Investigation of Factors Influencing Ambient Release of Metofluthrin from Various Polymeric Substrates.

THESIS

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By

REENA BIBALS

Under the Supervision of

Dr. DEBOJIT CHAKRABARTY

BIRLA INSTITUTE OF TECHNOLOGY AND SCIENCE
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BIRLA INSTITUTE OF TECHNOLOGY AND SCIENCE
PILANI (RAJASTHAN)

CERTIFICATE

This is to certify that the thesis entitled **Investigation of Factors Influencing Ambient Release of Metofluthrin from Various Polymeric Substrates a**nd submitted by **Reena Bibals** ID No **2008PHXF437P** for award of Ph. D. Degree of the Institute embodies original work done by her under my supervision.

Signature in full of the Supervisor: ______________________

Name in capital block letters: **DR. DEBOJIT CHAKRABARTY**

Designation: Associate Vice President -R&D -GCPL

Date:

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SUMMARY

In recent times, the household insecticide industry globally has witnessed a rapid surge in development in response to the growing incidence of mosquito menace on human population. Typically, household insecticidal compounds consist of synthetic pyrethroids as active ingredients which are primarily responsible for exhibiting insecticidal efficacies, when incorporated within a suitable delivery vehicle. Recent efforts on synthesizing newer generation pyrethroid compounds have placed greater emphasis on their enhanced safety, efficacy, and toxicity potential in comparison to their old congeners. The current study attempts to address key factors impacting the release of metofluthrin, a relatively recent synthetic pyrethroid exhibiting a relatively high vapor pressure under ambient conditions, when incorporated onto various substrate types.

While examples of few commercially available insecticidal formats containing metofluthrin do exist, it has proven difficult to reasonably predict their end-of-life given the influence of external variable factors on metofluthrin release. To our knowledge, a systematic study of the influence of external variables influencing metofluthrin release has not been undertaken, hitherto. In absence of this data, designing an optimal product format is fraught with uncertainty as regards claiming unambiguously a clear end of life. The current study attempts to bridge this understanding by studying the influence of some of the factors affecting release by designing relevant experiments that generate diffusion related data. Metofluthrin release profiles have been studied from different substrate types, all of which were incorporated with identical amounts. The data obtained experimentally has been subsequently used to build a generalized diffusion model. It is interesting to note that metofluthrin diffusivity under ambient conditions from various metofluthrin-impregnated substrates was found to be extremely low, of the order of 10^{-16} m^2/s. This value is typically three to four orders of magnitude lower than the normal diffusivity of gases and liquids. Such low metofluthrin diffusivities suggest the presence of strong cohesive interaction forces between metofluthrin and substrates under investigation.

Studies on physical characteristics of various polymeric substrates along with spectral studies that probe molecular level interactions between metofluthrin and various surfaces was conducted. Initial studies focused on measuring physical characteristics of various substrates. BET was

employed for determination of surface areas, pore sizes and pore volumes, while, MIP was used to quantify a) intrinsic porosities and b) the extent of pore occupancy upon metofluthrin impregnation. Thermo-analytical tools, viz., DSC, TGA, and TPD were employed to gain a qualitative understanding of the energetics of metofluthrin–substrate interactions.

HS-GC and TGA measurements in conjunction corroborate the experimentally observed higher diffusivity of metofluthrin in cellulose, and, provide a rational explanation for order of diffusivities noted from various substrates. Powder XRD, FTIR, surface FTIR, and solid-state ^{1}H and ^{13}C NMR investigations were conducted to probe substrate crystallinities, as well as, molecular level interactions between metofluthrin and the substrates, in the bulk or surface. Spectral studies both on the surface as well as bulk scale revealed negligible chemical interactions, suggesting that physical properties of substrates play an important role in diffusivity. These experiments have demonstrated that for all conditions maintained constant, metofluthrin diffusivity followed the order cellulose ~~ nylon > PET > polypropylene. The observed diffusivities correlate with the overall surface areas and surface spread abilities as demonstrated by contact angle observations.

