A Review on the Comparative Analysis of Synthetic Insect Repellents and Essential Oil Based Sustained-release Insect Repellent Formulations

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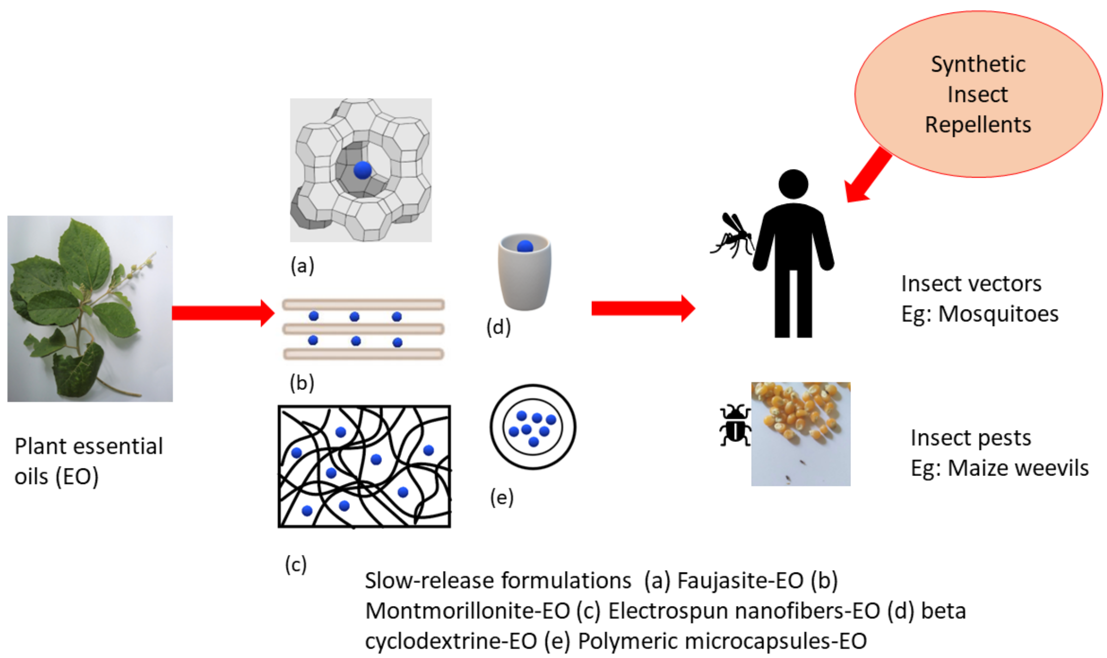
Graphical Abstract



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Abstract:

The necessity of developing insect repellents with highly effective sustained release properties has attracted more attention due to the vast spread of arthropod-borne diseases such as dengue and malaria, which must be controlled with proper measures, and also due to the devastating damage caused by severe infestation of insect pests on crops and stored food. Natural and synthetic insect repellents are used against insect vectors and insect pests. Topical insect repellent formulations should be less toxic, less irritant, and less skin permeable. Irrespective of the type and form of the repellent, the mechanism of action depends on the formation of a vapour barrier/ odour barrier, that would deviate the insect from reaching the host. Synthetic insect repellents are highly efficient but due to their high toxicity, degradation resistance, and bio accumulation, they raise environmental and ecological issues. Due to the adverse effects caused by synthetic insect repellents, more attention is given to insect repellents consisting of natural products. Essential oils are among the widely used natural insect repellents available due to their biocompatibility and non-toxicity. High volatility of essential oils is the major problem that hampers the application of essential oils as insect repellent agents. The high volatility that reduces the length of application, and its activity can be successfully addressed by the formulation of slow-release insect repellent composites by incorporating essential oils into adsorbing or encapsulating matrices. Zeolites, montmorillonite, β-cyclodextrin, polymeric materials, and electrospun nanomaterials are commonly used to develop slow-release formulations with essential oils. Among these, polymeric microcapsules are the most extensively studied and developed slow-release insect repellent systems that are based on natural and synthetic active compounds.

