RADIATION-

~~RADIASI~~ INDUCED DEGRADATION OF PIRIPHOS methyl IN AERATED SOLUTION.

Hendig Winarno, Agustin N. M.Bagyo, Winarti Andayani, Ermin K., Winarno dan Endrawanto Widayat.

RADIATION-INDUCED DEGRADATION OF PIRIMIPHOS METHYL IN AERATED SOLUTION*

Hendig Winarno, Agustin N. M. Bagyo, Winarti Andayani,
Ermin K. Winarno, and Endrawanto Widayat**

ABSTRACT

RADIATION-INDUCED DEGRADATION OF PIRIMI'HOS METHYL IN AERATED SOLUTION. Degradation of pirimiphos methyl insecticide as Minawet 250 EC formulation in aqueous solution was studied. The absorbance, pH, COD (chemical oxygen demand) in aerated solution, and the analyses of degradation products a various irradiation doses with dose rate of 5 kGy/h were measured. The absorbance decrea:ed with the increasing dose. At low doses (≤ 10 kGy), the absorbance decreased rapidly at a :id pH (pH 3.6), while at high doses (> 10 kGy) decreased slowly. The optimum irradiati:n dose for pirimiphos methyl degradation in aerated solution of Minawet 250 EC was found o be 15 kGy at pH 3.6. At that condition, more than 99% of pirimiphos methyl has been de graded and the COD decreased about 82%. Meanwhile, at doses ≤ 5 kGy, the pHs of solution s decreased sharply to 3.5, and at doses > 5 kGy the pHs decreased slowly. The analysis of irradiated samples at optimum condition showed that 2-ethylamino-6-methyl-4-oxo-3,4-dihy dropyrimidine and oxalic acid were formed, as identified by GC-MS and HPLC, respectively.

ABSTRAK

PENGARUH RADIASI PADA DEGRADASI PIRIMIFOS METIL DALAM LARUTAN YANG DIAERASI. Penguraian pirimifos metil sebagai formulasi Minawet 250 EC dalam larutan telah dipelajari. Pengukuran dilakukan terhadap absorbansi, pH, COD (kebutuhan oksigen kimiawi) dalam larutan yang diaerasi, dan analisis produk degradasi pada berbagai dosis dengan laju dosis 5 kGy/jam. Absorbansi larutan berkurang dengan bertambahnya dosis. Pada dosis rendah (≤ 10 kGy), absorbansi menurun dengan cepat pada pH asam (pH 3,6), sedangkan pada dosis tinggi (> 10 kGy) menurun secara perlahan. Kondisi iradiasi optimum untuk penguraian pirimifos metil dalam larutan Minawet 250 EC yang diaerasi ialah dosis iradiasi 15 kGy dan pH 3,6. Pada kondisi tersebut > 99% pirimifos metil

---

* **Jika disetujui Ketua KPTP**, akan dipresentasikan *dalam bentuk porter* pada "Int. Symposium on Environmental Engineering", Kyongju, Korea, 28 Sept.-1 Okt. 1997).

** Centre for the Application of Isotopes and Radiation, National Atomic Energy Agency, P.O. Box 7002 JKSKL, Jakarta 12070, Indonesia

telah terurai dan COD berkurang sebanyak 82%. Selain itu, pada dosis ≤ 5 kGy, pH larutan menurun dengan tajam sampai 3,5, dan pada dosis > 5 kGy pH larutan menurun dengan perlahan. Analisis sampel yang telah diiradiasi menggunakan GC-MS and HPLC menunjukkan bahwa 2 diantara senyawa hasil degradasi ialah 2-etilamino-6-metil-4-okso-3,4-dihidropirimidin dan asam oksalat.

INTRODUCTION

Along with rapid development of industry, the use of various organic compound are increasing. In Indonesia, pesticide industries have developed fastly, and this will produce waste from the raw materials and active ingredients. If it is not managed by good handling, the waste will cause pollution to the environment.

Some methods for treatment of waste water such as by absorption using activated charcoal, aeration, coagulation, or oxidation using ozon had been conducted, but so far no satisfactory results was obtained. So, more effective and efficient methods are still needed.

