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IRRADIATION EFFECTS ON INSECTICIDES AS A POLLUTANT MODEL IN AQUEOUS SOLUTION

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ABSTRACT

IRRADIATION EFFECT ON INSECTICIDES AS A POLLUTANT MODEL IN AQUEOUS SOLUTION. Degradation of some insecticides i.e.: fenitrothion, prothiofos, and cypermetrin as a model pollutant was carried out using gamma irradiation of ^{60}Co. Irradiation-induced of fenitrothion in solution acid medium gave the significant effect on the decrease of its concentration. The optimum condition for degradation of fenitrothion (55.5 mg/L) was irradiation at 6 kGy with aeration in initial pH 5.6. At this condition, the concentration of fenitrothion decreased up to 97%. Determination of organic acids in irradiated product by HPLC method showed that oxalic acid and formic acid were clarified as organic acid-degraded products of fenitrothion with the concentration of 23.0 mg/L and 2.5 mg/L respectively. The irradiation of prothiofos in aqueous solution (50 mg/L), showed that irradiation at a dose of 8 kGy and initial pH 7 gave the optimum degradation. At this condition, the concentration of prothiofos decreased up to 98%. Determination of irradiated product by HPLC method showed that oxalic acid (18 mg/L) was clarified as organic acid-degraded product of prothiofos. In the case of cypermetrin, the optimum condition for its degradation was irradiation with aeration of cypermetrin (40 mg/L) at a dose of 20 kGy, initial pH 11, and adding the catalyst 0.05% of $FeCl_3$. At that condition, cypermetrin decreased up to 87% and COD of solution decreased up to 78%. The organic acid detected at optimum condition as degradation products were oxalic acid (1.1 μg/L), maleic acid (9.0 μg/L), formic acid (127.0 μg/L), and acetic acid (286.0 μg/L). From these results, it could be concluded that ionizing radiation can be used as a tool to degrade insecticides as organic pollutants.

Keywords: ionizing radiation, organic pollutants, insecticides, fenitrothion, prothiofos, cypermetrin

INTRODUCTION

The increased in population caused the activities of industries increase as well as people activities, subsequently the negatives impact to the environment problems such as the increased contamination on the environment with the various industrial waste materials, pesticides, fertilizer in modern agriculture resulted in a strong overloading of water resources [1,2].

One of the industry which contribute to the wastewater is pesticide industries. Wastewater conventionally treatment such as coagulation method, aeration, and adsorption are done by the industries to decrease the pollution of environment. Un fortes this way could not be applied optimally. The dangerous pollutants are still found in waters. Many researches had been done to find the organic pollutants degradation techniques. One of the alternative method for degrading the organic pollutants is the oxidation using hydroxyl radical. The hydroxyl radical can be produced by UV irradiation that combined with Fenton reagent (UV/H_2O_2/Fe^{+2} or UV/H_2O_2/O_3/Fe^{+2}), UV/semiconductor (UV/TiO_2, UV/$ZrTiO_2$), UV/ozon, ionizing radiation (gamma, electron beam) [3]. At the last decades, the study on the use of the ionization radiation technique for removing the organic pollutants have been conducted [1-9].

THEORY

Insecticide

Based on the target, pesticide is divided into 8 kinds, i.e.: insecticide, herbicide, fungicide, acaricide, moluscicide, rodenticide, nematicide, and bactericide. Insecticide is one of the most highly produced and used pesticide. Based on the functional group of the active ingredients, insecticide is divided into four classes, namely organophosphorous, organochlorine, carbamate, and pirethroid.

Ionizing radiation

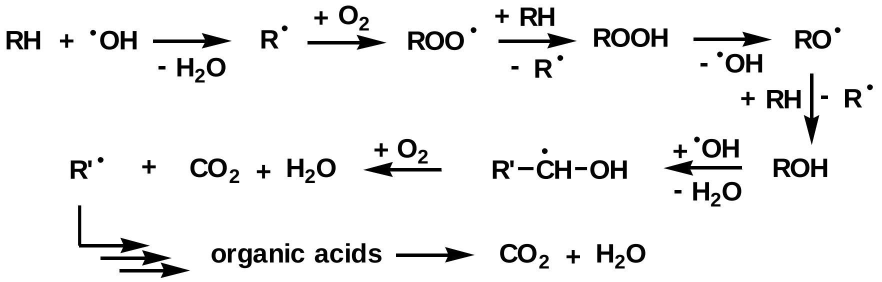
Ionization radiation of water produce the active species such as $^{\bullet}OH$ and H_2O_2 that act as an oxidizer and has a function to degrade organic pollutants in water. Ionized radiation can be produced by gamma rays from ^{60}Co, ^{137}Cs, and electron scatter machine. Radiation as well as electron scatter on water cause the degradation of water molecules to form primary products as follows [4]:

$$H_2O \xrightarrow{\gamma} {}^{\bullet}OH,\ H^{\bullet},\ H^{+},\ e^{-}_{eq},\ H_2,\ H_2O_2 \qquad (1)$$

