Comparison of Thermal Storage on Stability of Two Fungicides Mancozeb and Mancozeb Modified Dimethomorph and Their Impurities Ethylenethiourea.

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Abstract

Two fungicides under trade name uthane80% (mancozeb) wettable powder (WP)and volar mz 69% WP (mancozeb 60% modified dimethomorph 9%)were stored for 14 days at 54°C according to FAO specification 1980 to study stability of active ingredients dimethomorph and mancozeb and study behavior of its impurities ethylenethiourea (ETU) under storage conditions also physical properties of two fungicides studied. The results illustrated that dimethomorph and mancozeb active ingredientin volar mz formulation were slightly affected by thermal temperature of storage and become conformity with FAO specification and it became 8.55% and 58.51% after 14 days of storage respectively. But in uthane formulation mancozeb active ingredient was decomposed to reached 77.60% after 14 days of storage and become nonconformity with FAO specification. Ethylenethiourea was more stable in fungicide mancozeb modified dimethomorph than mancozeb and it was increased with increasing time of storage to reached 0.146% in volar mzformulation and reached to 0.40% in uthaneformulation after 14 days of storage. All physical properties pass successfully and conformity with FAO specification under storage for 14 days at 54°C.**Keywords:** Pesticides; Soil enzymes activity; Soil Respiration.

Keywords: Mancozeb, Ethylenethiourea, Degradation, Fungicides.

Introduction

Dithiocarbamate pesticides one of the important organic fungicides groups which used to control many diseases in a many crops whichhave low acute toxicity, but some of bisdithiocarbamates EBDCs mancozeb, maneb zineb can decompose Ethylenethioureawhich shown carcinogenic activities in animals test (Larsson et al., 1976). Ethylenethiourea is of major toxicological concern which shown a large spectrum of adverse effects in animal experimental studies. High occupational exposure can be found in agricultural workers or during manufacturing of ethylenbisdithiocarbamates (Eva et al., 2013).ETU is a metabolite of ethylenebisdithiocarbamates and it is agood indicator of exposure with fungicides and determined bν highperformance chromatography combined with photodiodearray detector (Souleiman et al., 2005). During the manufacture of mancozeb technical a small amount of ethylenethiourea (ETU) is also produced. In good manufacturing practice this should not exceed, at the time of manufacture, 0.5% of the mancozeb. During storage more ETU may be formed by decomposition. To minimize decomposition all products mancozeb should be stored under cool, dry conditions (FAO 1980). Ethylenethiourea in mancozeb modified copper and mancozeb modified metalaxyl were more stable than mancozeb where, ethylenethiourea increased to be 0.133%, 0.197 % and 0.5% after 14 days of storage at $54^{\circ}C$ for Primotox Fort, Kure M and Diethan formulations respectively. Also illustrated that half-life ($t_{0.5}$) for mancozeb active ingredient was 270.53, 93.7 and 145.17 days for Diethan 80%, Kure M 72% and Primotox Fort 41%, respectively (Hala et al., 2016).

MATERAL AND METHODS Tested Chemicals

All organic solvent methanol and acetonitrile were grade HPLC obtained from Fisher Scientific Ltd. All anhydrous salts magnesium chloride and calcium chloride and all buffer pH 4, pH 7 and pH 9 solutions obtained from Panreac Applichem Germany. Used water was deionized water which prepared by a Milli-Q water purification system. Dimethomorph and Ethylenethiourea standards obtained from Sigma-Aldrich.Fungicide {mancozeb 60% (C8H12MnN4S8Zn) + dimethomorph 9% (C21H22CINO4)} used under trade name Volar MZ 69% WP which obtained from Jiangsu Rotam chemistry Co., Ltd China. But the other mancozeb fungicide used under trade uthane 80% name WPwasobtained fromUttar Pradesh Power Co. Ltd India.

Tested Apparatus

Dionex UltiMate 3000 UHPLC from GmbH, Germany combinedwith photodiode array detector used as illustrated by Gamon et al. (1998) with the following conditions, mobile phase for dimethomorph was methanol: water (80/20 v/v) with flow rate 0.3 ml/min with wavelength detection 210 nm and retention

time was 5.52and 6.05min. But ethylenethiourea mobile phase was methanol: acetonitrile: water (60:25:5 v/v/v) with flow rate 0.5 ml/min with wavelength detection 235 nm and retention time 3.18 min.

Determination of active ingredient

Percent of mancozeb active ingredient determined before one day of storage and after 14 days of storage at 54 ± 2°C according to (CIPAC 1A, 1980) by decomposition with sulfuric acid to release carbondisulfide using lead acetate solution then the released carbondisulfide trapped through digestion with methanolic KOH solvent and determined by iodometric titration. But its impurities ethylenethioureawas determined by (CIPAC F, MT 162. p.399) and dimethomorph active ingredientdetermined by (CIPAC, 1994 and 1995).

