

**DEVELOPMENT OF BIODIESEL  
BYPRODUCTS BASED BIO-PESTICIDAL  
FORMULATIONS**

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FORMULATIONS**

by

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Submitted

**In fulfillment of the requirements of the degree of Doctor of Philosophy**

to the



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Dedicated  
To  
The Almighty  
&  
My family

## **CERTIFICATE**

This is to certify that the thesis entitled **“Development of Biodiesel Byproducts based Bio-pesticidal formulations”** submitted by Ms. Megha Pant has been prepared under our guidance with the rules and regulations of Indian Institute of Technology Delhi India. The research report results presented in this thesis have not been submitted for any degree or diploma in any other institute or university.

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## ABSTRACT

The biodiesel production in india utilizes two main crops, karanja (*Pongamia pinnata*) and jatropha (*Jatropha curcas*) as major source of non-edible oils. The technology of biodiesel production consumes only extracted vegetable oil from non-edible seeds and leaves behind a large amount of unutilized mass as seed cake. Majority of industrial products employ only purified glycerol as a raw material, and therefore biodiesel waste liquid is often discarded as a waste product. This liquid biodiesel waste creates disposal problems and in future, liquid biodiesel waste is likely to be produced in large amounts, with detrimental effects on the environment. With increasing awareness about the harmful effects of synthetic chemical based pesticides, the demand for technologies and products based on biological processes has been increasing steadily worldwide. Keeping all these facts into consideration, the present work entitled, “Development of Biodiesel By-products based Bio-pesticidal formulations” was focussed on the developing biodiesel by-products based bio-pesticidal formulations for controlling stored grain and household pests i.e. *Tribolium castaneum* (Red flour beetle), *Periplaneta americana* (American cockroach), *Blattella germanica* (German cockroach) and *Aedes aegypti* (mosquito). The study was started with the screening of non-edible oil seed cakes and other active ingredients used viz. eucalyptus oil, chlorpyrifos, citronella oil, dillapiole and biodiesel waste against the four targeted insect pests along with the characterization using ATR-FTIR, GC-MS, Particle size analysis etc. Seed cakes as crude or their aqueous extracts were evaluated for their efficacy before formulating them. Karanja and jatropha cakes were tested against the stored grain pest, *Tribolium castaneum* (red flour beetle). Aqueous filtrate of the cakes was used to evaluate its efficacy against the beetle. Eucalyptus oil was also tested for its efficacy against *Tribolium castaneum*. GC-MS analysis of the oil was done to find the percentage of its constituents. Non-aqueous filtrate of karanja

and jatropha cake powder was tested against the american cockroach, *Periplaneta americana*. Chlorpyrifos was also tested to evaluate its efficacy against the american cockroach. GC-FPD of the filtrate was done pre and post micro/nanoemulsion. Solid karanja and jatropha cakes were tested against the *Aedes aegypti* adults. Liquid Biodiesel by-products along with citronella oil and dillapiole were tested against *Blattella germanica* individually and in combination. Liquid Biodiesel by-products along with citronella oil and dillapiole were tested against *Aedes aegypti* larvae individually and in combination. After the successful testing of the actives selected, they were used to develop the bio-pesticidal formulations to increase the effectiveness and shelf life. The characterization of the formulations developed was also done to confirm the presence of active ingredient. Aqueous filtrate of Karanja and jatropha cakes along with eucalyptus oil were used to develop nanoemulsions against *Tribolium castaneum*. The nanoemulsions developed were tested for the shelf studies along with ATR-FTIR and GC-MS analysis to confirm the presence of active components. The Efficacy of nanoemulsions containing aqueous filtrate of karanja and jatropha against *Tribolium castaneum* was also better as compared to nanoemulsions containing only essential oil due to the reduction in volatility of the active component. Non-aqueous filtrate of Karanja and jatropha cakes along with Chlorpyrifos was used to develop microemulsions against *Periplaneta americana*. The microemulsions developed were tested for the shelf studies along with ATR-FTIR and GC-FPD analysis to confirm the stability and study the degradation pattern of active component. The results confirm the better performance of the chlorpyrifos microemulsions with non-aqueous filtrate of karanja & jatropha as dispersed phase. Solid karanja and jatropha cakes were used to develop coil formulations along with other ingredients against *Aedes aegypti*. The coil formulations developed were tested for their burning efficiency and efficacy against the mosquitoes. Liquid Biodiesel by-products along with citronella oil and dillapiole were used to develop tablets against *Blattella germanica*.

