Studing the effect of chemical additives on physico-chemical properties and pesticidal efficiency of some recommended pesticides

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The present work was conducted to investigate the role of chemical additives to increase the insecticidal efficiency and reduced the dosage rate of recommended concentrations to about 75% of candidate insecticides against the cotton leafworm, Spodoptera littorals in order to reduce the hazards and costs. Insecticides used: Dursban 44.5% EC, Curacron 72% EC, Axone 5% EC and Super alpha 10% EC. Additive materials included lipophilic agents (kerosene, xylene and CAPL1), acidifying agents (citric acid, sulphonic acid, oxalic acid and tartaric acid), Surfactant agents poly ethylene glycol 600 dilurate (DL600), poly ethylene glycol 600 monolurate (ML600) and Sisi6, sticking agents (glue and Arabic gum) and thickening agents (polyacryl amid and HMC).The following principle points were considered throughout the present study.1- The effect of adding local chemical additive materials on the physico-chemical properties of candidate insecticides.The physico-chemical properties of additive materials were studied. Solubility in both water and insecticides was considered as a limiting factor for mixing technique i.e direct or indirect method. The free acidity or alkalinity were studied for those materials, also HLB and CMC were studied for surfactants. The physical compatibility between different additive materials and candidate insecticides was then investigated.Emulsion stability test was consider as a limiting factor for the successful combination and would be an important guide for the physical compatibility of the mixed materials. Also the physico-chemical properties:iifree acidity or alkalinity, cold test and accelerated storage were carried out in case of -direct-mix method.The effect of physically compatible materials on the physico chemical properties of insecticidal spray solution in tap water under field dilution rate was studied. Surface tension, viscosity, electrical conductivity and pH value were measured.2- Physico-chemical properties of tested additive materials alone.Data indicated that all tested oils were miscible with Dursban, Curacron, Axone and super alpha, but they were not soluble in water. Therefore oils were added to insecticides using direct mix technique. On the other hand citric acid, sulphonic acid, oxalic acid, tartaric acid, glue, Arabic gum, polyacryl amid, HMC and surfactant Sisi6 were soluble in water, therefore, they could be mixed with insecticides using tank-mix method. Acidity modifiers, sulphonic acid, surfactants: Poly ethylene glycol 600 dilurate (DL600) and poly ethylene glycol 600 mono lurate (ML600) were soluble with all insecticides and water, therefore they added to

insecticides using direct mix technique and water using indirect mix technique. Data obtained indicated that all tested additives decrease pH value, Surface tension and increase viscosity, electrical conductivity; therefore they gave a prediction of increasing the efficiency and residual activity of insecticides spray solution.1.2. Physical compatibility of tested additive materials and candidate insecticides under field dilution rate.In case of direct mixing method, data indicated that all tested oils were compatible with all insecticides at ratio 10%. Also most of surfactantsiiipoly ethylene glycol 600 dilurate (DL600), poly ethylene glycol 600 mono lurate (ML600) and sulphonic acid were compatible at ratio 10% in emulsion stability, free acidity or alkalinity, cold test and heat storage tests. In case of tank-mix method, most of chemical additives used which soluble in water were compatible with tested insecticides.1.3. Effect of compatible additive materials on the physico-chemical properties of candidate insecticides under field dilution rate.The results indicated that most additive materials showed improvement in the physico-chemical properties of candidate insecticidal spray solution. Such improvement gave a prediction of increasing in their retention and deposit on treated plant surface. In case of direct mix technique, data indicated that, the tested oils (kerosene, xylene and CAPL1), poly ethylene glycol 600 dilurate (DL600), poly ethylene glycol 600 mono lurate (ML600) and sulphonic acid gave slight decrease in surface and pH values. On the other hand they gave decrease in viscosity and increase in electrical