SUN and PIGNATELLO [1] reported that 60% of 2,4-dichlorophenoxy acetic acid could be degraded by UV irradiation combined with the addition of Fe^{3+}/H_2O_2 as catalyst. Oxalic acid was identified as an intermediate compound.

The use of ionizing radiation to eliminate non biodegradable organic pollutants in raw material of drinking water and waste water had been investigated by many researchers [2-4]. Based on the previous research, the degradation of fenitrothion and prothiophos insecticides in aerated aqueous solution using gamma radiation could reach 90% (initial concentration was 50 mg/L) at the dose of 6 and 8 kGy, respectively [5,6]. One of the degradation products was oxalic acid.

In this research, degradation of pirimiphos methyl insecticide as Minawet 250 EC formulation was studied. Generally, this insecticide is used for controlling a wide range of pests of building and stored products, namely fruits, vegetables, and other crops [7]. The chemical name of pirimiphos methyl is *O*-(2-diethylamino-6-methylpyrimidin-4-yl)-*O*,*O*-dimethyl phosphorothioate. Its structural formula can be seen in Figure 1.

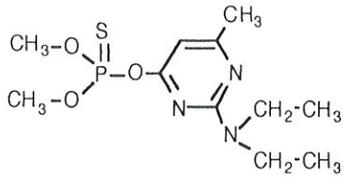


Figure 1. Structural formula of pirimiphos methyl

EXPERIMENTAL

Reagents. The Minawet 250 EC insecticide formulation containing 55% of pirimiphos methyl was used without purification. The other reagent used i.e. methanol, potassium dichromate, and ferro ammonium sulfate were of a reagent grade.

Irradiation Procedure and Analysis. As much as 500 ml of Minawet 250 EC solution containing 100 ppm of pirimiphos methyl was placed in a reaction vessel (∅ = 5.5 cm, l = 22 cm) and was bubbled through a porous plate at the bottom of the reaction vessel. The solution was bubbled with air during irradiation. It was then irradiated with Cobalt-60 gamma rays with doses of 5, 10, 15, 20, and 25 kGy at room temperature. The dose rate (5 kGy/h) was determined using Fricke dosimeter ($G[Fe^{3+}]= 15.6$) [9]. The absorbance was measured using a Shimadzu spectrophotometer uv-vis 160 at 304 nm. The pirimiphos methyl and the other compounds in Minawet 250 EC solution were analyzed using a Shimadzu LC-9A HPLC (High Performance Liquid Chromatograph) and a Finnigan MAT GC-MS (Gas Chromatography Mass Spectrometer). The organic acids were identified by HPLC using Aminex HPX 87H ion exclusive column.

RESULTS AND DISCUSSION

Effect of pH on Radiolysis of Pirimiphos Methyl in Minawet 250 EC Solution. The solution of Minawet 250 EC has λ_{max} at 304 nm. The absorbance of solutions before and after irradiation are shown in Figure 2. The pirimiphos methyl with concentration of 100 mg/L in aerated solution at various pHs (3.6 - 8.6) was irradiated with doses of 0 - 25 kGy. Figure 2 shows that the percentage of absorbance at doses up to 10 kGy at pH 3.6 decrease fastly, then the decrease becomes slow at doses > 10 kGy. The absorbance at pH 3.6 is greater than at neutral and basic pHs.

