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Original Article

Preparation, Characterization of Some Nanocationic Surfactants and Their Effectivness on the Physico-chemical Properties, Efficacy and Persistance of Some Insecticides against Cotton Leafworm (*Spodoptera littoralis* (Boisd.))

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Abstract

Some nanocationic tetra hallo cuperate surfactants, cetrimonium phenyl hydrazine-bromo-trichloro cuprate, cetrimonium-2-chloro phenyl hydrazineium -bromo-trichloro cuprate and cetrimonium-2-bromo phenyl hydrazinium-bromo-trichloro cuprate were prepared and characterized by micro elemental analysis, raman spectra, infrared spectra, uv spectrophotometer, atomic absorption spectroscopy (AAS) and transmission electron microscopy (TEM).These prepared surfactants were examined as additives on some insecticides formulations, organophosphorus as chlorpyrifos, pyrothroids as lambda-cyhalothrin and insect growth regulator as lufenuron insecticides against second and fourth instars larvae of cotton leafworm (*Spodoptera littoralis* (Boisd.)). The insecticidal activities of the tested compounds were affected by changing their physico-chemical properties (surface tension and pH values) which changed by adding synthesized nano surfactants.

1. Introduction

Surfactants are chemical compounds which lower the surface tension between two liquids, or that between a solid and a liquid. Surfactants can act as wetting agents, detergents (Mulligan *et al.,* 2001), dispersants, foaming agents and emulsifiers. For exactly performing of pesticides function, a spray droplet must be able to damp the foliage and be located over a leaf. The area of pesticide coverage is increased by surfactants so increasing the pests allergic to the chemical.

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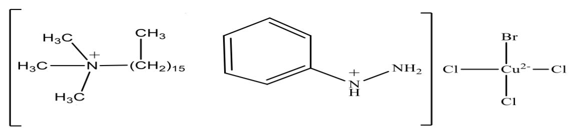
Also surfactants play an important role in several applications including: dyestuffs, fibers, mineral processing, oil field chemicals (Al-Sabagh *et al.,* 2003), paints, pesticides (Cremlyn, (2009) pharmaceutical or plastics (Chen *et al.,* 2011). Nanoemulsions are systems that greatly cover the size ranges 50-100 nm (Forgiarini *et al.,* 2001). Also they are defined as mini-emulsion (Caruso, 2006) and are stable kinetically. There are three main processes of nanoparticle synthesis and these are solid-state, solution precipitation and vapor phase processes. The major common and widely used process is solid state because it is the cheapest process used for production of micron- sized particles (Morsy, 2014). To reduce the side effects of super use of agrochemicals on the ecosystem, chemicals with less stability and greater specificity, nanoemulsions have assortment of applications in agrochemical industry.

Negm *et al.* (2011) prepared three cationic surfaces by chemically modification of vanillin. The synthesized surfactants, chemical structures were approved using IR, NMR spectra and elemental analysis. Hegazy *et al.* (2013) synthesized some colloidal copper Nano particles (CuNPs) in water by chemically reduction of the synthesized cationic surfactant. The characterization of prepared copper Nano particles were occurred by transmission electron microscopy (TEM) and FTIR spectrum. Morsy (2014) reported that the formation of Nano particles surfactants occurs by high dispersion method. Their present properties and characteristics depend on the preparation method and their composition. Piscureanu *et al.* (2001) measured the surface activity of some pesticide on colloidal systems by using nonionic surfactants. Krogh *et al.* (2003) investigated the destiny of adjuvants in environmental after application on the agricultural land. This paper discussed the fate and effect of two adjuvants (ANEOs and AEOs) on the hydrous and terrestrial environment and they are applied as technical mixtures.

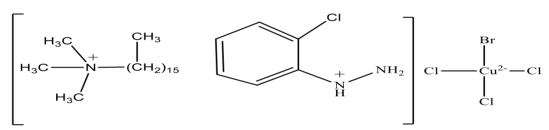
Ying (2006) reported that the widest used materials in industrial products and in household are surfactants. Surfactants have various conduct and effect in the environment. Mahmoud *et al.* (2007) prepared a chain of some cationic surfactants. These cationic surfactants have been estimated by studying their surface parameters, surface properties, antimicrobial, antifungal activities and biodegradability. Raman *et al.* (2008) discussed the effect of Schiff-base derived from acetoacetanilide and anthranilic acid and its copper complex on 4^{th} instar larvae of S. litura (Fabaceae) for insect pest control by using leaf dip method. Castro *et al.* (2014) used surfactants to improve the pesticide efficacy. Surfactants were used to decrease cost, pollution and increase in the absorption of foliar to be useful for bicides, defoliants and growth regulators. Pan *et al.* (2015) prepared nanosuspension solution of 5% lambda-cyhalothrin with 0.2% surfactants by the melt emulsification method under high pressure. The prepared surfactants were used to prepare lambda-cyhalothrin nanosuspension with high dispersity and stability. The use of organic solvents and reduce surfactants for reducing residual pollution and improving bioavailability of pesticide in agricultural products and environment.