H_2O_2 and $^{\bullet}OH$ are oxydizers, while e_{aq}^{-} and $H^{\bullet}$ are reducers. The oxidyzer cause organic compounds, including pollutant, to undergo degradation to form simple organic compounds such as organic acids until finally become the more simple compounds such as cations, anions, CO_2 , and H_2O.

Degradation of Organic Pollutants in Aqueous Solution

Degradation of organic pollutants in aqueous solution indirectly occurs through the reactive species such as hydroxyl radical ($^{\bullet}OH$). The $^{\bullet}OH$ produced from radiolysis of water subsequently react with organic pollutants (RH) following the mechanism of [4]:



(2)

Further degradation of R'• with the same mechanism will form organic acids, which is subsequently degraded to CO_2 and H_2O. The organic acids formed, such as formic, acetic, meleic, oxallic, and succinic acids could be detected by high performance liquid chromatography (HPLC), making the determination of the degradation products possible. The degradation of organic compounds reduce the chemical oxygen demand (COD) values and total organic carbon (TOC) values which are water quality parameters.

The Effect of Dissolved Oxygen in Water Solution

In the water, the dissolved oxygen react with $H^{\bullet}$, e_{aq}^{-}, and H^{+} to form perhydroxyl radical ($HO_2^{\bullet}$) that then act as additional oxidizing species. Subsequently, this species will also react with pollutant organic (RH) causing the increase of the pollutant degradation. The reaction mechanism is as follows [4]:

$$H^{\bullet} + O_2 \longrightarrow HO_2^{\bullet} \qquad (3)$$

$$e_{aq}^{-} + O_2 \longrightarrow O_2^{-} \xrightarrow{+H^{+}} HO_2^{\bullet} \qquad (4)$$

$$RH + HO_2^{\bullet} \rightrightarrows \text{organic acids} \longrightarrow CO_2 + H_2O \qquad (5)$$

IRRADIATION EFFECT ON ORGANOPHOSPOROUS AND PYRETHOID INSECTICIDES

In this report, 2 kinds of organophosphorous insecticides, namely: fenitrothion and prothiofos; and one of pirethroid insecticide, namely cypermetrin were used as models of organic pollutants. The chemical structure of these pesticides are shown in Fig. 1.

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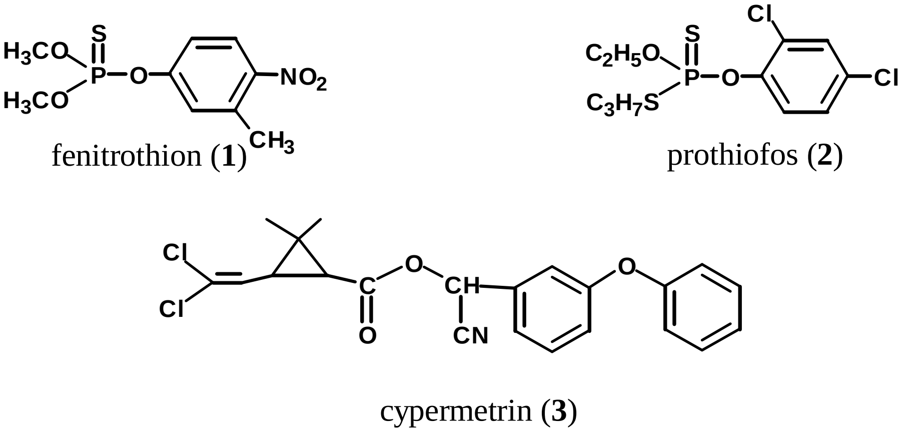

fenitrothion (**1**)

prothiofos (**2**)

cypermetrin (**3**)

Fig. 1. Chemical structure of insecticides as pollutant model

Fenitrothion

Fenitrothion with the chemical name of *O,O*-dimethyl-*O*-(3-methyl-4-nitrophenyl) phosphorothioate is an organophosphorous insecticide, moderately toxic with a 250 mg/kg and a 2.500 mg/kg dermal LD_{50} in rats [10]. This insecticide is usually used to control *Spodoptera exigua* on onion plant, *Atherigona sp.* on corn plants and commercially sold in some formulations (Sumithion 50 EC, Fenthron 50 EC) [11].