conductivity.In case of indirect mix technique, data indicated that, all tested surfactants (DL600, ML600 and Sisi6), sulphonic acid and HMC decreased the surface tension of candidate insecticide spray solution. Polyacryl amid and HMC increased the viscosity of candidate insecticide spray solution. The increase in viscosity gave a prediction of decreasing the drift and increasing retention of insecticides. All acids showed high increase in the electrical conductivity. Also most additive materials decreased the pH values of insecticide spray solution. This decrease in pH value indicated increase inivpositive charge of insecticide spray solution and therefore increased the attraction between the spray solution and the treated plant leaves which have negative charge.3- Evaluation the insecticidal efficiency of candidate insecticides and their combination with chemical additives against the 4th instar larvae of cotton leafworm.The tested insecticides at their full and 3/4 recommended rate of application alone and with chemical additives at 3/4 recommended rate were applied on cotton plants. Insecticidal efficiency was determined according to Ministry of Agriculture Protocol (Field – Laboratory Experiment). It could be concluded that the dosage rate of candidate insecticides could be reduced to about 3/4 of the recommended dose when mixed with chemical additives as a result of increasing their insecticidal efficiency to be the same as complete rate. In case of direct mix technique, the dosage rate of Dursban could be reduced to about 3/4 of the recommended rate when used in combination with Kerosene, Xylene and CAPL1. Also the dosage rate of Axone could be reduced to about ¾ rate when combined with Kerosene, Xylene, CAPL1 and. On the other hand, Kerosene, Xylene, CAPL1, poly ethylene glycol 600 dilurate (DL600) and Sulphonic acid when combined with Super alpha reduced the dosage rate to be about 3/4 the recommended rate. In case of tank- mix technique, the dosage rate of Dursban could be reduced to about ¾ rate when combined with citric acid, oxalic acid,

tartaric acid, poly ethylene glycol 600 dilurate (DL600), poly ethylene glycol 600 mono lurate (ML600), Sisi6, Glue, Arabic gum and HMC. On the other hand all the above additives reduced the dosage rate of Curacron to about ¾ rate except ML600, Glue and HMC. Also the dosage rate of Axone could be reduced to about ¾ rate when combined with citric acid, oxalic acid and polyveyhylene glycol 600 dilurate (DL600). The dosage rate of Super alpha could be reduced to about ¾ rate when combined with citric acid, oxalic acid, tartaric acid, poly ethylene glycol 600 dilurate (DL600), Glue, Arabic gum, polyacryl amid and HMC.4- Persistence of Dursban and Axone on cotton leaves.for determination the persistence of pesticides alone and pesticide – additive mixture on cotton plants, 3 leaves samples of treated cotton plant were taken at 0.0 time and after 6 days of treatment and kept at deep freezer at less than 0.0 C0 up to determination the chemical stability as the following method of extraction and cleaning up.A- Persistence of DursbanResults showed that the remaining quantity of pesticide Dursban after one hour from cotton leaves treatment with recommended rate, ¾ recommended rate, 3/4 recommended rate plus poly ethylene glycol 600 dilurate (DL600) were 96.04, 51.43 and 65.49 respectively. This amount decreased after 6 days of treatment to 9.65, 4.14 and 5.36.B- Persistence of Axone.Obtained results showed that the amount of pesticide residue after one hour from cotton leaves treatment with recommended rate, 3/4 recommended rate, and 3/4 recommended rate plus CAPL1 were 24.95, 7.18 and 7.63 respectively. This amount decreased after 6 days of treatment to 6.19, 3.44 and 5.23.Chapter (I)This chapter deals with the theoretical consideration of the subject about the surface active agent especially which containing heterocyclic moieties and their dividing into anionic, cationic, nonionic and amphoteric surfactant beside their industrial applications, Also it includes dividing according to ring size and the number of hetero atoms present in the heterocycle.Chapter (II)It divided into three parts:Part(1):It includes the synthesis of oxazolone and oxazolone derivatives from alkoylglycine which was prepared from the reaction of the (fatty acids) such as palmetic and stearic acid with glycine in presence of pyridine.4-Arylidene-2-alkyl-5(4)-oxazolones (1a-b) were obtained from