Photo and thermal degradation of Glyphosate and Fluazifop-butyl herbicides with and without additives


1Desert Research Center, Ministry of Agriculture, El -Mataria, Cairo, Egypt.
2Faculty of Agriculture, Ain Shams University, Shoubra El-Kheima, Cairo Egypt.

Received: 29 January 2014 / Accepted: 30 October 2017
Doi: https://doi.org/10.54172/mjsc.v32i2.184

Abstract: The study investigated the effect of some additives on glyphosate and fluazifop-butyl herbicides light-decomposition by ultraviolet rays and temperature were studied under laboratory conditions. Based on the results, additives have a varying influence on their photo and thermal decomposition of both studied herbicides substance. Generally, additives of glue, dioleate, monoleate and mineral oil were the most effective material for lowering the rate of glyphosate degradation by UV rays. Meanwhile, the effect of paraffin oil and urea were not significant in glyphosate thermal degradation, and the dual combination of glyphosate with additives reduced degradation rate regardless of the thermal exposure especially when mixed with glue and then dioleate and monoleate. Glyphosate was more susceptible to the thermal decomposition than photolysis by UV radiation. The change in fluazifop-butyl herbicides without or with binary mixture additives amount under the studies UV radiation and temperature was very low and was stable in the studied systems. On the others side, the effect of temperature on fluazifop-butyl degradation was very low in the absent or present of additives, but using additives with the herbicide gave a relative protection to herbicides. The mixture of fluazifop-butyl with rapeseed oils or mineral oils slightly accelerate the herbicide photodecomposition curves. In conclusion,. Some additives gave a relative protection to glyphosate to face deterioration by UV radiation and temperature. Therefore, using glyphosate for weed control requires avoiding direct sunlight with the help of any of the above additives, as it should be noted not to fear from the accumulation of glyphosate residue in these agro-environment areas for the rapid deterioration and degradation.

Key words: Glyphosate, fusilade, additives, photodecomposition, thermal degradation.

INTRODUCTION

More attention was being directed towards using additives to be developed for the sake of reducing the applied herbicides dose. While, total herbicides formulation efficacy can be expressed as a function of deposition: retention: uptake: translocation: a.i toxicity(Zabkiewicz 2000). Tank added additives often improve the performance of post emergence herbicides(Cabanne et al., 1998). The addition of oil and surfactants as additives can increase the foliar penetration of some pesticide formulation(Sharma and Singh 2000). On the other side, the activity of herbicides depends on the environmental factors (light, temperature, humidity, and soil moisture)(de Ruiter and Meinen 1998). Special attentions have been given to the decomposition reactions because they usually are the main factors governing the persistence of the chemical. Many compounds when present in the
environment are subject to decomposition reaction by temperature and UV light, which is the main process for disappearance from soil/plant surface and during application. Degradation of light has been reported for some herbicides. Photodecomposition and volatility may be important factors in the fate of pesticides which greatly affect their residual activity or toxicological characters (Nassar and Ebing 1978). Glyphosate was photodegraded strongly by UV light but not by long wavelength light. The half-life of 1 and 20 000 ppm of the herbicide in deionized water exposed to UV light was 4 days and 3-4 weeks, respectively. The main photolytic breakdown product of the glyphosate, aminomethylphosphonic acid, proved to be more stable to photodegradation than the parent compound itself (Lund-Høie and Friestad 1986). Complete loss of pure glyphosate AI occurred in the majority of cases in <30 min under the following conditions 5.0X10-5 M Fe(III), 1.0X10-2 M H2O2, T=25.0°C, pH 2.8, and 1.2X1019 quanta/liter per second with fluorescent black light UV irradiation (300-400 nm) (Huston and Pignatello 1999) The thermal decomposition temperature of glyphosate was studied (Chen et al., 2012). On the others side, many reviews recorded a high suitability of fluazifop-butyl regardless of photo and thermal decomposition (Burger et al., 1962).

The aim of this work was to study the effect of mixing additives with glyphosate and fluazifop-butyl on the photodegradation and thermal reaction. This type of study is urgently needed in order to correlate the fate of massive herbicides used under the Egyptian conditions.

**MATERIALS AND METHODS**

**Herbicides**

A-Round up (Glyphosate, (N (Phosphonomethyl) glycine) 48%WSC; supplied by Monsanto.

B-Fusilade (Fluazifop-butyl, (Fluazifop-butyl (I), butyl 2- [4 - (5-trifluoromethyl - 2-pyridyloxy) phenoxy] propionate) 12.5 EC supplied by Syngenta.

**Additives**

The additive materials was listed in table (1).

**Table (1).** List of the studied additives added to herbicides:

<table>
<thead>
<tr>
<th>Names of additives</th>
<th>Classifications and suppliers</th>
</tr>
</thead>
<tbody>
<tr>
<td>Glue</td>
<td>Sticking agent (local product in granular formulation)</td>
</tr>
<tr>
<td>Urea</td>
<td>H2N-CO-NH2 (El-Nasar Company)</td>
</tr>
<tr>
<td>Rape seed oil</td>
<td>Deposition aids (Agriculture Research Center)</td>
</tr>
<tr>
<td>Paraffin oil</td>
<td>Deposition aids (Local production)</td>
</tr>
<tr>
<td>Mineral oil (KZ)</td>
<td>KZ oil (Kafr El-Zayat Company)</td>
</tr>
<tr>
<td>Monoleate</td>
<td>Non-ionic: Monoethylene glycol mono-oleate (Egyptian Company for Starch, Yeast and Detergents, Alexandria)</td>
</tr>
<tr>
<td>Dioleate</td>
<td>Non-ionic: Monoethylene glycol Di-oleate (Egyptian company for Starch, Yeast and Detergents, Alexandria)</td>
</tr>
<tr>
<td>Glycerin</td>
<td>Non-ionic and Spreading agent (El-Gomhoria Medical Company)</td>
</tr>
</tbody>
</table>

**UV- radiation exposure**

The trial was implemented with 30ug ml⁻¹ from glyphosate and fluazifop-butyl herbicides plus 30ug ml⁻¹ from each additive dissolved in acetonitrile, all of which were spread as a thin film on the surface of Petri dishes to be exposed to ultraviolet radiation using UV lamp between 254-336 nm then incubated in a dark room at room temperature. The samples were placed at a distance of 20cm from the lamp surface for 30, 60,120,240 minutes according to (Barakat et al., 1999; Masoud 1988, Falb et al., 1990, Harrison and Venkatesh 1999, Lin et al., 2000 ; Orr and Hogan, 1984).

**Temperature exposure**

The experiments were conducted by using 30 µg ml⁻¹ from glyphosate or fluazifop-butyl herbicides plus 30 µg ml⁻¹ from each additive dissolved in acetonitrile and were put in test tubes. The tubes were placed in a water bath at 60 °C for 30, 60,120,240 minutes according to (Barakat, et al., 1999). The treatments were done in three replicates and maintained in the dark room at 25±2 °C during the experiments.
Procedure for glyphosate and fluazifop-butyl herbicides determination

Samples were taken and analyzed for glyphosate after extracted, cleaned up, and determined calorimetrically and the obtained average from triplicates samples modified by HPLC value according to (Yoza et al., 1977, Glass 1981). While fluazifop-butyl samples determined according to (Zhemchuzhin and Kononova 1988a, b). The t ½ values for each parameter were calculated mathematically though trend line equation of each treatment.

RESULTS AND DISCUSSION

Photodecomposition of the studied herbicides in relation to the tested additives

Photodecomposition occurs when energy from the sun breaks down the herbicide. Only a limited number of herbicides are sensitive to sunlight. To prevent photodecomposition, soil or additives application of these herbicides are often incorporated.

Figure (1) shows the considerable effect of additives on glyphosate degradation by UV-irradiation dependent on time exposure. In zero time UV-rays exposure, combination of glyphosate with monoleate showed loss by 8.73%, followed by glyphosate mixtures with urea, paraffin, and glycerin showing loss percent in glyphosate by 5.73, 4.6 and 4.33%, respectively. Dual mixture with Glyphosates such as dioleate or glue showed loss of 10.67 and 10.60% respectively from the initial amount. Meanwhile, glyphosate alone and its mixture with mineral oil showed loss of 2.86 and 1.73% respectively. After 30 minutes of UV exposure, mixture of glyphosate with paraffin and glyphosate alone showed the highest loss by 66.27 and 64.33 %, followed by the minimum loss of glyphosate mixtures reached 63.73 and 51.66%(glycerin or glue), 43.66, 48 and 44 % (urea, monoleate and mineral oil) respectively. The prolongation of UV-exposure to 60 minutes, glyphosate without additives was greatly deteriorated by 87.53%. Addition of paraffin or urea additives to glyphosate caused less deterioration reached 84.86 and 76.07% respectively than glyphosate mixtures with glue, glycerin, mineral oil, and monoleate causes loss by 62.67,70 63.6%.and 57 %, respectively, while glyphosate -dioleate mixture showed the lowest deterioration by 47.93%. UV-exposure to 120 minutes showed that glyphosate without additives and with urea suffered the highest loss by 94.67 and 91.87% respectively. The mixture of glyphosate with mineral and paraffin oil came next with 86.46 and 85.33% respectively. Mixtures with glue and glycerin reduced the amount of glyphosate loss by 79.73 and 74.06 % respectively. Glyphosate mixture with dioleate showed glyphosate loss by 64.2%. When exposure period to UV-irradiation extended to 240 minutes, the mixture of glyphosate with urea and the herbicide alone showed the maximum loss by 98.33 and 97.33 % respectively. Glyphosate mixtures with glycerin and paraffin showed loss by 95.73 and 94.86% respectively comparing to the initial amount. Glyphosate mixed with monoleate, glue, and mineral oil resulted in glyphosate loss by 91.8, 86.46 and 90.07 % respectively. Meanwhile, a slight loss was recorded with glyphosate -dioleate mixtures (74.53%). Data in figure (2) showed the stability of fluazifop-butyl against UV-irradiation when used alone or when mixed with additives. At zero exposure, The rate of decomposition of fluazifop-butyl either without or with additives such as paraffin, dioleate, mineral oil, monoleate, and rape seed oil was very low from its initial amount. The rate of fluazifop-butyl decomposition after 30 minutes of exposure reached 29.67% in case of fusilade- dioleate mixtures, followed by fusilade mixture with rape seed oil and fusilade alone (19.71 and 23.00%), respectively. Fluazifop-butyl mixtures with paraffin oil and mineral oil showed decomposition by 12.27 and 16.93% respectively. © 2017 The Author(s). This open access article is distributed under a CC BY-NC 4.0 license.

ISSN: online 2617-2186 print 2617-2178
Figure (1). Degradation rate of Glyphosate with and without additives regardless of UV radiation.
Initial concentration 30 μg ml⁻¹. Average from triplicates samples, Standard deviation ≤ 3.1.

Figure (2). Degradation rate of fluazifop-butyl with and without additives regardless of UV exposure
Initial concentration 30 μg ml⁻¹. Average from triplicates samples, Standard deviation ≤ 1.3.
Mixture with monoleate resulted in fluazifop-butyl decomposition by 10.68%. Exposure to UV-irradiation for 60 minutes showed considerable deterioration by 29.58% in case of fluazifop-butyl mixture with paraffin oil. Addition of fluazifop-butyl to rape seed oil and dioleate additives caused reduction by 25.10 and 25.85% respectively. Fluazifop-butyl alone and its mixture with monoleate showed loss of 22.30 and 21.74% in herbicide amount respectively. Applying mineral oil with fluazifop-butyl reduced herbicide residues by 11.89% than the added amount. The prolongation of UV-irradiation to 120 minutes showed that the mixture of fluazifop-butyl with mineral oil suffered the highest loss by 26.50%, followed by fluazifop-butyl-paraffin oil mixture (23.61%). The loss of with rape seed oil mixture and fluazifop-butyl alone reached 20.76 and 20.25% respectively. Mixtures of fluazifop-butyl with dioleate and monoleate showed a loss in herbicide amount by 19.78% and 18.33% respectively. At the end of the exposure period (240 minutes), Figure (2) indicates that fluazifop-butyl-dioleate mixture recorded the maximum reduction by 24.07%. Fluazifop-butyl mixture with rape seed oil and fluazifop-butyl without additives showed a loss by 23.70 and 23.93% respectively. Fluazifop-butyl mixture with paraffin oil resulted in loss amount of fluazifop-butyl by 22.07%. Meanwhile, a slight loss was recorded with fluazifop-butyl mixtures with mineral oil and monoleate, reached 18.15% and 12.22%, respectively from the initial amount. The above mentioned results reported the important effect of UV radiation on the tested herbicides deterioration and the elimination from the environment. The degradation pattern of the studied herbicide proved to be influential in this respect. The longer the time of exposure to UV rays was the higher the degradation was and vice versa. This was pronounced with glyphosate when used alone and when mixed with additives such as rape seed oil, mineral oil, paraffin oil, dioleate and monoleate, showed the longer half lives. This indicates that glyphosate was more susceptible to UV-irradiation than fluazifop-butyl. The photochemical degradation of herbicide is attributed to the absorption of energy from UV rays through direct exposure, reactions raising the molecule to an excited state. A small fraction of the electronically excited molecules releases the excess energy in a chemical reaction such as bond cleavage, dimerization, oxidation, hydrolysis or rearrangement affects. The rate of photochemical reaction depends on the radiation intensity at the wavelength absorbed by the chemical which caused a change in the vibration and rotation properties of molecules that depending on the structure of the compound, and on specific environmental conditions. Generally, it was found that photo-decomposition positively correlated with the exposure period (Hegazy et al. 1987). Ultraviolet light accelerates the disappearance of glyphosate, it may be because its energy was sufficient for the quick appearance of such compound, and probably due to an adsorption of UV rays from the direct source. It can be concluded from this study that photodecomposition is a major factor in glyphosate loss. Based on the above results, it could be stated that UV proved to be more effective in glyphosate deterioration. Chemical modification may affect the activity of the compound or its biodegradability may introduce ecological problem related to soil and water pollution. (Lund-HØie and Friestad 1986, Rozen and Margulies 1991, McMullan 1996, Huston and Pignatello 1999) stated that Cyclohexanedione (CHD) herbicides are approximately four-fold more sensitive to photodegradation by UV light than aryloxyphenoxypropionate for a sufficient uptake of the herbicide to occur.

**Thermal decomposition of the studied herbicides in relation to tested additives.**

Temperature tends to increase rates of both uptake and elimination of pesticides in the environment, so heat exposure can reduce accumulation of herbicide in the environment.
Data in figure (3) indicates that the addition of additives to glyphosate caused considerable loss in its residues. At zero time exposure to heat, glyphosate either with or without additives in binary mixture recorded an observed stability against thermal decomposition. Meanwhile, after 30 minutes heat exposure the rate of decomposition in glyphosate mixture with urea, glycerin, and paraffin reached 66.80%, 64.80%, and 62.27% respectively. Loss from the initial amount followed by glyphosate without additive and with glue mixture showed a loss by 57.80 and 59.20% respectively. A mixture of dioleate and monoleate reduced the recovered amount of glyphosate by 55.40% and 52.0% respectively. Elsewhere glyphosate mixture with mineral oil caused the minimum loss of the herbicide (30.47%). Heat exposure for 60 minutes indicates that the addition of urea to glyphosate greatly deteriorated glyphosate herbicide by 94.40%. Addition of paraffin and glyphosate alone caused a loss by 80.80 and 80.87% respectively. Glyphosate mixture with glycerin and monoleate showed the loss of 76.73 and 70.07% as initial, respectively. Applying a dual mixture of glyphosate with dioleate and glue resulted in a loss of 55.47% and 55.33% respectively. The lowest loss recorded by 37.33% achieved from mixing glyphosate with mineral oil. The prolongation of heat exposure to 120 minutes greatly affects glyphosate residue when used without additive by 99.73% (loss), followed by glyphosate mixture with urea, monoleate, paraffin, dioleate, and mineral oil, i.e. 97.93, 94.07, 92.73, 84.67 and 87.87% respectively. While the mixture with glue showed the lowest loss of glyphosate amount by 59.93%, the exposure to 240 minutes heat exposure of glyphosate-glycerin mixture and glyphosate alone showed the maximum loss by 99.80 and 99.73% respectively. Glyphosate mixture with urea, paraffin, and mineral oil showed a loss decreasing by 98.33, 97.93 and 96.80% respectively as an initial amount. Glyphosate mixture with dioleate and glue showed a loss in glyphosate amount by 84.93 and 62.20% respectively. Generally, it could be stated that heat proved to be more effective in glyphosate deterioration. Chemical modification may affect the herbicidal activity of the compound, or its biodegradability may introduce an ecological problem related to soil and water pollution (Rozen and Margulies 1991).

Our results agreed with (Frigerio et al., 1987).

**Figure (3).** Degradation rate of Glyphosate with and without additives regardless of temperature exposure. Initial concentration 30 µg ml⁻¹, Average from triplicates samples, Standard deviation ≤ 2.6
Data in Figure (4) indicates that fluazifop-butyl alone or with additives at zero time appeared to be more stable against degradation as compared with the direct exposure to temperature. However, deterioration was also observed in the fluazifop-butyl mixture after 30 minutes of heat exposure at decomposition rate reached the highest loss (17.12 %), followed by fluazifop-butyl when exposed alone (12.11%). Fluazifop-butyl mixtures with rapeseed oil and dioleate showed a loss by 11.38 and 11.38% respectively. Mixtures of paraffin and mineral oil with fluazifop-butyl caused a herbicide loss by 5.69% and 2.47 % respectively. Extending the heat exposure period to 60 minutes indicates that mixture with monoleate greatly deteriorated fusilade by 20.21%. In addition, fluazifop-butyl alone showed a loss by 13.66%. Fluazifop-butyl mixtures with rapeseed oil and dioleate caused a loss by 7.93 and 7.18 % respectively as an initial. Fusilade mixtures with paraffin and mineral oil showed a herbicide loss by 4.66% and 2.09% respectively. The prolongation of thermal exposure to 120 minutes of fluazifop-butyl without additives showed the highest loss by 23.58%, followed by mixing fluazifop-butyl -dioleate and monoleate by (11.38 and 10.12 % respectively). The combination of fusilade with minerals and paraffin showed a fusilade loss by 3.68 and 4.52 % respectively.

Heat exposure of fluazifop-butyl during 240 minutes without additives showed the maximum loss by 27.71 %. Fluazifop-butyl mixtures with mineral oil and paraffin came next showing a loss of 22.63 and 21.97% as initials respectively. Monoleate- fluazifop-butyl mixture resulted in herbicide loss by 17.73%. Meanwhile, a slight loss occurred in the case of fusilade mixtures with dioleate and rapeseed oil by 7.18% and 8.04% respectively from the initial amount. Reviewing the aforementioned results it could be concluded that the occurrence of thermal degradation of exposed herbicide is among the important factors in studying their behavior in the environment. The degradation pattern of each herbicide proved to be influential in this respect. This was evident with glyphosate alone and its mixtures with the additives glue, urea, glycerin, dioleate monoleate, paraffin, and mineral oil. The half-lives were 20, 45, 12, 25, 28, 20 and 40 minutes respectively. Whereas the corresponding of the half lives of fluazifop-butyl herbicide alone and when mixed with the additives rapeseed oil, mineral oil, paraffin oil, dioleate, and monoleate. Our results are in agreement with several studies and confirmed the role of temperature in degradation of insecticide residues (Barakat et al., 1999). These studies have reported that there was a positive relationship between temperature and the rate of degradation of pesticide.

The effect of additives was varying when mixed with glyphosate and it showed diversity of its influence during the photodecomposition process of glyphosate substances. Generally, additive materials gave some relative protection to glyphosate to face deterioration by UV radiation. Meanwhile, the combination with glue, dioleate, and monoleate and mineral oil materials were the most appropriate materials for lowering the rate of glyphosate degradation, while urea, glycerol, and paraffin oil did not have a significant effect on the photo-degradation of glyphosate.