ATR-FTIR analysis of the active components as well as the tablet formulation was done to assess the stability parameters. Bioefficacy of the tablets was evaluated against the German cockroach, (*Blattella germanica*) along with shelf life studies. Liquid Biodiesel by-products along with citronella oil and dillapiole were used to develop floating tablets against *Aedes aegypti* larvae. The bioefficacy trials along with ATR-FTIR analysis of the active components and tablets were conducted. The percent mortality rate decreased more with the tablets containing only citronella oil as compared to the tablets containing citronella along with dillapiole and biodiesel within a week time.

## सार

भारत में बायोडीजल उत्पादन गैर-खाद्य तेलों के प्रमुख स्रोत के रूप में दो मुख्य फसलों, करंजा (पोंगामिया पिन्नता) और जेट्रोफा (जेट्रोफा क्यूकस) का इस्तेमाल करता है! बायोडीजल उत्पादन की तकनीक ने केवल गैर-खाद्य बीज से निकाले वनस्पति तेल का सेवन किया है और बड़े पैमाने पर अप्रयुक्त जन (unutilized mass) को केक के रूप में छोड़ दिया है। अधिकांश औद्योगिक उत्पाद कच्चे माल के रूप में शुद्ध ग्लिसरॉल का इस्तेमाल किया गया है, और इसलिए तरल बायोडीजल अपशिष्ट पदार्थ को अक्सर अपशिष्ट उत्पाद (waste product) के रूप में त्याग दिया जाता है। यह तरल बायोडीजल कचरा निपटान की समस्याएं पैदा करता है और भविष्य में, तरल बायोडीजल कचरे की बड़ी मात्रा में उत्पादन की संभावना है, साथ ही पर्यावरण पर हानिकारक प्रभाव पड़ता है। सिंथेटिक रासायनिक आ धारित कीटनाशकों के हानिकारक प्रभावों के बारे में जागरूकता के साथ, जैविक प्रक्रियाओं के आधार पर प्रौद्योगिकियों और उत्पादों की मांग निरंतर दुनिया भर में बढ़ रही है। इन सभी तथ्यों को ध्यान में रखते हुए वर्तमान कार्य, "बायोडीजल बाय-प्रोडक्ट्स आधारित बायो-पेस्टीसीडल फॉर्म्यूलेशन का विकास" भंडारणित अनाज कीटों और घरेलू कीटों को नियंत्रित करने के लिए बायोडीजल द्वारा बायोपेस्टीसाइड आधारित बायो-कीटनाशक योगों पर केंद्रित था, अर्थात् ट्राइबोलियम कास्टेनियम (लाल आटा बीटल), पेरिप्लानेटा अमरीकाना (अमेरिकी तिलचट्टा), ब्लैटला जर्मनिका (जर्मन तिलचट्टा) और एडीस इजिप्सी (मच्छर)। अध्ययन गैर-खाद्य तेल के बीज केक और अन्य सक्रिय सामग्रियों की स्क्रीनिंग के साथ शुरू किया गया था। एटीआर-एफटीआईआर, जीसी-एमएस, कण आकार के विश्लेषण आदि का उपयोग कर लक्षण वर्णन के साथ चार

लक्षित कीटों के खिलाफ नीलगिरी का तेल, क्लोरोप्रिफॉस, सीट्रॉनला ऑयल, डिलिपियोल और बायोडीजल अपशिष्ट। बीज केक और उनके जलीय अर्क का मूल्यांकन उनके प्रभावकारिता के लिए उन्हें तैयार करने से पहले किया गया। भंडारित अनाज कीट, ट्राइबोलियम कास्टेनियम (लाल आटा बीटल) के खिलाफ करंजा और जेट्रोफा केक के जलीय अर्क का परीक्षण किया गया। नीलगिरी के तेल को भी ट्राइबोलियम कास्टेनियम के खिलाफ इसकी प्रभावकारिता के लिए परीक्षण किया गया था। तेल के जीसी-एमएस विश्लेषण में इसके घटकों का प्रतिशत जानने के लिए किया गया था। अमेरिकन तिलचट्टा, पेरिप्लानेटा अमरीकाना के खिलाफ करंजा और जेट्रोफा केक पाउडर के गैर जलीय अर्क का परीक्षण किया गया था। क्लोरोप्रिफॉस को भी अमेरिकी तिलचट्टा के खिलाफ इसकी प्रभावकारिता का मूल्यांकन करने के लिए परीक्षण किया गया था। एडीज इजिसी वयस्कों के खिलाफ ठोस करंजा और जेट्रोफा केक का परीक्षण किया गया। तरल बायोडीजल उप-उत्पाद, सिट्रोनेला तेल और डिलिपियोल का ब्लैटला जर्मैनिका और एडीस के खिलाफ व्यक्तिगत रूप से और संयोजन में जांच की गई। चुने गए सक्रियों के सफल परीक्षण के बाद, उन्हें प्रभावशीलता और शेल्फ जीवन को बढ़ाने के लिए जैव-कीटनाशक योगों को विकसित करने के लिए उपयोग किया गया। सक्रिय सामग्रियों की उपस्थिति की पुष्टि करने के लिए विकसित किए गए योगों का लक्षण वर्णन भी किया गया था। नीलगिरी के तेल के साथ करंजा और जेट्रोफा केक के जलीय अर्क का उपयोग ट्रावोलीयम कास्टेनियम के खिलाफ नैनोमुल्शन को विकसित करने के लिए किया गया था। सक्रिय घटकों की उपस्थिति की पुष्टि के लिए विकसित किए गए, नैनोमुल्शन का एटीआर-एफटीआईआर और जीसी-एमएस विश्लेषण के साथ शैल्फ अध्ययन के लिए परीक्षण किया गया। सक्रिय घटक की