the condensation of aromatic aldehydes with alkoylglycine, via Erlenmeyer synthesis.It -reacted with primary amines in ethanol solution to give α-arylcarboxamido-β alkylacrylamides (2,3)a-c and α-arylcarboxamido-β-arylacrylamides (2,3)d-g.As well as the oxazolone derivatives (1a-b) react with secondary amines namely piperidine to yield α-(p-hydroxybenzamido)-β-alkylacrylic acid piperidine (4a-b).However -2-alkyl-4-arylidene-2-oxazol-5-ones react with amino acids in ethanol to give α-aryl β-alkyl-aceylamido-acryloamino-acetic acid (5a-b).Also compound (1a-b) react alcoholic solution of hydrazine hydrate afforded the corresponding α-arylamido cinnamic acid hydrazides (6,7)a.Similary it condensed with phenyl hydrazine in boiling ethanol and yielded the corresponding phenylhydrazides (6,7)b.All trials of cyclisation of the hydrazides by treatment with acetic acid and sodium acetate to the corresponding 1:2:4-triazine derivatives were unsuccessful and no crystalline products were obtained . It seemed that decomposition took place with rapid evolution of nitrogen.On the other hand , the phenylhydrazides were readily cyclised under the above conditions to give the corresponding triazines (8a-b).Thus, The oxazolones (1a-b) react with hydroxylamine hydrochloride in boiling pyridine

and DMF to give the corresponding 4-arylidene-1-hydroxy-2-alkyl-5-imidazolones (9a-b).Thus the imidazolone derivatives react with phenylhydrazine in ethanol or -acetic acid to give the corresponding triazines(8a-b).4-arylidene-2-p hydroxyphenyl-5(4)-oxazolones react with sodium azide in acetic acid to give -α-[tetrazolyl-(1)-]-5-(2-p-hydroxyphenyl)-cinnamic acid derivatives (10a -b).Part(2):This part based on the synthesis of 2N-(pht-amino acid) and 2N-(tos amino acid) imidazolones (11a-g) and (12a-g) were prepared via the carbodiimide method,then the amino acid derivatives were performed by hydrazinolysis of the corresponding pht-amino acid derivatives (11a-d) and (12a-d)Part(3):In this part nonionic surfactants were prepared by addition of proplylene oxide (5,10,15 moles) to any active hydrogen in the molecule, the surface active properties like Surface tension, Interfacial tension, Cloud point, Wetting time, Emulsion stability, Foam height and critical micelle concentration of these compounds were measured and shows a pronounced surface activities, good emulsifying properties and highly foaming in some of these compounds. The biodegradability was evaluated and it was found that all the tested compounds showes a good biodegrability properties which manifested the importance of their application avoiding pollution problems, and make them safe for humen as well as environement.Chapter (III)This chapter concerned with the experimental in addition to surface active properties and biodegrability properties of the synthesized compounds.Wadi El Rayan depression consists of two main man-made lakes occupy the area between Latitudes of 29° 05’ and 29° 18’ N and Longitude 30° 21’ and 30° 32’ E. The desert in all directions with only source of El-Wadi drain of agricultural drainage water borders the two lakes. Depression provided the excess agricultural wastewater over the capacity of Lake Qarun. The Depression with its huge area (703 km2) was thought to be a suitable natural flood-water reservoir. After construction of the High Dam, Wadi El-Rayian project was converted to a large drainage reservoir. Since Lake Qarun is the natural place for the accumulation of the drainage water of El-Fayium Governorate.A project was therefore implemented in order to improve the drainage of the cultivated lands, reclaim more soils in El-Fayium and finally to lower the underground water level which was inundating the arable lands and led to the collapse of homes and buildings in several villages. The project began in 1968 and has been operated in 1973. The Depression receives about 200 million m3 of agricultural water per year. This led to the formation of an immense reservoir of agricultural wastewater, which will finally contain 2 billion m3 of water.The present work includes three chapters; a brief description of these chapters is given as follow:The first chapter is related to introduction of the thesis where the environmental status of Wadi El-Rayan lakes is given from the historical background and the literature survey for Aquatic Environment of Wadi El-==========The second chapter contains the experimental parts including sampling techniques, description of the selection and investigated sampling stations and describing the methods applied to determine the physico-chemical parameters in water and heavy metals in water and sediment.The third chapter included the obtained results and their discussion and data analysis as the following during the period of study and discussion of these results obtained which can be summarized as follow: -A preliminary assessment of two lakes showed