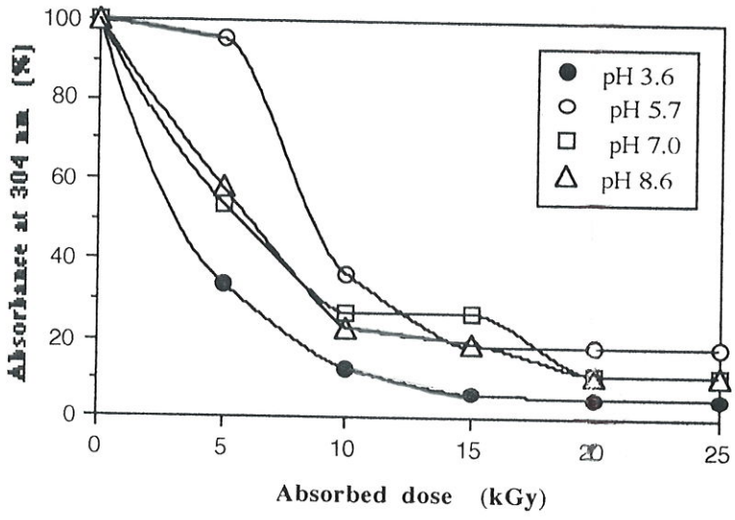


Fig. 2. Effect of pH of Minawet aqueous solution on the reduction of absorbance at 304 nm

This shows that pirimiphos methyl degrade faster due to irradiation at acid medium (pH 3.6). In an acidic aerated solutions, the following tranformations occur [10, 11] :

$$e^-_{aq} + H^+ \longrightarrow H\cdot \quad (1)$$

$$H\cdot + H_2O_2 \longrightarrow H_2O + OH\cdot \quad (2)$$

$$OH\cdot + H_2O_2 \longrightarrow H_2O + HO_2\cdot \quad (3)$$

In a basic aerated solutions, the following tranformations occur [10-12] :

$$H\cdot + OH \longrightarrow e^-_{aq} + H_2O \quad (4)$$

$$O_2 + e^-_{aq} \longrightarrow O_2^{-}\cdot \quad (5)$$

$$OH\cdot \longrightarrow O^{-}\cdot + H^+ \quad (6)$$

$$H_2O_2 \longrightarrow HO_2^- + H^+ \quad (7)$$

Degradation of pirimiphos methyl at acid pH is greater than at basic or neutral medium, since at acidic medium the oxidizing species ($\cdot OH$ and $HO_2\cdot$) increase due to the transformation reactions (1) - (3), while at basic pH, the $O_2^{-}\cdot$ formed from reactions (4) and (5) is less reactive than $HO_2\cdot$ and $OH\cdot$ to attack pirimiphos methyl. Besides, $\cdot OH$ and H_2O_2 molecules will dissociate producing less reactive species as shown in reactions (6) and (7). Therefore, the irradiation of pirimiphos methyl at acid condition will be more effective to degrade the insecticide as the oxidicing species will attack the aromatic ring.

Change of pH, Concentration of Pirimiphos methyl Remained, and Its Degradation Products. Pirimiphos methyl (100 mg/L) as Minawet 250 EC in aerated solution was irradiated at various pHs and absorbed doses.

