Storage Effect on Degradation of Copper Fungicide and its Relevant Impurities.

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Abstract Copper fungicide formulation wettable powder (WP) was stored under accelerated storage temperature at 54 °C for 14 days to study the degradation of copper active ingredient and effect of storage temperature on relevant impurities of copper which determined by ICP.MS. The physical properties according to FAO specification (1989) such as pH values, suspensibility, wet sieve test, wetting without swirling test and persistent foam test before and after storage periods were also studied. Data showed that the active ingredient effected by long time of storage and the degradation rate increase with increasing the long time of storage but the amount of relevant impurities of copper were slightly increased and not effected by storage. All physical properties tests pH values, suspensibility, wet sieve test, wetting without swirling test and persistent foam were passed successfully through all storage periods at 54 °C for 14 days.

Keywords: Storage, Stability, copper, fungicide, ICP-MS.

1.Introduction

Fungicides are biocidal chemical compounds or biological organisms used to kill or inhibit fungi or fungal spores. Fungi can cause serious damage in agriculture, resulting in critical losses of yield, quality, and profit. Fungicides are used both in agriculture and to fight fungal infections in animals. A very common active ingredient is copper.

Temperature is known to be one of the most important factors influencing the stability, persistence and degradation of pesticides. It may affect other factors which are mainly responsible for the decomposition of pesticides Harris (1971) and Suett (1975). Pesticide degradation is the process by which a pesticide is transformed into a benign substance that is environmentally compatible with the site to which it was applied. Globally, an estimated 1 to 5.2 million tons of active ingredients are used each year, mainly in agriculture. Forty percent are herbicides, followed by insecticides and fungicides. Since their initial development in the 1940s, multiple chemical pesticides with different uses and modes of action have been employed. Pesticides are applied over large areas in agriculture and urban settings. Pesticide use therefore represents an important source of diffuse chemical environmental inputs. Fungicide residues have been found on food for human consumption, some fungicides are dangerous to human health, so it is urgently needs to clarify the degree of food safety from pesticides.

2. MATERAL AND METHODS

Copper oxychloride is used as fungicide;
Chemical structure: $3Cu(OH)_2.CuCl_2$.
Common name: Copper oxychloride.
IUPAC name: dicopper chloride trihydroxide (approximate composition); copper oxychloride.
CAS RN: [1332-40-7].
Formulation type: WP.
Molecular weight: 427.1.
Molecular formula: $Cl_2Cu_4H_6O_6$.

2.1. Applications:

Biochemistry: Copper-II ion is taken up by the spores during germination and accumulates until a sufficiently high concentration is achieved to kill the spore cell; the activity is limited to the prevention of spore germination.
Mode of action: Foliar fungicide with preventative action. Deposits must be on the crop before fungal spores begin to germinate.

2.2. Chemical analysis:

Determination of active ingredient percentage:
Total copper determined before and after storage according to method (CIPAC A1, 44.0/3K.1/1.4, p.236). Total copper content shall be declared (g/kg) and when determined the content obtained shall not differ from that declared by more than +/-5 % of the declared content.

2.3. Determination of impurities:

Arsenic, lead and cadmium were determined before and after storage by (CIPAC 1A, 44.0/ 2/M2/2.6, p.1168) and (MT 92, CIPAC 1A, p.1603) with using ICP MS.

2.4. ICP-MS (ICAP-MS) parameters:

Forward power : 1550 w.
Nebulizer gas : 0.80 L/min.

Injector : 2mm I.D., quartz.
Interface : Ni sampler and skimmer.
Qcell He gas flow : 4.8 ml/min.
Qcell KED voltage : 2 V.
75 As dwell time : 300ms.

2.5. Physical properties:

Physical properties were determined before one day of storage and after different storage periods
Suspensibility: (CIPAC A1,44/3/M1/1.7,p.236).
Wet sieve test: (MT 59.3, CIPAC 1, p.981).
Wetting of product: (MT53.3.1, CIPAC1,p.967).
Persistent foam: (MT 47.2, CIPAC 1C, p2249).
pH range: (MT 75.2 , CIPAC 1A, p. 1590)

2.6. Stability at 54 °C:

Storage at 54 ± 2 °C for 14 days according to FAO specification by the method (MT 46.1.1, CIPAC A1, p.951) after storage at 54 °C the samples was determined and the average of active ingredient percentage must not be lower than 95 % for copper oxychloride relative to the determined average content found before storage, the product shall continue to comply with physical properties of pesticides such as suspensibility, Wet sieve test.

