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Impact of Formulation Type on Stability of Metribuzin Herbicide Under Certain Environmental Conditions

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Abstract

This study examined the stability of active ingredient (a.i) and three different commercial formulations of metribuzin herbicide (suspension concentrate (SC), water dispersible granules (WG) and wettable powder (WP)) after exposure to UV-rays, direct sunlight, different temperature degrees, and different pH values at different intervals. In addition, the effect of accelerated storage at 54 ± 2 ℃ for 14 days under laboratory conditions and the degradation rate of metribuzin for test samples were evaluated. The metribuzin content and degradation products were determined using GC–FID and GC–MS. Results indicated that direct sunlight and high temperatures were more effective than ultraviolet rays in accelerating the rate of metribuzin degradation. In contrast, the degradation rate of metribuzin was faster in acidic and alkaline pH than in neutral medium. The formulations of metribuzin are stable after accelerated storage at 54 ± 2 ℃. There were no discernible differences in metribuzin content before and after 14 days of storage. Metribuzin formulation in SC was more stable than metribuzin in formulation WG and WP, but overall, formulation type had a limited effect on the metribuzin degradation rate. Analysis of metribuzin a.i after exposure to direct sunlight using GC-MS identified four photodegradation products: deamino metribuzin (DA), diketo metribuzin (DK), 6-(tert-butyl) -1,2,4-triazin-5(4H)-one and 4-amino-6-(tert-butyl)-3-(methylsulfonyl)-1,2,4-triazin-5(4H)-one.

Keywords: Metribuzin, degradation products, UV-rays, direct sunlight, different temperature degrees, pH, GC–FID, and GC–MS.

1. Introduction

The contamination of crops, soil, and water quality by flame-retardant pesticides has become a significant environmental issue in recent years, and a solution is required. Metribuzin is a selective, systemic triazinone herbicide designed for pre- and post-emergence control of numerous grass species and broadleaf weeds in a variety of crops [1].

Some of the first insecticide formulations developed in the agricultural industry (granules, aqueous solutions, powders, mineral oil-in-water emulsions) were based on simple technologies. However, since the 1980s, the agrochemical industry has made significant advances in the development of new formulations, with a focus on discovering more effective chemicals. Improved stability optimized biological activity, differentiation, and use safety [2]. In addition, efforts are being made to reduce the required dose per hectare in order to reduce the amount of pollutants. Due to the prevalence of pesticides in the environment, there has been a focus on the

development of new formulations [3, 4]. Solubility characteristics of the active ingredient (ai), manufacturing costs, and intended use are the primary factors determining formulation design. Therefore, the development of new formulations requires interdisciplinary science [5]. In general, the efficacy of pesticides as crop protection agents is determined by the intrinsic properties of the active ingredients. B. toxicity, plant movement, systematicity, and mode of action [6]. The effectiveness of pesticides as crop protection agents depends on the active ingredients' intrinsic properties, B. toxicity, plant movement, systematicity, and mode of action [7]. Different formulations can promote photodegradation stability or reduce the amount of active ingredients required for pest control, making formulation a vital tool [8]. Various studies propose that a formulation can improve handling safety and play a crucial role in the active ingredient's delivery duration [9, 10]. The formulation may also contribute to preventing

phytotoxicity [11] or incompatibility on mixes with other agrochemicals [12].

The type of formulation can affect the proportionality of residues, particularly if the rate (kg of active substance per hectare) is altered by changing the spray concentration, thereby increasing the amount of spray based on the formulation type. Moreover, it affects the residue fraction. Increased surfactants and other adjuvants increase the concentration of the spray solution, allowing plants to retain the residue for a more extended period of time [13].

Metribuzin is a valuable organic herbicide that is widely used throughout the world and in some countries. This type of herbicide has been demonstrated to be hazardous to lipid tissue and to be highly persistent in soil [14, 15]. Metribuzin has significantly substituted many public organic herbicides, such as chlorinated hydrocarbons. Numerous public herbicides, such as chlorinated hydrocarbons, have been largely replaced by metribuzin. In addition, metribuzin is an effective organic pesticide used to prevent the growth of broadleaf weeds and dangerous grasses between various crops. The mode of action is determined by the inhibition of electron transfer during photosynthesis [16]. Metribuzin belongs to the group of triazinone herbicides that is highly soluble in water (1.05 g/L) but rather weakly adsorbed in sandy soils with low organic content. Adsorption coefficients range from 0.56 for extremely sandy loams to 31.7 for soils with 60% organic matter [17]. Metribuzin is considered to be of short to moderate persistence in soils, with measured half-lives ranging from 5 to 50 days [18]. Residues of metribuzin are affected by environmental factors, particularly ultraviolet rays, direct sunlight, pH, and varying temperatures [19, 20]. Therefore, it is highly expected that the compatibility of the commonly used compound and its residues could reveal different behaviors under various application conditions [21]. The herbicides metribuzin (MTZ) and metamitron (MTT) are effectively degraded by catalytic ozonation. On the catalytic degradation of MTZ and MTT, the effects of catalyst dosage, pH, temperature, and ozone concentration were studied. Gas chromatography-mass spectrometry and liquid chromatography-tandem mass spectrometry identified 12 MTZ degradation products and 5 MTT degradation products. The degradation products of the two contaminants demonstrated different toxicity profiles [22].

The purpose of this study was to investigate the stability of active ingredient (a.i) and three different commercial formulations of metribuzin herbicide [Suspension concentrate (SC), water dispersible granules (WG), and Wettable powder (WP)] after exposure to UV-rays, direct sunlight, different temperature degrees, and different pH values at different intervals, as well as accelerated storage at 54 ±2 °C for 14 days according to FAO specifications. Furthermore, the study aimed to identify some photodegradation products for metribuzin a.i after exposure to direct sunlight. The identification and determination of metribuzin content and its degradation products were confirmed using gas chromatography equipped with a flame ionization detector (GC–FID) using external standard and gas chromatography-mass spectrometry (GC-MS).