2. Materials and Methods

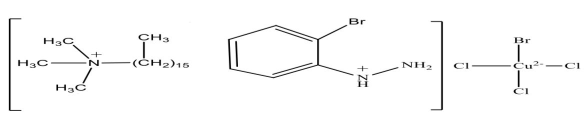
2.1. Preparation of Nanocationic Tetra Halo Cuperate Complexes: cupper chloride (II) with phenyl hydrazine and their derivatives salts in presence of CTAB in the mortar until all components mixed well to produce tetra halo cuprate complexes and this indicate by change color of mixture.



Cetrimonium phenyl hydrazine-bromo-tri chloro cuprate



Cetrimonium-2-chloro phenyl hydrazinium-bromo-trichloro cuprate



Cetrimonium-2-bromo phenyl hydrazinium-bromo-trichloro cuprate

Fig.1. Structures of the prepared nanocationic tetra halo cuperate surfactants.

2.2. Characterization of the Prepared Surfactant Complexes: by micro elemental analysis, raman spectra, infrared spectra, uv spectrophotometer, atomic absorption spectroscopy (AAS) and transmission electron microscopy (TEM).

2.3. Determination of the Physico-chemical Properties of the Prepared Surfactants

2.3.1. Surface Tension Measurements: surface tension measurements were obtained by using De-Nöuy Tensiometer krüss K-6 with a platinum ring (Mariano *et al.,* 2014).

2.3.2 pH Meter Measurement: by Automatic pH Meter-2601.

2.4. Determination the Effect of Prepared Nanocationic Surfactants on the Physico-chemical Properties of Spray Solution of Some Insecticides: by measurement of surface tension and acidity of the tested insecticides alone and their mixture spray solution (surfactant + insecticide).

2.5. ImInsecticidal Efficacy:

2.5.1. Insecticidal Activity of Prepared Nanosurfactants adding to Some Tested Insecticides Formulations, Chlorpyrifos, Lambda-cyhalothrin and Lufenuron against 2nd Instar Larvae of Cotton Leafworm: by dipping of plant leaf on the spray solutions then feeding of the tested instar and the mortality ratios were recorded. The toxicity lines were drawn and LC_{50} and LC_{90} were calculated.

2.5.2. Persistence of Tested Insecticides Alone and Its Tank Mix with Surfactant Complexes Additives against 2nd Instar Larvae of Cotton Leafworm: a hand sprayer equipped with one nozzle was used for spraying (spray volume was 200 liter / feddan) with different synthetic surfactants adjuvants against 2nd instars larvae of cotton leaf worm). Samples were taken immediately after one hour of spraying (zero time) and then after 3,6,9,12,15 and 21 days from application to evaluate the residual performances in cotton field during the period from 2 to 23 July, 2015.

3. Results

3.1. Micro Elemental Analysis: the data are shown in the following Table (1).

3.2. Raman Spectrum

Raman spectra were taken with a Perkin- Elmer 301 double beam Spectrophotometer. The 4000-70 cm^{-1} region was investigated. Raman spectra of cetrimonium phenyl hydrazine bromo -tri chloro – cuprate showed three bands at (112, 132 and 178 cm^{-1}) at low wavenumber region, two bands at (1406 and1423 cm^{-1}) and six

Table 1. Micro Elemental Analysis of The prepared Nanocationic Surfactants.

Surfactant	$M.W_t$	%C	%H	%N	% Cl	%Br	%Cu
Cetrimonium phenyl hydrazine-bromo-Tri chloro cuprate	643.50	Calculated 46.66 Found 46.66	Calculated 7.92 Found 7.99	Calculated 6.53 Found 6.53	Calculated 16.53 Found 16.53	Calculated 12.43 Found 12.42	Calculated 9.79 Found 9.88
Cetrimonium-2-chloro phenyl hydrazinium-bromo-trichloro cuprate	677.95	Calculated 44.29 Found 44.29	Calculated 7.37 Found 7.43	Calculated 6.20 Found 6.20	Calculated 20.91 Found 20.92	Calculated 11.80 Found 11.79	Calculated 9.37 Found 9.37
Cetrimonium-2-bromo phenyl hydrazinium-bromo-trichloro cuprate	722.40	Calculated 41.56 Found 41.57	Calculated 6.92 Found 6.98	Calculated 5.82 Found 5.84	Calculated 14.72 Found 14.72	Calculated 22.15 Found 22.12	Calculated 8.79 Found 8.80

bands (2774, 2823, 2836, 2864, 2885 and 3000 cm^{-1}) at high wavenumber region, Figure (2.a). Raman spectra of cetrimonium-2-chloro phenyl hydrazinium bromo-trichloro-cuprate showed three bands at (60, 133 and 179 cm^{-1}) at low wavenumber region, two bands at (1395 and1410 cm^{-1}) and six bands (2823, 2845, 2874, 2895, 2934 and 2998 cm^{-1}) at high wavenumber region, Figure (2.b). Raman spectra of cetrimonium-2-bromo phenyl hydrazinium bromo-trichloro-cuprate showed three bands at (108, 133 and 176 cm^{-1}), one single band at 413 cm^{-1} at low wavenumber region, one single bands at(1498 cm^{-1}) and five bands (2828, 2871, 2894, 3001, and 3021 cm^{-1}) at high wavenumber region, Figure (2.c). Bands below 400 $cm^{-1}$are attributed to lattice modes (Lattice vibrations in crystals). Bands from 1000 to 1500 cm^{-1} are attributed to υ(CC) aromatic ring chain. Bands from 2800 to 3000 cm^{-1} are attributed to υ(C-H), υ(C-NH). The four Cu-Cl and Cu-Br distances being almost identical, two opposite angles of about 133^{o} and the others of about 108^{o}. The copper complexes are distorted tetrahedral structure has been found. For cetrimonium-2-chloro phenyl hydrazinium bromo-trichloro-cuprate , the band presents at about 60 cm^{-1} equires some additional discussion. This band may be assigned to the υ_2 frequency, activated by site symmetry, or alternatively to a lattice mode, Figure (2.b).