3. RESULTS AND DISCUSSION

3.1. Effect of storage temperature at 54 °C on copper active ingredient percentage.

Table (1) indicates the effect of storage temperature on copper active ingredient through 14 days of storage at 54 °C according to FAO specification (1989).

Data in Table (1) illustrate that initial deposits of copper percentage determined one day before storage was 48.50% recording loss 3.0 %. Such deposits values were degraded with storage time to reach 47.46% recording dissipation 5.08 % after 10 days of storage. According to the tolerances (±2.5 %) for pesticide formulated in FAO specifications (1989), the used pesticide become non conformity with this specifications when it stored after 8 days.

Table (1) Thermal stability of copper content percentage fungicide formulated (WP) and it's impurities during storage at 54 °C according to FAO Specification (1989).

Storage period (days)	Active ingredient 50 %		Impurities mg/kg		
	%	Loss %	Arsenic	Lead	Cadmium
Initial	48.50	3.00	0.061	0.00	0.069
2	48:12	3.76	0.066	0.00	0.073
4	47:76	4.48	0.069	0.00	0.078
6	47:68	4.64	0.072	0.00	0.085
8	47:52	4.96	0.079	0.00	0.091
10	47:46	5.08	0.083	0.00	0.095
12	47:35	5.30	0.086	0.00	0.099
14	47:05	5.90	0.091	0.00	0.099

By long period of storage the rate of degradation was increased, whereas copper active ingredient percentage was 47.05% recording a dissipation of 5.90 % at the end of experiment after 14 days of storage. The obtained results are in line with Marei et al (1979), El-Sayed et al (1980), Hegazy et al (1982), Singh et al (1999), Shereen (2008), El-badry and kamal El-din.(2007) and Kamal El-Din and Ola (2007).

3.2. Effect of storage temperature at 54 °C on relevant impurities of copper fungicide.

Table (1) showed the effect of storage temperature on relevant impurities of copper through 14 days of storage at 54 °C according to FAO specification (1989). Results showed that there are slightly increasing in copper relevant impurities arsenic, lead and cadmium where, it recorded one day before storage 0.062, 0.00 and 0.069 mg/kg respectively. And at the end of storage after 14 days it reached 0.091, 0.00 and 0.099 mg/kg respectively. According to FAO specifications (1989), which mention that maximum of arsenic, lead and cadmium were 0.1, 0.5 and 0.1 mg/kg of copper content, the used pesticide pass successfully and not effected by storage for 14 days. The obtained results are agree with Mohamed (2013).

3.3. Effect of storage temperature at 54 °C on suspensibility percentage for copper.

Data in table (2) showed the effect of storage temperature on suspensibility for copper fungicide during storage at 54 °C for 14 days.

The results indicated that the suspensibility percentage of copper through the experiment passed successfully during storage for 14 days at 54 °C. The limits of suspension complete was a minimum of 80 % of copper content found according to FAO specifications (1989). The suspensibility percent of copper formulation in the initial was 99.52 % at one day before storage and it was gradually decreased by time lapse period of storage to 85.78 % recording loss of 13.81 % after storage for 14 days at 54 °C.

Results are agree with Duraipandian and Regupathy (1989), Morpth (1995), Kamal El-Din (2007) and El-badry and Mohsin (2007).

3.4. Effect of storage temperature on pH value for copper during storage at 54 °C.

Data presented in table (2) indicated the influence of storage temperature on pH value for copper fungicide formulation through 14 days storage at 54 °C. Data showed that pH value proved stable one day before storage until the end of storage for 14 days at 54 °C.

The pH value was 6.78 at one day before storage and reached to 6.50 after 14 days from storage. Results showed that the pH value was more stable and the change of values of pH was little until the end of storage. Results are agree with FAO specifications (1989) which reported that pH for copper fungicide ranged from 6 to 9.5. Results agree with El-badry and Mohsin (2007), Kamal El-Din and Ola (2007), Hirahara et al (1997), Ola and Sheren (2007), Abou–Donia et al (1985) and Barakat et al (1999).

Table (2): Thermal stability of copper fungicide formulated (WP) during storage at 54 °C according to FAO specifications (1989).