Key words: Formulation, Insects, Microcapsules, Repellents, Zeolite

1 Introduction

Insects have an origin of existence that extends back to millions of years, making them one of the ancient groups of terrestrial organisms to exist on earth. Having survived some of the major events of extinction that eliminated some of the plant and animal species, insects however have managed to successfully adapt to natural and anthropogenic changes that have been taking place ever since. Out of the estimated (4-10 million) insect species, only about one million insect species have been detailed, out of which only a several thousand are described as pests.

Due to the vast distribution, adaptability, and diversity, insects have become an essential part of the eco-system, playing an important role in delivering ecosystem services that are essential to sustain human life on earth. But also, they have become one of our major competitors for food resources, and vectors of serious diseases such as malaria, dengue, Lyme disease.

Among the globally concerning diseases, insect-vectored diseases are causing a significant health threat to humans, and hence need to be dealt with thoroughly. 'Arboviruses' are the disease causing viruses that are biologically transmitted by a hematophagous arthropod to a vertebrate and maintained in a cycle (Shope and Meegan, 1997). Out of the many incidents that were contributing to the increasing global mortality, arboviral diseases were given the least attention and that resulted in a sudden increase of epidemic arboviral diseases. This eventually had to be dealt by the WHO, researchers, and the

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governmental parties to come up with better solutions to strengthen the awareness programs, to develop better vector control measures, vaccines, diagnostics and carry out more research regarding aedes-transmitting diseases such as dengue and chikungunya (Wilder-Smith et al., 2017). Initiating suitable vector control measures is a vital step in this process and the proper use of insect repellent formulations plays an important role.

In addition to causing diseases such as dengue and chikungunya, insects also cause devastating losses to crops, and stored food products. Eliminating or controlling such issues is costly and could lead to significant economic losses. One reason for the higher susceptibility of agriculture crops to crop pests is the reduced genetic diversity of the crops, resulted due to the plantation of monocultures of a single plant species. This reduces the probability of insect pests searching for better hosts. Although most of the crop pests are limited to crops in their innate range, due to the worldwide transportation of crops or infested sources, many crop pest species are distributed out of their native environments. Although synthetic insecticides are widely used to control insect pest outbreaks, they result in certain unfavorable effects such as causing insect pest resistance with time and accumulating in different levels of the food chain. Due to that, the leniency of using insect repellents formulated with natural sources as a promising control measure is given more attention.

Application of insect repellents is widely used in controlling insect-vectored diseases such as arboviral diseases, as the main intention of insect repellents is to repel insects from the vicinity, in this case impeding any chances of causing insect bites. Insect repellent formulations can be natural or synthetic, based on the origin. These volatile, oily formulations contain active chemical compounds that are responsible for repelling the insects. Based on the application, such as using as an ointment that can be applied on skin or fabric, or as a formulation that is used in the open environment close to the stored grains and food items to repel insect pests, the desirable features of the repellents are described. If the insect repellent is used as an ointment that is directly applied on the skin, it is important that the repellent is less toxic, and does not cause any skin irritation after its application, and has low permeability on the skin (Tavares et al., 2018). If the repellent is applied on fabric, it is important not to stain the fabric; and if it is used in food storages to repel insect pests, it is highly important that it does not contain any toxic compound that can contaminate the food items, which would result in food poisoning and other harmful effects. Despite the variations in application, one of the important features that is expected in an insect repellent is the long-lasting nature that would reduce reapplication, and hence make it more cost effective.

The dialkyl phthalates were among the earliest synthetic insect repellents to be discovered, and by 1956, N, N-diethyl-3-methylbenzamide (DEET) was made available to the public (Brown and Hebert, 1997, Katz et al., 2008). In addition to that, IR3535 (ethyl butylacetylaminopropionate), and Icaridin are among the widely used synthetic insect repellents. Natural insect repellents are plant-derived insect repellents, which are mainly formulated using plant essential oils, such as citronella and lemon eucalyptus essential oils. Plant-derived essential oils are commonly used as ointments that can be directly applied on the skin, on surfaces such as fabric, or by impregnating into solid wax in candles which releases the aroma when it burns. In comparison to some of the synthetic insect repellents, plant-derived essential oils are low in toxicity, however, the length of application is limited to a few hours due to their high volatility. To address this issue, slow-release insect repellent formulations are developed using suitable matrices such as inorganic porous materials, polymeric microcapsules and cyclodextrins.

