The Thermal Impact on the Stability of Physical Properties in Flonicamid, hexythiazox, Nicosulfuron, and Quinclorac Formulations

التأثير الحراري على ثبات الخصائص الفيزيائية في مستحضرات الفلونيكاميد والهيكسيثيازوكس والنيكوسلفورون والكوينكلوراك

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Abstract :

The impact of storage temperatures on the stability of the physical properties of flonicamid, hexythiazox, nicosulfuron, and quinclorac formulations in Teppeki 50% WG, Efdal hexzarun 5% EC, Shield 4% OD, and Queen 75% WG, respectively was investigated. The wettability, dispersibility, suspensibility, pH value, free acidity, emulsion stability, crystallization, and dispersion stability were investigated before and after storage at 35, 40, 45, and 54°C for 14 weeks. The change in pH values and acidity for the studied formulations was confirmed with GC/MS analysis. According to the obtained results, there was a relationship between pH value or free acidity, storage period, and temperature. Nicosulfuron formulation must be stored at a temperature of 40°C or less and its formulations must have appropriate adjuvants to stabilize it and maximize its potency at higher temperatures. Economically, it is recommended that the quantity of pesticides purchased per season do not exceed the requirements in order to limit the period of these chemicals' storage. The pH and hardness of water sources influence pesticide effectiveness and some physical properties such as emulsion stability, re-emulsification, and dispersion stability; thus, water must be analyzed before spraying pesticides to determine cation and anion concentrations. Pesticide package labels must contain the pH range in which the pesticide is sprayed, as well as the appropriate temperature range for maintaining the pesticide's best storage shelf life.

Keywords: Storage temperatures, Suspensibility, pH value, GC/MS, Emulsion and dispersion stability.

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المستخلص:

تم التحقق في تأثير درجات حرارة التخزين على ثبات الخصائص الفيزيائية للفلونيكاميد، هيكسيسيازوكس، نيكوسلفيرون و كوينكلوراك في مستحضرات تيبيكي ٥٠% حبيبات قابلة للانتشار في الماء، افدال هيكزرن ٥% مركز قابل للاستحلاب، شيلد ٤% مركز زيتي قابل للانتشار في الماء وكوين ٧٥% حبيبات قابلة للانتشار في الماء على الترتيب. تم دراسة القابلية للبلل والتشتت والتعلق وقيمة الأس الهيدروجيني والحامضية الحرة وثبات الاستحلاب والتبلور وثبات الانتشار قبل وبعد التخزين عند ٣٥ و ٤٠ و ٤٥ و ٥٤ درجة مئوية لمدة ١٤ أسبوعًا. تم تأكيد التغيير في قيم الأس الهيدروجيني والحموضة للتركيبات المدروسة من خلال تحليل GC/MS. وفقًا للنتائج التي تم الحصول عليها، كانت هناك علاقة بين قيمة الأس الهيدروجيني أو الحموضة الحرة وفترة التخزين ودرجة الحرارة. يجب تخزين تركيبة النيكوسلفورون عند درجة حرارة 40 درجة مئوية أو أقل ويجب أن تحتوي تركيباتها على مواد مساعدة مناسبة لتثبيتها وتعظيم فعاليتها عند درجات حرارة أعلى. ومن الناحية الاقتصادية، يوصى بألا تتجاوز كمية مبيدات الآفات المشتراة في الموسم المتطلبات من أجل الحد من فترة تخزين هذه المواد الكيميائية. يؤثر الأس الهيدروجيني وصلابة مصادر المياه على فعالية مبيدات الآفات وبعض الخصائص الفيزيائية مثل استقرار المستحلب وإعادة الاستحلاب واستقرار التشتت ؛ وبالتالي، يجب تحليل المياه قبل رش مبيدات الآفات لتحديد تركيزات الكاتيون والأنيون. يجب أن تحتوي ملصقات عبوات المبيدات على نطاق الأس الهيدروجيني الذي يتم فيه رش المبيد، بالإضافة إلى نطاق درجة الحرارة المناسب للحفاظ على أفضل مدة تخزين للمبيد.

1. Introduction:

Storage stability testing provides some evidence on how the quality of a product varies with time under the influence of environmental factors such as temperature, humidity and light. The test requirement for stability during storage can normally be established in one or more ways, such as accelerated testing, ambient testing, cold stability testing, testing for reactivity towards container material **(Aksoy *et al.*, 2007)**. These studies provide indications of the effect of and the influence that these factors may have on the product quality, safety and performance.

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The main objective of testing is to determine how long the product will retain the percent active ingredient in its packaging and provide data on the change in product composition over time. If certain ingredients decompose under conditions such as high or low temperature or humidity, then new toxic chemicals may be formed whose effects must be considered**.**

A pH-safe spray solution for the majority of pesticide compounds is generally between 4.5 and 7.0, with the best possibly between 5.0 and 6.0. The high alkalinity of the spray solution can cause the pesticides' active ingredients to hydrolyze, which will decrease their effectiveness. Hydroxyl ions break down the pesticides molecules in an irreversible chemical reaction known as alkaline hydrolysis, which transforms them into other compounds that lack pesticidal properties. When pesticides such as organophosphates, carbamates and synthetic pyrethroids are mixed with alkaline spray solutions, they undergo hydrolysis **(Whitmore, 1986)**.

Decreased spray solution pH values would increase the spray solution's attraction to treated plants, resulting in more of the spray solution depositing and penetrating the tested surface, which would increase the effectiveness according to (**Molin and Hirase, 2004)**. **Green and Hale (2005)** reported that weak acid herbicides' solubility and ionic state are controlled by the pH of the spray mixture, which in turn affects their uptake and biological activity. When the herbicide's solubility limits absorption, increasing pH can increase solubility and improve activity when the pH of the spray water is below the pKa of the herbicide. The weak acid becomes more anionic when the pH is raised above the pKa, which may make it more difficult to pierce the lipophilic cuticle, the negatively charged membrane, and the cell wall. The weak acid is transformed into a neutral or unionized form by lowering pH below the pKa, which facilitates

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penetration through these lipophilic and negatively charged barriers. Other herbicide properties such as chemical stability, volatility, and chemical compatibility, are also influenced by the pH. As a result, when manufacturers modify the pH value of their adjuvant and herbicide compositions, they must balance a variety of factors.