2. Experimental:

2.1- Chemical used:

The three different commercial formulations of metribuzin herbicide (metribuzin 60% SC), (metribuzin 70% WG) and (metribuzin 70% WP) were purchased from Egyptian market. The certified reference standard of metribuzin was obtained from LGC Dr. Ehrenstorfer-Germany with 99.5% purity. All used organic solvents and the water were of analytical grade or HPLC Grade quality (Merck). Chemical structure of metribuzin is shown in Fig. 1.
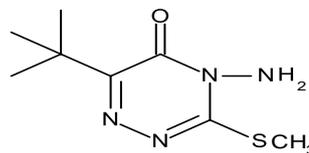
Fig. 1. Chemical structure of metribuzin

2.2- Accelerated storage procedures.

Water dispersible granules (WG) and Wettable powder (WP).

The metribuzin 70% WG and metribuzin 70% WP formulations were evenly distributed by placing approximately 20 g of each formulation into separate beakers. The disc was placed onto the surface of the powder within the beaker, where it rests with a loose fit. The dimensions of the disc are such that it can apply a pressure of 25 g/cm^2 to the sample's surface within the beaker. Subsequently, the beakers were subjected to a temperature of 54 ±2 °C for a duration of 14 days within the confines of an oven. Samples of WG and WP formulations were collected at different periods of 0, 3, 7, and 14 days [23, 24].

Suspension concentrate (SC).

The Metribuzin 60% SC formulation was dispensed into bottles with a volume of approximately 50 ml. The bottles were securely sealed and subjected to a temperature of 54 ±2 °C in an oven for a duration of 14 days. Upon reaching the designated time, the bottle was extracted from the oven, the cap was removed, and both the bottles and their contents were subsequently allowed to undergo natural cooling until they reached room temperature. The cap was then replaced once the cooling process was complete [25].

The samples of SC formulation were collected at different periods of 0, 3, 7, and 14 days.

Preparation of samples:

Metribuzin after accelerated storage at 54 ±2 ºC.

Standard Preparation

Metribuzin's analytical standard of known purity was weighed into a 25 ml grade (A) measuring flask, dissolved, and completed with methanol.

Sample Preparation

A specific weight equivalent to 10 mg of Metribuzin analytical standard was taken from each formulation, transferred to a 25 ml grade (A) measuring flask, and completed with methanol. The concentration was then determined using GC-FID.

2.3- Effect of UV-rays, direct sunlight, different temperatures exposure and extraction.

A stock solution (100 µg ml^{-1}) of metribuzin standard and metribuzin formulations were prepared and dissolved in ethyl acetate. One milliliter ethyl acetate containing 100 µg ml^{-1} metribuzin. 1 ml from stock solution was taken and spread uniformly as possible in uncovered Petri dishes (5 cm i.d.) and were left to dry at room temperature when were subjected to the different treatments at successive periods. The petri – dishes were divided into three groups and the first group was exposure to sun light while the second group was exposure to short uv – rays at 254 nm at distance of 12 cm. samples were taken from the first and second groups of 0,1,3,6,15,30,60,90 and 120 hours of exposure. The third group was exposure to different temperature degrees (30,40 and 50ºC) for 0,1,3,6,12,24,48,96,144 and 240 hours inside a dark electric oven with a temperature regulating system. Residues in Petri dishes were quantitatively transferred to known volumes with ethyl acetate, and then determined using GC-FID [26].

2.4- Effect of pH on the degradation of metribuzin.

Aqueous buffers pH 4, 7 and 9 were prepared by using pH tablets. Certain metribuzin standard and metribuzin formulations were added to buffer to obtain a solution of 100 µg ml-1. The studied hydrolysis was conducted in a dark incubator at approximately 30°C±2. Samples were collected after 0, 1, 3, 6, 12, 24, 48, 96, 144 and 240 hours. Samples were extracted and determined using GC-FID.

2.5- Measurements
Gas Chromatography Determination

This procedure was conducted according to [27]. Agilent 7890B gas chromatograph with autosampler 7693 equipped with Flame Ionization Detector (FID) at 250 ºC, capillary column HP-50+ (30 m x 0.53 mm

I.D., 1 µm film thickness). Nitrogen was used as a carrier gas with a constant flow of 8 ml/min. The oven temperature program was held at 200 ºC for 1 min, then ramped 20 ºC /min to 260 ºC. The injector temperature was 250 ºC with splitless mode. The injection volume was 1 µl. Under these conditions, the typical retention time of metribuzin was 3.855 min. The standard for metribuzin is depicted in Fig. 2.
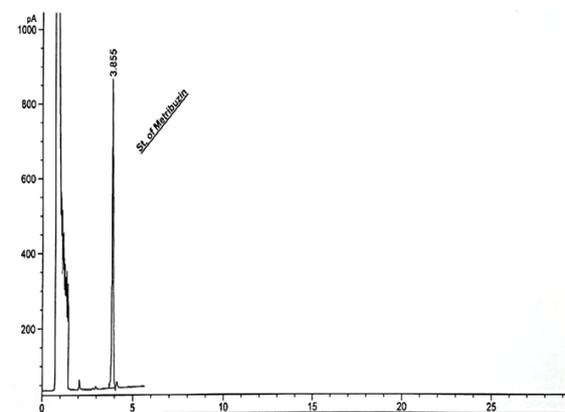
Fig. 2. Chromatogram of metribuzin Standard

Gas chromatography-mass spectrometry analysis (GC-MS)

The GC-MS analysis was performed with an Aglient 7890B gas chromatograph equipped with 5977 A MSD Aglient mass spectrometric detector, with a direct capillary interface and fused silica capillary column HP-5MS (30 m x 0.25 mm x 0.25 µm film thickness). Helium was used as the carrier gas at a pulsed split rate of approximately 1.0 ml/min. The volume of the injection was 1 l. The GC temperature program was held at 10 ºC /min, then ramped 10 ºC /min to 190 ºC for 1 min, and ramped 10 ºC/min to 300 ºC for 2 minutes (total run time 29.5 minutes). The injector temperature was set to 280 ºC ºC. Wiley mass spectral database Library was used to identify the mass spectra. Fig. (3, 4) depict the full scan spectrum and mass spectrum of metribuzin a.i.
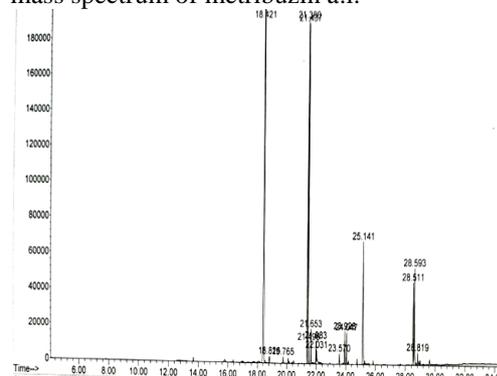
Fig. 3. The full scan spectra of metribuzin a.i
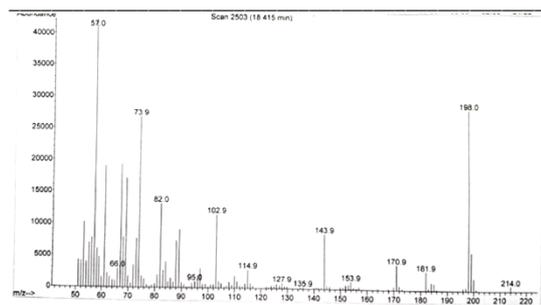
Fig. 4. Mass spectrum of metribuzin a.i