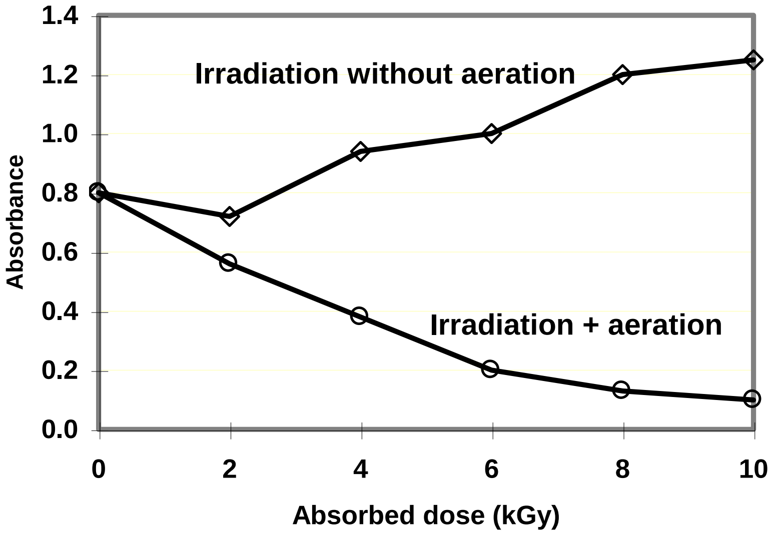

Fig. 2. The effect of gamma irradiation at pH 5.5 with and without aeration on the UV absorption (279 nm) of fenitrothion in aqueous solution

Gamma irradiation on fenitrothion in aqueous solution with a concentration of 55.5 mg/L and at pH 5.6, showed that irradiation without aeration caused the increase of UV absorption at 279 nm (maximum wavelength) (Fig. 2). This fact suggested that the additive ingredients reacted to each other or reacted with fenitrothion to form new compounds that cause UV absorption. As explain in eq. (3) to (5), irradiation with O_2 added cause the increase of the oxidizer species, resulting in more intensive degradation of fenitrothion and additive ingredients [12].

Irradiation of fenitrothion in various pH showed that irradiation in acid pHs (pH 3 and 5.6) is rather more efective than irradiation in neutral and basic pHs (Figure 3).

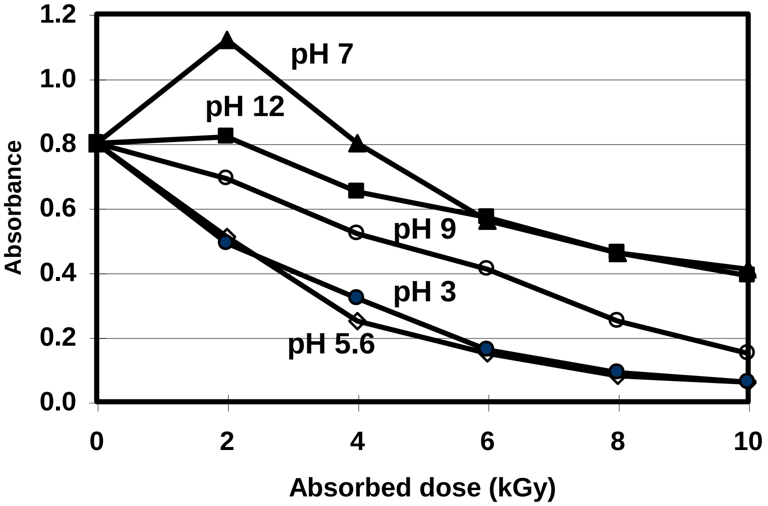

Fig. 3. The effect of gamma iradiation with aeration at various pH 5.5 on the UV absorption (279 nm) of fenitrothion in aqueous solution (concentration of fenitrothion = 55.5 mg/L)

This was shown clearly with $G_{(degradation)}$ value of fenitrothion at a dose of 4 kGy (Table 1). $G_{(degradation)}$ value is the degradation of molecules or chemically changed at every 100 eV of

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energy adsorbed. $G_{(degradation)}$ value at acid pHs (3 and 5.6) was higher than at neutral and basic pHs (7-11), this showed that fenitrothion molecules degraded effectively at acid pH.

Table 1. G values of fenitrothion degradation by gamma irradiation in aqueous solution

pH	**G values**
3	0.27
5.6	0.32
7	0.19
9	0.19
12	0.18

Determination of fenitrothion concentration by HPLC on reverse-phase column decreased with increasing irradiation doses (Fig. 4). At a dose of 6 kGy, fenitrothion decreased from 55.5 mg/L to 1.63 mg/L (> 97%), and the colloidal solution changed to a clear solution.