Alvarado Aguilar *et al*. (2019) reported that the potential of hydrogen (pH) is a useful indicator of an EC's stability after extended storage. Long- term pH changes during storage periods or ageing treatments may indicate component incompatibility, bacterial proliferation, degradation of the active ingredient, or instability.

The emulsifiers used in agricultural formulations are blends of anionic and non-ionic types. The emulsifiers are used in the emulsifable concentrates and are mixed with water where a complex interfacial layer which governs emulsion stability covers the resultant droplets. The emulsifier blend must be carefully selected and used in right quantities to provide better stability at higher dilution rate they improve spontaneity, increase stability and good performance even in hard water.

Because of the different types of the water hardness found in different agricultural regions, stability of emulsifiability with different levels of water hardness is an important factor for an agricultural product. Some agricultural regions use groundwater that is frequently hardened, but some surface water supplies are also affected. Calcium concentrations in groundwater can reach and exceed 100 mg/L. In contrast, magnesium is typically found in lower concentrations in the groundwater than calcium (around 50 mg/L, and rarely around 100 mg/L), and calcium-based hardness predominates **(WHO, 2010)**.

Several factors can influence emulsion stability, including Hydrophile- Lipophile Balance (HLB) **(Losada-Barreiro *et al*.,**

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2013), active ingredient concentration **(Hallouard *et al*., 2015)** and surfactant type addition **(Feng *et al*., 2016)**. Emulsifiable concentrates, which can also include surfactants and other additives, are typically optically transparent oily liquid formulations that are made by dissolving a specific quantity of pesticide in organic solvents (such as benzene, toluene, xylene and solvent oil). Prior to use, these systems are diluted with water, which causes an oil-in-water emulsion to spontaneously develop and include insecticides inside the oil droplets **(Feng *et al*., 2018)**.

Zimdahl (2018) reported that when herbicide is dissolved in an organic solvent with enough emulsifier, it results in the formation of an emulsifiable concentration that may be added to water to produce an oil/water emulsion. Because the herbicide may react with the metallic ions in water, precipitating the active ingredient and clogging spray equipment, salts of acidic herbicides that are soluble in the water and can be made as solution concentrates are formulated as emulsifiable concentrates.

Water dispersible granules are solid, non-dusty granular formulations that quickly dissolve or disperse when mixed with water in a spray tank to create a suspension of small particles.

Dong *et al.* (2013) reported that the suspensibility of the formulation is inversely proportional with particle size because, as particle size decreases, Brownian motion may become dominant over the gravitational force, while **Yang *et al*. (2020)** found that the electrokinetic properties of the suspensions are directly related to their stability. The surface charge density of the particle can be increased to produce stronger repulsion forces that will stabilize the suspension.

Important indicators of re-dispersibility in water and spreadability on leaves of solid formulations are wettability and

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suspensibility. These features have a significant effect on pesticide retention in targeted organisms, which has an impact on pesticide efficacy **(Cui *et al*., 2018)**.

According to **(CIPAC MT 39.1, 1995)**, the allowed normal maximum amount of separated solid and liquid after storage at 0^{o}C for 7 days was 0.3 mL. The goal of cold storage is to ensure that the formulations properties are not harmed by storage during periods of extreme cold. The cold stability test should be performed at 0^{o}C or lower if a product is expected to be stored in a refrigerator, where the active ingredient may crystallize, or phase separation may occur **(BPU-HSE, 2004)**.

Hence, the purpose of this study is to investigate the effect of different storage temperatures on the physical properties of flonicamid, hexythiazox, nicosulfuroun, and quinclorac formulations in Efdal hexzarun 5% EC, Shield 4% OD, Teppeki 50% WG, and Queen 75% WG. Furthermore, GC/MS analysis will be performed to confirm the change in pH and free acidity.

2. Materials and methods

2.1. Stuied formulations:

Efdal hexzarun 5% EC, Shield 4% OD, Teppeki 50% WG and Queen 75% WG.

2.2. Thermal degradation studies:

Accelerated high-temperature storage procedures were carried out according to CIPAC MT 46.1 (1995). About 20 g of the solid formulation was put in a glass beaker, and about 50 mL of the liquid formulation was put in a glass bottle. The glass beakers and bottles were introduced into an electrical oven at the following temperatures: 35, 40, 45, and 54 °C. The oven temperature was regulated for the following predetermined period of (1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, and 14 weeks) per temperature. After withdrawal, each formulation was investigated to determine the effect of temperature on the

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stability of the physical properties and identify the thermal degradation products of the tested pesticide that were responsible for the changes in pH and free acidity if they occurred.

2.3. Preparation of standard water used.

CIPAC MT 18.1 (1995), MT 18.3 Non-CIPAC Standard Waters,18.3.1 WHO Standard Hard Water (342 ppm hardness) was used for the determination of emulsion stability and persistent foaming of formulations under study. WHO standard hard water was prepared by dissolving 0.304 g of anhydrous calcium chloride ($CaCl_2$) and 0.139 g of magnesium chloride hexahydrate ($MgCl_2$. 6 H_2O) in distilled water and made up to 1000 mL.

2.4. Determination of the physical properties for pesticides under study

2.4.1. Determination of the wettability for the WG formulations.

The wettability of WG formulations was determined according to **CIPAC MT 53.3 (1995)**. 5±0.1g of a non-compacted representative sample of the formulation were added all at once by dropping it on the hard water (100± 0.1 ml) from a position level with the beaker's rim, without agitating the liquid surface. When the granules were added, the stop watch was started, and the time taken for it to become completely wet was noted. The suitable wetting time required for complete wetting of the formulation was 1 min.

2.4.2. Determination of the dispersibility for the WG formulations.

The degree of dispersion was determined according to **CIPAC MT 174 (1995)**. Tarred beaker filled with 900 mL of the hard water, with the stirrer centrally located and positioned so that the bottom of the stirrer blades are 15 mm above the beaker's base. The stirrer was switched on, and a sample of WG

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(approximately 9 g weighed to ± 0.1 g) was added to the stirred water. The stirring continued for 1 min, then the stirrer was switched off, and the suspension was allowed to stand undisturbed for 1 min. Nine-tenths (810 ml) of the suspension is withdrawn by means of a vacuum pump. The solid particles obtained in the remaining 90 mL of the beaker were determined gravimetrically. The dispersibility of the WG calculated by the formula:

Dispersibility = 10/9 × (m-W)/m × 100%, where W= mass of residue after drying (g) and m= mass of sample taken

2.4.3. Determination of the suspensibility for the WG formulations.

Suspensibility of the formulation was determined according to **CIPAC MT 168 (1995)**. A sufficient sample of the formulation was weighted in a beaker, and a small quantity (about 5 mL) of hard water was added. After shaking the suspension, it was transferred quantitatively to a measuring cylinder of 250 mL; the volume was completed to 250 mL with the hard water; the cylinder was inverted 30 times in 1 min; and then placed in a water bath maintained at 30±2°C for 30 min. At the end of this time, the separated materials or sediment, if any, were measured.