अस्थिरता में कमी के कारण केवल आवश्यक (essential) तेल युक्त नैनोमुल्शन की तुलना में ट्राइबोलियम कास्टेनियम के विरुद्ध करंजा और जट्रोफा के जलीय अर्क युक्त नैनोमुल्शन की प्रभावकारिता भी बेहतर थी। क्लोरीफ्रीफोस के साथ करंजा और जट्रोफा केक के गैर-जलीय अर्क का उपयोग पेरिप्लानेटा अमेरिकाना के खिलाफ सूक्ष्म-ईमुल्शन को विकसित करने के लिए किया गया था। करंजा और जट्रोफा के गैर-जलीय अर्क के साथ क्लोरोप्रिफॉस सूक्ष्म-ईमुल्शन के बेहतर प्रदर्शन की पुष्टि करते हैं। ठोस करंजा और जट्रोफा केक का उपयोग एडीज इजिप्सी के विरुद्ध अन्य सामग्रियों के साथ कॉइल फॉर्म्युलेशन को विकसित करने के लिए किया गया था। विकसित कॉइलस को मच्छरों के खिलाफ उनकी बर्निंग दक्षता (efficiency) और प्रभावकारिता के लिए परीक्षण किया गया। तरल बायोडीजल बाय-प्रोडक्ट, सिट्रोनेला ऑयल और डिलिपियोल का ब्लैटला जर्मैनिका के खिलाफ टैबलेट्स विकसित करने के लिए इस्तेमाल किया गया। सक्रिय घटकों के एटीआर-एफटीआईआर विश्लेषण के साथ-साथ टैबलेट तैयार करने के लिए स्थिरता मापदंडों का आकलन किया गया। गोलियों की जैव-दक्षता का मूल्यांकन जर्मन तिलचट्टा, (ब्लैटला जर्मैनिका) के साथ किया गया था, जिसमें शेल्फ लाइफ स्टडीज भी शामिल थे। तरल बायोडीजल बाय-प्रोडक्ट, सीट्रोनेला ऑयल और डिलिपियल ऐडिस इजिप्टी लार्वा के खिलाफ फ्लोटिंग टैबलेट्स विकसित करने के लिए इस्तेमाल किए गए थे। सक्रिय घटकों और टैबलेट्स के एटीआर-एफटीआईआर विश्लेषण के साथ जैव दक्षता परीक्षण किया गया। सीट्रोनेला, डिलिपियल और तरल बायोडीजल बाय-प्रोडक्ट युक्त टैबलेट्स में प्रतिशत मृत्यु दर अधिक पई गई।

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## ***ABBREVIATIONS***

<b>ANOVA</b>	Analysis of Variance
<b>ME</b>	Microemulsion
<b>NE</b>	Nanoemulsion
<b>EC</b>	Emulsifiable Concentrate
<b>CRF</b>	Controlled Release Formulation
<b>ATR-FTIR</b>	Attenuated Total Reflectance Fourier Transformer Infrared Spectroscopy
<b>GC-MS</b>	Gas Chromatography- mass spectrometry
<b>GC-FPD</b>	Gas Chromatography- flame photometric detector
<b>HPLC</b>	High Performance Liquid Chromatography
<b>SEM</b>	Scanning Electron Microscopy
<b>LC<sub>50</sub></b>	Lethal Concentration-50
<b>LD<sub>50</sub></b>	Lethal Dose-50
<b>KD<sub>50</sub></b>	Knockdown-50
<b>NEOC</b>	Non edible oil cake
<b>Fig.</b>	Figure
<b>°C</b>	Degree Centigrade
<b>g</b>	Gram
<b>L</b>	litre
<b>mg</b>	Milligram
<b>ml</b>	Millilitre
<b>min</b>	Minutes
<b>ppm</b>	Parts per million

/	Per
<b>mg<sup>-1</sup></b>	Permilligram
<b>ml<sup>-1</sup></b>	Per millilitre
<b>%</b>	Percentage