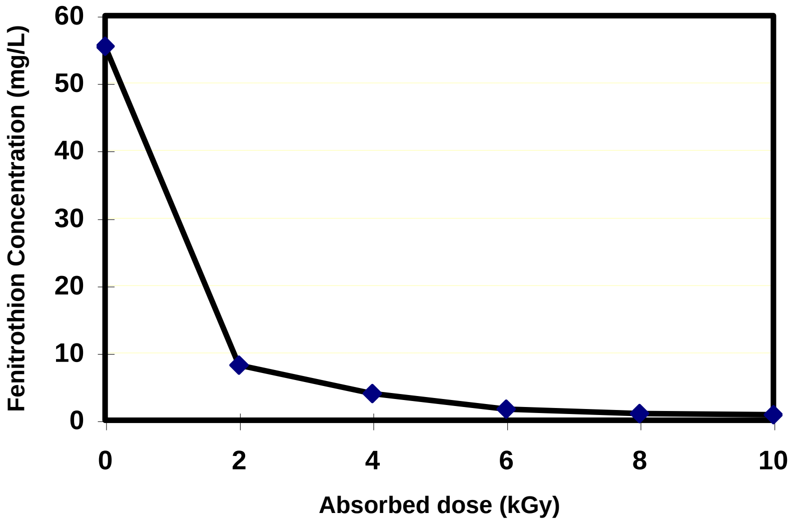

Figure 4. The concentration decreased of irradiated fenitrothion in aerated solution (pH = 5.6, initial concentration = 55.5 mg/L) measured with HPLC method

Irradiation also caused the decrease of pH solution from 5.6 to 2.8 at a dose of 10 kGy. The decrease of pH showed that fenitrothion molecules degraded to acid products. Detection of organic acids in irradiated fenitrothion at a dose of 6 kGy by HPLC method (Shimadzu LC-9A, UV detector at 210 nm, Aminex HPX-87H column, eluent: 4.0 mM of H_2SO_4 at flow rate of 1.0 ml/min) are shown in Table 2.

Table 2. The organic acids determination of irradiated fenitrothion in aerated solution by HPLC method

Irradiation Dose (kGy)	Organic acid concentration (mg/L)		
	Oxalic acid	Maleic acid	Formic acid
0	< 0.01 mg/L	< 0.01 mg/L	< 0.01 mg/L
2	11	0.18	4.5
4	18	0.27	4.5
6	23	< 0.01 mg/L	2.5
8	25	0.18	4.5
10	27	< 0.01 mg/L	1.7

The plausible mechanism of the fenitrothion degradation is described in Fig. 5.