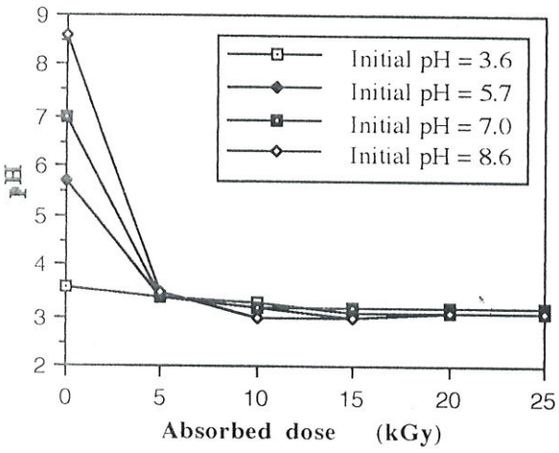


Fig 3. Effect of irradiation dose on the pH of Minawet 250 EC solution

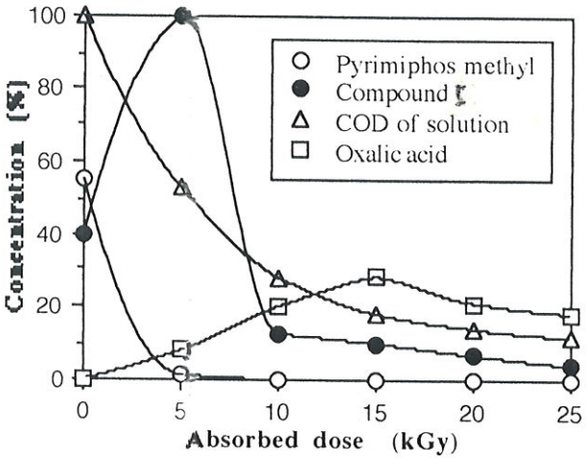
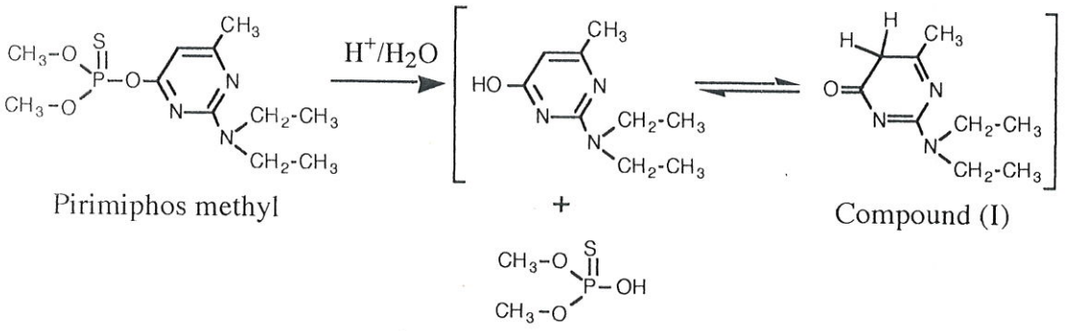


Fig 4. Conc. of pirimiphos methyl, 2-diethyl amino-6-methyl-4-oxo-3,4-dihydropyrimidine (I), oxalic acid and COD of the solutions

The results of pH measurements are shown in Figure 3. It appears that pH of the solutions decreased fastly after irradiation at 5 kGy, but at doses > 5 kGy the pH decreased slowly, or even almost no significant change. From initial pH 3.6 to 8.6, the pH decreased until pH 3 due to irradiation. The decrease of pH showed that pirimiphos methyl molecules and the other compounds in the Minawet 250 EC aqueous solution were degraded into acid products.

The concentration of pirimiphos methyl , compound (I) COD of solution, and oxalic acid produced due to radiolysis of Minawet 250 EC in aerated solution at pH 3.6 (initial concentration of pirimiphos methyl was 100 mg/L) are shown in Figure 4. Figure 4 shows that the concentration of pirimiphos methyl before irradiation was only 57% (checked by HPLC, retention time = 5.825 min), and the second peak (compound I) appeared at retention time = 2.675 min. At the dose of 5 kGy, the peak of compound ( ) was greater than the control solution (0 kGy), while pirimiphos methyl almost degraded completely (98%). It suggests that 57% of pirimiphos methyl had been hydrolyzed into compound (I) when the pH was adjusted to acid pH using H_2SO_4 solution. The concentration of compound (I) could not be determined quantitatively because no standard compound was available. However if the highest peak of compound I curve in irradiated sample of 5 kGy was assumed as 100%, the proporsions of compound (I) present in every dose are as shown in Fig. 4 The HPLC chromatogram of

pirimiphos methyl and compound (I) is shown in Fig. 5. Analyses of compound (I) by GC-MS showed that compound (I) is 2-diethylamino-6-methyl-4-oxo-3,4-dihydropyrimidine (Fig. 6). It is agreeable with the theory that organophosphate insecticides will be hydrolyzed easily in acid medium producing 2-diethylamino-6-methyl-4-oxo-3,4-dihydropyrimidine (I) (*m/z* 181) and *O,O*-dimethyl phosphorothioate compounds as the following reaction :



(8)

At the dose of 5 kGy, the amount of OH radicals was not enough to attack compound (I), because the OH radicals will be catched by scavenger radical that may be formed from radiolysis of the other compounds in Minawet aqueous solution. Therefore the amount of OH radical for attacking the aromatic ring in compound (I) was not effective. At 10 kGy, the compound (I) concentration decreased sharply, then at doses higher than 10 kGy decreased slightly.

