



Angstrom void polymer (AVP) gel matrix – An organo-inorganic matrix formulation development for slow and sustained release of methyl eugenol

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Abstract

A new unique and novel formulation was developed using microporous and mesoporous zeolites 4A, loaded with methyl eugenol (ME) and in combination with the ME loaded and pH adjusted carbopol 940 aqueous gel. The developed formulation with the entrapped ME in the organo-inorganic matrices resulted in slow and sustained release of ME at constant rate for 56 days when deployed in the agriculture fields. The formulation can be effectively used for monitoring, mass trapping and controlling of fruit fly pest. Molecular sieves in the inorganic matrix of zeolites 4A helps in the sorption of the pheromones and exhibits the synergic sustained release effect, when combined with the pH stabilized ME loaded carbopol 940 gel. By adjusting the pH of the matrix system, an average sustained release of 33.33 ± 0.06 mg of ME per day was achieved continuously for 56 days, by a loading dose 2gms of ME into the zeolite 4A dispersed carbopol 940 gel; angstrom void polymer (AVP) gel matrix formulation (patent applied).

Keywords: Methyl eugenol, Carbopol 940 gel, Zeolites 4A

Introduction

Pest control in the agricultural fields is big challenge in the present days. Irrational and unscientific usage of pesticides, impact of industrialization and its effect to name few, deforestation, greenhouse effect, pollution due to increased human activities, increase in earth's surface temperature, glacier meltdown at poles, and increase in sea levels, all these turbulence in the nature has caused the harsh resistance development in the pests. Another surprising fact is that some of the pests are also resistant to even genetically modified crops posing the bigger challenges to the scientific community, whose efforts are in vain to contain these pests. These stubborn pests are posing a bigger challenge for the cultivation process bringing enormous loss to the farmers. Need of the hour is to develop safe and effective methods to control these intractable pests.

Thus, there is a need for the development of pheromone-based pest control methods to contain these pests without harming the nature. While developing the pheromone-based products to address the pests, another bigger challenge to the scientific community is to develop a pheromone dispersion system that works effectively in the open agricultural fields. These dispersion systems should work effectively for longer duration of time even under the unpredictable weather conditions including variations in wind flow, temperatures, and humidity and allow the release of pheromones from the formulation into the surroundings at a constant rate.

Evaluating the need for the effective pheromone dispersion system, we have developed a new unique and novel formulation by amalgamating the specifically selected inorganic zeolites 4A matrix with the organic pH stabilised carbopol 940 gel (AVP gel matrix; patent applied). The newly developed organo-inorganic matrix formulation demonstrated slow, sustained, and constant release of ME into the atmosphere for a prolonged time. Sustained release

capacity of the pheromone charged zeolites 4A dispersed in pheromone charged carbopol 940 gel can be altered and adjusted by modulating the pH and the addition of moisture retaining agents to the matrix.

The unique property of the zeolites with variable properties such as unique framework based on Si/Al ratio, pore dimension and the presence and absence of Lewis acid [1-4] sites are explored to control the sorption of organic pheromone molecules in their cages [5, 6], facilitating the inward and outward movement of molecules under the influence of pH of the surrounding system [9-12].

Since the change in pH alters the inductive and electromeric effects of organic polymer of the carbopol 940 gel, altering this weak attraction forces between the ME molecules with organic polymer carbopol 940 gel, influences the slow release of ME to the surrounding air. Also, pH influences the altering of Lewis acid base interaction of zeolites [7,8] with the methyl eugenol. Molecular sieves of the zeolite 4A act as release control for the pheromones to migrate from these molecular sieves to the surrounding gel base. Thus, pH influenced interaction of organic ME molecules with the inorganic zeolites 4A and organic carbopol 940 gel plays an important role in the sustained release effect of the matrix. Water absorption capacity of the carbopol 940 gel, its water retention capacity was found to influence by the pH of gel and molecular structure of the polymer [13-15].

It was observed that, sustained release of ME molecules into the surrounding air from the matrices was influenced by the ME sorbed in the porous framework of cavities and channels present in the selected zeolites 4A and pH stabilised carbopol 940 gel. The ionic interaction of the inorganic zeolite 4A matrix and the carboxyl groups present in the polymerised acrylic acid groups in carbopol 940 gel with the organic ME play an important role for the sustained release effect.

Materials and method

Active pheromone ingredient (API), ME of 95% - 98% purity, was procured from in-house Advanced Pheromone development (APD) dept., Barrix Agro Sciences, Molsieve-13X, Molecular Sieve Zeolites of 2-4mm (Zeolites 4A), the specific variant was obtained from Gujarat Multi Gas Base Chemicals Pvt. Ltd., carbopol 940 was purchased from s d fine-chem limited. All the other chemicals and reagents used in the formulation development and its evaluation were of analytical grade.