2.6- Kinetic study

The half-life time (RL50) of metribuzin was calculated according to [28].

$$RL50 = \ln2/K$$
$$K = (1/tx) \ Ln \ (a/bx)$$

Where, RL50= the time required to reach 50% of the initial concentration.

K = rate of degradation

a = initial concentration

tx = time in hours

bx = concentration at x time

3. RESULTES AND DISSCUSSION

3.1. Effect of accelerated storage on the content of metribuzin formulations.

The effects of storage at 54 ±2 °C for 0, 3, 7, and 14 days on the stability of three commercial formulations of metribuzin are detailed in Table 1. There were no discernible differences in metribuzin content between the three formulations before and after 14 days of storage at at 54 ±2 °C. The results indicated that the loss percentages at 14 days were 2.34, 2.71, and 2.63% for the SC, WG, and WP formulations, respectively, indicating that the formulations are stable at 54 ± 2 °C for 14 days without a change in specifications.

3.2. Effect of direct sunlight on the degradation rate of metribuzin formulations.

Table 2 and Fig. 5 show the effect of exposure to direct sunlight on the degradation rate of a.i and the three tested commercial metribuzin formulations. After 120 hours of exposure to direct sunlight, the loss percentages of metribuzin increased to 83.19, 84.03, 84.37, and 84.7%, as demonstrated by the results. In addition, the half-life (RL50) was 15.6, 15.03, 14.88, and 14.59 h, and the degradation rates were 0.019 and 0.020, 0.020, and 0.021 for a.i, SC, WG, and WP, respectively. There were no significant differences in the degradation rates of metribuzin formulations following exposure to direct sunlight.

Table (1): Effect of accelerated storage on the content of metribuzin formulations at 54 ±2 °C for 14 days.

Storage Periods (Days)	SC		WG		WP	
	metribuzin content 60 % (w/v)	Loss %	metribuzin content 70 % (w/w)	Loss %	metribuzin content 70 % (w/w)	Loss %
0*	59.91±0.53**	0	69.84±0.4	0	69.48±0.83	0
3	59.2±0.65	1.19	69.4±0.1	0.63	69.1±1.14	0.547
7	58.85±0.3	1.77	69.24±0.51	0.859	68.55±0.67	1.34
14	58.51±0.2	2.34	67.95±0.37	2.71	67.65±0.92	2.63

* Samples before and after accelerated storage stability test analyzed together to reduce the analytical error.

** Each value represents an average of three replicates: FAO tolerance ±2.5%: mean or average and STDEV.

Table (2): Effect of direct sunlight on the degradation rate of metribuzin formulations.

Times (hours)	a.i		SC		WG		WP	
	µg**	% loss	µg	% loss	µg	% loss	µg	% loss
0*	100 ±1	0	100 ±1	0	100 ±1	0	100 ±1	0
1	88.95 ±0.06	11.05	84.5 ±1.3	15.5	82.72 ±1.1	17.28	80.94 ±1.33	19.06
3	75.43 ±0.05	24.57	71.66 ±1.1	28.34	70.15 ±1	29.85	68.64 ±0.98	31.36
6	68.23 ±0.04	31.77	64.82 ±1.5	35.18	63.45 ±0.8	36.55	62.09 ±0.56	37.91
15	52.91 ±0.1	47.09	50.26 ±0.8	49.74	49.21 ±0.3	50.79	48.15 ±1.26	51.85
30	44.02 ±0.03	55.98	41.82 ±0.6	58.18	40.94 ±0.4	59.06	40.06 ±0.81	59.94
60	35.74 ±0.08	64.26	33.95 ±0.2	66.05	33.24 ±0.1	66.76	32.52 ±0.65	67.48
90	23.06 ±0.91	76.94	21.91 ±1.1	78.09	21.45 ±0.2	78.55	20.98 ±0.39	79.02
120	16.81 ±0.17	83.19	15.97 ±0.7	84.03	15.63 ±0.34	84.37	15.3 ±0.11	84.7
K***	0.019		0.020		0.020		0.021	
RL50**** (hours)	15.6		15.03		14.88		14.59	
LOD*****	0.01 ppm							

*: Samples were collected directly after the quantitative transfer (zero time)

**: Each value represents an average of three replicates: mean or average and STDEV.

K***: Constant of degradation rate.

RL50****: Half-life value   LOD*****: limit of detection.

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Fig. 5. Effect of direct sunlight on the degradation rate of metribuzin formulations.

3.3. Effect of short UV rays (245 nm) on the degradation rate of metribuzin formulations.

The effect of short UV rays (245 nm) on the degradation rate of a.i and three commercial formulations of metribuzin is depicted in Table 3 and Figure 6. The data revealed that exposure to direct sunlight accelerated the photodecomposition rate more effectively than exposure to short UV rays. Following 120 h of exposure to short UV rays, the loss percentages were 83.215%, 83.6%, 83.54 %, and 83.95 %, respectively. The estimated RL50 values for a.i, SC, WG, and WP were 43.50, 38.55, 28.99, and 27.31 hours, and the degradation rates were 0.007, 0.008, 0.010, and 0.011, respectively. After exposure to short UV rays (245 nm), the results revealed no significant differences in the degradation rates of metribuzin formulations..
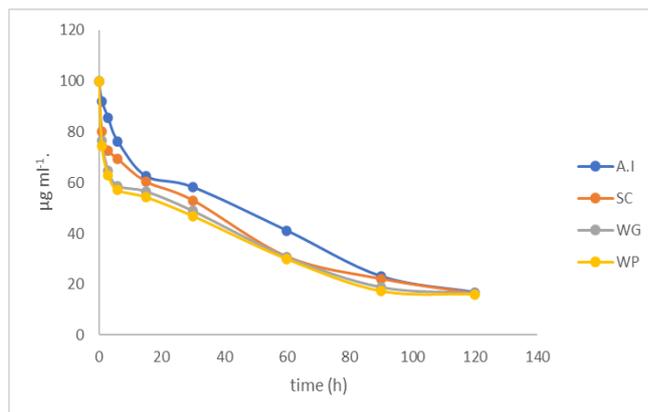
Fig. 6. Effect of short UV rays (245nm) on the degradation rate of metribuzin formulation.

3.4. Effect of temperature at 30°C on the degradation rate of metribuzin formulations.

Table 4 and Fig. 7 show the effect of exposure to temperature at 30°C on the degradation rate of a.i and the three commercial metribuzin formulations. Data indicated that metribuzin was very stable and did not influence by exposure to temperature at 30°C for 240 h. The loss percentage values of metribuzin were 20.94, 21.34, 21.49, and 21.65%, and the estimated RL50 values were 573.07, 562.32, 558.4, and 554.27 h, and the degradation rates were 0.0005 for a.i, SC, WG, and WP, respectively. The absence of statistically significant differences in the rates of degradation of metribuzin formulations after exposure to 30 °C temperatures demonstrated the metribuzin's high stability.

Table (3): Effect of short UV rays (245nm) on the degradation rate of metribuzin formulations.

Times (hours)	a.i		SC		WG		WP	
	µg**	% loss	µg	% loss	µg	% loss	µg	% loss
0*	100 ±1	0	100 ±1	0	100 ±1	0	100 ±1	0
1	92.1 ±0.9	7.9	79.98 ±0.6	20.02	76.49 ±0.44	23.503	74.36 ±2.1	25.64
3	85.53 ±0.5	14.47	72.71 ±0.2	27.29	64.87 ±0.23	35.1302	63.06 ±0.37	36.94
6	76.35 ±1	23.655	69.33 ±0.1	30.67	58.68 ±0.66	41.3222	57.04 ±0.57	42.96
15	62.59 ±1.2	37.411	60.41 ±0.9	39.59	56.50 ±0.19	43.4974	54.23 ±1.25	45.77
30	58.24 ±0.8	41.764	53.02 ±0.6	46.98	48.86 ±1.1	51.1428	46.8 ±0.97	53.2
60	41.13 ±0.6	58.87	30.83 ±0.3	69.17	30.74 ±1.3	69.2636	29.88 ±0.81	70.12
90	23.14 ±0.2	76.858	22.11 ±0.08	77.89	18.83 ±0.99	81.1684	17.28 ±0.41	82.72
120	16.79 ±0.4	83.215	16.4 ±0.02	83.6	16.46 ±0.81	83.54	16.05 ±0.26	83.95
K***	0.007		0.008		0.010		0.011	
RL50**** (hours)	43.5		38.55		28.99		27.31	
LOD*****	0.01 ppm							

*: Samples were collected directly after the quantitative transfer (zero time)

**: Each value represents an average of three replicates: mean or average and STDEV.

K***: Constant of degradation rate.

RL50****: Half-life value   LOD*****: limit of detection

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Table (4): Effect of temperature at 30°C on the degradation rate of metribuzin formulations.

Times (hours)	30 °C							
	a.i		SC		WG		WP	
	μg **	% loss	μg	% loss	μg	% loss	μg	% loss
0*	100±1	0	100±1	0	100±1	0	100±1	0
1	99.87±0.1	0.13	99.37±0.5	0.63	99.17±0.6	0.83	98.97±0.11	1.03
3	99.64±0.3	0.36	99.14±0.3	0.86	98.95±0.8	1.05	98.75±0.15	1.25
6	99.32±0.14	0.68	98.82±0.1	1.18	98.63±0.21	1.37	98.43±0.26	1.57
12	98.95±0.6	1.05	98.46±0.26	1.54	98.26±0.47	1.74	98.06±0.38	1.94
24	98.5±0.9	1.5	98.01±0.48	1.99	97.81±0.19	2.19	97.61±0.9	2.39
48	93.69±1.2	6.31	93.22±0.91	6.78	93.03±0.44	6.97	92.85±0.88	7.15
96	91.15±0.29	8.85	90.7±0.73	9.3	90.51±0.68	9.49	90.33±0.61	9.67
144	89.26±0.36	10.74	88.81±0.56	11.19	88.64±1.1	11.36	88.46±0.34	11.54
240	79.06±0.24	20.94	78.66±0.48	21.34	78.51±0.96	21.49	78.35±0.28	21.65
K***	0.0005		0.0005		0.0005		0.0005	
RL$_{50}$**** (hours)	573.07		562.32		558.4		554.27	
LOD*****	0.01 ppm							

*: Samples were collected directly after the quantitative transfer (zero time)

 **: Each value represents an average of three replicates: mean or average and STDEV.

K***: Constant of degradation rate.