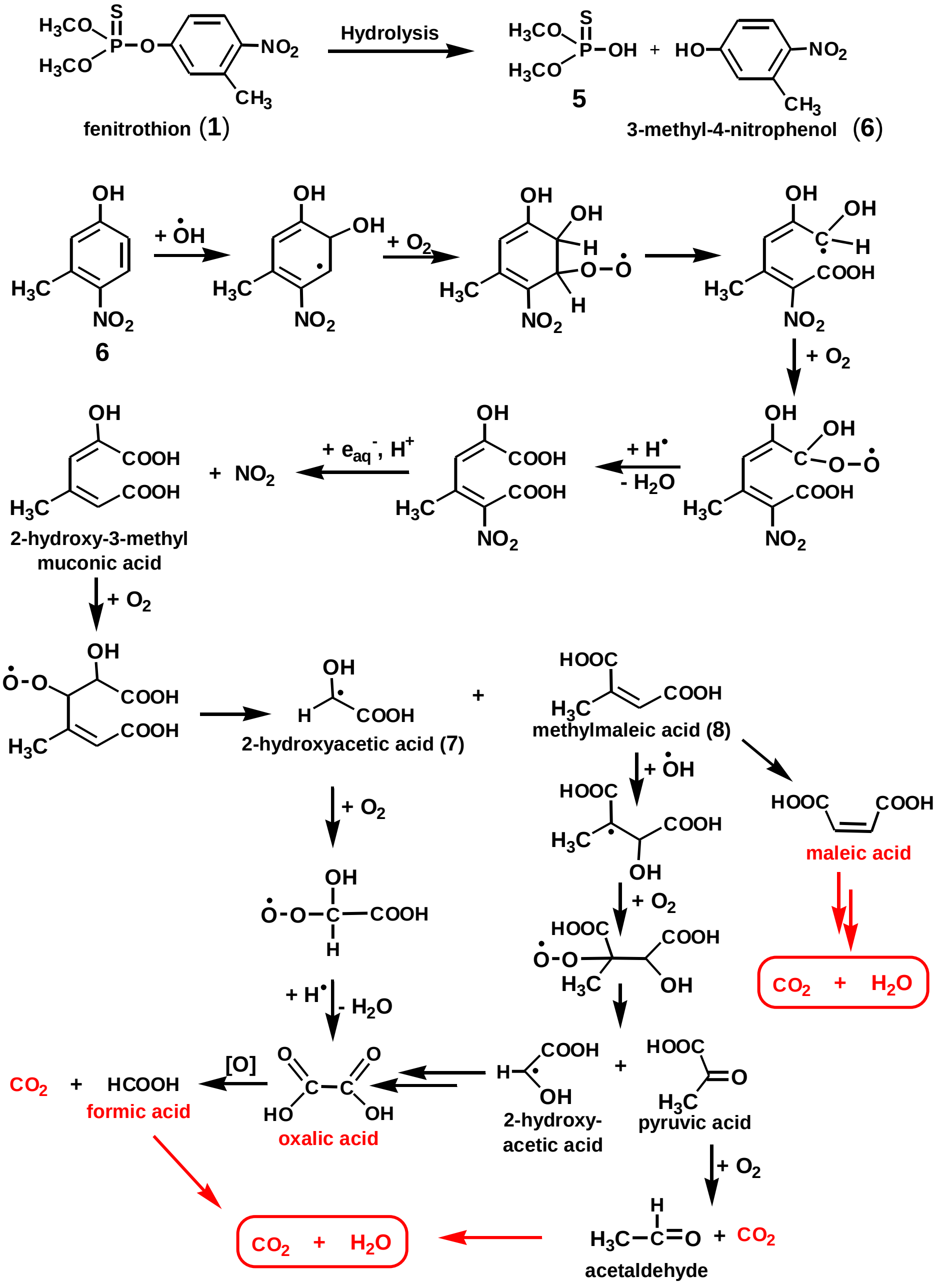

Fig. 5. The plausible mechanism of fenitrothion degradation induced by gamma irradiation in aerated solution

Firstly, fenitrothion (**1**) is hydrolized into dimethyl phosphorothioate (**5**) and 3-methyl-4-nitrophenol (**6**). Dimethyl phosphorothioate is an organic acid and easily degraded to acid mineral, while 3-methyl-4-nitrophenol is still toxic, but it underwent degradation to form organic acid via free radical mechanism by gamma irradiation.

There were three organic acids detected, i.e.: oxalic acid, maleic acid and formic acid from the irradiated solution. The formic acid concentration was very low, because of it's unstable characteristic it was easily oxidized to CO_2 and H_2O. Pyruvic acid and acetaldehyde have not been identified, due to the unavailability of standard solution. It is suggested that acetaldehydes were oxidized to acetic acid and after that it was degraded to CO_2 and H_2O, resulting in the undetected of acetic acid. Based on the analysis result shown fenitrothion could be degraded by gamma irradiation to simple compounds which not are toxic and the colloidal solution changed to clear solution.

Prothiofos

Prothiofos (**2**) with the chemical name of *O*-ethyl-*O*-(dichlorophenyl)-*S*-propyl dithiophosphate is an organophosphorous insecticide, moderately toxic with a oral LD_{50} of 1.500 mg/kg and dermal LD_{50} of > 5.000 mg/kg in rats [10]. This insecticide is general used for protection of fruit from leaf-eating catepillar *Pseudococus sp.*, cutworms, thrips and commercially sold in some formulations (tokuthion 500 EC, Carolit 500 EC) [11]. In aqueous solution, prothiofos is hydrolyzed into *O*-ethyl-*S*-propyl dithiophosphate (**9**) and 2,4-dichlorophenol (**10**). Compound **9** is easily degraded into mineral acid, but compound **10** contained the benzene ring, making it difficult to degrade [13].

The degradation of prothiofos (concentration = 50.0 mg/L) without aeration was low, at a dose of 10 kGy the absorbance of solution at λ_{max} 284 nm was only decreased to 4 %, but irradiation at a dose of 8 kGy with aeration decreased up to 98 % (Fig. 6) [13]. The dissolved oxygen in the solution caused the formation of $HO_2^\bullet$ as oxidizing species increased (eq. 3-5) and further degradation of prothiofos could increased too.

