



Egyptian Journal of Plant
Protection Research Institute

www.ejprii.eg.net



Influence of storage thermal on some fungicide compounds and their impurities

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ARTICLE INFO

Article History

Received: 18 / 1 /2021

Accepted: 25 / 3 /2021

Keywords

Storage thermal,
fungicides, copper ,
mancozeb and
impurities.

Abstract:

The present work was carried out to study the effect of storage under high temperature fungicides of mancosil plas (Metallic copper + metalaxyl)50 %WP and mancosil (Mencozeb and metalaxyl) 70 % WP. The stability of active ingredient of the tested pesticides under storage 54 °C for 28 days and influence UV ray were studied . The active ingredient was metallic copper active ingredient 35.11 before storage become after storage the end experiment 33.81% for 28 days stability of metallic copper active ingredient was 35.59 before storage UV 36 and 48 hours become after influence UV 33.56 and 33.32, respectively . Also, the effect of the influence UV ray on the stability of mancozeb active ingredient (a.i) in mancosil formulation 72 % , The active ingredient of mancozeb was before 64.94 % become after influence UV ray 58,33% and 58.21% at 36 and 48 hours respectively. Cadmium has not detected in both mancosil plas , also showed decreased the amount of lead and arsenic (mg/kg)in mancosil plas 50 % , whereas the percentage loss of lead , and arsenic were 153% and 3.11% respectively, for storage 28 days on 54°C. Also, show that the impurities ethylene thiourea (ETU) and 2,6 dimethyl aniline of mancozeb 72 % WP before storage were 0.09 and 0.0041, respectively , before an influence UV ray become 0.49% and 0.069 % after influence UV ray 48 hrs.

Introduction

Fungicides are useful and important in agricultural production despite the increasing interest of the new concept called biological agriculture. This practice is not without risk on animal and human health and, in wide consideration, on environmental conditions due to the residues of fungicides that may persist many weeks or months after application

(Sparling *et al.*, 2001). Mancozeb (Ethylene bis-dithiocarbamate fungicide (EBCD)) was first registered in the United States in 1948 (Runkle *et al.*, 2017) and introduced in the global fungicide market in 1962 (Palmerini *et al.*, 2018). Mancozeb fungicidal efficacy has been applied in different agricultural and industrial contexts, for example, in major agricultural crops (Potato, tomato and grapevine), and its

use will likely increase by the 2020s due to its low price, global demand for vegetables and fruits, and non-selective fungicidal efficacy (Runkle *et al.*, 2017). Mancozeb influence induces a wide range of environmental hazard, such as, thyroid hormone dysfunctions, Parkinson-like symptoms and defects in fetal development (Goldner *et al.*, 2010 and Runkle *et al.*, 2017) . The aim of this work to determine (Mencosil plus
Table (1): The formulation of pesticides.

50 % and mancosil 70 %) active ingredient and the impurities heavy metal , ethylen thiourea and 2,6 dimethyl analine content through storage at 54°C for 28 days .

Materials and methods

1. Source of Sample: Center Agric. Pesticides Laboratory. Table (1) showed that the formulation of pesticides used.

Trade name	Formulation types	Active ingredient	Impurities
Mancosil plus 72 %	WP	Mixture metalaxyl + Cupper oxychloride	2,6 dimethyl analine in metalaxyl + AS,Cd, Pb in cupper
Mencosil 50 %	WP	Mixture metalaxyl + Mencozeb	2,6 dimethyl analine in metalaxyl +Ethylen thiourea (ETU) in mencozeb

2. Sample preparation for tested pesticides:

Accurately weighed enough samples formulation equivalent to 10 mg of standard in a different 25 ml volumetric flask for each sample, and slowly mixed with methanol and the volume was completed with methanol.

3. Sample preparation for impurities:

1 g tested formulation samples in 25 ml volumetric flask for each sample were prepared and slowly mixed with methanol and the volume was completed with methanol .

4. Storage conditions:

The tested fungicide formulation was stored at 54°C for 14 days according to FAO (1989 and 1998). During the storage period , samples were taken at 1,3,7, 14 , 21 and 28 days to determine the active ingredient and their impurities content for the tested formulations under testes .

5. Influence of UV ray :

The pesticides mencosil plus 50 %WP and mancosil WP 72 %) formulation were influence of direct UV ray .The samples were taken at 0,

1,5 ,12 , 24 , 36 and 48 hours from influence direct UV to determine the active ingredient and impurities content for formulation under testes.