RL$_{50}$****: Half-life value   LOD*****: limit of detection.
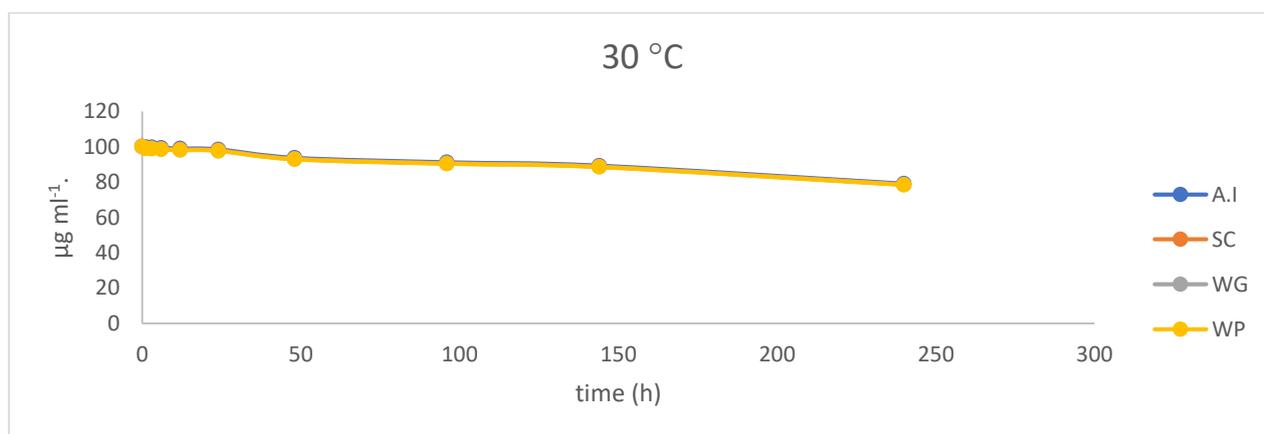
Fig. 7. Effect of temperature at 30°C on the degradation rate of metribuzin formulations.

3.5. Effect of temperature at 40°C on the degradation rate of metribuzin formulations.

Table 5 and Fig. 8 show the effect of exposure to temperature at 40°C on the degradation rate of a.i and the three commercial metribuzin formulations. According to the data, metribuzin is affected by increasing temperatures and exposure durations. After 240 h, the loss percentages of metribuzin were 41.99, 44.89, 50.11, and 54.17%, and the estimated RL50 values were 279.15, 267.32, 239.47, and 221.52 h. The degradation rates were 0.0011, 0.0011, 0.0013, and 0.0014 for a.i, SC, WG, and WP, respectively. The results elucidated very slight statistically significant differences in the degradation rates of metribuzin formulations exposed to 40 °C.
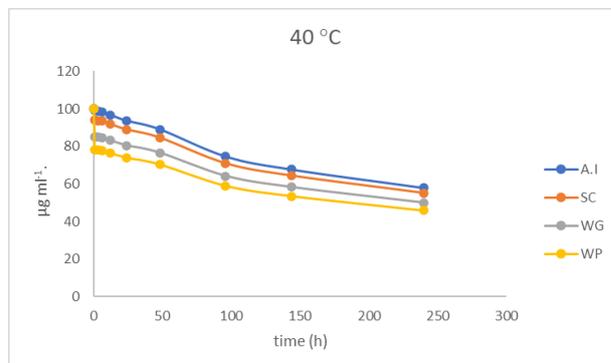
Fig. 8. Effect of temperature at 40°C on the degradation rate of metribuzin formulations.

Table (5): Effect of temperature at 40 °C on the degradation rate of metribuzin formulations.

Times (hours)	40 °C							
	a.i		SC		WG		WP	
	µg**	% loss	µg	% loss	µg	% loss	µg	% loss
0*	100±1	0	100±1	0	100±1	0	100±1	0
1	99.02±0.2	0.977	94.07±1.6	5.93	85.16±0.67	14.84	78.23±1.41	21.77
3	98.69±0.29	1.312	93.75±0.8	6.25	84.87±0.26	15.13	77.96±1.23	22.04
6	98.41±0.32	1.59	93.49±0.33	6.51	84.63±0.48	15.37	77.74±0.87	22.26
12	96.67±0.61	3.33	91.84±0.15	8.16	83.14±0.95	16.86	76.37±0.93	23.63
24	93.52±0.9	6.484	88.84±0.96	11.16	80.42±0.38	19.58	73.88±0.68	26.12
48	89.01±0.87	10.989	84.56±0.66	15.44	76.55±0.59	23.45	70.32±0.29	29.68
96	74.63±0.95	25.375	70.89±0.29	29.11	64.18±0.77	35.82	58.95±0.36	41.05
144	67.73±0.99	32.275	64.34±0.46	35.66	58.24±0.33	41.76	53.5±0.44	46.5
240	58.01±1.3	41.99	55.11±0.24	44.89	49.89±0.25	50.11	45.83±0.89	54.17
K***	0.0011		0.0011		0.0013		0.0014	
RL$_{50}$**** (hours)	279.15		267.32		239.47		221.52	
LOD*****	0.01 ppm							

 * *: Samples were collected directly after the quantitative transfer (zero time)
***: Each value represents an average of three replicates: mean or average and STDEV.
 K***: Constant of degradation rate.
 RL$_{50}$****: Half-life value   LOD*****: limit of detection

Table (6): Effect of temperature at 50 °C on the degradation rate of metribuzin formulations.

Times (hours)	50 °C							
	a.i		SC		WG		WP	
	µg**	% loss	µg	% loss	µg	% loss	µg	% loss
0*	100±1	0	100±1	0	100±1	0	100±1	0
1	88.72±1.92	11.277	82.51±0.63	17.49	71.87±0.26	28.13	69.2±0.86	30.8
3	82.34±1.36	17.66	76.58±0.49	23.42	66.7±0.39	33.3	64.23±0.19	35.77
6	78.06±0.87	21.937	72.6±1.26	27.4	63.23±1.15	36.77	60.89±0.42	39.11
12	70.54±0.69	29.46	65.6±0.91	34.4	57.14±0.66	42.86	55.02±0.29	44.98
24	66.41±0.45	33.59	61.76±0.88	38.24	53.79±0.38	46.21	51.8±0.53	48.2
48	52.04±0.36	47.96	48.4±0.94	51.6	42.15±1.61	57.85	40.59±0.99	59.41
96	35.09±0.51	64.911	32.63±1.4	67.37	28.42±0.28	71.58	27.37±1.13	72.63
144	11.21±0.22	88.795	10.42±0.44	89.58	9.08±0.39	90.92	8.74±1.08	91.26
240	4.52±0.14	95.48	4.21±0.27	95.79	3.66±0.48	96.34	3.53±0.16	96.47
K***	0.0033		0.0082		0.0090		0.0100	
RL$_{50}$**** (hours)	90.68		36.88		33.45		30.22	
LOD*****	0.01 ppm							

*: Samples were collected directly after the quantitative transfer (zero time)
 **: Each value represents an average of three replicates: mean or average and STDEV.
 K***: Constant of degradation rate.
 RL$_{50}$****: Half-life value   LOD*****: limit of detection..

