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Fatty acid metallic salts and pyrethroids environmental friendly pesticides

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Abstract
The most important challenge of the third millennium will be to further develop sustainable agricultural production systems that can meet the food needs of the world population without damaging the environment. New agricultural technologies must follow several objectives such as better quality of agricultural products, healthier and better value food to ensure disease prevention, increasing sustainability [1]. Potassium salts of fatty acid are commonly called soap salts. They are used as insecticides, herbicides, fungicides, and algaecides. The synthesized soap compounds were characterized by elemental analysis, IR spectral studies and molar conductance measurements. When the soap is mixed with required synthetic pyrethroides, it is found to be an effective combination to provide enhanced non-persistent insecticidal properties. They may also remove the protective waxes that cover the insects, causing death through excess loss of water, it is found to be an effective combination to provide enhanced insecticidal efficacy and residuality.

Keywords: soap, fatty acid, IR, whiteflies, insecticidal soap, non-persistent pesticides

Introduction
Pesticides play an important role in agriculture, to prevent loosing of considerable part of vegetable, fruit, cereals and flowers crop every year. Each of the commercial products has utility in a certain field and to a certain extent being suitable for killing certain species of pests, on certain hosts, and in certain conditions of temperature, light and humidity. Much effort is still requested for improving the aspects concerning toxicity, phytotoxicity, biodegradability or staining and killing pests [2].When synthetic pyrethroids mixed with potassium salt of fatty acids, it is found to be an effective combination to provide enhanced insecticidal efficacy and residuality. Fatty acids are natural occurring substances, in animal and vegetal organs, and can be obtained from by-products resulted from industrial processing of animal greases and vegetal oils. Some chemical derivation techniques can provide a diversity of semi-chemicals able to substitute the synthetic pesticides for the organic agricultural practice, in order to combine their high biologic activity, low toxicity for plants, humans and domestic animals with a total protection of the environment. Among these derivatives, fatty acid metallic salts can be obtained by very clean and relatively simple technologies, without using chemical solvents or other substances non-admitted by the international legislation about the environment protection. The low solubility in water of the fatty acid metallic salts contributes to the low phytotoxicity and no propagation in the environment of the formulation [3, 4]. On the other hand, the fatty acid based pesticides are readily biodegradable. This liquid soap-based pesticides which is easy to handle and to apply and safe to use, which act largely by a physical mode of action, which overcomes to know problems of powder-based insecticides, to provide an environmentally friendly insecticide having insect repellent activity are reported in the present paper.

Material and Methods
Fatty acids metallic salts was prepared by refluxing equivalent amounts of corresponding fatty acids and aqueous solution of KOH for 6-8 hours on a water bath. The Fatty acids metallic salts was purified by recrystallization with benzene-methanol mixture and dried under reduced pressure. The purity of the Fatty acids metallic salts was checked by the determination of their melting point.

$$C_{15}H_{31}COOH \quad + \quad KOH \longrightarrow C_{15}H_{31}COOK \quad + \quad H_2O$$

Palmitic Acid   Pot. Hydroxide   Potassium Palmitate (Soap)

The conductivity measurements of the solution of Potassium palmitate in distilled water was made with "BIOCRAFT" direct reading Conductometer and a dipping type glass conductivity cell with platinumized electrodes at a room temperature [5].

Results and Discussion
Infra-red Absorption spectra: The infrared absorption spectra of palmitic acid and of corresponding potassium palmitate were obtained with a Perkin-Elmer grating spectrophotometer in the region 4000-400 cm^{-1}, using potassium bromide technique. In the IR spectrum of Potassium Palmitate the absorption bands of C-H stretching vibrations viz. the symmetrical vibration of CH_2 at 2860-2850 cm^{-1}, the asymmetrical stretching vibration of CH_2 at 2920-2910 cm^{-1}, the asymmetrical stretching vibration of CH_3 at 2960-2940 cm^{-1} and the deformation of CH_2 at 1498-1320 cm^{-1} are observed

in the spectra of potassium palmitate as well as in palmitic acid [6, 7]. The evenly spaced progressive bands near 1350-1188 cm^{-1} which are characteristic of the hydrocarbon chain of acid remain unchanged on preparing the carboxylate from the corresponding fatty acid. The absorption bands observed near 2660-2640, 1700, 930-900, 575-530 cm^{-1}, in the spectra of fatty acid have indicated the presence of localized –COOH group in the form of dimeric structure and the existence of intermolecular hydrogen bonding between two molecules of the acid.

The appearance of two absorption band of carbonyl group corresponding to the symmetric and asymmetric vibrations of carboxylate ion near 1470-1410 and 1560-1540 cm^{-1} respectively in the spectra of potassium palmitate indicate that there is a complete resonance in the C-O bonds of carbonyl group of the carboxylates molecules and the two bonds become identical with the force constant assuming the value intermediate between those of normal double and single bonds.

It is therefore concluded that the resonance character of the ionized carboxyl group is retained in these metal carboxylates and the fatty acids exist with dimeric structure through hydrogen bonding whereas the metal-to-oxygen bonds in these metal carboxylates are ionic in character.

Specific Conductance: The Specific conduction, K of the solution of potassium palmitate soap in a mixture of KOH and Palmitic Acid increase with increasing concentration of carboxylate, C and temperature. The increase in specific conductance may be due to ionisation of potassium palmitate into simple metal cations, K^+ and palmitate anions $C_{15}H_{31}COO^-$ in dilute solutions and due to the formation of ionic micelles at higher carboxylate cooncentrations. The micellization occurs when the energy released as a result of aggregation of hydrocarbon chains of the monomer is sufficient to overcome the electrical repulsion between the ionic head groups and to balance the decrease in entropy accompanying aggregation. The CMC increase with increasing temperature since the kinetic energy of the monomers increases with temperature.

The result shows that the solute-solvent interaction is larger than the solute-solute interaction of dilute soap solutions. It is therefore concluded that the soap molecules do not show appreciable aggregation below the CMC and there is a marked increase in the aggregation of the soap molecules at this definite soap concentration. The CMC (critical micelle concentration) of potassium palmitate is 3.1 x 10^{-3} dm^3/l on plotting specific conductance Vs concentration at various concentrations. Many samples of various concentration having different pH have been prepared by mixing potassium palmitate of concentration of different dilution (%), and then sprayed on plant to check the efficacy of this insecticidal spray on daily and bi-weekly interval.

Conclusion

Potassium fatty acids are a non-selective insect control product. Insecticidal works only on direct contact with the pests [8, 9]. They wash away the protective coating on the surface of the insect's body. They will break the cell membrane and the insects will dies. That in our experiment we conclude that, the liquid spray insecticide contains Potassium palmitate of 10% having pH 10.29 (table: 2) is found to be more effective than other solutions. Other solutions were found to be less effective in destroying insects viz. whiteflies. Insecticidal soap is a contact insecticide and has no residual activity [10, 11]. It is readily broken down by light, so there is no soap residue.

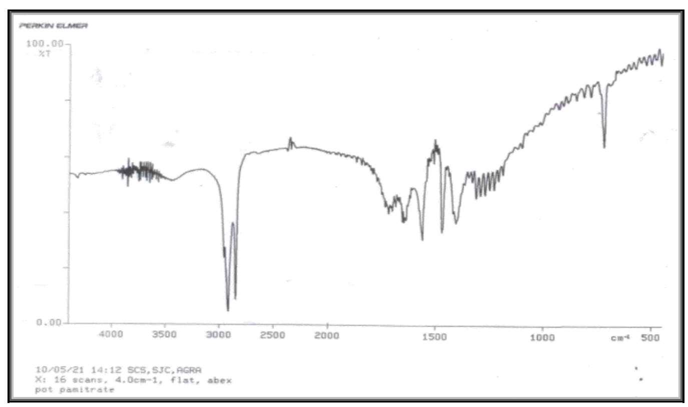

Fig 1: IR Spectra of Potassium Palmitate

Table 1: Infrared absorption spectral frequencies (Cm^{-1}) with their assignment

S. No	Assignment	Palmitic acid	Potassium palmitate
1	CH_3, C-H asymmetrical stretching	2960 V W	2940 W
2	CH_2, C-H asymmetrical stretching	2910 V S	2920 S
3	CH_2, C-H symmetrical stretching	2850 S	2850 S
4	OH Stretching	2650 W	__
5	C=O stretching	1700 VS	__
6	COO^-, C-O asymmetrical stretching	___	1600 W
7	COO^-, C-O symmetrical stretching	___	1460 MS
8	C-O, stretch, -OH in plane deformation	1440 W	__
9	CH_2, (adjacent to –COOH group) deformation	1410 W	__
10	CH_3, symmetrical deformation	1350 W	1350 W
11	Progressive band (-CH_2, twisting and waging)	1200-1180 W	1300-1170 W
12	CH_3, rocking	1110 W	1110 W
13	OH out of plane deformation	930 W	__
14	CH_2, rocking	720 M	720 S
15	COOH, bending mode	690 MS	__
16	COOH, wagging mode	550 MS	__
17	KOH bond	__	__

Table 2: Specific conductance of different solution of potassium palmitate soap

Sr. No.	Concentration C x 10^3 (dm^3/l)	Specific conductance K x 10^6 (mhos cm^{-1})	P^H	Impact on Whiteflies
1	4.7	6.44	8.42	No impact
2	4.9	6.65	8.52	No impact
3	5.1	6.68	8.61	No impact
4	5.3	6.73	8.68	No impact
5	5.5	6.83	8.76	No impact
6	5.8	6.94	8.86	Less effective
7	6.0	7.12	8.94	Less effective
8	6.4	7.28	9.15	Less effective
9	6.7	7.43	9.40	Less effective
10	7.1	7.49	9.80	Effective
11	7.6	7.67	9.95	Effective
12	8.0	7.91	10.15	Effective
13	8.6	8.18	10.29	Most Effective
14	9.2	8.29	10.46	Less effective
15	10.0	8.79	10.70	Less effective

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