The combination of fluazifop-butyl with the rapeseed oil and mineral oil possess an observed slightly acceleration of the herbicides photodecomposition curves. On the contrary, its combination with paraffin oil, dioleate and monoleate did not have any significant effect on fluazifop-butyl photo decomposition. Most of Glyphosate treatments showed the largest response to the thermal decomposition than photolysis by UV radiation. In this respect, the dual combination of glyphosate with additives reduced degradation rate regardless of the thermal exposure, special mix with glue, then dioleate and monoleate. Meanwhile, the effect of paraffin oil and urea is not clearly significant to consider. On the other hand, the effect of temperature on fluazifop-butyl degradation was very low in the absent or present of additives, while in the presence of additives gave a relative protection of fluazifop-butyl herbicides. Finally, it could be concluded that using glyphosate in weed control in the newly cultivated desert area where there are temperature and light during the day is possible, but a good application requires avoiding direct
sunlight with the help of any of the above additives to avoid the loss of effectiveness of the pesticides. From environmental point, the risk of glyphosate residues should be very limited in

**REFERENCES**


التدهور الضوئي والحراري لمبيد الجليفوسات و الفلفزي فوب بيوتيل العشبي في وجود وغياب المواد الإضافية

محمد عبد العزيز بلح، عبد الرحمن جمال الدين، زيدان هندى عبد الحميد، سيد عبد الطيف دحروج

مركز بحوث الصحراء، المطرية، القاهرة- مصر
كلية الزراعة، جامعة عين شمس، شبرا الخيمة، القاهرة- مصر

تاريخ الاستلام: 29 يناير 2014 / تاريخ القبول: 30 أكتوبر 2012
DOI: https://doi.org/10.54172/mjsc.v32i2.184

المستخلص: استهدفت الدراسة إقامة الضوء على تأثير بعض المواد الإضافية على تحمل مبيد الأعشاب الجليفوسات والفلفزي فوب بيوتيل بواسطة الأشعة فوق البنفسجية والحرارة تحياً، حيث أظهرت النتائج تتبع دور المواد الإضافية واختلاف تأثيرها أثناء تحمل المبيدات ضوئياً وحرارياً. عموماً أعطت مادة الغراء والدائى أوليتي والمونوموليتي والزيت المعدني حماية نسبية للجليفوسات من التحلل الضوئي، على العكس من ذلك مادة البوريا والجزيرين زيت البارافين لم يكن له أي تأثير معنوي، كما كان لمعظم المواد الإضافية دور مهم في تقليل التدحرج الحراري للجليفوسات وخاصة الغراء ثم الدائى أوليتي والمونوموليتي بينما مادة البوريا زيت البارافين لم يكن له تأثير معنوي على تحمل الجليفوسات حرارياً حيث أظهر الجليفوسات استجابة أكبر للتحلل الحراري عن التحلل الضوئي في جميع المعاملات، من جهة أخرى أوضحت الدراسة الثبات النسبى للمبيد الفلفزي فوب بيوتيل عند تعرضه للأشعة فوق البنفسجية (UV) وعدع التعصر للحرارة، عند حل خلط المبيد مع المواد الإضافية حدد فقد طفيف لثبات المبيد بزيادة فترة التعصر، كما أدى خلط الفليزيتود لزيت الرباب والزيت المعدني إلى زيادة ملحوظة في منحنى تحلل الفلفزي فوب بيوتيل وعلى العكس من ذلك لم يكن لزيت البارافين والمونوموليتي والذي أوليتي أي تأثير معنوي على الفلفزي فوب بيوتيل. عموماً يمكن التتويه أن المواد الإضافية وفرت بعض الحماية النسبية للجليفوسات من تأثير الأشعة فوق البنفسجية وقلق مع محلل ظنياً وحرارياً، لذا عند استخدام الجليفوسات في مكافحة الحشائش يستلزم الرش بعد انكسار أشعة الشمس مع الاستعانة بنوع من المواد الإضافية السابقة لتتجنب فقد المبيد لفاعليته، كما يجب التتويه بعدم الخوف من تراكم مخلفات الجليفوسات في منتجات هذه المناطق لسرعة تحمل وتلاشيها من البيئة.

الكلمات المفتاحية: غليفوسات، فوسيلود، إضافات، فتوتوفيكومبيسيتيون، التدهور الحراري.