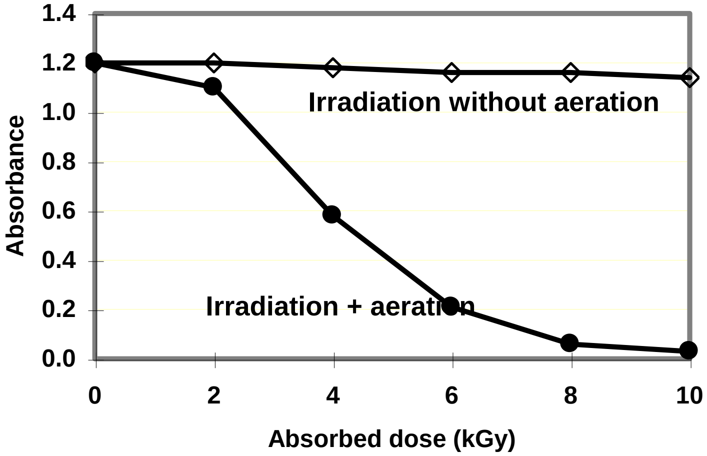

Figure 6. The absorbance decreased of irradiated prothiofos in aerated solution (pH = 7, initial concentration = 50.0 mg/L)

Determination by HPLC method on reverse-phase column showed the concentration of prothiofos could decreased up to 98% at the irradiation dose of 8 kGy (Fig. 7) [13].

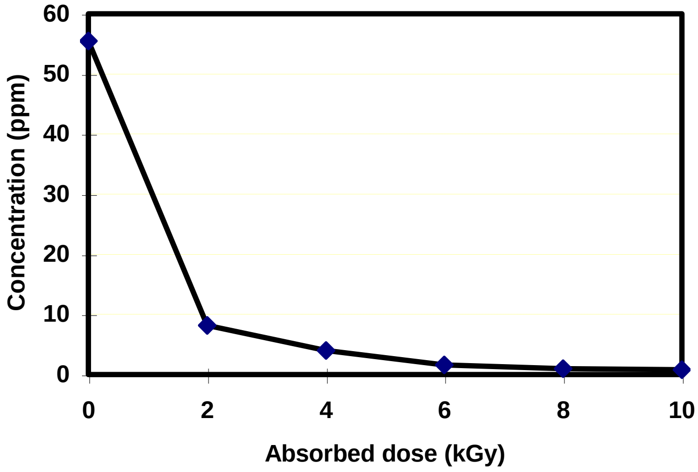

Figure 7. The concentration decreased of irradiated prothiofos in aerated solution (the initial pH = 7, the initial concentration = 50.0 mg/L)

$G_{(degradation)}$ value presented in Table 3, showed that at a dose of $\geq$ 6 kGy and at the initial pH 7 the prothiofos degradation was clearly shown. $G_{(degradation)}$ value of prothiofos were

0,132 – 0,212 at 100 eV. G $_{\text{(degradation)}}$ value of prothiofos at pH 7 was the highest compared to G values at acid and basic pHs.

Table 3. G value of prothiofos degradation by gamma irradiation at dose of 6 kGy (dose rate 5 kGy/h)

pH	**G$_{\text{(degradation)}}$ value**
3	0,190
5	0,181
7	**0,212**
9	0,132
12	0,189

The organic acids analysis of irradiated prothiofos at an optimum dose (8 kGy) using HPLC method showed that oxalic acid was detected as a degradation product. The plausible degradation is described in Fig. 8.

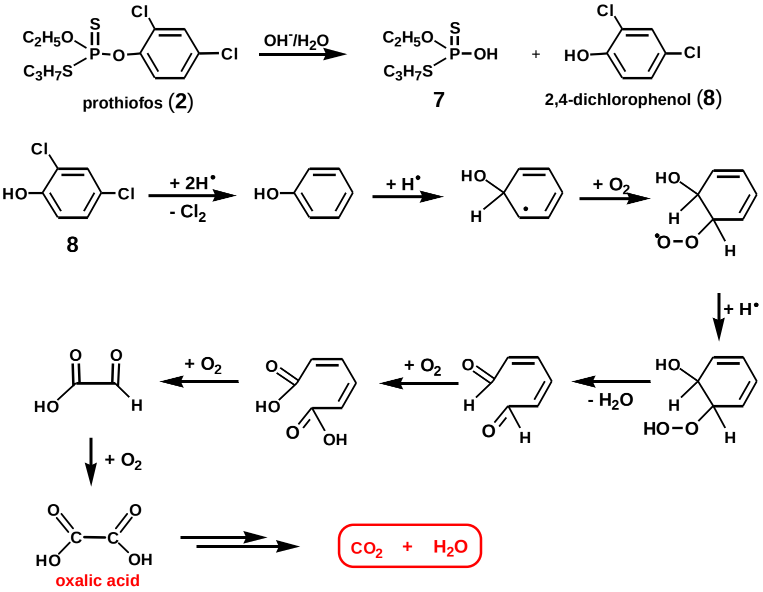

Fig. 8. The plausible mechanism of prothiofos degradation induced by gamma irradiation in aerated solution