A generalized metofluthrin diffusion model was developed using temperature, velocity and surface area as external variables and validated by applying it on an earlier reported system. Modelling studies were conducted using unsteady state mass balances while assuming that the diffusivity of metofluthrin inside the matrix follows an Arrhenius dependence on temperature, and, that the mass transfer coefficient is linearly dependent on the bulk fluid velocity. A “hindered pore diffusion model” has been proposed to explain the unusually low mass transfer coefficients of metofluthrin from substrates.

Spectral studies at the bulk and surface level revealed absence of chemical interactions between metofluthrin and substrates. Studies show that the unusually lower diffusivities of metofluthrin are fundamentally dependent on physical properties of substrates. Factors like surface area, spreading ability of active on substrate, pore volume, pore size and intrinsic porosities are key to metofluthrin release, and, do explain the order of metofluthrin diffusivities experimentally determined from various substrates. ‘A hindered pore diffusion model’ has been invoked to rationalize and explain the extremely low metofluthrin diffusivity which has been observed.

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LIST OF ABBREVIATIONS / SYMBOLS

Abbreviation / Symbol	Meaning
Pf	Plasmodium falciparum
DDT	Dichlorodiphenyltrichloroethane
WHO	World Health Organization
CDC	US center for disease control
DEET	N,N-Diethyl meta-toluamide
LD_{50}	Lethal Dose 50
Cx	Culex
EPA	US Environmental Protection Agency
RH	Relative Humidity
GC	Gas Chromatography
PP	Polypropylene
PET	Polyethylene Terephthalate
DSC	Differential Scanning Calorimtery
DTG	Differential Thermogravimetry
TPD	Temperature Programmed Desorption
GSM	Grams per square meter
D_{eff}	Effective Diffusion Coefficient
E_a .	Activation energy of diffusing molecule
R	Universal gas constant = 8.314 J/K/Mol
VOC	Volatile organic compound
HS-GC	Head Space Gas Chromatography
BET	Brunauer–Emmett–Teller
SEM	Scanning electron microscope
MIP	Mercury intrusion porosimtery
TGA	Thermogravimtery analysis
ATR-FTIR	Attenuated total reflectance-Fourier transform Infrared spectroscopy
^{13}C NMR	13 C nuclear magnetic resonance spectroscopy
HPLC	High performance liquid chromatography
UV-Spectrophotometer	Ultraviolet –visible spectroscopy
GC-ECD	Gas chromatography- electron capture detector
MS	Mass spectroscopy
GC-FID	Gas chromatography with flame ionization detector
TDS	Thermal desorption spectroscopy
MAS	Magic angle spinning
XRD	X-ray diffraction spectroscopy
KT_{50}	Knock down time 50
% m//m	Percentage mass/ mass
Pa	Pascals
K_c	Mass transfer co efficient
IRS	Indoor residual spray
Bt	Bacillus thuringiensis

LIST OF ABBREVIATIONS / SYMBOLS

Abbreviation / Symbol	**Meaning**
OBP	Odorant-binding proteins
CIB	Central Insecticide Board
EPA	Environmental Protection Agency
rpm	Rotations per minute
FWHM	Full Width at Half Maximum
cps	Cycles per second
M	Molecular Weight of metofluthrin, 360.34 gm/mol
D_a	Diffusivity of metofluthrin in Air, 1×10^{-5} m^2/s
D_{eff}	Effective Diffusivity of metofluthrin in the Matrix
Mt	Amount released at time t, mg
C_1	Concentration of metofluthrin inside the matrix
C_2	Concentration of metofluthrin inside the room
E_a	Energy of Activation, J/mol
A	Pre-exponential factor, m^2/s
R	Universal Gas Constant, 8.314 J/K/mol
T	Matrix Temperature, K
v	Velocity of Air, m/s
t	Time, s
x, y, z	Spatial coordinates

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