6. Determination of impurities heavy metal:

The cadmium, lead and Arsenic were determined before and after storage according to **CIPAC (1970)** Thermo element (Atomic absorption spectra photometric (Model 4200 MP - AES) was used for all the measurement

7. Determination of metallic copper:

The metallic copper percentage was determined before and after storage according to **CIPAC E 44/TC/M3.1p.42.**

8. Determination of mencozeb :

The active ingredient percentage was determined before and after storage according to (**CIPAC . IA;34/3/M/6.3).**

9. Determination of 2, 6 dimethyl analine and ETU by HPLC :

The Impurities for ETU were evaluated by HPLC apparatus according to the method of Luke *et al.* (1981). A revise phase high-

performance liquid chromatographic was used for quantitative analysis . Aglient technologies 1200 series HPLC in student equipped with degasser , quaternary pump, photodiode array detector connected with injection system and computer (Model vectra was used for analysis . The stationary phase consisted of lichrosphere on Rp-8 packed stainless steel column (15 cm X4.6 mm id)

Results and discussion

1. Effect of storage thermal stability mancosil plas 35 %WP and mancosil 72 %WP at 54°C.:

Date in Table(2) showed that stability of metallic copper active ingredient 35.11 % before storage become after storage the end experiment 33.81% for 28 days .these results indicated that all test copper formulation was passed successfully and comply with FAO Specification (1989 and 1998) . These results are similar obtained by Abd El-Aal *et al.*, 1993 and El-Deep *et al.*, 1991), who report the correlation between temperature and storage temperature and decomposition of patricides formulation. Also, the effect

Table (2): Effect of storage thermal stability mancosil plas 35 %WP and mancosil 72 %WP at 54°C.

Storage period days	Mancosil plas 50%				Mencosil 70 %			
	Metallic Copper 35 %	Loss %	Metalaxyl 15 %	Loss %	Mencozeb 64 %	Loss %	Metalaxyl 8%	Loss %
0	35.11	00	15.44	0	64.34	00	8.59	00
1	35.11	00	15.31	0.84	64.34	0.01	8.51	1.04
3	35.00	0.31	15.01	0.90	63.88	0.52	8.09	5.82
7	35.00	0.31	14.60	2.78	63.03	0.730	7.82	8.96
14	34.81	0.85	13.89	5.44	62.92	2.05	7.55	12.10
21	34.00	3.16	13.59	10.03	61.56	2.22	6.99	18.62
28	33.81	3.70	12.55	18.71	59.33	8.40	6.64	22.70

0* one hour before exposure to storage

2. Effect of influence UV ray stability mancosil plas 35 %and mancosil 72 % at UV ray :

Data in Table (3) stability of metallic copper active ingredient were 35.59 before storage UV 36 and 48 hours become after influence UV 33.56

of storage at 54°C on the stability of Mancozeb active ingredient (a.i) in mencosil formulation 72 % . The active ingredient of Mancozeb was before storage 64.35% at become after storage 62.92% after 14 days of storage at 54°C .According to this results FAO specification (1992) but decreasing 28 days become after storage 59.33 % . The primary source of these exposure is the use of ethylene bisdithio carbamate (EBDCs) fungicides of which ethylenethiourea is an environmental degradation product, metabolite and impurity. Ethylenthiourea content in (EBDCs) fungicides formulation depend on the pesticides storage conditions and increased by increasing temperature , a moisture and length of storage period Comoni *et al.* (1988) and Sue Xu (2000) . The stability of metalaxyl active ingredient were 15.44 and 8.59 before storage 54 °C all mencosil plas and mancosil become after thermal storage 54 °C at the end of experiment 12.55% and 6.64% for 28 days There obtained result were agreement with (Khozimy and Ramdan , 2018) .

and 33.32respectively . Also, the effect of influence UV ray on the stability of mancozeb active ingredient (a.i) in mencosil formulation 72 % , The active ingredient of mancozeb was before 64.94 % become after influence UV ray 58,33% and 58.21% at 36 and 48

hours, respectively. The stability of metalaxyl active ingredient were 15.44 and 8.59 before influence UV ray all mencosil plas and mancasil become

after influence UV ray 54 °C at the end of experiment 12.32 % and 6.34 % for 48 hours.

Table (3): Effect of influence UV ray stability mancasil plas 50 % and mancasil 72 % at UV ray .

Storage period hours	Mancosil plas 50 Metallic cupper + metalaxyl				Mencosil 70 % Mencozeb + metalaxyl			
	Metallic cupper 35 %	Loss %	Metalaxyl 15 %	Loss %	Mencozeb 64 %	Loss %	Metalaxyl 8%	Loss %
0	35.59	00	15.44	00	64.94	00	8.59	00
1	35.59	00	15.44	00	64.94	00	8.20	4.54
5	35.00	1.66	15.00	2.93	64.55	0.54	8.00	6.94
8	34.85	2.00	14.78	4.27	64.31	0.97	7.98	18.26
12	34.11	4.10	14.78	4.27	62.55	3.68	7.88	18.16
24	33.56	5.70	14.50	6.08	60.25	7.22	7.03	22.19
36	33.56	5.8	13.91	9.90	58.33	10.18	6.95	19.09
48	33.32	6.37	12.32	20.20	58.21	10.36	6.34	26.19

0* one hour before exposure to storage

3. Effect of storage at 54 °C on level impurities mancasil plas 50% and mancasil 72 % :

The Data illustrate in Table (4) show the effect of storage at 54 c on the level Cadmium and arsenic mg/kg in testes copper products. Cadmium not detected in both mencosil plas , also showed decrease the amount of Lead and Arsenic (mg/kg)in im mencosil plas 50 % , whereas the percentage loss of Lead , and Arsenic were 153 and 3.11%, respectively, for storage 28 days on 54°C . Some pesticides are suspected carcinogenic properties . The trace element can be associated with ligaud , colloids or particles of organic and inorganic forms according to their chemical structure Digild and Best (1994) .