The COD of solution decreased from 288 mg/L before irradiation to 33 mg/L after irradiation at the dose of 25 kGy. The concentration of oxalic acid produced was determined by HPLC. Oxalic acid concentration increased until the dose of 15 kGy, then decreased at doses > 15 kGy (Figure 4). It suggests that the oxalic acid degrade further into smaller compounds (CO_2 and H_2O). From Figure 4, it can be seen that 15 kGy is the optimum dose for pirimiphos methyl degradation. At this condition, the pirimiphos methyl had been degraded completely, 92% of compound I was also degraded, and COD of the solution decreased 82% (from 288 to 52 mg/L).

CONCLUSION

Gamma irradiation can degrade the compounds in Minawet 250 EC aqueous solution to acid compound. The optimum condition for degrading pirimiphos methyl and other compounds in aerated solution of Minawet 250 EC is irradiation at the dose of 15 kGy and pH

3.6. At this condition, pirimiphos methyl and a hydrolytic product of pirimiphos methyl, i.e. 2-diethylamino-6-methyl-4-oxo-3,4-dihydropyrimidine can be degraded 100% and 92%, respectively, and COD of the solution decreases 82%. The organic acid produced from radiolysis of this insecticide is oxalic acid.

ACKNOWLEDGMENTS

The authors are grateful to Mr. Syurhubel, Mrs. Christina Tri Suharni, and Mr. Armanu for their technical assistances.

REFERENCES

1. SUN, Y. and PIGNATELLO, J., Photochemical reactions involved in the total mineralization of 2,4-D by $Fe^{3+}/H_2O_2/UV$, *Environ. Sci. Technol.*, **27** (1993) 304.

2. PROKSCH, E., GEHRINGER, P., SZINOVATZ, W. and ESCHWELER, H., Radiation induced decomposition of small amounts of trichloroethylene in drinking water, *Appl. Radiat. Isot.*, **40** (1989) 133.

3. GETOFF, N., Radiation-induced degradation of water pollutants - state of the art, *Radiat. Phys. Chem.*, **47** (1996) 581.

4. GETOFF, N., Advancements of radiation-induced degradation of pollutant in drinking and waste water, *Appl. Radiat. Isot.*, **40** (1989) 585.

5. WINARNO, E. K., LINDU, W. A., ARMANU, and WINARNO, H., "Degradation of fenitrothion insecticide in aqueous solution by gamma radiation", (Presented at JNK Seminar, Yogyakarta, Oct. 12, 1996), (Proceeding will be published). (in Indonesian).

6. WINARNO, E. K., LINDU, W. A., and WINARNO, H., "Radiolysis of tokuthion 500 EC insecticide in aqueous solution", (Presented at Seminar of Application of Isotopes and Radiation, National Atomic Energy Agency, Jakarta, February 18-19, 1997), NAEA, Jakarta (1997). (Proceeding will be published). (in Indonesian).

7. ANONYMOUS, Farm Chemicals Handbook 1996, Willoughby, Meister Publishing Co., (1996), C305.

8. SEHESTED, K., "The Fricke Dosimeter", Manual on Radiation Dosimetry (HOLM, N.W. and BERRY, R.J., Eds.), Marcel Dekker, New York (1970) 313.

9. QUINT, R. M., PARK, H.R., KRAJNIK, P., SOLAR, S., GETOFF, N. and SEHESTED, K., γ-Radiolysis and pulse radiolysis of aqueous 4-chloroanisole, *Radiat. Phys. Chem.*, **47** (1996) 835.

10. EL-ASSY, N.B., EL-WAKELL, E. I., and FATTAH, A. A. A., The degradation of triazo dye chlorantine fast green BLL in aqueous solutions by gamma radiation-III, *Appl. Radiat. Isot.*, **42** (1991) 89.