3.6. Effect of temperature at 50°C on the degradation rate of metribuzin formulations.

Table 6 and Fig. 9 show the effect of exposure to temperature at 50°C on the degradation rate of a.i and the three commercial metribuzin formulations. Data indicated that metribuzin is strongly affected by increasing temperature degrees and periods of exposure. The loss percentages values of metribuzin after 240 h increased to reach 95.48, 95.79, 96.34, and 96.42%, and the estimated RL50 values were 90.68, 36.88, 33.45, and 30.22 h, and the degradation rates were 0.0033, 0.0082, 0.0090, and 0.010 for a.i, SC, WG, and WP, respectively. The indicated results clarified statistically significant differences in the degradation rates of metribuzin formulations after exposure to temperature at 50 °C, as well as the apparent effect of increasing temperatures on the metribuzin's stability.
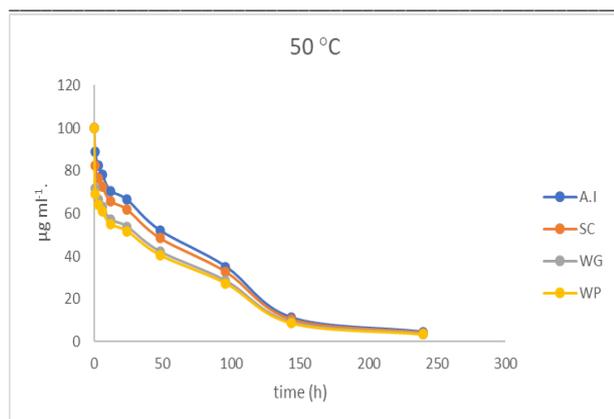
Fig. 9. Effect of temperature at 50 °C on the degradation rate of metribuzin formulations.

3.7. Effect of pH 4 at (atmosphere temp. about 30°C±2) on the degradation rate of metribuzin formulations.

Table 7 and Fig. 10 show the effect of hydrolysis at pH 4 on the degradation rate of a.i and the three commercial metribuzin formulations. According to the data, metribuzin is influenced by hydrolysis in the acidic medium at pH 4 and the exposure period. The loss percentages values of metribuzin after 240 h were 36.23, 40.05, 46.43, and 47.71%, and the estimated RL50 values were 331.24, 299.63, 258.45, and 251.52 h, and the degradation rates were 0.0009, 0.0010, 0.0012, and 0.0012 for a.i, SC, WG, and WP, respectively. The results demonstrated very slight statistically significant differences in the degradation rates of metribuzin formulations after hydrolysis at pH 4.

Table (7): Effect of pH 4 at (atmosphere temp. about 30°C±2) on the degradation rate of metribuzin formulations.

Times (hours)	pH 4							
	a.i		SC		WG		WP	
	μg **	% loss	μg	% loss	μg	% loss	μg	% loss
0*	100±1	0	100±1	0	100±1	0	100±1	0
1	97.32±0.59	2.681	91.48±2.33	8.52	81.75±0.26	18.25	79.8±1.11	20.2
3	94.96±0.22	5.04	89.26±1.54	10.74	79.77±0.97	20.23	77.87±0.38	22.13
6	91.74±0.31	8.265	86.23±0.25	13.77	77.06±0.36	22.94	75.22±0.42	24.78
12	85.38±1.23	14.62	80.26±0.99	19.74	71.72±1.61	28.28	70.01±0.16	29.99
24	81.73±0.78	18.275	76.82±0.56	23.18	68.65±0.84	31.35	67.01±0.44	32.99
48	80.27±0.49	19.73	75.45±0.48	24.55	67.43±0.16	32.57	65.82±0.29	34.18
96	75.15±0.82	24.853	70.64±1.27	29.36	63.12±0.29	36.88	61.62±0.52	38.38
144	73.43±0.66	26.57	69.02±0.66	30.98	61.68±0.11	38.32	60.21±0.12	39.79
240	63.77±0.42	36.23	59.95±0.79	40.05	53.57±0.51	46.43	52.29±0.87	47.71
K***	0.0009		0.0010		0.0012		0.0012	
RL$_{50}$**** (hours)	331.24		299.63		258.45		251.52	
LOD*****	0.01 ppm							

*: Samples were collected directly after the quantitative transfer (zero time)
**: Each value represents an average of three replicates: mean or average and STDEV.
K***: Constant of degradation rate. RL$_{50}$****: Half-life value   LOD*****: limit of detection.

3.8. Effect of pH 7 at (atmosphere temp. about 30°C±2) on the degradation rate of metribuzin formulations.

Table 8 and Fig. 11 show the effect of hydrolysis at pH 7 on the degradation rate of a.i and the three commercial metribuzin formulations. Data indicated that metribuzin is very stable and did not influence by hydrolysis in the neutral medium at pH 7. The loss percentages values of metribuzin after 240 h were 21.48, 23.05, 25.41, and 24.62%, and the estimated RL50 values were 558.56, 520.61, 472.26, and 465.41 h, and the degradation rates were 0.0005, 0.0006, 0.0006, and 0.0006 for a.i, SC, WG, and WP, respectively. The absence of statistically significant differences in the rates of degradation of metribuzin formulations after hydrolysis in a neutral medium at pH 7 demonstrated the metribuzin's high stability.

Fig. 10. Effect of pH 4 at (30°C±2) on the degradation rate of metribuzin formulations.

Table (8): Effect of pH 7 at (atmosphere temp. about 30°C±2) on the degradation rate of metribuzin formulations

Times (hours)	pH 9							
	a.i		SC		WG		WP	
	μg**	% loss	μg	% loss	μg	% loss	μg	% loss
0*	100±1	0	100±1	0	100±1	0	100±1	0
1	96.64±1.17	3.36	85.04±0.99	14.96	75.38±0.21	24.62	71.51±1.09	28.49
3	90.93±0.81	9.07	80.02±0.81	19.98	70.93±0.39	29.07	67.29±0.26	32.71
6	89.93±0.36	10.069	79.14±0.66	20.86	70.15±0.15	29.85	66.55±0.18	33.45
12	83.69±0.41	16.311	73.65±0.49	26.35	65.28±1.24	34.72	61.93±1.37	38.07
24	80.84±0.55	19.16	71.14±0.82	28.86	63.06±0.81	36.94	59.82±0.88	40.18
48	78.92±0.29	21.076	69.45±0.57	30.55	61.56±0.46	38.44	58.4±0.49	41.6
96	70.5±1.36	29.5	62.04±1.26	37.96	54.99±0.34	45.01	52.17±0.16	47.83
144	64.6±1.45	35.4	56.85±0.85	43.15	50.39±0.25	49.61	47.8±0.56	52.2
240	57.52±0.92	42.48	50.62±0.34	49.38	44.87±0.73	55.13	42.56±0.19	57.44
K***	0.0011		0.0012		0.0014		0.0014	
RL$_{50}$**** (hours)	282.49		243.01		217.67		208.91	
LOD*****	0.01 ppm							

*: Samples were collected directly after the quantitative transfer (zero time)

**: Each value represents an average of three replicates: mean or average and STDEV.

K***: Constant of degradation rate. RL$_{50}$****: Half-life value   LOD*****: limit of detection.

Fig. 11. Effect of pH 7 at (30°C±2) on the degradation rate of metribuzin formulations.

3.9. Effect of pH 9 at (atmosphere temp. about 30°C±2) on the degradation rate of metribuzin formulations.

Table 9 and Fig. 12 show the effect of hydrolysis at pH 9 on the degradation rate of a.i and the three commercial metribuzin formulations. Data indicated that metribuzin is strongly affected by hydrolysis in the alkaline medium at pH 9 and the period of exposure compared to hydrolysis in acidic and neutral mediums. The loss percentages values of metribuzin after 240 h were 42.48, 49.38, 55.13, and 57.44%, and the estimated RL50 values were 282.49, 243.01, 217.67, and 208.91 h, and the degradation rates were 0.0011, 0.0012, 0.0014, and 0.0014 for a.i, SC, WG, and WP, respectively. The results indicated very slight statistically significant differences in the degradation rates of metribuzin formulations hydrolysis in the alkaline medium at pH 9, as well as the extent of the precise effect of hydrolysis in the alkaline medium on the stability of the metribuzin.

The previously mentioned results demonstrated that the rate of degradation of a.i and the three commercial metribuzin formulations under investigation were influenced by exposure to direct sunlight compared to exposure to short UV rays in accelerating the photodecomposition rate. Metribuzin is significantly affected by increasing temperatures and exposure times, as the rate of degradation was observed to be faster after exposure to 50 °C compared to lower temperatures. The rate of metribuzin degradation is influenced more by hydrolysis in acidic and alkaline media than in neutral media. The indicated results elucidated very slight statistically significant differences in the degradation rates of a.i and the three commercial metribuzin formulations; additionally, the metribuzin formulation in SC was more stable than metribuzin in formulations WG and WP; nevertheless, metribuzin formulations are affected by numerous factors, including the manufacturing process, sources of starting materials, type of adjuvants, chemical structure, exposure to air, sunlight, and elevated temperatures. Therefore, all these factors can affect the degradation rate of metribuzin.

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Table (9): Effect of pH 9 at (atmosphere temp. about 30°C±2) on the degradation rate of metribuzin formulations

Times (hours)	pH 7							
	a.i		SC		WG		WP	
	µg**	% loss	µg	% loss	µg	% loss	µg	% loss
0*	100±1	0	100±1	0	100±1	0	100±1	0
1	98.32±0.33	1.679	96.35±0.67	3.65	93.4±0.92	6.6	94.39±0.55	5.61
3	96.55±0.54	3.45	94.62±0.28	5.38	91.72±0.83	8.28	92.69±0.13	7.31
6	92.3±0.31	7.7	90.45±0.88	9.55	87.69±0.44	12.31	88.61±0.09	11.39
12	91.29±0.16	8.71	89.46±0.21	10.54	86.73±0.58	13.27	87.64±0.17	12.36
24	88.94±0.46	11.058	87.16±0.34	12.84	84.49±0.74	15.51	85.38±0.03	14.62
48	87.26±0.29	12.74	85.51±0.86	14.49	82.9±0.98	17.1	83.77±0.19	16.23
96	84.46±0.98	15.54	82.77±0.49	17.23	80.24±0.29	19.76	81.08±0.78	18.92
144	81.82±1.16	18.177	80.19±0.36	19.81	77.73±1.23	22.27	78.55±0.38	21.45
240	78.52±0.85	21.48	76.95±0.57	23.05	74.59±1.12	25.41	75.38±0.91	24.62
K***	0.0005		0.0006		0.0006		0.0006	
RL$_{50}$**** (hours)	558.56		520.61		472.26		465.41	
LOD*****	0.01 ppm							

*: Samples were collected directly after the quantitative transfer (zero time)

**: Each value represents an average of three replicates: mean or average and STDEV.

   K***: Constant of degradation rate. RL$_{50}$****: Half-life value   LOD*****: limit of detection.

Fig. 12. Effect of pH 9 at (30°C±2) on the degradation rate of metribuzin formulations

The formulation type can affect biological efficacy and efficacy protection. Pesticide residues can also be influenced by the relationship between formulation, type and concentration of auxiliaries and adjuvants, the concentration of active ingredients, growth stage, environmental conditions, and application method [29]. The biological efficiency of metribuzin WG and SC formulations was studied in field experiments. It was found that herbicide formulations containing metribuzin in SC formulation were more effective than WG at controlling grassy and broadleaf weeds [30].

Our findings are consistent with [19-21, 31] using the same herbicide or other pesticides, when exposed to ultraviolet light, pesticides undergo numerous chemical changes, including hydrolysis, oxidation, and isomerization. Radiation energy produced by ultraviolet rays and direct sunlight may be absorbed by pesticide molecules, thereby increasing their transitional, rotational, vibrational, or electronic energy. This makes sunlight more effective than UV rays at accelerating the photodecomposition rate, which can be attributable to thermal, evaporation, and light intensity factors [31]. Metribuzin residues are affected by environmental factors, including ultraviolet rays, direct sunlight, pH, and varying temperatures [19]. Direct sunlight was more effective than ultraviolet rays at accelerating pesticide degradation [21]. Metribuzin showed a high degradation when exposed to direct sunlight and high-temperature degrees (50°C), so it is recommended to use metribuzin not exceeding 30°C. Additionally, short UV rays have a positive correlation with the duration of exposure and chemical structure [20].