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The main objective of this work is to conduct a literature review on the types of plant essential oil based slow-release insect repellent formulations, and to elaborate the importance of utilizing sustained-release technology to develop such insect repellent formulations. In addition to that, different types of synthetic and natural insect repellent formulations that are currently available will be discussed. Information regarding the areas of study was obtained from a comprehensive survey of electronic databases in the period from 1982 to 2022.

2 Insect repellents

Irrespective of the different types of insect repellents that are available, the repellent activity is resulted due to the release of volatile compounds from the relevant insect repellent product. An insect repellent can be of a natural origin or a synthetic formulation, but the mechanism of action despite its type and form depends on the formation of a vapor-layer with an unbearable odor that would deviate the path of an insect from reaching the host (Islam et al., 2017). Insect repellents can be categorized into five categories according to the type of insect behavior that is observed: 1) True repellents 2) Contact irritants 3) Deterrents 4) Odor maskers 5) Visual maskers (Deletre et al., 2016). Insect repellents are commonly used to repel insects such as mosquitoes, that spread arboviral diseases such as dengue, chikungunya, and Lyme disease. Hence, there are certain factors that should be taken into consideration when formulating an insect repellent. Some important characteristics of an insect repellent include its low-toxicity, low-irritancy when applied on the human skin, long lasting repellent activity, less skin permeation and affordability. These conditions differ with the application of the insect repellents; as in addition to using it to control insect-vectored diseases, they are also used to control insect pest infestations in stored products, and to control the damage that is caused to fabrics.

2.1 Synthetic insect repellents

Synthetic insect repellents are developed industrially on a larger scale for commercial distribution. The dialkyl phthalates were among the first synthetic chemical insect repellents to discover back in 1929, which was followed by DEET, that was made available to the public in 1956 (Brown and Hebert, 1997, Katz et al., 2008). Currently, DEET is among the major synthetic insect repellents in use. In addition to that, insect repellents such as Icaridin and IR3535 are widely used, and these insect repellents will be discussed further in detail.

2.1.1 DEET

DEET (N,N-Diethyl-3-methylbenzamide) which was initially used by the United States armed forces in 1946, was first marketed to the public in 1956 (Brown and Hebert, 1997). It is a slightly yellowish, volatile liquid with an oily texture at room temperature, which is generally considered as the most effective insect repellent that is available in the market (Wylie et al., 2016). In comparison to other insect repellents such as IR3535 and synthetic products containing plant derived oils such as citronella oil, DEET is considered to outperform, especially in providing extended protection against mosquito bites (Fradin and Day, 2002). Due to the effectiveness in performance, DEET is available in the market in various formulations such as lotions, sprays, gels, and wipes with varying strengths from (5-100) % (Diaz, 2016). When the effectiveness of DEET is considered regarding its repellent activity, the toxicity of the chemical to mammals and humans is often discussed. In a previous study which was conducted on the neurotoxicity and the mode of action of DEET, the authors have reported about acetylcholinesterase having a low sensitivity to DEET in both insects and mammals, which would otherwise cause serious issues regarding the neurotoxicity, by the inhibition action of acetylcholinesterase (Swale et al., 2014).

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The authors have further stated that the toxicity resulted in houseflies and mosquitoes was resulted due to a combinatory effect of the excitatory octopaminergic effect and the peripheral neurosuppressive action (Swale et al., 2014). DEET is reportedly more effective against *Culex* and *Aedes* species and shows less effectiveness to *Anopheles* species (Tavares et al., 2018).

