Fatty Acid Metallic Salts and Pyrethroids - Environmental friendly Pesticides

Jain Dheeraj *, Verghese .P Susan, Sidhardhan Nisha

School of Chemical Sciences, St.John's College Agra (U.P)

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. Potassium salts of fatty acid are commonly called soap salts. They are used as insecticides, herbicides, fungicides, and algaeicides. The synthesized soap compounds were characterized by elemental analysis, IR spectral studies and molar conductance measurements. When the soap is mixed with required synthetic pyrethroids, 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, I.R, whiteflies, insecticidal soap, non-persistent pesticides

Corresponding Author:-
Dheeraj Jain
School of Chemical Sciences,
St.John's College Agra (U.P)
E-mail: jaind44@yahoo.co.in
INTRODUCTION:

Pesticides play an important role in agriculture, to prevent loosing of considerable part of vegetable, fruit, cereals and flowers crop every year\(^1\). 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 required 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:

(1) 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.

\[
\text{KOH} + \text{C}_{15}\text{H}_{31}\text{COOH} \rightarrow \text{C}_{15}\text{H}_{31}\text{COOK} + \text{H}_2\text{O}
\]

Pot. Hydroxide Palmitic Acid Potassium Palmitate (Soap)
(2) 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.

(3) 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 platanized electrodes at a room temperature \(^5\).

RESULTS AND DISCUSSION:

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.

Conductivity measurement of Potassium Palmitate:

The Specific conduction, K of the solution of potassium palmitate soap in a distilled water increase with increasing concentration of carboxylate, C and temperature. The increase in specific conductance may be due to ionization 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 $3.1 \times 10^{-3}$ 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.

**Application of Potassium Palmitate and Pyrethroids as Insecticides:**

Insecticidal soaps (mixture of Potassium palmitate and pyrethroids), individually Potassium palmitate and pyrethroids these three insecticides were applied weekly and bi-weekly on the whiteflies and note down the results after fourth week of application. After the single application of potassium palmitate these was little impact on plants whiteflies. After fourth week of application some whiteflies were dead but not much improvement in the plants leaf as they were still affected and unhealthy.

Synthetic insecticides that mimic the action of pyrethrins are known as pyrethroids when pyrethroids spray applied on the plant many whiteflies were dead after the weekly and bi-weekly application. Pyrethroids are synthesized pyrethrins these materials disrupt the nervous system of insects and cause paralysis a few minutes after application the insect cannot move or fly away. Since pyrethroids has some toxic effects to human other mammals plants leaf fruits and stem etc. so it also damage the plant growth. So it can not be used as good insecticide.

Insecticidal soaps (mixture of Potassium palmitate and pyrethroids) works only on direct contact with the pests. We have prepared many spray solution of mixture of potassium Palmitate and pyrethroids of different concentration having various pH and spray. They wash away the protective coating on the surface of the insects body. These formulation contains insecticidal soap penetrate an insects body covering and disrupt the cell membranes causes it to dehydrate and die. They are fast acting and often used for their “knock-down” effects to quickly reduce large insect pest populations. They are less toxic to humans and other mammals and break down quickly form sunlight moisture and oxygen leaving no residues. The percentage mortality of these solutions was also high. (Graph: 1)
CONCLUSION:

Insecticidal soaps (mixture of Potassium palmitate and pyrethroides) are a non-selective insect control product. Insecticidal works only on direct contact with the pests\textsuperscript{8,9}. They wash away the protective coating on the surface of the insects body. They will break the cell membrane and the insects will die. That in our experiment we conclude that, the liquid spray insecticide contains Potassium palmitate and pyrethroides of 10\% having pH 10.29 (table: 2, graph: 1) is found to be more effective than other solutions. Other solutions were found to be less effective in destroying insects viz. whiteflies. Insecticidal soap (mixture of Potassium palmitate and pyrethroides) is a contact insecticide and has no residual activity\textsuperscript{10,11}. It is readily broken down by light, so there is no soap residue.

![IR Spectra of Potassium Palmitate](image)

Fig. - 1   I R Spectra of Potassium Palmitate
Graph: 1 Concentration vs Mortality of Potassium Palmitate and Pyrethroids

Table: 1 Infra-Red absorption spectral frequencies (cm\(^{-1}\)) with their assignment