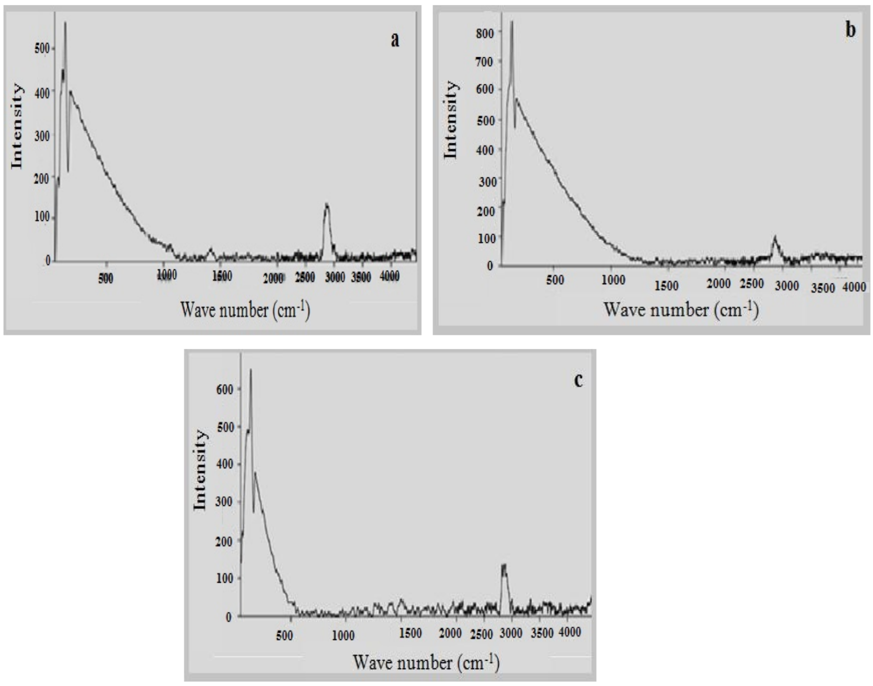


Fig. 2. Raman Spectra of a) Cetrimonium phenyl hydrazine bromo -tri chloro – cuprate, b) Cetrimonium -2-chloro phenyl hydrazinium bromo-trichloro-cuprate and c) Cetrimonium-2-bromo phenyl hydrazinium bromo-trichloro-cuprate.

3.3. *Infrared spectra*

IR spectra of cetrimonium phenyl hydrazine-bromo -tri chloro – cuprate) showed a band at (3424 for C-NH_2 group), bands at (3023, 2917, 2851 cm^{-1} for C-H (SP^3) stretching of alkane group) and (1630, 1468 cm^{-1} for C=C stretching in aromatic ring), (780, 719cm^{-1} of meta disubstituted aromatic), Figure (3.a). The IR spectra of cetrimonium-2-chloro phenyl hydrazinium-bromo-trichloro cuprate showed a band at ((3421 for C-NH_2 group), bands at (3018, 2916, 2850 cm^{-1} for C-H (SP^3) stretching of alkane group) and (1631, 1469 cm^{-1} for C=C stretching in aromatic ring), (788,719 cm^{-1} of meta disubstituted aromatic), (600-800 cm^{-1} for C-Cl group), Figure (3.b). The IR spectra of cetrimonium-2-bromo phenyl hydrazinium bromo-trichloro cuprate showed a band at (3418 for $C\text{-}NH_2$ group, bands at (3016, 2918, 2850 cm^{-1} for C-H (SP^3) stretching of alkane group) and (1631, 1467 cm^{-1} for C=C stretching in aromatic ring), (755,721cm^{-1} of meta disubstituted aromatic), (500-600 cm^{-1} for C-Br group), Figure (3.c).

3.4. UV Spectra:

UV spectra were recorded with a Perkin-Elmer S52 Spectrophotometer. The quaternization of tetra halo cuprate complexes formation was proved by the appearance of new uv bands, the data was obtained in Figure (4).