Cypermetrin[14]

The effect of gamma irradiation on cypermetrin showed that by adding 0.05% of $FeCl_3$ and H_2O_2 as catalysts, irradiation at pH 11 exhibit decreasing of UV absorbance compared to the addition of TiO_2 or $CuSO_4$ (Fig 9). The hyperchomic effect suggested that this is a result from the reaction of additive agents in insecticide formulation with the primer species of radiolysis products, or the reaction between additive ingredients in the formulation, forming new polymer compounds that would be difficult to degrade.

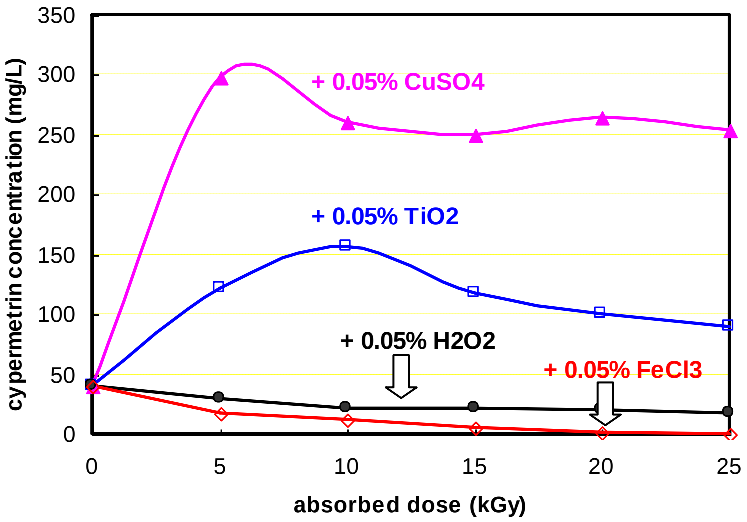

Figure 9. The effect of irradiation with adding the catalyst on cypermetrin degradation (cypermetrin concentration = 40 mg/L, pH adjusted to 11, catalyst = 0,05 %)

Irradiation at dose of 15 kGy with the addition of 0,05% $FeCl_3$ as a catalyst resulted in the best condition of degradation. At this condition, the UV absorbance of solution decreased to 87%.

The aerated and irradiated cypermethrin solution at the best condition (pH 11 and added with catalyst $FeCl_3$ 0,05 %) has its COD values measeured and the organic acids content formed as the products of cypermethrine degradation. COD values are shown in Table 4. The irradiation dose at 20 kGy could decrease COD value from 581 mg/L to 130 mg/L (a decrease of 78 %). Organic acids formed are shown in Table 4, they are formic acid, acetic acid, oxalic acid, and maleic acid. These organic acids are unstable, so they are further easily degraded to H_2O and CO_2.

Table 4. COD value and organic acid concentration of irradiated cypermetrin solution on the optimum condition

Irradiation	COD of solution	Formic acid	Acetic acid	Oxalic acid	Maleic acid

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Dose (kGy)	mg/L	%	(μg/L)	(μg/L)	(μg/L)	(μg/L)
0	581	100	-	-	-	-
5	293	50	318	286	422	52
10	217	217	254	429	626	41
15	193	33	191	286	1004	26
20	130	23	127	286	1136	19
25	87	15	191	286	829	24

Based on these results, it could be estimated that initially cypermetrin underwent hydrolitic cleavage at position 1, 2, 3, and 4 to form intermediates benzene (**9**), m-cresol (**10**), cyclic carboxylic acid (**11**), and mineral acids HCl and HCN as shown in Figure 10.