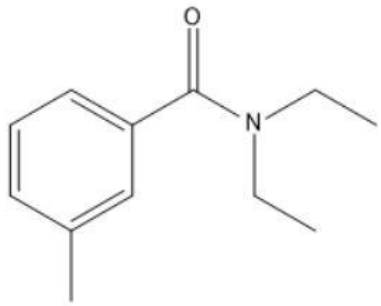

Figure 1: Chemical structure of DEET

2.1.2 Icaridin

Icaridin, which is also known as Picaridin or KBR3023, is a synthetic insect repellent in the piperidine chemical family, which is effective against mosquitoes, ticks, and other types of biting-flies. Icaridin, being a synthetic insect repellent was first developed in 1980 using a ligand based molecular modelling technique on different types of derivatives of known repellents (Boeckh et al., 1996). Icaridin is less toxic compared to DEET, however it can cause irritation to the skin and eyes upon exposure. When the chemistry of the repellent activity of Icaridin is concerned, it is imperative to mention about the major role played by the chirality at the stereogenic centers of Icaridin in binding to the receptor proteins in the olfactory system, to result in the 'repellence' phenomenon. There are two stereogenic centers in Icaridin, which are available as a 1:1 mixture of four racemic diastereomers (Drakou et al., 2017, Natarajan et al., 2005). In a study conducted by Drakou et al. (2017), it is mentioned that the four individual diastereoisomers depict a specific order of mosquito repellency as 1R,2S> 1R,2R> 1S,2R> 1S,2S (Drakou et al., 2017, Natarajan et al., 2005).

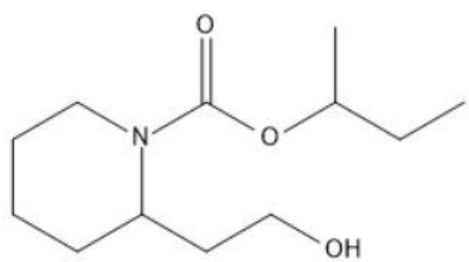

Figure 2: Chemical structure of Icaridin

2.1.3 IR3535

IR3535 (ethyl butylacetylaminopropionate) is a synthetic insect repellent which was developed by Merck, which contains the chemical structure based on beta alanine. IR3535 is effective against

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mosquitoes, bees, ticks, and insects such as lice. Compared to DEET, the effectiveness in repellent activity is lower in this, however it has lower toxicity and biocompatibility (Tavares et al., 2018). The mechanism of action of most of the insect repellents are poorly understood. Synthetic repellents such as DEET and IR3535 act by forming a layer of vapor on the skin, impeding the biting of some hematophagous arthropods (Islam et al., 2017).

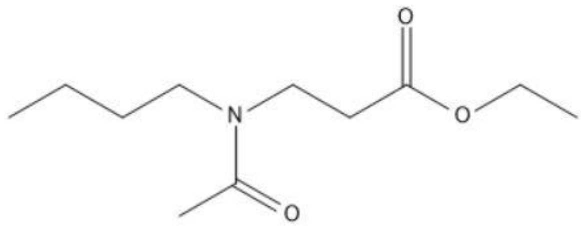

Figure 3: Chemical structure of IR3535

2.2 Natural insect repellents

There are different alternatives in the nature, that can be used as potential insect repellents, in place of synthetic chemicals. There are certain native methods in practice, such as burning plant leaves to generate smoke and repel insects, spreading plant leaves in cultivations, and using essential oil to repel insects that cause serious health issues such as dengue. Some of the examples for the aforementioned methods in practice are, the usage of 'Keppetiya' (*Croton laccifer*) plant leaves to repel insect pests in paddy cultivations by sweeping the cultivations with the plant leaves after beating them on the floor, to release the phytochemicals that are responsible for the insect repellent activity, burning of 'Kaduru' (*Cerberamanghas*) bark which contains phenylpropionic acid that has insecticidal properties, and the usage of citronella, and lemon eucalyptus essential oils as insect repellents against mosquitoes (Widanapathirana and Dassanayake, 2013).

Out of these methods, the most common practice is the usage of essential oils as insect repellents. Essential oils can be mentioned as a mixture of volatile, organic compounds that are present in a plant, which are released when subjected to any aggression as a defensive mechanism against predatory insects (Rehman et al., 2014, Tavares et al., 2018). These chemical compounds that are found as a measure of defensive mechanism against predatory insects are mainly classified as repellents, toxins, feeding deterrents and growth regulators, and they belong to the chemical categories representing phenolics, primary alkaloids, terpenoids, growth regulators, and protein inhibitors (Debboun et al., 2006). It has been found that many plant volatiles have repellent or deterrent activity due to their higher vapor toxicity (Jang et al., 2005).