11. BURTON, M. and MAGEE, J., Advances in Radiation Chemistry, Vol. 1, John Wiley & Sons Inc. (1969) 109.

12. SPINKS, J. W. T., and WOODS, R. J., An Introduction to Radiation Chemistry, New York, John Wiley & Sons (1976) 256.

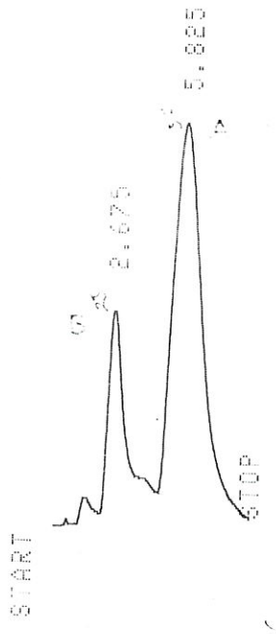


Fig. 5. HPLC chromatogram of Minawet 250 EC in aqueous solution containing pirimiphos methyl 100 mg/L

A. Pirimiphos methyl, r. t. = 5.825 min (47% checked by standard compound))
B. Compound I, r. t. = 2.675 min

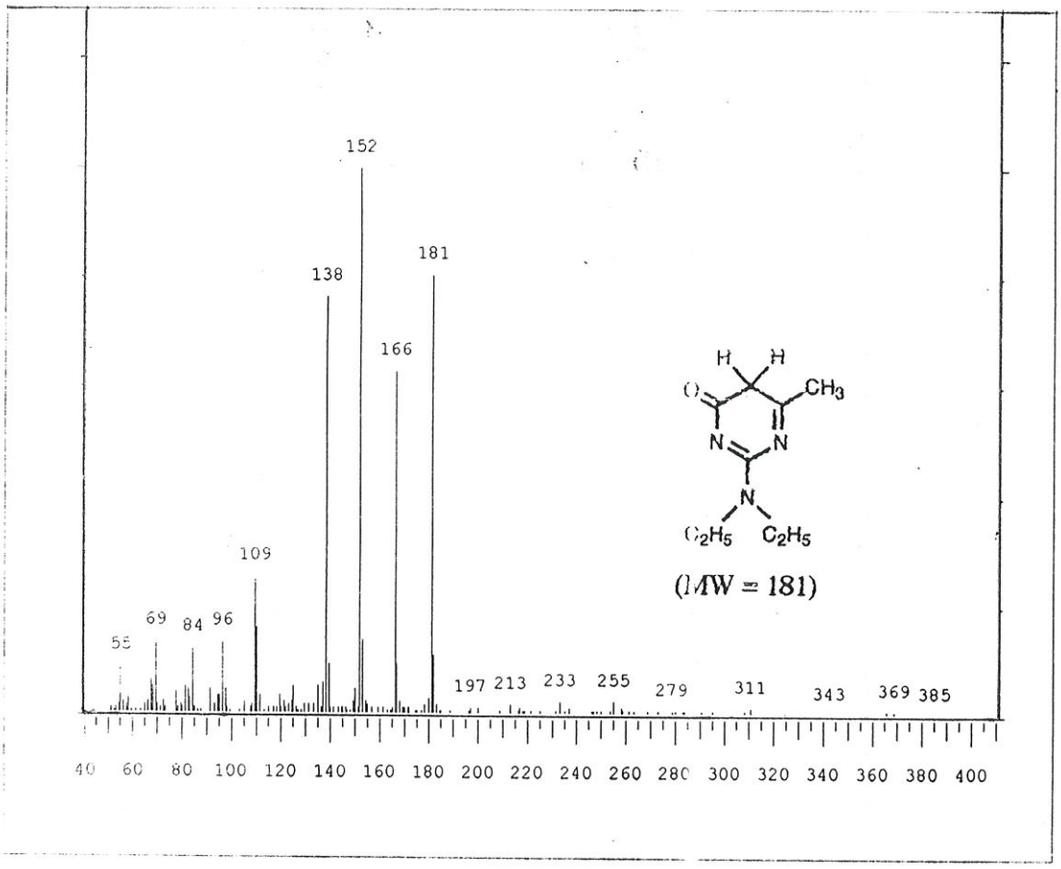


Fig. 6. Mass spectrum (*CI mode*) of 2-diethylamino-6 methyl-4-oxo-3,4-dihydropyrimidine (compound I)