Samplespreparation

All samples for uthane 80% WP and Volar MZ 69% WP formulationsone day before storage and after 14 days of storage at 54 ± 2^oCwere extracted with methanol and then filtrated to carryout by UHPLC to determined percentage of dimethomorph and ethylenethiourea. But for mancozeb determination all samples determined by iodometric titration after digestion by acid according to (CIPAC 1A, 1980).

Standard preparation

Suitable weight 0.01 gm of dimethomorph and ethylenethiourea with purity 100% in 25 ml volumetric flask completed with methanol to prepare calibration solutions with methanol containing 1, 5, 10, 15, 20, 40 and 50 μg per ml for dimethomorph and ethylenethiourea.

Storage stability at 54°C

The tested fungicides formulation were stored for 14 days at $54 \pm 2^{\circ}$ C by the method (CIPAC,

1985). During storage the samples were taken at 2, 4, 6, 8, 10, 12 and 14 days to determined active ingredients, their impurities and their physical properties for tested fungicides formulations. After storage the minimum permitted mancozeb content shall be 90% of that found before storage and the product shall continue to comply with physical properties pH values, Wet sieve test, suspensibility and wettability of powder according to FAO Specifications (1980).

Physical properties

Physical properties of tested fungicides determined before one day of storage and after storage periods as the following, Wet sieve test, Suspensibility, pH range, Persistent foam andd wettability of the powder (CIPAC, 1985).

RESULTS AND DISCUSSION

I. Effect of thermal storage at 54 ± 2 °C for 14 days on stability of mancozeb and their impurities ethylenethiourea in formulation uthane 80% WP Date in Table (1) illustrated that active ingredient of mancozeb in formulation uthane 80% WP one day before storage was 79.89% recording loss 0.14% and degradation rate of mancozeb increased with increasing long time

of storage and decomposed to 77.60% recording loss 3.0% after 14 days of storage at 54 ± 2°C. According to FAO specifications (1980) which reported that tolerances of mancozeb was (±2.5%) the used uthane 80% WP formulation become non conformity with FAO specifications when stored for 14 days and can store only for 8 days of storage at 54 ± 2°C (FAO, 1980). Also, results showed that ethylenethiourea impurities of mancozeb one day before storage was 0.24% and it was increased due to mancozeb decomposition during thermal storage to reached 0.40% and the increasing percent of ethylenethiourea was 66.67% after 14 days of storage. According to FAOspecifications (1980) which reported that maximum percentage of ethylenethiourea 0.5% the tested formulation successfully in stability of ethylenethiourea test but failed in stability of mancozeb active ingredient. So that uthane 80% WP formulation can be stored for 8 days only under thermal storage at 54 ± 2°C. Results agree with Hala et al., (2016) whom reported increasing percentage ethylenethiourea was 65.6% after 14 days of storage at 54 °C. Also agree with Attala et al., (2009).

Table (1): Effect of thermal storage at 54 ± 2 °C for 14 days on stability of mancozeb and their impurities ethylenethiourea in formulation uthane 80% WP

Storage period (days)	Mancozeb active ingredient 80%		Ethylenethiourea (ETU) impurities of mancozeb		
	Mancozeb %	Loss %	ETU %	Increase %	
Initial	79.89	0.14	0.24	0.00	
2	79.54	0.57	0.25	4.17	
4	79.21	0.99	0.27	12.50	
6	78.97	1.29	0.29	20.83	
8	78.76	1.55	0.31	29.17	
10	78.25	2.19	0.34	41.67	
12	77.95	2.56	0.38	58.33	
14	77.60	3.00	0.40	66.67	

II. Effect of thermal storage at 54±2 °Cfor 14 days on stability of mancozeb modified dimethomorph and their impurities ethylenethiourea in formulation volar mz 69% WP

Date in Table (2) indicated that active ingredient of mancozeb in formulation volar mz 69% WP one day before storage was 59.93% recording loss 0.12% and it was slightly decomposed to reached 58.51% recording loss 2.48% after 14 days of storage at 54 \pm 2 $^{\circ}$ C. According to FAO specifications (1980) which reported that tolerances of and mancozeb was (±2.5%) the mancozeb active ingredient in volar mz 69% WP formulation become conformity when stored for 14 days at 54 ± 2 ^oC. Also results showedthat dimethomorph active ingredient in the same formulation one day before storage was 8.85% recording loss 1.67%. Dimethomorph was stable with slightly degradation during storage and became 8.55% recording loss 5% after 14 days of storage. According to FAO/WHO specification (2006) the permitted tolerance (± 10 %) for dimethomorph fungicide formulated, the used volar mz become conformity and can store for 14 days at 54 \pm 2 $^{\circ}$ C. Also results showed that ethylenethiourea impurities of mancozeb in the same formulation not affected by thermal storage and still stable during storage periods and it was 0.132% one day before storage and it became 0.146% at the end of experiment after 14 days of storage with increasing percent 10.61% after 14 days of storage. According to FAO specifications (1980) which reported that maximum percentage of ethylenethiourea 0.5% the tested formulation successfully in stability of ethylenethiourea test. Results agree with Attala et al., (2009) and Hala al., (2016)whom indicated ethylenethiourea mancozeb modified in copper and mancozeb modified metalaxyl were more stable than mancozeb.