Storage period (days)	pH	Suspensibility test		Wet sieve test	Persistent foam	Wetting of the product
	value	Suspensibility %	Loss %	Retained %	ml	
Initial	6.78	99.52	—	None	6.0	Completely wetted
2	6.73	92.13	7.43	None	6.0	Completely wetted
4	6.70	88.91	10.66	None	6.0	Completely wetted
6	6.68	88.10	11.48	None	5.5	Completely wetted
8	6.64	87.95	11.63	None	5.5	Completely wetted
10	6.61	87.20	12.38	None	4.0	Completely wetted
12	6.58	86.99	12.60	None	4.0	Completely wetted
14	6.50	85.78	13.81	None	4.0	Completely wetted

3.5. Limits of wet sieve test of copper fungicide during storage at 54 °C.

Data in table (2) showed the effect of storage temperature on stability of wet sieve test of copper fungicide during storage for 14 days at temperature 54 °C. The retained percentage of copper fungicide before one day of storage until the end of experiment after 14 days of storage at 54 °C were none and results pass successfully according to FAO specification (1989) which reported that a maximum of 1 % retained on a 45 µm test sieve. These results are in line with Smith (1976) and Morpeth (1995).

3.6. Limits of persistent foam amount for copper fungicide during storage at 54 °C.

Data in table (2) showed limits of stability of persistent foam of copper fungicide formulation (WP) during storage for 14 days at 54 °C. The volume (ml) after 1 min of foam after one day before storage were 6ml. By the elapse of time of storage the foam amount slightly decreased to the end of experiment to reach 4 ml after 14 days storage. From this results it is clearly note that copper foam volume not affected by storage and become conformity with FAO specification (1989) which reported that maximum is 10 ml of foam after 1 min. The obtained results are agree with El-Attal (1979) and Kamal El-Din.A. Ibrahim and Ramadan (2011).

3.7. Wetting limits of the product for copper fungicide during storage at 54 °C.

Data in table (2) illustrate the wetting of copper fungicide through storage for 14 days. The results indicated that the powder was completely wetted for Copper formulation before one day of storage until 14 days at 54 °C. According to FAO specification (1989) which reported that the product shall be completely wetted in 1 min without swirling. The product was completely wetted in 1 min without swirling and become conformity with FAO specification. The obtained results are agree with Kamal El-Din.A.Ibrahim and Ramadan (2011).

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تأثير التخزين على تكسير مبيد النحاس والشوائب المصاحبة له

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تلقى الدراسة المقدمة الضوء على تأثير حرارة التخزين المختلفة على ثبات الخواص الطبيعه والكيميائية لمسحوق قابل للبلل مبيد أوكسى كلور النحاس٨٥ %. تم التخزين السريع لمستحضر المبيد الفطري أوكسى كلور النحاس٨٥ % مسحوق قابل للبلل الذى يحتوى على (نحاس معدنى٥٠ %) على درجة ٥٤ م° لمدة ١٤ يوم لدراسة ثبات نسبة المادة الفعالة من النحاس المعدني والشوائب السائدة المصاحبة له. أيضا شملت الدراسة بعض الخواص الطبيعية طبقا لمواصفات FAO لسنة (١٩٨٩) مثل اختبار التعلق ومدى pH واختبار النعومة المبتله واختبار البلل بدون تقليب واختبار ثبات الرغاوى. كما تم تقدير نسبة المادة الفعالة للمبيد والشوائب المصاحبة له باستخدام جهاز ICP MS .

النتائج تبين الأتي :

- تتأثر نسبة المادة الفعالة النحاس المعدني مسحوق قابل للبلل بحرارة التخزين بعد ٨ يوم من التخزين على درجة حرارة ٥٤ م° .
- وعلى العكس لم تتأثر الشوائب المصاحبة للنحاس المعدني حيث مرت بنجاح خلال جميع فترات التخزين على الرغم من وجود زيادة ضئيلة فى نسبة الشوائب وذلك كلما زادت فترة التخزين إلا أنها كانت مطابقة لمواصفة FAO 1989 .
- لم يتأثر اختبار قيمة pH والنسبة المئوية للتعلق وكذلك اختبار النعومة المبتلة ومقاومة الرغاوى بطول فترة التخزين حتى ١٤ يوم على درجة حرارة ٥٤ م° ومرت جميعها بنجاح.