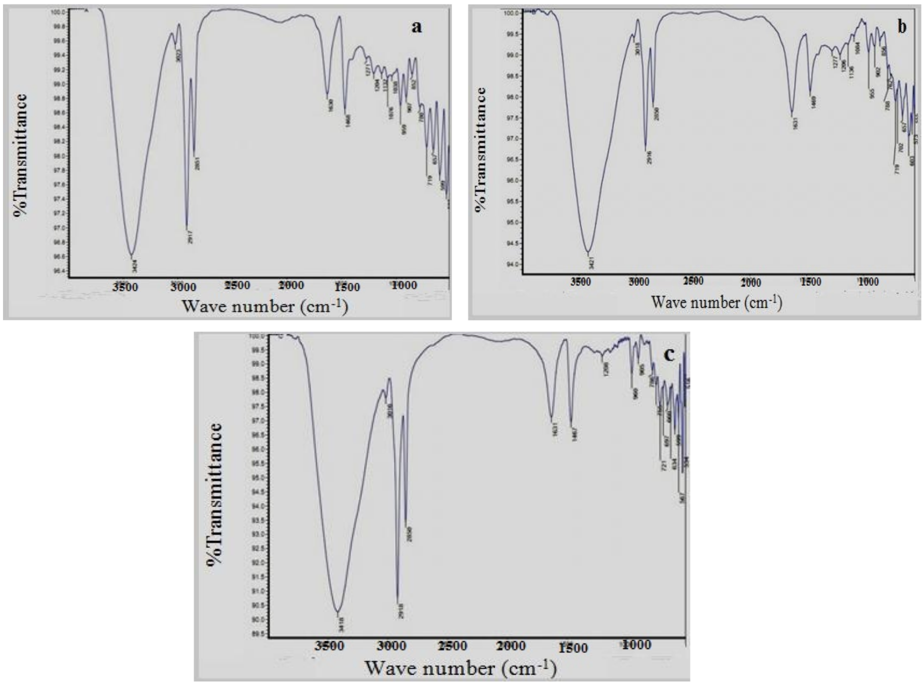


Fig. 3. IR Spectra of a) Cetrimonium phenyl hydrazine-bromo-tri chloro – cuprate, b) Cetrimonium-2-chloro phenyl hydrazinium-bromo-trichloro cuprate and c) Cetrimonium-2-bromo phenyl hydrazinium-bromo-trichloro cuprate.

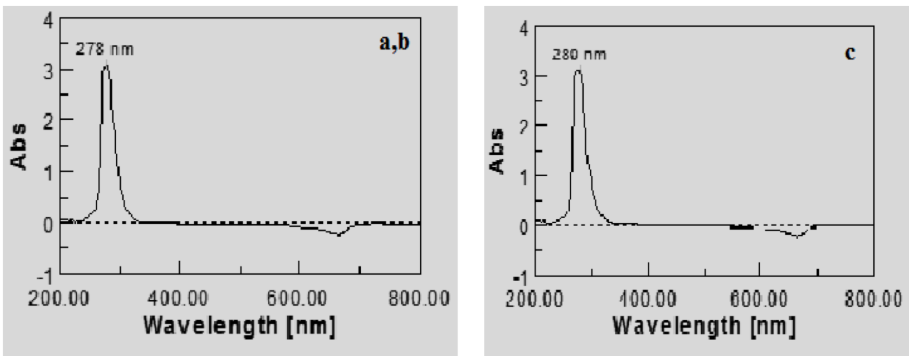


Fig. 4. UV Spectra of a) Cetrimonium phenyl hydrazine-bromo-tri chloro – cuprate, b) Cetrimonium-2-chloro phenyl hydrazinium-bromo-trichloro cuprate and c) Cetrimonium-2-bromo phenyl hydrazinium-bromo-trichloro cuprate.

3.5. Atomic absorption spectroscopy (AAS): atomic absorption spectrometry (AAS) is a technique for measuring quantities of chemical elements present in environmental samples by measuring the absorbed radiation by the chemical element of interest. This is done by reading the spectra produced when the sample is excited by radiation. The concentration is usually determined from a calibration curve, obtained using standards of known concentration.

Table 2. Atomic Absorption Spectroscopy (AAS) of the Prepared Nanocationic Surfactants.

Tested Surfactants	Found Metal	Concentration (mg/L)
Cetrimonium phenyl hydrazine-bromo-tri chloro cuprate	Cu	0.16
Cetrimonium-2-chloro phenyl hydrazinium-bromo-trichloro cuprate	Cu	0.16
Cetrimonium-2-bromo phenyl hydrazinium-bromo-trichloro cuprate	Cu	0.18

3.6. Transmission Electron Microscopy (TEM): (by JEM-2100 – high resolution (200KV)):

The TEM images of the synthesized cationic surfactants were represented in Figure (5). The TEM images showed the self- assembling of the prepared surfactants on nano particles which causes the stabilization of these surfactants due to the formation of nano shells in the prepared surfactants. The particle size of the prepared surfactants showed in Table (3).

Table 3. Particle size of the synthetic surfactants.