3.10. Identification of the photodegradation products of metribuzin by GC-MS

The samples of metribuzin a.i were analyzed after exposure to sunlight using GC-MS to identify the degradation products and found that the characteristic ions at m/z 214, 199, 184, 154, and 246, were molecular ions of metribuzin, deamino metribuzin (DA), diketo metribuzin (DK), 6-(tert-butyl) -1,2,4-triazin-5(4H)-one   and   4-amino-6-(tert-butyl)-3-

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(methylsulfonyl)-1,2,4-triazin-5(4H)-one, respectively. However, according to Table 10, identification of the degradation products of metribuzin a.i by GC-MS.

Numerous factors, including photolysis, hydrolysis at varying pH levels, and high temperatures, can play a significant role in the degradation of metribuzin and the formation of its degradation products. These factors can result in the formation of numerous degradation products, as demonstrated by the current research. According to the chemical structure of metribuzin, it contains an N-NH2 bond. Deamination occurs rapidly upon exposure to direct sunlight or UV rays, resulting in the formation of deamino metribuzin (DA) m/z 199 [32, 33], followed by desulfuration reaction via cleavage -SCH3 bond to form 6-(tert-butyl)-1,2,4-triazin-5(4H)-one m/z, 154 [34]. Metribuzin can be degraded by photolysis and hydrolysis under acidic and alkaline conditions by desulfuration reaction followed by oxidation to form diketo metribuzin (DK) m/z 184. Both deamination of DK and desulfuration of DA resulted in the formation of deaminodiketo metribuzin (DADK) [35]. In addition, there is another transformation of metribuzin by oxidation to form 4-amino-6-(tert-butyl)-3-(methylsulfonyl)-1,2,4-triazin-5(4H)-one m/z, 246 [33].

Table (10). Identification of the photodegradation products of metribuzin a.i by GC-MS

Name	Structure	RT (min)	Mass (m/z)
Metribuzin		18.42	214
Deamino metribuzin (DA)		18.36	199
Diketo metribuzin (DK)		16.90	184
6-(tert-butyl) -1,2,4-triazin-5(4H)-one		23.57	154
4-amino-6-(tert-butyl)-3-(methylsulfonyl)-1,2,4-triazin-5(4H)-one		21.98	246
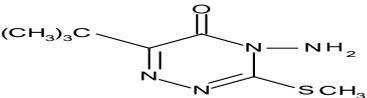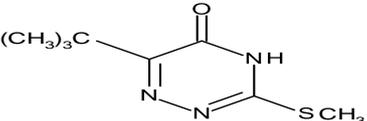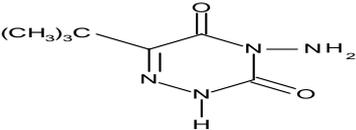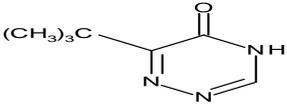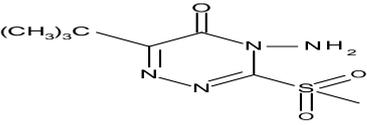
All the previous reactions can be explained in Fig. 13, which demonstrates the possible photodegradation pathways of metribuzin a.i.

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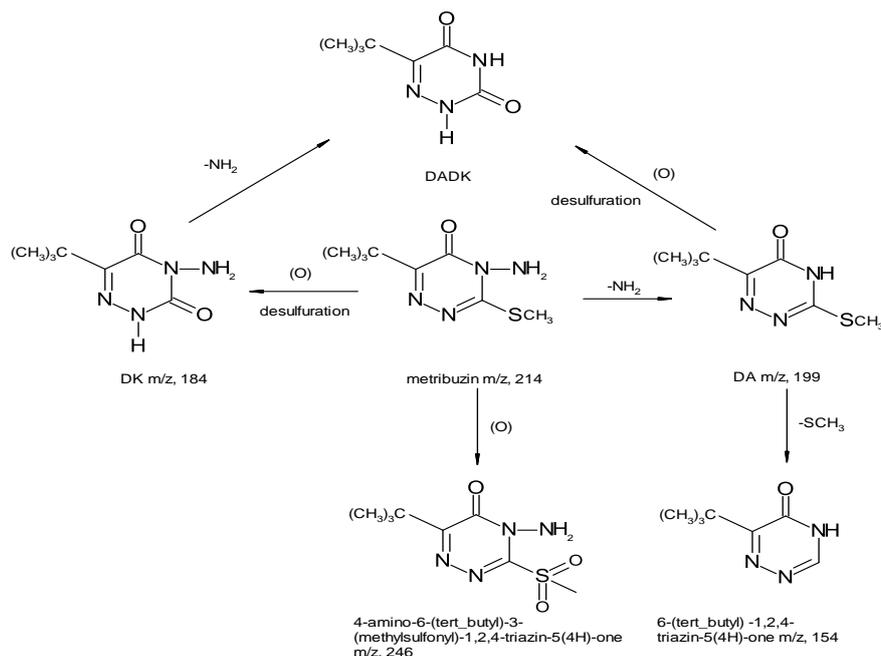
Fig 13. The possible photodegradation pathways of metribuzin a.i.

4- CONCLUSIONS

In the present study, metribuzin formulations (SC, WG, and WP) were not affected by accelerated storage at 54 ±2 °C for 14 days. The type of formulation had a limited effect on the metribuzin degradation rate. However, the current study revealed that the metribuzin formulation in SC was more stable than formulations WG and WP. Metribuzin formulations were more affected by exposure to sunlight and high temperatures than by exposure to ultraviolet rays and low temperatures. Hydrolysis by different pH values plays a significant role in the degradation rate of metribuzin formulations, particularly in alkaline and acidic media, whereas it was stable in neutral media. Photolysis can quickly degrade metribuzin into numerous degradation products. Based on the current study results, it can be concluded that the rate of degradation and the quality of metribuzin formulations can be affected by several factors that affect the quality of formulations, such as the manufacturing process, sources of technical materials, environmental conditions, and the use of different types of adjuvants.

5- Conflicts of interest
There are no conflicts to declare

6- Acknowledgment

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