Gravimetric analysis was used to determine the amount of particles in the sediment. After removing nine-tenths of the suspension, the residual tenth was transferred into a tared Petri dish by rinsing with distilled water and drying to constant weight. The residue's mass was noted.

Suspension stability= 111 (1- (a /w)), where: a= dry mass of the lower 25 ml of the suspension (g). w= the mass of the sample taken (g).

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2.4.4. Determination of the emulsion stability for EC formulation.

The test was carried out according to **CIPAC MT 36 (1995)**. 5 mL of the formulation was added to 95 mL of WHO standard hard water in a 100 mL measuring cylinder to produce 100 mL of an aqueous emulsion. The cylinder was stoppered and inverted 30 times in one min and then placed in water bath at 30±2°C for 30 min. The volume, if any, of free oil, froth, cream that separated at the top of the emulsion or the volume, if any, of solid matter or sedimentation that separated at the bottom of the emulsion was recorded at the end of the 30 min period.

2.4.5. Determination of the dispersion stability for OD formulation.

The test was carried out according to **CIPAC MT 180 (1995)**. 5 g of the formulation was added to 240 mL of WHO standard hard water in a 250 mL measuring cylinder to produce dispersion and then the cylinder was filled to the mark with standard water. The cylinder was stoppered and inverted 30 times in one min and then placed in a water bath at 30±2°C for 30 min. The volume, if any, of free oil or cream that separated at the top of the cylinder, or sedimentation that separated at the bottom of the cylinder was recorded at the end of the 30 min period.

2.4.6. Determination of the pH value for the studied formulations.

The pH value of a mixture of a sample or of an undiluted aqueous formulation was determined by using a pH meter **(Model: Jenway 3510).** The system was initially standardized using buffered solution of pH 4 and 7. one gram of sample was weighed and transferred into a measuring cylinder containing about 50 mL distilled water, the volume was completed to 100

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mL with water and shaken vigorously for 1 min until completely mixed. The suspension, if any, was allowed to be settled for 1 min at room temperature then the electrode was immersed into the sample and the pH of the supernatant was measured. The electrode was thoroughly washed between samples using a stream of distilled water to remove all traces of the previous sample **(CIPAC MT 75, 1995)**.

2.4.7. Determination of the free acidity in the studied pesticides.

The free acidity was determined according to **CIPAC MT 31.2 (1995),** using **(HANNA 901)** automatic titrator with glass electrode and pH meter. 10 g of the pesticide was dissolved in a beaker containing 50 mL of acetone and 5 mL of distilled water was then added to the beaker contents and stirred to homogenize. The final solution was titrated electrometrically with NaOH 0.5 mol/L (0.5 N) to the apparent pH of the acetone/buffered mixture (100 mL acetic acid (2 N) and 100 mL NaOH (1 N)) and made up to 1000 mL with distilled water at 20°C.

Acidity (g/kg) was calculated as H_2SO_4 = (4.904× t × N × 10) / w, where:

N= Normality of sodium hydroxide (0.5 N).

t= Volume (mL) of the end point titrated with NaOH solution.

w= 10 g of the pesticide.

2.4.8. The influence of cold storage on the crystallization of formulations under investigation.

For the stability test at 0ºC, 100 mL of each pesticide formulation under test was transferred to a centrifuge tube and the tube and its contents were placed in a refrigerator at 0±1°C for 1 hour. During this period, the contents of the tube were stirred at intervals of 15 min. After this period, the volume of any separated solid or oily matter was recorded. Then the tube and its contents were placed in the refrigerator and remained at

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0±1°C for a total period of 7 days. At the end of 7 days, the tubes were removed from the refrigerator and allowed to remain undisturbed at room temperature for 3 hours. The volume of any separated material at the bottom of the tubes was subsequently recorded. The permitted normal maximum amount of separated solid and liquid is 0.3 mL after storage at 0ºC for 7 days **(CIPAC MT 39.1, 1995)**.

3. Results and Discussion:

3.1. Effect of thermal conditions on flonicamid's physical properties in the Teppeki 50% WG formulation.

3.1.1. Effect on the wettability.

The results indicate that the Teppeki 50% WG formulation passed the wettability test before and after 14 weeks of storage at 35, 40, 45, and 54°C. The results showed that the wettability of flonicamid was unaffected during the study periods at different temperatures and the formulation completely wetted in less than 1 min without swirling.

The obtained results are consistent with the specifications of **APVMA (2005)** and **JMPS (2016)**, which stated that the formulation is acceptable if complete wetting occurs in 1 min without swirling. Overall, the results indicate that the formulation wets easily when used in the spray tank or other equipment, and the wetting agents in the formulation are unaffected by storage at high and low temperatures, as well as the length of storage duration.

3.1.2. Effect on the dispersibility.

The results indicate that the Teppeki 50% WG formulation passed the dispersibility test before and after 14 weeks of storage at 35, 40, 45, and 54°C. The results showed that the dispersibility of flonicamid was unaffected during the study periods at different temperature degrees, and there was no sedimentation or separation. This complied with **APVMA (2005)** and **JMPS**

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(2016), which stated that the average determined active dispersibility must not be lower than 60% nor higher than 105% after 1 min of stirring if any sediment appeared.

Overall, the obtained results demonstrate that the formulation disperses easily and quickly when diluted with water; therefore, when it applied using appropriate application equipment, the preparation will be homogeneous and free of blockages.

3.1.3. Effect on the Suspensibility.

Suspensibility is determined to show that enough active ingredients are suspended in the spray liquid to produce a satisfactory, homogeneous mixture throughout spraying.