Tested Surfactants	Particle size(nm)
Cetrimonium Phenyl hydrazine-Bromo-Tri chloro Cuprate	14.70 – 19.80
Cetrimonium-2-Chloro Phenyl hydrazinium-Bromo-Trichloro Cuprate	3.50 – 5.02
Cetrimonium-2-Bromo Phenyl hydrazinium-Bromo-Trichloro Cuprate	11.01 – 51.02

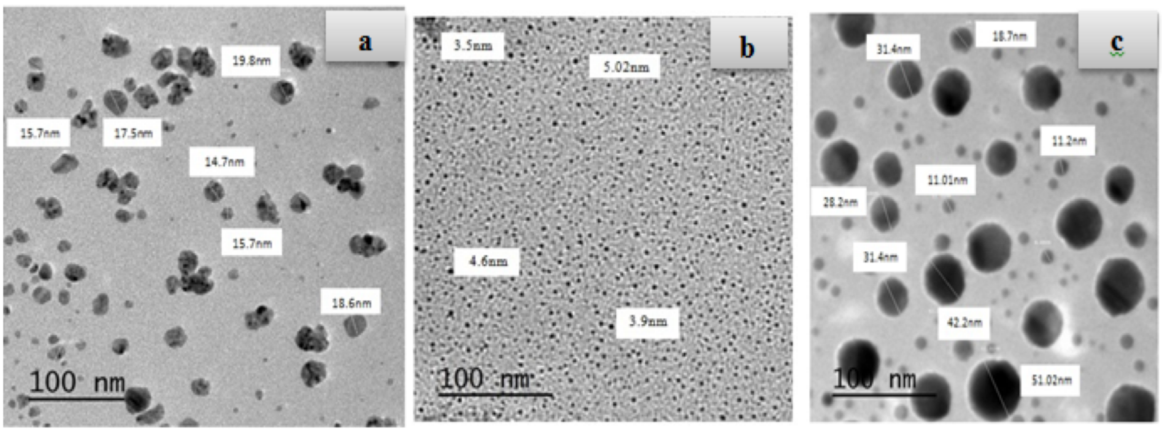


Fig. 5. TEM image of The Synthesized Surfactants a) Cetrimonium phenyl hydrazine-bromo-tri chloro – cuprate, b) Cetrimonium-2-chloro phenyl hydrazinium-bromo-trichloro cuprate and c) Cetrimonium-2-bromo phenyl hydrazinium-bromo-trichloro cuprate.

3.7. Surface Tension Measurements of Synthetic Cationic surfactants :

Figure (6) represent the relation between the surface tension values in (mN/m) and the concentration (Log C) at 25˚C. These curves are characterized by two regions, one at lower concentration at which is greatly sensitive towards concentration reaction, the other at which the surface tension is almost constant up on variation of surfactant concentration. Extrapolation of these two regions determines the so-called critical micelle concentration (CMC) (Tao *et al.,* 2009 and Behpour *et al.,* 2009). The equilibrium happened at the concentration of complete surface tension (CMC) (Zhang and Hua, 2009; (Zhang *et al.,* 2009). The CMC value is dependent on the chemical structure of the surfactant molecules (Abboud *et al.,* 2009). The molecules tend to lower that unfavorable situation via forming more stable aggregative structures which are micelles (thermodynamically stable). Therefore the CMC occurred at lower concentration (Negm *et al.,* 2010). The surface tensions of the synthesized metal complexes (cationic surfactants) were often decreased remarkably compared with their parent, i.e., A > C >B for phenyl hydrazine hydrochloride and its derivatives salts. The critical micelle concentration of cationic tetra halo cuperate surfactants are shown in Table (4). When the surface tension decreases by increase the hydrophobic chain length, this leads to effectiveness (πcmc) increase. The effectiveness of the synthesized surfactants is arranged as follow: B>C>A (by decreasing surface tension). It is clear from Table (4) that the synthesized surfactants have ability to decrease the surface tension by 20mN/m at very low surfactant concentration at 25˚C and that is defined as efficiency (Pc_{20}), (Badr, 2009). The maximum surface excess (μmax) for synthesized cationic surfactants have different rearrangement for phenyl hydrazine hydrochloride and its derivatives salts (A > B increase by increasing surface tension, C > A increase by decreasing surface tension). Minimum surface area (A_{min}) for cationic synthesized surfactants is arranged as B > A > C. The standard free energy of micellization and adsorption of the prepared surfactants at 25˚C can be calculated using the following thermodynamic equations (Negm *et al.,* (2011)): ΔG_{mic} = - RT lin (CMC), $\Delta G_{ads} = \Delta G_{mic} - (0.006 \text{ X } \pi CMC \text{ X } A_{min})$, $\Delta G^o_{mic} = \Delta G^o (CH_3) + m\Delta G^o (CH_2) + \Delta G^o$ (head group). From Table (4) it is clear that ΔG_{mic} and ΔG_{ads} values of all prepared surfactants are negative. The negativity of these values suggests the spontaneous behavior and equilibrium between the two phases of the surfactant molecule.

3.8. pH Meter Measurements of The Prepared Surfactants: the data are shown in the following Table (5).