that physico-chemical characteristics and heavy metals in the 1st lake are controlled by the intrusion of drainage water through El-Wadi Drain. However, the rate of evaporation and the amount of water discharged from the 1st lake are the main factors control these concentrations in the 2nd lake.1. Water analyses1.1. Physical characteristics1.1.1. Temperature:Minimum and maximum temperature recorded ranged from 14.50 oC (winter) to 31.30 oC (summer), respectively. There was no significant difference between two lakes. On the other hand, the results show temporal highly significant difference. In El-Wadi Drain, temperature ranged between 16.10-29.10 oC.1.1.2. Electrical conductivity (EC):EC ranged between 2.63-3.01 ms/cm and 18.67- 25.84 ms/cm in 1st and 2nd lake respectively with a maximum in summer and a minimum in winter. The significant differences between two lakes are highly. In addition, there were sites significant differences in the 2nd lake. In addition, EC in El-Wadi Drain ranged between 1.49-1.84 ms/cm.1.1.3. Total solids (TS):TS varied in the 1st and 2nd lake between (1710.00-1898.00 mg/l) and (11325.00-15340.00 mg/l) respectively, where highest values in hot period (summer & spring) and lowest values in cold period (winter & autumn). The results were highly significant differences between the 1st and 2nd lake. In El-Wadi Drain, TS ranged between 1346.00-1526.00 mg/l.1.1.4. Total Dissolved Solids (TDS):TDS increased in summer, while the lowest values were recorded in winter. It varied between (1586.00-1811.00 mg/l) and (11060.00-14908.00 mg/l) in the 1st and 2nd lake, respectively. The differences were a significant between two lakes, as well as spatial significant differences in the 2nd lake. In El-Wadi Drain, TDS ranged between 1238.00-1412.00 mg/l.1.1.5. Total Suspended Solids (TSS):TSS ranged between (62.00-136.00 mg/l) and (146.00-432.00 mg/l) in the 1st and 2nd lakes respectively. On the other hand, there is a significant difference between two lakes. In addition, the results show temporal significant difference. In El-Wadi Drain, TSS ranged between 96.00-114.00 mg/l.1.2. Chemical characteristics:1.2.1. pH:pH of Wadi El Rayan Lakes lies in alkaline side and it ranged from 8.47 in (winter) to 8.96 in (spring) and from 8.26 in (winter) to 8.71 in (autumn) in the 1st and 2nd lakes respectively. In addition, pH in El-Wadi Drain ranged between 7.95- 8.19.1821.2.2. Dissolved oxygen (DO):The water of Wadi El-Rayan Lakes was will oxygenated all year round. DO varied between (6.40–12.00 mg/l) and (4.80-11.40 mg/l) in the 1st and 2nd lakes respectively, with seasonally significant difference with no local difference. The lowest value was recorded during summer, while the highest one during autumn. In El-Wadi Drain, DO was ranged between 6.60-7.80 mg/l.1.2.3. Biological oxygen demand (BOD):BOD ranged between (3.08-7.20 mg/l) and (2.80-6.54 mg/l) in the 1st and 2nd lakes respectively, where minimum and maximum values recorded in autumn and summer seasons, respectively. On the other hand, there was temporal significant difference. In El-Wadi Drain, BOD was ranged between 4.80-6.80 mg/l.1.2.4. Chemical oxygen demand (COD):COD ranged from 4.80 to 12.00 mg/l and 6.40 to 12.40 mg/l in the 1st and 2nd lake, respectively with significant difference between winter and autumn. The highest value was recorded during spring, while the lowest one during winter. On the other hand, COD in El-Wadi Drain ranged between 11.60-2.40 mg/l.1.2.5. Nutrient salts:The nutrient salts include compounds that contain nitrogen (NH3, NO2-, NO3-), phosphours -(ortho-P, TP) or silicate (SiO22-) in different forms either in available or non

available forms. The ranges of NH3, NO2- and NO3- in the 1st lake were (85.70-376.80 µg/l), (1.90- 40.80 µg/l) and (26.55 - 290.00 µg/l), respectively while the ranges of ortho-P and TP were (27.50-75.90 µg/l) and (154.80-434.00 µg/l) respectively, with spatial significant difference. In the 2nd lake, the ranges of NH3, NO2- and NO3- were (56.50-159.00 µg/l), (1.63-16.86 µg/l) and (28.38- 97.20 µg/l), respectively while the ranges of ortho-P and TP were (11.00 - 59.40 µg/l), and (186.00-358.40 µg/l), respectively. The SiO22- ranged (5.79-12.97 mg/l) and (6.64-17.74 mg/l) in the 1st and 2nd lake, respectively. During the seasons, there were non-significant a difference in nutrient salts levels except ortho-P and SiO22- in the 2nd lake. In El-Wadi Drain, The ranges of NH3, NO2-, NO3-, ortho-P, TP and SiO22- fluctuated between 648.20-320.90, 88.60-66.46, 824.08-366.80, 288.10-202.40, 358.40-186.00 and 8230-5420 µg/l, respectively.1.2.6. Major anions and cations ions:The major ions include (HCO3-, CO32-, SO42-, Cl-, Ca2+ and Mg2+). The SO42-, Cl-, Ca2+ and Mg2+ have been the same distribution trend and their concentrations in the 2nd lake were very higher than the 1st lake. They ranged between 281.65-372.00, 563.24-712.00, 51.10-68.12 & 98.20-119.82 mg/l and 2155.74-3418.00, 5073.94- 6987.00, 142.14-188.00 and 405.19-594.00 mg/l for SO42-, Cl-, Ca2+ and Mg2 in the 1st lake and 2nd lake respectively, with significant difference between two lakes. On the other hand, HCO3-, CO32- showed irregular distribution and varied between 194.56-261.12 & 12.00-32.00 mg/l and 208.32-276.48 & 4.00-18.00 mg/l in the 1st lake and 2nd lake, respectively. In El-Wadi Drain, The ranges of HCO3-, CO32-, SO42-, Cl-, Ca2+ and Mg2+ fluctuated between 266.24-256.00, Nil, 246.00-142.94, 432.00-286.00, 56.70-44.89 and 92.77-73.75 mg/l, respectively.1.3. Trace metals in waterThe concentrations of trace metals (Fe, Mn, Cu, Pb, Ni, Co, Cr and Cd) in Wadi El Rayan lakes water were increase at inlet the 1st lake during all seasons which may be attributed to the effect of agricultural influx drained into the 1st lake from El-Wadi Drain.The trace metal results in Wadi El Rayan lakes water can be summarized as:a. Fe ranged between 132.00-990.00 µg/l -and 146.00-676.00 µg/l in the 1st and 2nd lakes respectively. However, Fe in El Wadi Drain ranged between 2346.00-1142.00 µg/l.b. Mn ranged between 16.00-121.08 µg/l and 2.00-79.00µg/l in the 1st and 2nd lakes respectively. However, Mn in El-Wadi Drain ranged between 422.30-116.00 µg/l.c. Cu ranged between 10.60-27.68 µg/l and 7.60-14.25 µg/l in the 1st and 2nd lakes respectively. However, Cu in El-Wadi Drain ranged between 32.66-16.40 µg/l.d. Co ranged between 6.28-16.23 µg/l and 4.12-14.30 µg/l in the 1st and 2nd respectively. However, Co in El-Wadi Drain ranged between 18.60-12.66 µg/l.e. Pb ranged between 6.10-16.40 µg/l and 4.67-10.14 µg/l in the 1st and 2nd lakes respectively. However, Pb in El-Wadi Drain ranged between 24.40-12.40 µg/l.f. Ni ranged between 8.02-24.80 µg/l and 5.80-15.80 µg/l in the 1st and 2nd lakes respectively. However, Ni in El-Wadi Drain ranged between 44.80-12.60 µg/l.185□g. Cr ranged between 6.14-21.60 µg/l and 6.22-16.35 µg/l in the 1st and 2nd lakes respectively. However, Cr in El-Wadi Drain ranged between 44.80-12.60 µg/l.h. The concentration of Cd in Wadi El Rayan lakes and El-Wadi Drain was less than 0.20 µg/l.2. Sediment analyses2.1. Carbonate in sediment:The ranges of carbonate fluctuated between 22.24-38.10and 27.22-18.60 % in the 1st and 2nd lakes respectively.2.2. Organic matter in sediment:The ranges of organic matter fluctuated between 3.66-13.22

and 1.25-7.11 % in the 1st and 2nd lakes respectively.2.2. Trace metals in sediment:The contents of trace metals (Fe, Mn, Cu, Pb, Ni, Co, Cr and Cd) in Wadi El Rayan lakes sediment were increase at inlet the 1st lake during all seasons which -may be attributed to the effect of agricultural influx drained into the 1st lake from El Wadi Drain.The trace metals results in Wadi El Rayan lakes sediment can be summarized as:a. Fe ranged between 1300.50-2600.00 µg/g and 764.80-1805.00 µg/g in the 1st and 2nd lakes respectively.b. Mn ranged between 110.30-612.50 µg/g and 102.80-267.90 µg/g in the 1st and 2nd lakes respectively.c. Cu ranged between 12.36-38.50 µg/g and 3.61-18.60 µg/g in the 1st and 2nd lakes respectively.d. Co ranged between 10.22-37.45 µg/g and 11.50-35.10 µg/g in the 1st and 2nd respectively.e. Pb ranged between 4.76-42.20 µg/g and 5.10-12.60 µg/g in the 1st and 2nd lakes respectively.f. Ni ranged between 13.63-68.30 µg/g and 11.49-70.40 µg/g in the 1st and 2nd lakes respectively.g. Cr ranged between 11.90-54.50 µg/g and 10.50-34.12 µg/g in the 1st and 2nd lakes respectively.h. The content of Cd in Wadi El Rayan lakes sediment was less than 0.10 µg/l.