Results indicate that the teppeki formulation passed the suspensibility test before and after 14 weeks of storage at 35, 40, 45, and 54°C. There was no sediment or precipitated materials formed at the end of the 30-minute suspension test before and after the storage period at each temperature and this complied with the requirements of **APVMA (2005)** and **JMPS (2016)** that reported that the average determined active suspensibility must not be below 60% and not more than 105%. Overall, the results showed that the suspensibility of flonicamid was unaffected during the study periods under elevated temperatures and this an indication that the formulation will be homogeneous on application through appropriate equipment and the dispersing agents are unaffected by storage at higher and lower temperature degrees, as well as storage periods of varying length.

3.1.4. Effect on the free acidity.

Table (1) and **Fig.(1)** show the free acidity calculated as H_2SO_4 in the Teppeki 50% WG formulation before and after storage for 14 weeks at 35, 40, 45 and 54°C. The results indicate that the free acidity of flonicamid before storage was 0.4555 g/kg.

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Table (1): Effect of storage at 35, 40, 45 and 54 °C on the free acidity of flonicamid in Teppeki 50% WG.

Storage conditions	Volume (mL) of NaOH (0.43 N) consumed during titration	Acidity of flonicamid as H_2SO_4 (g/kg)
Before storage	0.216	0.4555
After 14 weeks of storage at 35°C	0.418	0.8814
After 14 weeks of storage at 40°C	0.524	1.1050
After 14 weeks of storage at 45°C	0.640	1.3496
After 14 weeks of storage at 54°C	0.798	1.6828

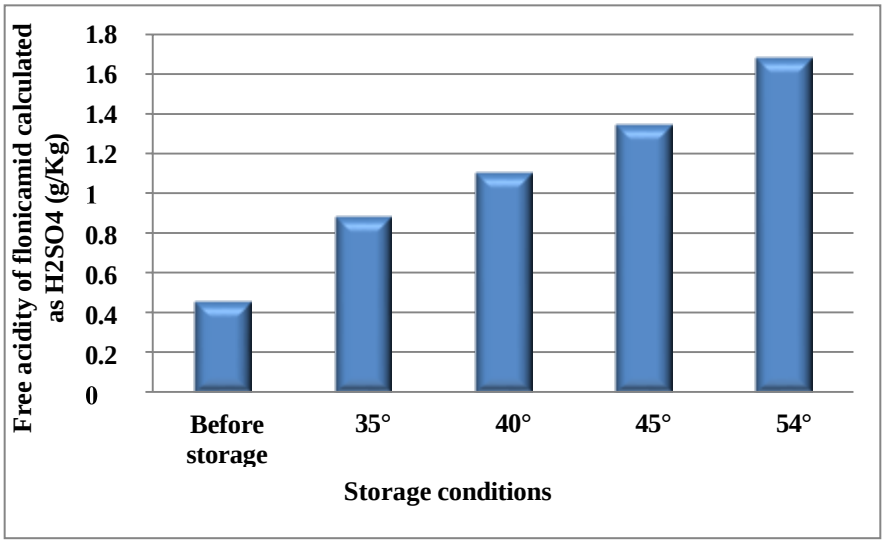

Fig.(1): Effect of storage at 35, 40, 45 and 54 °C on the free acidity of flonicamid in Teppeki 50% WG.

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The results clearly demonstrated that acidity values changed during storage, increasing as the temperature increased, indicating the instability of flonicamid, which has a pKa value of 11.9.

The increase in acidity values was confirmed by GC/MS analysis in **Mansour *et al*. (2024)**, which demonstrated the formation of 4-(trifluoromethyl) pyridine, N'-acetyl-2-cyanoacetohydrazide, and 4-acetylpyridine, all with pKa values of 2.92, 4.45, and 3.505, respectively. The lower the pKa of the thermal degradation products of flonicamid, the greater their ability to donate their protons and hence their acidity. Additionally, GS/MS revealed the formation of N-(2-aminoethyl)isonicotinamide, which hydrolyzed in water to produce the appropriate acid.

According to the results, there was a positive relationship between the acidity of flonicamid, storage period, and temperature. Generally, the free acidity of flonicamid increased as storage time and temperature increased.

3.2. Effect of thermal conditions on hexythiazox's physical properties in the Efdal hexzarun 5% EC formulation.

3.2.1. Effect on the emulsion stability.

The data in **Table (2)** shows the emulsion stability of Efdal hexzarun 5% EC formulation before and after storage for at 35, 40, 45 and 54°C.

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Table (2): Effect of storage at 35, 40, 45 and 54°C on the emulsion stability of Efdal hexzarun 5% EC formulation.

Storage conditions (weeks)		Cream layer (mL)	Free oil (mL)	Sedimen t (mL)
Before storage		0	0	0
At 35°C	After 12 weeks	0	0	0
	After 14 weeks	1	0	0
At 40°C	After 8 weeks	< 1	0	0
	After 14 weeks	< 2	0	0
At 45°C	After 6 weeks	< 1	0	0
	After 14 weeks	2.5	0.5	0
At 54°C	After 2 weeks	< 1	0	0
	After 14 weeks	3.5	1	0

The results showed that the Efdal hexzarun 5% EC formulation passed the FAO emulsion stability test before and after storage at 35, 40, 45 and 54°C for 12, 8, 6, and 2 weeks, respectively. This complies with **APVMA (2005)** and **JMPS (2016)** which reported that the maximum level of cream or free oil and precipitate layer does not exceed 2 mL after 30 min of dilution. However, after storage for 14 weeks at 45 and 54°C, the emulsion stability failed to fulfill the specifications of an emulsifiable concentrate.

According to the data, the Efdal hexzarun 5% EC formulation has good emulsion stability after each specified temperature and time duration due to the hexythiazox stability, adjuvants, and emulsifying constituents.

3.2.2. Effect on the pH value.

Data in **Table (3)** show the pH values of the Efdal hekzarun 5% EC formulation before and after storage at 14

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weeks of storage at 35, 40, 45, and 54°C. The results show that the pH value of the formulation before storage was 6.02.

Table (3): Effect of storage at 35, 40, 45 and 54 °C on the pH value of hexythiazox in Efdal hekzarun 5% EC.