Experiment

After initial assessment of all the available forms of zeolites, Zeolites 4A pellets were chosen considering the pellets size, Al/Si ratio, pore dimensions and its framework. Zeolites 4A were activated, by dry heating the zeolites 4A at 150°C for half hour in temperature regulated hot air oven.

ME gels were made in accordance with the formula in table 1.

STEP 1: Stabilized ME formulation was added to activated Zeolite 4A, and allowed for complete sorption, ensuring the incorporation of ME into the molecular sieves of the Zeolite 4A.

STEP 2: Alkaline purified water (made alkaline with potassium citrate) was slowly incorporated into the polyacrylate 940 (carbopol 940) with continuous stirring and allowed to swell, after gelation the gel is stabilized by the addition of antimicrobial agent, antioxidant and photo stabilizer. Later moisture retaining agent was added with continuous stirring to ensure uniform mixing and finally the pheromone ME was slowly incorporated into the gel.

STEP 3: Pheromone charged Zeolites 4A was slowly and uniformly dispersed into the pheromone charged carbopol 940 Gel. Desired pH of the matrix was adjusted using organic acids or organic bases, thus forming ME charged Angstrom void polymer (AVP) gel matrix.

Table 1: Composition of formulations of zeolites 4A dispersed carbopol 940 gel; angstrom void polymer (AVP) gel matrix.

Ingredients	Role in formulation	F1	F2	F3	F4	F5
Methyl Eugenol	Active Pheromone ingredient	0.5	0.75	1	0.5	0.75
Pheromone-Zeolite ratio	In-organic Matrix	0.5:2	0.75:2	1:2	0.5:2	0.75:2
Pheromone-dry Carbopol-940 ratio	Organic Gelling agent	0.5:2	0.75:2	1:2	0.5:2	0.75:2
Pheromone-Carbopol-940 gel ratio	Organic gel Matrix	0.5:100	0.75:100	1:100	0.5:100	0.75:100
Glycerol	Moisture Retaining agent	1	3	5		
Propylene glycol					1	3
pH	Release rate modifier	4.5	5.5	6.5	4.5	5.5
Zeolite-dry Carbopol-940 ratio	Combined in-organic and organic dry Matrix	1:1	1:1	1:1	1:1	1:1
Zeolite-Carbopol-940 gel ratio	Combined in-organic and organic gel Matrix	2:100	2:100	2:100	2:100	2:100

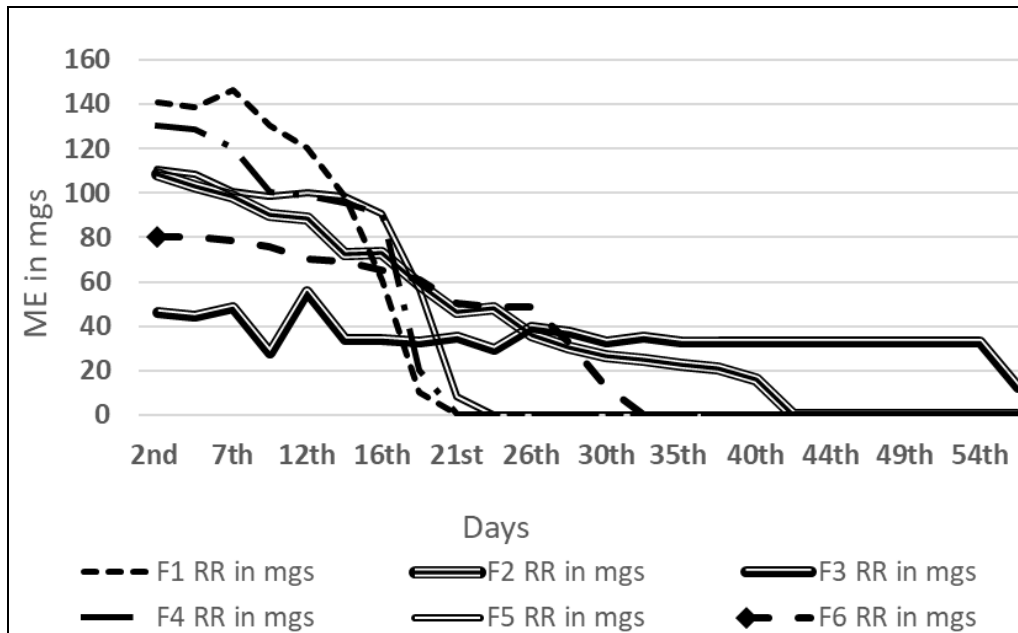


Fig 1: Methyl Eugenol release rates in various formulations of ME loaded zeolites dispersed in ME loaded carbopol 940 Gel.

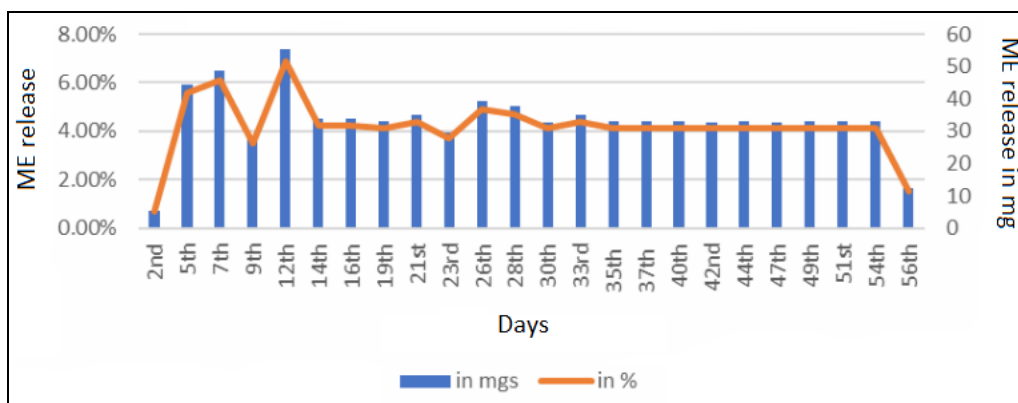


Fig 2: Controlled, sustained and constant release rate of methyl eugenol by zeolites 4A dispersed carbopol gel matrix [AVP] gel matrix] - F3 formulation.

Results and discussion

The organo-inorganic matrix interactions influencing the inorganic zeolite 4A matrix and the carboxyl group terminals present in the selected carbopol 940 gel, changes in the weak induced dipole moment, i.e., ionisation of the carboxylic groups in the acrylic acid units of the carbopol 940, resulting in variable ionic attraction of organic ME molecules play an important role for the sustained release effect.

As the pH of the designed formulation changes from more acidic to less acidic pH the ME molecules were held strongly in the organic carbopol 940 matrix. Gel formation influenced by the pH of the surrounding medium, which in turn influences the uncoiling of the acrylic polymer and increases the water retention and gelling capacity of the carbopol 940. When the surface ME molecules from the carbopol 940 gel were dispersed into the flowing air, diffusion of ME from the zeolites 4A into the gel was observed in order to sustain induced dipole movement changes or ionic changes in the organo-inorganic matrix by pH of the surrounding medium and the presence of glycerol. When ME was loaded into the zeolites 4A at a ratio of 1:2, prolonged and sustained release of ME was observed. By adjusting the pH of the matrix system to 6.5 and modulating the humectant glycerol content in a ratio of 5:100, the

resultant gel exhibited a good prolonged and sustained release effect, it was observed that slow and sustained release of ME for a period of 56days effectively in the newly developed organo-inorganic gel matrix (AVP gel matrix). As glycerine modulates the solubility of the carbopol 940 by increased unwinding of the acrylic polymer, there by influencing the interaction of ME with the dipole induced acidic groups of the acrylic acid units of the carbopol 940 polymer. The newly developed formulation exhibited effective release an average 33.33 ± 0.06 mg of ME per day constantly for 56 days, making the zeolite 4A dispersed carbopol 940 gel; angstrom void polymer (AVP) gel matrix formulation (patent applied), a novel formulation.

Conclusions

The present experimental results, it was concluded that by amalgamating the pH modulated organic matrix carbopol 940 gel with inorganic zeolites 4A, a unique and novel angstrom void polymer (AVP) gel matrix was obtained, and it was also established that, this pH modulated organo-inorganic matrix formulation demonstrates slow, sustained, and extended release of methyl eugenol in field studies. Sustained and extended-release effect of the matrix depends on the pH of the organic gel, moisture retaining agent used and chemical nature of the pheromone. This pH induced

changes in the dipole interactions affects the weak attraction forces between the gel and the pheromone. The pH surrounding the zeolites 4A also affects the in and out movement of pheromone molecules in the 3d molecular sieves of the zeolites 4A. Numerous pheromones can be charged into the variable pH modulated AVP gel matrix to attain slow, sustained, and extended release of pheromones in the open-air fields for crop protection.

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