2.2.1 Phenols

Phenols are a class of chemical compounds that contain a hydroxyl group (-OH) attached to an aromatic hydrocarbon compound. The simplest compound of that class is phenol (C_6H_5OH). Flavanoids, are the most important group of phenolics that contribute to the insect repellent and insecticidal activity.

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Flavones, isoflavonoids, and tannins that are found in some plants contribute to the insect repellent and potential insecticidal properties.

2.2.2 Terpenoids

Terpenes are biosynthetically derived units of isoprene. Terpenes are sequentially categorised as hemiterpenes, monoterpenes, sesquiterpenes, diterpenes, triterpenes according to the number of isoprene units as the chain grows.

Monoterpenes are the most important group of terpenes that contribute to the insect repellent activity of essential oils. Limonene, is a monoterpene that exists as a colourless, clear liquid at room temperature, and it is a chiral molecule that biological sources produce majorly in one enantiomeric form (Debboun et al., 2006). Limonene is present in a wide range of plants that are used as insect repellents, such as, *Ocimum basilicum*, *Curcuma longa*, and *Thymus vulgaris*. In citrus fruits, limonene is present as its (R)-enantiomer/ *d*-limonene (Debboun et al., 2006). Geraniol, which is present in small quantities in citronella, and the essential oil obtained from Lamiaceae, is a monoterpene that is available as a pale-yellow coloured liquid at room temperature (Chen and Viljoen, 2010). It is found in a variety of plants such as *T. vulgaris*, *O. basilicum*, *Zingiber officinale*, and *Mentha longifolia* (Tavares et al., 2018).

2.3 Plant essential oils

Plant essential oils are among the widely used natural insect repellents, especially used to get protection from the arthropods that are vectors of serious diseases such as dengue, malaria, and chikungunya. When essential oils are considered, certain plant species or plant-families are best known to produce some of the commercially available plant essential oils. Some of such plant-families include the family Poaceae, Lamiaceae and Myrtaceae (Debboun et al., 2006).

2.3.1 Citronella oil

Citronella essential oil, especially extracted from the species *Cymbopogon nardus* is widely used as a commercial insect repellent, as it can be used at a low concentration as (5-10) % which is less irritant to cause any skin irritation upon application (Maia and Moore, 2011). The composition of citronella oil contains citronellol, citronellal, citral, geraniol, limonene, and α-pinene, and it was identified as an effective dose as DEET, but the fast evaporation results in a reduced efficacy (Curtis et al., 1987). To slow down the release of citronella oil, encapsulated citronella oil nanoemulsions are prepared by the homogenization of 2.5% surfactant and 100% glycerol, to make droplets that are stable, and retain the oil well (Sakulku et al., 2009).

2.3.2 *Ocimum basilicum* essential oil

Ocimum basilicum (Basil), is a culinary herb that is found in the Lamiaceae family. The essential oil of *O. basilicum* is reported to contain majority of terpenes, including linalool, eugenol, isocaryophyllene, cineole, methyl cinnamate and alpha-cubebene (Ismail, 2006). The essential oil of *O. basilicum* is reported to contain larvicidal properties, which is 100% effective against *Culex quinquefasciatus* at very low concentrations such as 0.12% (Chavan and Nikam, 1982).

2.3.3 Lemon eucalyptus oil

Lemon eucalyptus essential oil is extracted from the plant species *Corymbia citriodora*. The chemical composition of lemon eucalyptus essential oil contains citronellal, citronellol, geraniol and other sesquiterpenes, out of which citronellal is the key compound that shows higher effectiveness in insect

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repellent activity (Poaty et al., 2015). However, due to the high volatility of the essential oil, the repellent activity is reduced over time. In addition to the major volatile components, p-Menthane-3,8-diol is one of the other compounds that is found in the lemon eucalyptus essential oil that provides protection from a variety of insects, due to its lower vapour pressure compared to many of the monoterpenes (Carroll and Loye, 2006).