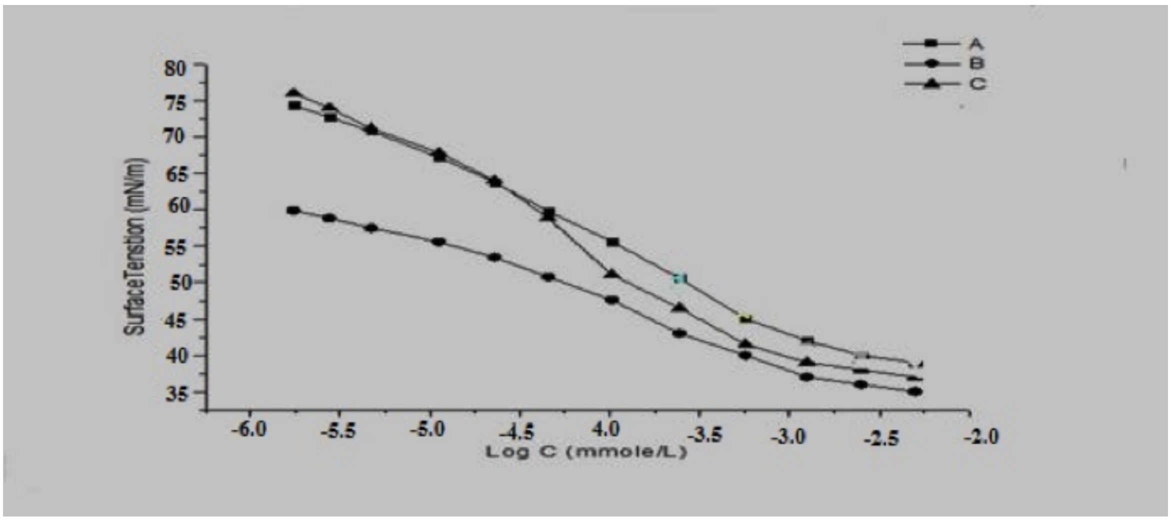


Fig. 6. Variation of Surface Tension against Concentration of The Prepared Cationic Surfactants, A) Cetrimonium phenyl hydrazine-bromo-tri chloro cuprate, B) Cetrimonium-2-chloro phenyl hydrazinium-bromo-trichloro cuprate and C) Cetrimonium-2-bromo phenyl hydrazinium-bromo-trichloro cuprate.

Table 4. Surface properties of the prepared surfactants in bidistilled water at 25°C.

Compound	pH
Cetrimonium phenyl hydrazine-bromo-tri chloro cuprate	4.3
Cetrimonium-2-chloro phenyl hydrazinium-bromo-trichloro cuprate	2.3
Cetrimonium-2-bromo phenyl hydrazinium-bromo-trichloro cuprate	2.2

Table 5. The pH values of the synthetic surfactants.

Compound	CMC X 10^7 Mole/L	γ_{CMC} mN/m	π_{CMC} mN/m	μ_{max} x10^{11} mol.k^{-1}.cm^{-1}	A_{min} nm^2	P_{c20} x10^7 (mol/L)	ΔG_{ads}	ΔG_{mic}
Cetrimonium phenyl hydrazine-bromo-tri chloro cuprate	6.61	41.66	30.14	22.8	7.30	1.90	-19.50	-18.10
Cetrimonium-2-chloro phenyl hydrazinium-bromo-trichloro cuprate	5.75	37.80	34.00	16.77	9.90	0.31	-20.50	-18.50
Cetrimonium-2-bromo phenyl hydrazinium-bromo-trichloro cuprate	4.36	39.36	32.44	27.05	6.14	1.17	-20.40	-19.20

3.9. Determination the Effect of Surfactants on the Physico-chemical Properties of Spray Solution of Some Tested Insecticides (the Effect of pH and Surface Tension) .

The data in Table (6) show that synthesized cationic surfactants have reduced of surface tension values. The reduction of the surface tension of the insecticidal spray solution would increase its wetability and spreading on the treated surface, thus increase insecticidal activity (Abd-alla *et al.,* 2013). Also, by pH measurement, we observe that by increasing pH value (to basicity), the insecticidal activity decreases (Hussein, 2002). So the effect of synthesized cationic surfactants on insecticidal activity of the tested pesticides depends on surface tension and pH values.

Table 6. Response of the pH and Surface Tension effect of different synthetic surfactant complexes adding as additive to tested insecticide formulations against laboratory strain of 2nd and 4th instar larvae of the cotton leaf worm.

Tested insecticides	Surfactants	pH	Surface Tension	2nd instar larvae			4th instar larvae		
				LC_{50} (ppm)	LC_{90} (ppm)	Toxicity Index	LC_{50} (ppm)	LC_{90} (ppm)	Toxicity Index
Chlorpyrifos		3.80	52	0.10	1.47	100.00	1.529	2.98	100.00
	A	6.00	38	0.93	17.62	8.14	4.06	37.55	37.70
	B	5.90	37	0.29	16.23	25.94	3.20	22.06	47.70
	C	5.80	36	0.20	10.27	37.80	2.37	16.08	64.50
Lambda-Cyhalothrin	--	9.0	39	0.02	68.24	2.38	9.26	662.44	0.01
	A	5.80	35.5	0.02	26.91	7.89	0.068	155.62	13.97
	B	5.60	35.5	0.01	16.67	12.50	0.024	65.143	39.58
	C	5.50	35	0.001	15.62	100.00	0.009	18.0	100.00
Lufenuron	--	7.00	40	0.15	57.19	86.49	14.01	995.04	100.00
	A	7.40	36	0.44	152.31	29.02	35.71	1972.9	39.24
	B	7.10	35	0.20	92.00	63.05	25.20	4822.5	55.60
	C	7.00	35	0.128	43.67	100.00	14.70	4660.4	95.29

Where: A) Cetrimonium phenyl hydrazine-bromo-tri chloro cuprate, (B) Cetrimonium-2-chloro phenyl hydrazinium-bromo-trichloro cuprate and (C) Cetrimonium-2-bromo phenyl hydrazinium-bromo-trichloro cuprate.