Table (2): Effect of thermal storage at 54 ± 2 Cfor 14 days on stability of mancozeb modified dimethomorph and their impurities ethylenethiourea in formulation volar mz 69% WP.

Storage period (days)	Mancozeb active ingredient 60%		dimethomorph active ingredient 9 %		Ethylenethiourea (ETU) impurities of mancozeb	
Initial	Mancozeb %	Loss %	dimethomorph %	Loss %	ETU %	increase %
2	59.93	0.12	8.85	1.67	0.132	0.00
4	59.72	0.47	8.81	2.11	0.134	1.52
6	59.34	1.10	8.77	2.56	0.137	3.79
8	59.03	1.62	8.71	3.22	0.140	6.06
10	58.97	1.72	8.68	3.56	0.142	7.58
12	58.67	2.22	8.63	4.11	0.145	9.85
14	58.51	2.48	8.55	5.00	0.146	10.61

III. Effect of thermal storage at $54 \pm 2^{\circ}$ Cfor 14 days on limits of wet sieve test of uthane 80% WP and volar mz 69% WP formulations Results in Table (3) showed that the retained percentageon a 75 μ m test sievefor fungicide formulationsuthane 80% WP and volar mz 69% WP in initial deposit one day before storage were none and this percentage gradually increased during storage for 14 days and

became 0.38% and 0.21% respectively.FAO specifications (1980) which reported a maximum2 % of retained on a 75 μ m test sieve the two fungicides formulation can be store for 14 days at 54 6 C.The results arein line with Morpeth (1995), Mohamed (2009), Mohamed (2013) and Mohamed et al. (2016).

IV. Effect of thermal storage at 54 ± 2 $^{\circ}$ C for 14 days on suspensibility percentageof uthane 80% WP and volar mz 69% WP formulations

Data in Table (3) illustrated that the suspensibility percentage of formulations uthane 80% WP and volar mz 69% WP during storage for 14 days at 54 °C passed successfully through the experiment with FAO specifications (1980) which reported that A minimum of 50% of the mancozeb content shall be in suspension after 30 min in CIPAC Standard Water A where, the initial percentage one day before storage were 95% for uthane and 98% for volar mz formulations. Those percentages were gradually decreased during storage periods to reached 83% and 91% for uthane and volar mz after storage for 14 days at 54 Ocrespectively. Results agree with Kamal El-Din (2007) and El-badry and Mohsin (2007) whom observed similar results.

V. Effect of thermal storage at 54 \pm 2 $^{\circ}$ C for 14 days on change on pH values of uthane 80% WP and volar mz 69% WP formulations

Date in Table (3) indicated changes of pH values in uthane 80% WP and volar mz 69% WP where, the initial deposits of pH determined one day before storage were 6.91 and 5.43 respectively. Through the storage period for 14 days pH values were little decreased to reached 6.49 and 5.25 for uthane 80% WP and volar mz 69% WP respectively. According to FAO specifications (1980) which reported that pH range for mancozeb wettable powder from 5 to 9 the two formulations pass successfully and can store for 14 days at $54 \pm 2^{\circ}$ C.Data agree with Ibrahim and Ramadan (2011) whom reported that pH value for fungicide milor-Cu 50% WP was slightly decrease under storage and data also in line with Mohamed (2009), Mohamed et al. (2013) and Khozimy et al., (2017).

Table (3): Effect of thermal storage at 54 ± 2 °C for 14 days on wet sieve test, suspensibility and change in pH values for uthane 80% WP and volar mz 69% WP formulations.

		alle 60% WP allu V	Voiai IIIZ O	т			
Storage	uthane 80 %	uthane 80 % WP			volar mz 69% WP		
period							
(days)	Wet sieve	Suspensibility	рН	Wet sieve	Suspensibility	рН	
	test	(%)		test	(%)		
	(%)	` '		(%)			
Initial	None	95	6.91	None	98	5.43	
2	None	95	6.88	None	98	5.43	
4	0.11	93	6.82	None	98	5.41	
6	0.15	92	6.75	None	97	5.39	
8	0.20	90	6.69	0.10	95	5.36	
10	0.22	87	6.60	0.13	93	5.32	
12	0.27	84	6.55	0.15	91	5.29	
14	0.38	83	6.49	0.21	91	5.25	