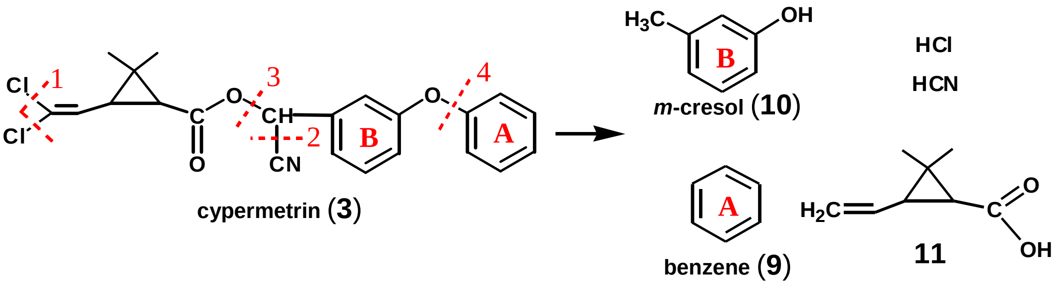

Fig. 10. The hydrolytic cleavage of cypermetrin

The intermediate **11** as an acid was easily degraded to mineral acids and intermediates **9** and **10** were further degraded as described in Fig. 11 and Fig. 12.

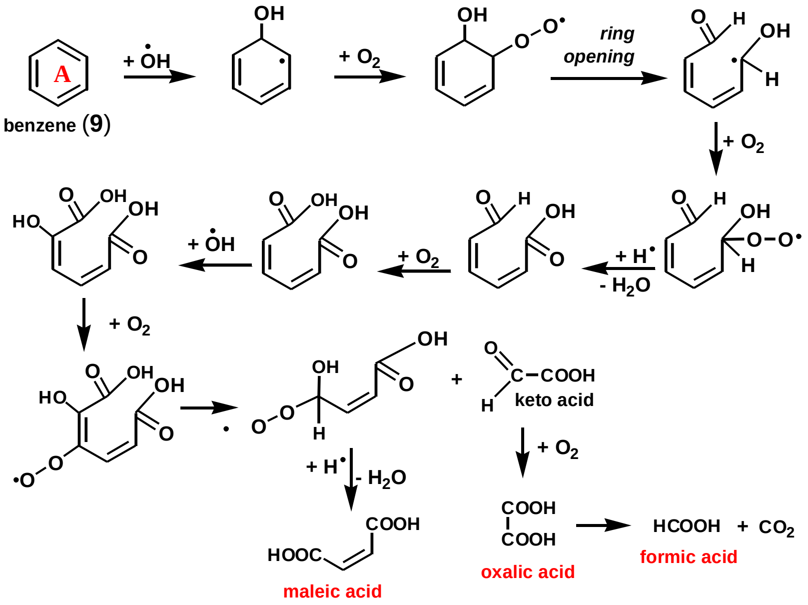

Fig. 11. The plausible mechanism of cypermetrin degradation induced by gamma irradiation in aerated solution from benzene to maleic, oxalic, and formic acids

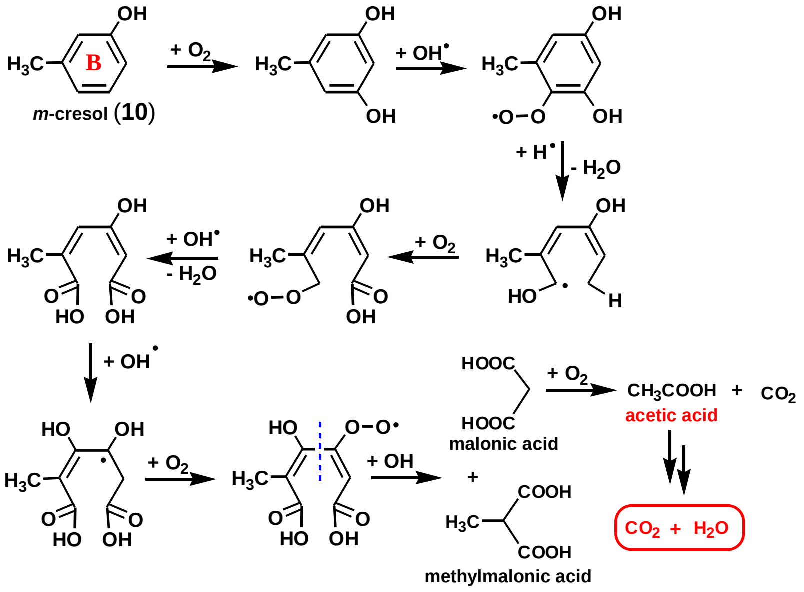

Fig. 12. The plausible mechanism of cypermetrin degradation induced by gamma irradiation in aerated solution from *m*-cresol to acetic acid

CONCLUSION

Ionizing radiation can degrade fenitrothion, prothiofos and cypermetrin as insecticide samples to simple and non toxic organic compounds such as organic acids which could further be degraded to CO_2 and H_2O, making ionizing radiation able be used as a tool to degrade insecticides as organic pollutants.

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