3.10. Study of the Insecticidal Activity: surface active agent plays a significant role on many fields especially in pesticides on both formulation and improvement of their biological efficiency (El-Sisi *et al.,* (2006).

3.10.1. Study of the Insecticidal Activity of Mixed Spray Solution (Insecticide+ Surfactant): the obtained results reflect the insecticidal activity of chlorpyrifos, lambda-cyhalothrin and lufenuron alone and with tested surfactants against laboratory strain of 2nd instar larvae of the cotton leaf worm *S. littoralis*. The results in Table (6), Figure (7.a) show that chlorpyrifos with synthetic cationic surfactants (C,B, A) showing less insecticidal activity than chlorpyrifos only. Also results show in Figure (7.b) that lambda-cyhalothrin with synthetic cationic surfactant(C, B, A) respectively proved to be the most effective compound than lambda-cyhalothrin only. In Figure (7.c) lufenuron with synthetic cationic surfactant (C) proved to be the most effective compound than lufenuron only. But synthetic cationic surfactants (B, A) showing less insecticidal activity than lufenuron only.

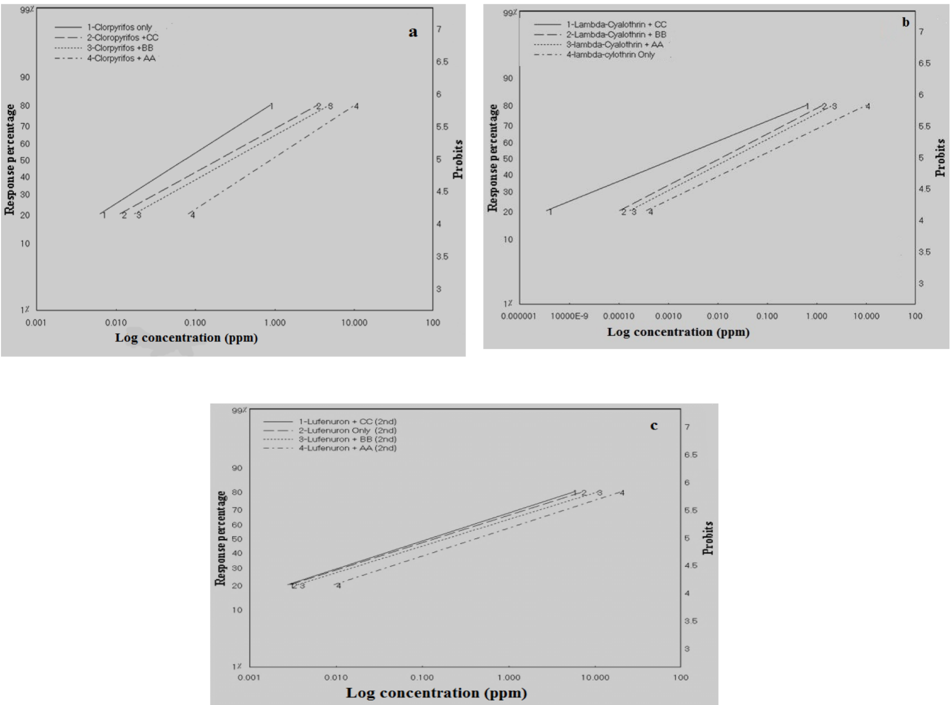


Fig. 6. Toxicity lines of different synthetic surfactant complexes, (A) Cetrimonium Phenyl hydrazine-Bromo-Tri chloro Cuprate, (B) Cetrimonium-2-Chloro Phenyl hydrazinium-Bromo-Trichloro Cuprate and (C) Cetrimonium-2-Bromo Phenyl hydrazinium-Bromo-Trichloro Cuprate adding as additive to some tested insecticides formulations against laboratory strain of 2nd instar larvae of the cotton leafworm.

3.10.2. Persistence of Mixed Spray Solution (Insecticide + Surfactant) on Cotton Leafworm: Data presented in Table (7) show that; all surfactants increase the percentage of larval mortality than that obtained with chlorpyrifos, lambda-cyhalothrin and lufenuron used alone at the recommended rate in field- lab. The general mean of mortality percentage for chlorpyrifos increases from 71.56% for chlorpyrifos alone to 88.51% by adding the prepared nanocationic surfactants. Also, for lambda-cyhalothrin, the general mean of mortality percentage increases from 64.70% for lambda-cyhalothrin alone to 79.74% and for lufenuron, the general mean of mortality percentage increases from 63.09% for lufenuron alone to 78.34% .

Table 7. Toxicity of singular tested insecticides and their tank mixed with synthetic surfactant additives against 2nd instars larvae of cotton leafworm .

Treatments	% of corrected mortality after treatment (days)								% of general mean of mortality
	1K	Residual effect						% of mean residual effect	
		3	6	9	12	15	21		
Chlorpyrifos alone	100	100	93.3	79.3	63.3	51.7	13.3	66.82	71.56
Chlorpyrifos + A	100	93.1	86.7	79.3	66.7	50.0	48.3	70.68	74.87
Chlorpyrifos + B	100	100	100	93.1	90	75.9	53.3	85.38	87.47
Chlorpyrifos + C	100	100	100	100	93.3	89.6	36.7	86.60	88.51
Lambda-Cyhalothrin alone	96.5	86.7	79.3	73.3	58.6	55.2	3.3	59.40	64.70
Lambda-Cyhalothrin +A	100	90.0	86.0	80.0	62.0	58.6	3.3	63.82	68.56
Lambda-Cyhalohrin + B	100	90.0	89.6	79.3	79.3	75.9	10.0	70.68	74.87
Lambda Cyhalothrin +C	100	90.0	89.6	86.7	82.8	72.4	36.7	76.37	79.74
Lufenuron alone	100	93.1	90.0	58.6	51.7	44.8	3.45	56.94	63.09
Lufenuron + A	100	82.7	66.7	58.6	58.6	58.6	48.3	62.25	67.64
Lufenuron + B	100	89.6	83.3	68.9	68.9	62.1	58.6	71.90	75.91
Lufenuron + C	100	96.5	93.3	72.4	65.5	62.1	58.6	74.73	78.34

Where: 1K: Initial kill after one hour from application, (A) Cetrimonium phenyl hydrazine-bromo-tri chloro cuprate, (B) Cetrimonium-2-chloro phenyl hydrazinium-bromo-trichloro cuprate and (C) Cetrimonium-2-bromo phenyl hydrazinium-bromo-trichloro cuprate.

4. Conclusion

The data reflects that by using the prepared nanocationic surfactants with lambda-Cyhalothrin insecticide formulations increases their toxicity and with all the tested insecticide formulations increase their persistence in the field than insecticide alone mixture and so decrease the rate of field application. This is because of the ability of the synthesized surfactants to change the physico-chemical properties of spray solution. So by decreasing pH and surface tension of insecticide spray solution, the wetability, spreading and depositing of the tested insecticides increase so the insecticidal efficiency increase. The use of surfactants with chemical insecticides may provide a great efficacy of insecticidal properties and decreases their application rates, pollution. From the last results, we recommend to use the prepared nanocationic surfactants with the tested insecticides to increase the persistence of adjuvant/insecticide mixture against the cotton leafworm.

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الملخص العربى

تحضير وتوصيف بعض المواد النانوكاتيونيه ذات النشاط السطحى وتأثيرها على الخصائص الفيزيائية والكيميائية وفعالية وثبات بعض المبيدات الحشرية المستخدمه لمكافحه دوده ورق القطن

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تم تحضير ثلاث مركبات نانوكاتيونيه جديده ذات نشاط السطحى من الفينيل هيدرازين هيدروكلوريد ومشتقاته وكلوريد النحاس الثنائى ومركب السيتاب عن طريق الطحن الصلب للمواد وقد استدل على اكتمال التفاعل بواسطه تغير لون الخليط. وقد تم توصيف هذه المتراكبات بواسطه عدة تحاليل وهى Micro elemental analysis, Raman Spectroscopy, Infrared Spectroscopy (IR) , 1H-NMR Spectroscopy, Ultra Violet (UV) and Transmission Electron Microscopy (TEM) وتم أختبار فاعليه هذه المتراكبات على الكفائه الحشريه وبقاء بعض المبيدات الحشرية المستخدمه لمكافحه دوده ورق القطن وهى الكلوربيروفوس (chlorpyrifos) كمبيد فسفورى و اللامداثيالوثيرين (lambda-cyhalothrin) كمبيد بيروثرويد والليوفنرون (lufenuron) كمبيد مثبط للنمو وذلك عن طريق تغير خواصها الفيزيائية الكيميائية باضافه هذه المتراكبات للمبيدات الحشريه محل الأختبار. وقد دلت النتائج على أن المركبات المحضره تقلل التوتر السطحى للماء المذيب لمحاليل المبيدات المختبره وأيضا تزيد حامضيه بعض محاليل المبيدات المختبره خاصه اللامداثيالوثيرين مما أدى الى زياده سميه هذا المبيد الحشري مع المتراكبات المضافه وزياده بقاء جميع مستحضرات المبيدات المختبره حتى بعد ٢١ يوم من الرش الحقلى. وأيضا دلت النتائج على زياده نسبه المتبقى المميت فى التجربه الحقليه - المعمليه لمبيد الكلوروبيروفوس من ٧١,٦٪ للمبيد وحده ل ٧٤,٩٪ و٨٧,٥٪ و ٨٨,٥٪ عند أضافه المتراكبات النانونيه المحضره. أيضا زياده نسبه المتبقى المميت فى التجربه الحقليه - المعمليه لمبيد اللامداثيالوثيرين من ٦٤,٧٪ للمبيد وحدة ل ٦٨,٦٪ و ٧٤,٩٪ و ٧٩,٧٪ وزياده نسبه المتبقى المميت لمبيداليوفنرون من ٦٣,١٪ للمبيد وحده ل ٦٧,٦٪ و٧٥,٩٪ و ٧٨,٣٪ عند أضافه المتراكبات النانونيه المحضره.

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Preparation, Characterization of Some Nanocationic Surfactants and Their Effectivness on the Physico-chemical Properties, Efficacy and Persistance of Some Insecticides against Cotton Leafworm (*Spodoptera littoralis* (Boisd.))

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