Storage conditions (weeks)	pH value of Efdal hekzarun 5% EC
Before storage	**6.02**
After 14 weeks of storage at 35°C	**5.59**
After 14 weeks of storage at 40°C	**5.37**
After 14 weeks of storage at 45°C	**5.29**
After 14 weeks of storage at 54°C	**5.15**

The results showed that the pH value of the formulation decreased with increasing in temperature and storage period. This change in pH value is an indication for instability of hexythiazox and formation of acidic degradation products during thermal storage. The obtained results are in agreement with **Agri Sciences (2015)** that reported that the pH value of 10% solutions of hexythiazox in the formulation of agrilex 50g/L EC ranged from 5 to 9. As well, **Lainco (2019)** reported that the pH values of hexythiazox in the formulation of shoshi 10% EC ranged from 5 to 6.

3.2.3. Effect on the free acidity.

Table (4) and **Fig.(2)** show the free acidity calculated as H_2SO_4 in Efdal hekzarun 5% EC before and after storage for 14 weeks at 35, 40, 45 and 54°C. Results indicate that the free acidity of hexythiazox before storage was 0.4977 g/kg.

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Table (4): Effect of storage at 35, 40, 45 and 54 °C on the free acidity of hexythiazox in Efdal hekzarun 5% EC.

Storage conditions (Weeks)	Volume (mL) of NaOH (0.43N) consumed during titration	Acidity of hexythiazox as H_2SO_4 (g/Kg)
Before storage	0.236	0.4977
After 14 weeks of storage at 35°C	0.252	0.5314
After 14 weeks of storage at 40°C	0.267	0.5630
After 14 weeks of storage at 45°C	0.280	0.5904
After 14 weeks of storage at 54°C	0.297	0.6263

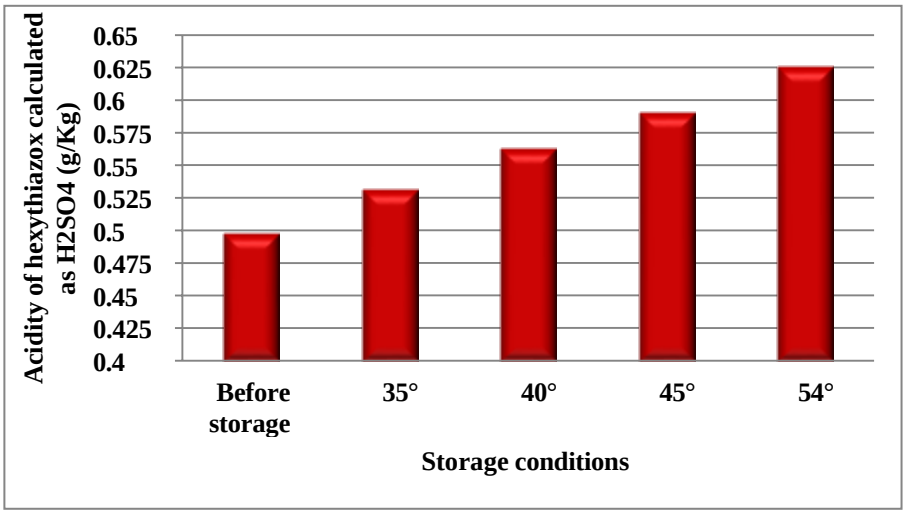

Fig.(2):Effect of storage at 35, 40, 45 and 54 °C on the free acidity of hexythiazox in Efdal hekzarun 5% EC

The results clearly showed that there was a change in the acidity values during thermal storage as they increased when the temperature increased. The increase in the acidity values was

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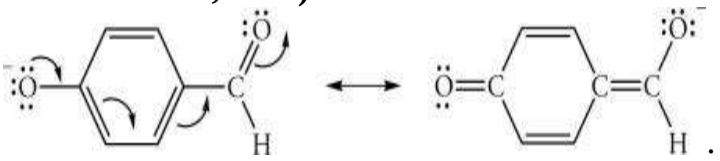
confirmed with the GC/MS analysis which revealed the formation of:

- ❖ N-methyl-N-phenyl formamide which has a pKa value of 0.53.
- ❖ N-benzyl formamide which is a very weak acid and partially soluble in water.
- ❖ Isocyanates reacted with water to form carbon dioxide that soluble in water leading to formation of carbonic acid (**Six and Richter, 2003**).

$$RCNO+H_20 \rightarrow RNH_2+CO_2$$
$$CO_2+H_20 \rightarrow H_2CO_3$$

- ❖ 4-chloro-2-hydroxy benzaldehyde, where the aldehyde group can aid in charge delocalization, thereby stabilizing the conjugate base. The resonance stabilization of the conjugate base promotes ionization and raises the acid dissociation constant **(Ouellette and Rawn, 2014)**.



Overall, there was a positive relationship between pH or free acidity value, storage period, and temperature. Generally, the acidity value increased (pH decreased) as storage time and temperature increased.

3.2.4. Effect of cold storage on the crystallization of Efdal hekzarun 5% EC.

The results demonstrated that the formulation of Efdal hekzarun 5% EC after storage at 0°C for 7 days did not exhibit crystallisation, delamination, any separated material at the bottom of the tube, or oily substance. These observations are consistent with **CIPAC MT 39.1 (1995)**, which stated that 0.3 mL of separated solid and liquid is the highest allowable normal

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amount. The mobility and emulsifying characteristics in Efdal hekzarun 5% EC were mostly unaffected by storage at 0°C or low temperature.

3.3. Effect of thermal conditions on nicosulfuron's physical properties in Shield 4% OD formulation.

3.3.1. Effect on the dispersion stability.

The data in **Table (5)** show the effective of thermal storage at 35, 40, 45 and 54°C on the dispersion stability for Shield 4% formulation. Results reveal that creamy and oily layers formed at the top of the cylinder at the end of the 30 min period of the dispersion test, and the volume of these layers increased as the temperature and storage duration increased.

Table (5): Effect of storage at 35, 40, 45 and 54°C on the dispersion stability of Shield 4% OD formulation

Storage conditions		Cream layer (mL)	Free oil (mL)	Sediment (mL)
Before storage		0	0	0
At 35°C	After 12 weeks	< 1	< 1	0
	After 14 weeks	2	1.5	0
At 40°C	After 8 weeks	1	1	0
	After 14 weeks	3	< 2	0
At 45°C	After 6 weeks	1.5	1	0
	After 14 weeks	4	2	0
At 54°C	After 2 weeks	2	1	0
	After 14 weeks	6	3	0

The results reveal that the formulation passed the dispersion stability after storage for 12 and 8 weeks at 35 and 40°C, respectively. This complies with **APVMA (2005)** and **JMPS (2016)**, which reported that the maximum level of cream

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or free oil and precipitate layer does not exceed 2 mL after 30 min of dilution. However, dispersion stability after storage for 6 and 2 weeks at 45 and 54°C, respectively, failed to fulfill the specification due to increasing the volume of creamy and oil layers above the maximum level. Also, the shield 4% OD did not comply with the specification of the dispersion stability after storage for longer than the specified periods reported by the **FAO/WHO (2010)** specification.

The increasing volume of the creamy and oily layers indicates that thermal storage had an impact on the active ingredient and dispersion agents. The color of the formulation and dispersion changed after 6 and 2 weeks of storage at 45 and 54°C, respectively. This meant that nicosulfuron was degraded and different degradation products were produced. Therefore, the best dispersion stability was achieved when stored at 35 and 40°C or 12 and 8 weeks, respectively.

3.3.2. Effect on the pH value.

The data in **Table (6)** show the pH values of the Nicosulfuron 4% OD formulation before and after storage at 14 weeks of storage at 35, 40, 45, and 54°C. The results clearly showed that the pH value of the formulation before storage was 6.51 and decreased when the temperature increased, indicating the instability of nicosulfuron, which has a pKa value of 4.22.

Table (6): Effect of storage at 35, 40, 45 and 54°C on the pH value of nicosulfuron in Shield 4% OD

Storage conditions	pH value of nicosulfuron 4%OD
Before storage	**6.51**
After 14 weeks of storage at 35°C	**5.70**
After 14 weeks of storage at 40°C	**5.26**
After 14 weeks of storage at 45°C	**4.87**
After 14 weeks of storage at 54°C	**4.69**

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The decrease in pH values was confirmed with GC/MS analysis which revealed the formation of the following: 2-Amino-4,6-dimethoxypyrimidine, Methanethioamide, N,N-dimethyl- and N,N-Dimethyl(methylthio)acetamide which have pKa values of 4.02, 1.71, and -0.8, respectively. The lower the pKa values of thermal degradation products of nicosulfuron, the greater their ability to donate their protons and hence their acidity increased; therefore, the pH values decreased.

According to the results, there was a positive relationship between the pH, storage period, and temperature. Generally, the pH value of nicosulfuron decreased as storage time and temperature increased.

3.4. Effect of thermal conditions on quinclorac's physical properties in the Queen 75% WG formulation.

3.4.1. Effect on the wettability.

Results indicate that the Queen formulation passed the wettability test before and after 14 weeks of storage at 35, 40, 45, and 54°C. The results showed that the wettability of quinclorac was unaffected during the studied periods at different temperature and the formulation completely wetted in less than 1 min without swirling. This met the specifications of **APVMA (2005), FAO (2002) and JMPS (2016)** which stated that a preparation is acceptable if complete wetting occurs in 1 min without swirling.

The results show that the studied formulation wets easily when used in the spray tank or other equipment and the wetting agents in the formulation are unaffected by storage at high and low temperatures, as well as storage periods of varying length.

3.4.2. Effect on the dispersibilty.

The results indicate that the Queen formulation passed the dispersibilty test before and after 14 weeks of storage at 35, 40, 45, and 54°C. The results showed that the dispersibility of

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quinclorac was unaffected during study periods at different temperature degrees, and there were no sedimentation or separation materials. This complied with **APVMA (2005)** and **JMPS (2016)**, which stated that the average determined active dispersibility must not be lower than 60% nor higher than 105% after one min of stirring if any sediment appeared, and with **FAO (2002),** which stated that a minimum of 70% of the formulation shall be dispersed after 1 min of stirring.

The results demonstrate that the Queen 75% WG disperses easily and quickly when diluted with water; therefore, when it applied using appropriate application equipment, the final preparation will be homogeneous and free of blockages.

3.4.3. Effect on the suspensibility.

Table (7) shows the percentage of suspensibility in the formulation of Queen 75% WG before and after 14 weeks of storage at 35, 40, 45, and 54°C. The results show that the suspensibility of quinclorac before storage was 99.04%.

Table (7): Effect of storage at 35, 40, 45 and 54 °C on the suspensibility of quinclorac in Queen 75% WG.

Storage conditions (Weeks)	Suspensibility of quinclorac (%)
Before storage	**99.04**
After 14 weeks of storage at 35°C	**98.50**
After 14 weeks of storage at 40°C	**97.83**
After 14 weeks of storage at 45°C	**96.89**
After 14 weeks of storage at 54°C	**95.51**

The results indicate that the Queen 75% WG formulation passed the suspensibility test before and after 14 weeks of storage at 35, 40, 45, and 54°C. This complied with the requirements of **APVMA (2005)** and **JMPS (2016)** specifications, which reported that the average determined active suspensibility must not be below 60% and not more than 105%, and with the specification of the **FAO (2002),** which stated that a

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minimum of 70% of the quinclorac content found shall be in the suspension after 30 min of the test. The results showed that the suspensibility of quinclorac was slightly affected during the study periods but remained within the specification limits, and the dispersing agents added to the formulation are unaffected by storage at higher and lower temperatures as well as storage periods of varying length; thus, the WG formulation of Queen will be homogeneous upon application using appropriate application equipment.

3.4.4. Effect on the pH value.

The pH values of the Queen 75% WG formulation before and after 14 weeks of storage at 35, 40, 45, and 54°C are shown in **Table (8)**. The results show that the pH value of the formulation before storage was 3.57.

Table (8): Effect of storage at 35, 40, 45 and 54 °C on the pH value of quinclorac in Queen 75% WG.

Storage conditions (Weeks)	pH value of quinclorac
Before storage	**3.57**
After 14 weeks of storage at 35°C	**3.54**
After 14 weeks of storage at 40°C	**3.48**
After 14 weeks of storage at 45°C	**3.41**
After 14 weeks of storage at 54°C	**3.32**

The results clearly showed that the pH value of the formulation slightly decreased after thermal storage because quinclorac was a weak acid and, at higher temperatures, its disassociation in water solution increased.

Results indicate that the Queen formulation passed the pH test before and after 14 weeks of storage at 35, 40, 45, and 54°C. This complied with the specification of **FAO (2002),** which stated that the pH range of quinclorac was from 3 to 6.

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3.4.5. Effect on the free acidity.