<table>
<thead>
<tr>
<th>S.NO.</th>
<th>ASSIGNMENT</th>
<th>PALMITIC ACID</th>
<th>POTASSIUM PALMITATE</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>CH(_3), C-H asymmetrical stretching</td>
<td>2960 V W</td>
<td>2940 W</td>
</tr>
<tr>
<td>2</td>
<td>CH(_2), C-H asymmetrical stretching</td>
<td>2910 V S</td>
<td>2920 S</td>
</tr>
<tr>
<td>3</td>
<td>CH(_2), C-H symmetrical stretching</td>
<td>2850 S</td>
<td>2850 S</td>
</tr>
<tr>
<td>4</td>
<td>OH stretching</td>
<td>2650 W</td>
<td>—</td>
</tr>
<tr>
<td>5</td>
<td>C=O stretching</td>
<td>1700 VS</td>
<td>—</td>
</tr>
<tr>
<td>6</td>
<td>COO(^-), C-O asymmetrical stretching</td>
<td>—</td>
<td>1600 W</td>
</tr>
<tr>
<td>7</td>
<td>COO(^-), C-O symmetrical stretching</td>
<td>—</td>
<td>1460 MS</td>
</tr>
<tr>
<td>8</td>
<td>C-O, stretch, -OH in plane deformation</td>
<td>1440 W</td>
<td>—</td>
</tr>
<tr>
<td>9</td>
<td>CH(_2), (adjacent to –COOH group) deformation</td>
<td>1410 W</td>
<td>—</td>
</tr>
<tr>
<td>Sr. No.</td>
<td>CH₃, symmetrical deformation</td>
<td>1350 W</td>
<td>1350 W</td>
</tr>
<tr>
<td>--------</td>
<td>-------------------------------</td>
<td>--------</td>
<td>--------</td>
</tr>
<tr>
<td>11</td>
<td>Progressive band (-CH₂, twisting and wagging)</td>
<td>1200-1180 W</td>
<td>1300-1170 W</td>
</tr>
<tr>
<td>12</td>
<td>CH₃, rocking</td>
<td>1110 W</td>
<td>1110 W</td>
</tr>
<tr>
<td>13</td>
<td>OH out of plane deformation</td>
<td>930 W</td>
<td>—</td>
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<tr>
<td>14</td>
<td>CH₂, rocking</td>
<td>720 M</td>
<td>720 S</td>
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<tr>
<td>15</td>
<td>COOH, bending mode</td>
<td>690 MS</td>
<td>—</td>
</tr>
<tr>
<td>16</td>
<td>COOH, wagging mode</td>
<td>550 MS</td>
<td>—</td>
</tr>
<tr>
<td>17</td>
<td>KOH bond</td>
<td>—</td>
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</tr>
</tbody>
</table>

Table: 2 Specific conductance of different solution of Insecticidal soaps (mixture of Potassium Palmitate and Pyrethroids)

<table>
<thead>
<tr>
<th>Sr. No.</th>
<th>Concentration C x 10³ (dm³/l)</th>
<th>Specific conductance k x 10⁶ (mhos cm⁻¹)</th>
<th>pH</th>
<th>Impact on Whiteflies</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>4.7</td>
<td>6.44</td>
<td>8.42</td>
<td>No impact</td>
</tr>
<tr>
<td>2</td>
<td>4.9</td>
<td>6.65</td>
<td>8.52</td>
<td>No impact</td>
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<tr>
<td>3</td>
<td>5.1</td>
<td>6.68</td>
<td>8.61</td>
<td>No impact</td>
</tr>
<tr>
<td>4</td>
<td>5.3</td>
<td>6.73</td>
<td>8.68</td>
<td>No impact</td>
</tr>
<tr>
<td>5</td>
<td>5.5</td>
<td>6.83</td>
<td>8.76</td>
<td>No impact</td>
</tr>
<tr>
<td>6</td>
<td>5.8</td>
<td>6.94</td>
<td>8.86</td>
<td>Less effective</td>
</tr>
<tr>
<td>7</td>
<td>6.0</td>
<td>7.12</td>
<td>8.94</td>
<td>Less effective</td>
</tr>
<tr>
<td>8</td>
<td>6.4</td>
<td>7.28</td>
<td>9.15</td>
<td>Less effective</td>
</tr>
<tr>
<td>9</td>
<td>6.7</td>
<td>7.43</td>
<td>9.40</td>
<td>Less effective</td>
</tr>
<tr>
<td>10</td>
<td>7.1</td>
<td>7.49</td>
<td>9.80</td>
<td>Effective</td>
</tr>
<tr>
<td>11</td>
<td>7.6</td>
<td>7.67</td>
<td>9.95</td>
<td>Effective</td>
</tr>
<tr>
<td>12</td>
<td>8.0</td>
<td>7.91</td>
<td>10.15</td>
<td>Effective</td>
</tr>
<tr>
<td>13</td>
<td>8.6</td>
<td>8.18</td>
<td>10.29</td>
<td>Most Effective</td>
</tr>
<tr>
<td>14</td>
<td>9.2</td>
<td>8.29</td>
<td>10.46</td>
<td>Less effective</td>
</tr>
<tr>
<td>15</td>
<td>10.0</td>
<td>8.79</td>
<td>10.70</td>
<td>Less effective</td>
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</table>
REFERENCES: