richardson, A.D Thruston Jr., T.W. Collette, K.S. Patterson, B.W. Lykins Jr. and J.C. Ireland, (1996), *Environmental. Science Technology*, 30 (11) 3327–3334.
4. L. Muszkat; D. Raucher; M. Mogaritz and D. Ronen (1994), U. Zoller (Ed.), Groundwater Contamination and Control, Marcel Dekker, New York, pp. 257–271.
5. R.M. Dowd, M.P. Anderson, M.L. Johnson (1988), Proceedings of the Second National Outdoor Action Conference on Aquifer Restoration, Groundwater Monitoring Geophysical Methods, National Water Well Association, Dublin, OH, pp. 1365–1379
6. R. Đurović, T. Đorđević, Lj. Šantrić, S. Gašić and Lj. Ignjatović (2010), Headspace Solid Phase Microextraction Method for Determination of Triazine and Organophosphorus Pesticides in *Soil. Journal of Environmental Science and Health,* Part B, 45 (7): 626-632
7. S. Gašić, M. Budimir, D. Brkić and N. Nešković, (2002), Residues of Atrazine in Agricultural Areas of Serbia. *Journal of the Serbian Chemical Society*, 67 (12): 887-892.
8. B. Gevao; K.T. Semple and K.C. Jones (2000), Bound Pesticide Residues in Soils: a Review. *Environmental Pollution,* 108 (1) : 3-14.
9. World Health Organization (2006), WHO gives indoor use of DDT a clean bill of health for controlling Malaria. Division of Environmental Health, WHO, 1211 Geneva 27, Switzerland.
10. K. D. Racke (1992), Degradation of organophosphorus insecticides in environmental matrices. San Diego, Academic Press.
11. W. Hai Bin., K. W. Ming and Y. M. Chp (1994), Comparative Study on the Quantum Yields of Direct Photolysis of Organophosphorus Pesticides in Aqueous Solution, *J. Agric. Food Chem* 42: 2625-2630.
12. A. Kiss, S. Rapi and Cs. Csutoras (2007), GC/MS studies on revealing products and reaction mechanism of photodegradation of peticides. *Microchemical Journal* 85: 13-20.
13. M. I. Pinto, R. Salgado, Barbara A. Cottrell, William J. Cooper, Hugh D. Burrow, C. Vale, G. Sontag and J.P. Noronha (2015), Influence of dissolved organic matter on the photodegradation and volatization kinetics of chlorpyrifos in coastal water. *Journal of Photochemistry and Photobiology A: Chemistry,* 310: 189- 196
14. J. E. Ukpebor, E. E. Ukpebor, and C. J. Halsall, (2012), Determination of Selected Organophosphorus Pesticides using GC-MS in aqueous samples, *Ife journal of Science* 14 (1): 23-29.
15. M.B Colovic., D.Z Kristic., T.D. Lazarevic-Pasti., A.M. Bondzic and V.M. Vasic (2013), Acetyl cholinesterase inhibitors: pharmacology and toxicology. *Curr. Neuropharmacology;* 11:315–335
16. J. Ukpebor, V. Llabjani, F. L. Martin and C. J. Halsall, (2011), Sublethal genotoxicity and cell alterations by organophosphorus pesticides in MCF—7 cells: Implications for environmentally relevant concentrations. *Environmental Toxicology and Chemistry,* 30 (3): 632-639.
17. G. L. Berg, (1986), Farm chemicals handbook. Willoughby, OH: Meister Publishing Company.
18. USEPA (2008); Fate, transport and transformation test guidelines - Hydrolysis
19. J. Ukpebor, J. Sama, A.Oseneboh, N. Osawe, and E. Ukpebor, (2014), Environmental Fate of Temephos: Photodegradation versus Hydrolysis, *Ilorin Journal of Science*, 1 (1):203-211.
20. R. Muhlmann and A. Schrader (1957), Hydrolysis of organophosphorus pesticides. *Z. Naturforsch* 12B, 196–208.
21. S. D. Faust and H. M. Gomaa (1972), Chemical hydrolysis of some organic phosphorus and carbamate pesticides in aquatic environments, *Environmental Letters* 3:171–201.
22. R. Lal, (1984) ed. Insect microbiology. NY: Springer-Verlag.
23. A Farran, J. De Pablo and D. Barceló (1988), Identification of organophosphorus insecticides and their hydrolysis products by liquid chromatography in combination with UV and thermospray-mass spectrometric detection. *Elsevier Journal of Chromatography A.* Vol. 455:163-172.