Table (9) and **Fig.(3)** show the free acidity calculated as H_2SO_4 in the Queen 75% WG formulation before and after storage for 14 weeks at 35, 40, 45 and 54°C. Results indicate that the acidity of quinclorac before storage was 0.4555 g/kg.

Table (9): Effect of storage at 35, 40, 45 and 54 °C on the free acidity of quinclorac in Queen 75% WG.

Storage conditions	Volume (mL) of NaOH (0.43N) consumed during titration	Acidity of quinclorac as H_2SO_4 (g/kg)
Before storage	1.921	4.0509
After 14 weeks of storage at 35°C	1.967	4.1479
After 14 weeks of storage at 40°C	1.990	4.1964
After 14 weeks of storage at 45°C	2.061	4.3451
After 14 weeks of storage at 54°C	2.207	4.6539

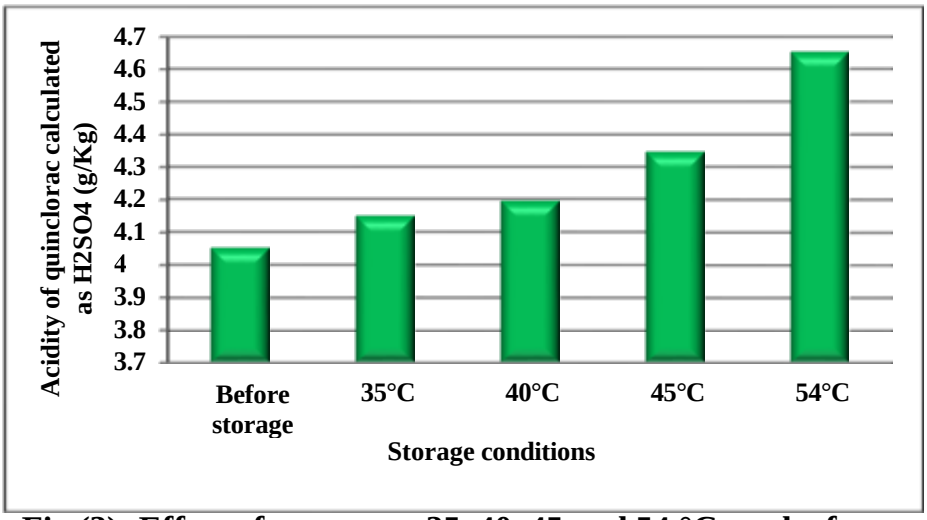

Fig.(3): Effect of storage at 35, 40, 45 and 54 °C on the free acidity of quinclorac in Queen 75% WG.

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The results clearly showed that there was a change in the acidity values during storage as they increased when the temperature increased. The results were confirmed by the GC/MS analysis in **Mansour *et al*. (2023)**, which revealed the formation of 7-chloroquinoline-8-carboxylic acid with a pKa value of -2.92. The lower the pKa, the greater the acidity. The greater the number of chlorine atoms in a molecule, the greater the electronegativity at the molecule end, resulting in the molecule's characteristics being highly ionic: the density, boiling point, and acidity increased. According to the obtained results, there was a relationship between free acidity, storage period, and temperature. Generally, the acidity of quinclorac increased (pH decreased) as storage duration and temperature increased.

4. Conclusion:

The impact of storage temperatures on the stability of the physical properties of flonicamid, hexythiazox, nicosulfuron, and quinclorac formulations in Teppeki 50% WG, Efdal hexzarun 5% EC, Shield 4% OD, and Queen 75% WG, respectively was investigated. The wettability, dispersibility, suspensibility, pH value, free acidity, emulsion stability, crystallization, and dispersion stability were investigated before and after storage at 35, 40, 45, and 54°C for 14 weeks. The change in pH values and acidity for the studied formulations was confirmed with GC/MS analysis. According to the obtained results, there was a relationship between pH value or free acidity, storage period, and temperature. Nicosulfuron must be stored at a temperature of 40°C or less and its formulations must have appropriate adjuvants to stabilize it and maximize its potency at higher temperatures. Therefore, the storage and handling of the formulation must be taken into consideration and be at suitable temperatures away from water and high humidity. Economically, it is recommended that the number of pesticides acquired per

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season not exceed the requirements in order to limit the duration of storage for these chemicals. The pH value and hardness of water sources in agricultural areas can vary; therefore, water must be analyzed before spraying pesticides to determine the concentrations of cations and anions because water pH and hardness affect effectiveness of the pesticide and some physical properties such as emulsion stability and re-emulsification, and dispersion stability. Pesticide package labels must contain the pH range in which the pesticide is sprayed, as well as the appropriate temperature range for maintaining the pesticide's best storage shelf life.

ISSN: 2537-0804 **eISSN: 2537- 0855**

References:

Agri science (2015). Material Safety Data Sheet of Agrilex 50 g/L EC based on preparation and distribution of safety data sheets about hazardous materials and preparations (O.G. issue no 27092 dated 26/12/2008). P: 1-8.

Aksoy, A.; Yavuz, O.; Guvenc, D. & Das, Y. K. (2007). Effects of the high temperature on the physical and chemical properties of some public health insecticide formulations. Asian J. Chem., Vol. 19(7): 5681-5687.

Alvarado Aguilar, M. C.; Recalde Coronel, P. C.; Leal Alvarado, D. A.; Villa Sanchez, F. E. & Tamayo Alcivar, R. (2019). Oil-in-water (o/w) emulsionable concentrate of Ishpink (Ocotea quixos) with thermodynamic stability. Rev Caatinga [Internet].Vol. 32(3):590–8. https://doi.org/10.1590/1983-21252019v32n303rc

Australian Pesticides Veterinary Medicines Authority (APVMA) (2005). Guidelines for the generation of storage stability data of agricultural chemical products. The data requirements that the APVMA adopts are derived from the 'Manual on development and use of FAO and WHO specifications for pesticides', first edition (2002).

Biocides and Pesticides Unit of Health & Safety Executive (BPU-HSE) (2004). Guidance on the storage stability data requirements for non- agricultural pesticide products. Available from: https://pdf4pro.com/cdn/pesticides-guidance-on-the-storage- stability-data-2fd1e7.pdf

CIPAC Hand book MT 168 (1995): Determination of the suspension stability of water dispersible granules. Vol. F: 417.

CIPAC Hand book MT 174 (1995): Dispersibility of water dispersible granules. Vol. F: 435.

ISSN: 2537-0804 eISSN: 2537- 0855

CIPAC Hand book MT 18.1 (1995): Preparation of standard waters A to G (MT 18.1.1 to 18.1.7). Vol. F: 59-63.

CIPAC Hand book MT 180 (1995): Dispersion stability, Vol., H, p.310.

CIPAC Hand book MT 31.2 (1995): Electrometric procedure. Vol. F: 98.

CIPAC Hand book MT 36 (1995): Emulsion characteristics of Emulsifiable Concentrate. Vol. F: 108-109.

CIPAC Hand book MT 39.1 (1995): Emulsifiable concentrate and solutions. Vol. F: 128-129.

CIPAC Hand book MT 46.1 (1995): General method of accelerated storage procedure.Vol. F: 149.

CIPAC Hand book MT 53.3 (1995): Wetting of wettable powder. Vol. F: 164.

CIPAC Hand book MT 75 (1995): Determination of pH values. Vol. F: 205-206.

Cui, B.; Wang, C.; Zhao, X.; Yao, J.; Zeng, Z.; Wang, Y.; … & Cui, H. (2018): Characterization and evaluation of avermectin solid nanodispersion prepared by microprecipitation and lyophilisation techniques. PLOS ONE, Vol. 13(1): e0191742. https://doi.org/10.1371/journal.pone.0191742

Dong, L. F.; Li, H. M.; Wang, Z. & Zhang, B. H. (2013). Determination of the types and dosages of dispersants and thickeners in pesticide SC. Mod. Agr., Vol. 12: 14-17.

FAO (2002). Specification and evaluation for quinclorac. Available from: https://www.fao.org/fileadmin/templates/agphome/documents/Pests Pesticides/Specs/quinclor.pdf

FAO/ WHO (2010). Manual on development and use of FAO and WHO specifications for pesticides, First edition, WHO/FAO -Rome.

ISSN: 2537-0804 **eISSN: 2537- 0855**

Feng, J.; Zhang, Q. I.; Liu, Q. I.; Zhu, Z.; McClements, D. J. and Jafari,S. M. (2018). Application of nanoemulsions in formulation of pesticides. Nanoemulsions p: 379-413. Academic Press. https://doi.org/10.1016/B978-0-12-811838-2.00012-6

Feng, W.; Wei, Z.; Song, J.; Qin, Q.; Yu, K.; Li, G.; Zhang, J.; Wu, W. & Yan, Y. (2017). Hydrolysis of nicosulfuron under acidic environment caused by oxalate secretion of a novel Penicillium oxalicum strain YC-WM1. Scientific Reports, Vol.7 (1):1-11.

Green, J. & Hale, T. (2005). Increasing the biological activity of weak acid herbicides by increasing and decreasing the pH of the spray mixture. J. ASTM Intern., Vol. 2(6): 62-71. Available from: www.astm.org and from https://doi.org/10.1520/JAI12907

Hallouard, F.; Dollo, G.; Brandhonneur, N.; Grasset, F. & Le Corre, P. (2015): Preparation and characterization of spironolactone-loaded nano-emulsions for extemporaneous applications. Int. J. Pharm., Vol. 478(1):193-201.

JMPS (2016). FAO and WHO Joint Meeting on Pesticide Specifications; Manual on development and use of FAO and WHO specifications for pesticides (3rd revision of the first edition), Rome. Italy, Specification guidelines for liquid formulated pesticides, Emulsions in water (EC).

Lainco (2019). Material Safety Data Sheet of Shoshi 10% WP based on regulation (EC) No. 1907/2006 and its modifications. Revision 2, p: 1-11. Available from: https://www.lainco.es/files/pdf/3233d93cb28096cc6d54170947d224ed.pdf

Losada-Barreiro, S.; Sánchez-Paz, V. & Bravo-Díaz, C. (2013). Effects of the emulsifier hydrophile-lipophile balance and the emulsifier concentration on the

ISSN: 2537-0804 eISSN: 2537- 0855

distributions of gallic acid, propyl gallate, and α-tocopherol in corn oil emulsions. J. Colloid Interface Sci., Vol. 389 (1):1-9.

Mansour, H. A. B., El-Dars, F., & Radwan, O. (2023). A study of quinclorac degradation during thermal and forced hydrolysis and soil photolysis. Egyptian Journal of Soil Science, 63(4), 593-608.

Mansour, H., El-Dars, F., & Radwan, O. (2024). Thermal And Forced Hydrolytic Degradation Studies Of Flonicamid And Its Photolysis In Egyptian Clay-Loam Soil. Egyptian Journal of Chemistry, 67(1), 563-580.

Molin, W. T. & Hirase, K. (2004). Comparison of commercial glyphosate formulations for control of prickly sida, purple nutsedge, morningglory and sicklepod. Weed Biol. Manag., Vol. 4(3): 136– 141. | https://doi.org/10.1111/j.1445-6664.2004.00130.x

Ouellette, R. J., and Rawn, J. D. (2014). Organic chemistry study guide: Key concepts, problems, and solutions. Elsevier.p.614.

Six, C. and Richter, F. (2003). Isocyanates, Organic. Ullmann's encyclopedia of industrial chemistry. Weinheim: Wiley-VCH. Available from: https://doi.org/10.1002%2F14356007.a14_611

Whitmore, T. E. (1986). Dealing with alkaline sprays. J. arboric., Vol. 12(8): 202-205.

World Health Organization (WHO) (2010). Hardness in drinking-water: background document for development of WHO guidelines for drinking-water quality (No. WHO/HSE/WSH/10.01/10). Available from: https://apps.who.int/iris/bitstream/handle/10665/70168/WHO_HSE_ WSH_10.01_10_Rev1_eng.pdf

ISSN: 2537-0804 **eISSN: 2537- 0855**

Yang, L.; Ji, W.; Mao, M. & Huang, J. N. (2020). An updated review on the properties, fabrication and application of hybrid-nanofluids along with their environmental effects. J. Clean. Prod., Vol. 257:120408. | https://doi.org/10.1016/j.jclepro.2020.120408

Zimdahl, R. L. (2018). Herbicide Formulation in Fundamentals of weed science. p. 501–509. Academic press. | https://doi.org/10.1016/b978- 0-12-811143-7.00017-2

ISSN: 2537-0804 eISSN: 2537- 0855