Although it is probable that the final product is not only affected by the source of primary minerals but also by trace elements introduce during pesticides production. Of the other

important use of mercury and Arsenic include manufacture of pesticides (Hutton and Symon , 1986). show that the impurities of Mancozeb 72 % WP before storage were 0.09 and % (ETU) Ethylen thio urea and 2, 6 dimethyl analine respectively, Become after storage, 1.10 and 0.04 % after 28 days from storage at 54 °C respectively.

There obtained result were agreement with Suzanne (1980) . According to FAO specifications (1992) which reported that maximum limit of 2, 6- dimethylaniline and Ethulenthourea (ETU) as relevant impurities are 0.1 % and 0.5 %)of the metalaxyl content the tested fungicide percentage became higher than FAO specification limit after 10 days of storage and tested fungicide became non conformity with FAO specifications when stored for 14 days at 54±2°C (Khozimy and Ramdan ,2018) .

Table (4): Effect of storage at 54 °C on level impurities mancosil plas 50% and mancosil 72 % .

Storage period days	Mancosil plas 50						Mencosil 70 %	
	Impurities Copper + metalaxyl						Impurities Mancozeb + metalaxyl	
	Cd Ppm	Pb Ppm	FAO Maximum g/kg	As	FAO Maximum g/kg	2, 6 dimethyl aniline	ETU	2, 6 dimethyl aniline
0	UND	134.11	175.55	2.34	35.11	00.00	0.09	0.0043
1	UND	134.11	175.55	2.35	35.11	00.00	0.09	0.0034
3	UND	151.00	175.00	2.31	35.00	0.0054	0.11	0.0076
7	UND	149.09	175.00	3.51	35.00	0.0068	0.11	0.0085
14	UND	153.08	174.05	3.43	34.81	0.079	0.27	0.0089
21	UND	154.00	170.00	3.55	34.00	0.080	0.35	0.0290
28	UND	153.00	169.05	3.11	33.81	0.089	0.46	0.040

FAO maximum(Cd) = 0.1 x b mg/dl where b copper content by g/kg.

FAO maximum(As) = 0.1 x b mg/dl where b copper content by g/kg.

FAO maximum(pb) = 0.5x b mg/dl where b copper content by g/k.

4. Effect of influence UV ray on level impurities mancosil plas 50% WP and mancosil 72 % WP :

The Data illustrate in Table (5) show the effect of influence UV ray on the level Cadmium lead and arsenic mg/kg in testes copper products. Cadmium not detected in both mancosil plas , also showed decrease the amount of Lead and Arsenic 154 and 3.34 (mg/kg)respectively in mancosil plas 50

, whereas the percentage loss of Lead , and Arsenic were 153% and 3.11 respectively, for influence UV ray 48 hours. Also show that the impurities ethylene thio urea (ETU and 2,6 dimethyl aniline of Mancozeb 72 % WP before storage were 0.09 and 0.0041 respectively , before influence UV ray become 0.49 % and 0.069 after influence UV ray 48 hrs.

Table (5): Effect of influence UV ray on level impurities mancosil plas 50% WP and mancosil 72 % WP.

Storage period hours	Mancosil plas 50%						Mencosil 70 %	
	Copper + metalaxyl						Mancozeb + metalaxyl	
	Impurities						Impurities	
	Cd	Pb	FAO Maximum g/kg	As	FAO Maximum g/kg	2, 6 dimethyl aniline	ETU	2, 6 dimethyl aniline
0	UND	134.11	177.95	2.89	35.59	00.00	0.09	0.0043
1	UND	134.11	177.95	2.43	35.59	0.0043	0.09	0.0043
5	UND	151.00	175.00	2.99	35.00	0.0067	0.09	0.0067
8	UND	149.09	174.25	3.31	34.85	0.0076	0.12	0.0076
12	UND	153.08	170.55	3.11	34.11	0.0079	0.21	0.0079
24	UND	154.00	167.80	3.34	33.56	0.045	0.29	0.045
36	UND	153.00	167.8	3.34	33.56	0.055	0.35	0.055
48	UND	154.00	166.60	3.34	33.32	0.069	0.49	0.069

FAO maximum (Cd) = 0.1 x b mg/dl where b copper content by g/kg.

FAO maximum (As) = 0.1 x b mg/dl where b copper content by g/kg.

FAO maximum (Pb) = 0.5x b mg/dl where b copper content by g/k.

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