VI. Effect of thermal storage at 54 ± 2 °C for 14 days onpersistent foamamount for uthane 80% WP and volar mz 69% WP formulations Data in Table (4) illustrated that foaming evaluated as volume (ml) after 1 min for

uthane 80% WP and volar mz 69% WP were 9 ml and 4.5 ml before one day of storage respectively. The foaming volume after 14 days of thermal storage was decreased and reached 3ml for uthane and 1.5ml for volar mz

formulations. According to FAO specifications (1980) which reported thatmaximum 20 ml of foam for mancozeb after 1 min the used fungicides formulation become conformity with FAO specifications and can be store for 14 days under thermal storage at 54 \pm 2 $^{\circ}$ C. The obtained results in line with Ismail (2010) and Mohamed et al. (2016) finding similarresults.

VII. Effect of thermal storage at 54 ± 2 $^{\circ}$ C for 14 days on wettability of the powder of uthane 80% WP and volar mz 69% WP formulations

Results in Table (4) showed the wetting of fungicide formulations uthane 80 % WP and volar mz 69% WP through storage for 14 days at 54 ± 2 $^{\circ}$ C. Data indicate that the powder was completely wetted for two formulations before

one day of storage until the end of experiment for 14 days and became conformity with FAO specification (1980) which reported that the product shall be completely wetted in 1 min without swirling. Data in line with Mohamed (2009), Ibrahim and Ramadan (2011) and Mohamed et al. (2016).

CONCLUSION

Active ingredients and its impurities in fungicide formulation volar 69% WP (mancozeb 60 % WP modified dimethomorph 9%) were more stable than fungicide formulation uthane 80 % WP containing mancozeb only.

Table (4): Effect of thermal storage at $54 \pm 2^{\circ}$ Cfor 14 days on persistent foam limits and wettability of the powder of uthane 80% WP and volar mz 69% WP formulations.

Storage period	uthane 80 % WP		volar mz 69% WP		
(days)	Persistent foam	Wettabiliy of the	Persistent foam	Wettabiliy of the	
	ml	powder	ml	powder	
Initial	9	Completely wetted	4.5	Completely wetted	
2	9	Completely wetted	4.5	Completely wetted	
4	8	Completely wetted	4.0	Completely wetted	
6	7	Completely wetted	3.0	Completely wetted	
8	5	Completely wetted	3.0	Completely wetted	
10	5	Completely wetted	2.5	Completely wetted	
12	4	Completely wetted	2.0	Completely wetted	
14	3	Completely wetted	1.5	Completely wetted	

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مقارنة التخزين الحراري على ثبات اثنين من المبيدات الفطرية مانكوزيب و مانكوزيب المضاف الى دايميثورف والملوثة بمادة الاثيلين ثيويوريا

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الملخص العربي

أجريت هذه الدراسة على المبيد الفطرى بوسان ٨٠ % WP المحتوى على مادة فعالة مانكوزيب والمبيد الفطرى فولار أم زد ٦٩ % WP المحتوى على مانكوزيب مضاف اليه دايميثومورف. حيث تم تخزينهم على درجة حرارة ٥٠ م لمدة ١٤ يوم طبقا لمواصفات منظمة الأغذية والزراعة لدراسة ثبات المواد الفعالة والملوثة بمادة الاثيلين ثيويوريا والخواص الطبيعية لهم وكانت النتائج كالتالي:

مبيد فولار أم زد ٦٩ % WP حدث تكسير بسيط بالمواد الفعالة مانكوزيب و دايميثومورف حيث كانت نسبتهم قيل التخزين ٥٩.٩٣ % و ٥٩.٩٣ % و الدايميثومورف على التوالى. كما أن المادة المادة مدين المادة المادكوزيب وهي الاثيلين ثيويوريا لم تتأثر بالتخزين حيث كانت نسبتها قبل التخزين ١٣٢. ١٣٢ وبعد التخزين كانت المدد المادكوزيب وهي الاثيلين ثيويوريا لم تتأثر بالتخزين حيث كانت نسبتها قبل التخزين ١٣٢. ١٩٠٠ وبعد التخزين كانت

مبيد يوسان ٨٠ % WP حدث به تكسير للمادة الفعالة مانكوزيب حيث كانت نسبتها ٧٩.٨٩ % واصبحت بعد التخزين ٧٧.٦٠ % وبعد التخزين ك٧٠.٦٠ أن وبعد التخزين حيث كانت نسبتها قبل التخزين ٢٤.٥ % وبعد التخزين أصبحت ٤٠.٤ % وبعد التخزين أصبحت ٤٠.٤ % و وبعد التخزين أصبحت ٤٠.٨ % و وبعد التخرين المستخدمين خلال التجربة.