2.3.4 Turmeric essential oil

Turmeric (*Curcuma longa*) is a household spice and a medicine that is especially used in South Asian countries like Sri Lanka and India. In addition to using it as a spice, turmeric is also used as an insect repellent and an insecticide, due to the presence of anti-insect properties. It is reported in previous literature that the insect repellent properties of turmeric are resulted due to the presence of two compounds, Turmerone and ar-Turmerone (Su et al., 1982). It has been reported about the efficacy of turmeric powder against stored grain insect pests such as *Tribolium castaneum*, and *Sitophilus oryzae*, and about the essential oil of turmeric bearing insect repellent and feeding deterrent properties against stored grain insect pests such as lesser grain borer, *S. oryzae* and *T. castaneum* (Chander et al., 1992, Harish et al., 1991). The chemical composition of the essential oil of turmeric rhizome is reported to contain ar-turmerone, α-turmerone, and β-turmerone, while the oil extracted from leaves contain α-phellandrene, p-cymene, and 1,8-cineole (Sharma et al., 1997).

3 Slow-release formulations of plant essential oils

There is a tendency to use natural insect repellents such as essential oils, in place of synthetic insect repellents, due to their less toxicity, and less harmful environmental and ecological impact. Essential oils such as citronella oil, and the oil obtained from lemon eucalyptus are developed commercially as insect repellent products containing different methods of application, such as spray bottles and towelettes containing the oil formulations, to provide a better and safe application (Tavares et al., 2018). Even though natural insect repellent formulations containing plant essential oils are a better alternative to synthetic insect repellents, the efficacy of plant essential oils is limited due to their high volatility, which limits the hours of protection that is obtained after application. To acquire high efficacy, advancements to the formulations containing plant essential oils are made, such as developing slow-release formulations by incorporating essential oils into suitable matrices.

The concept of slow-release formulations was initially applied to formulate slow-release drugs in the pharmaceutical industries, which was eventually utilized to formulate slow-release fertilizers and other composites that facilitate the slow release of fragrances and bio-active compounds, as in the case of plant essential oils. In pharmacology, slow release/sustained release activity helps to reduce side effects by preventing fluctuations in the therapeutic drug dose in the body, and improves the patient compliance by reducing the frequency of drug administration (Gupta and Ray, 2012). In agriculture, nutrient leaching from the applied fertilizers due to the poor retention capacity results in inefficient nutrient absorption by the crops, that would ultimately cause low yields and an additional cost of fertilizer (Khan et al., 2008, Mortain et al., 2004). This problem is addressed by the formulation of slow-release fertilizer, which has a low solubility, and hence providing the crops with a gradual nutrient supply over the time, which would prevent the leaching of nutrients and enhance the efficiency of the fertilizer (Fernández-Escobar et al., 2004). In addition to the formulation of slow-release fertilizers and drugs, studies regarding the slow-release of fragrance molecules have also been carried out using different solid matrices such as zeolites. In those studies, effect of the type of zeolite (synthetic or natural) on the adsorption of fragrance molecules,

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and how the particle size of zeolites would contribute to the desorption kinetics of the adsorbed fragrance molecules were further studied (Strzemiecka et al., 2012, Tekin et al., 2015).

When formulating a slow-release formulation, it is important to study about the type of matrix that is used to adsorb or encapsulate the desired compound/s, to acquire slow-release properties. The dimensions and the morphology of the material that is used to formulate a slow-release formulation contribute to the adsorption/encapsulation of the relevant compound/s, and the desorption kinetics that plays a major role in deciding if the formulation performs well in slow releasing.

3.1 Slow-release formulations incorporated with insect repellent active compounds

Volatility of the active compounds in an insect repellent formulation contributes to the insect repellent activity, by forming an aroma barrier that leads to the deviation of the insect's path. However, due to the presence of these volatile, active compounds, the longevity of application of an insect repellent formulation is reduced. To address this issue, advanced insect repellent formulations are currently being developed using the 'sustained-release' technology, by adsorbing or encapsulating such volatile, active compounds with insect repellent properties in suitable matrices.

3.1.1 Zeolites

Zeolites are microporous, aluminosilicate materials with a crystalline structure, that has a regular pore architecture containing channels and cages that run through the material (Spanakis et al., 2014). Zeolites contain unique structural characteristics, such as the availability of void spaces, pore dimensions, window size, the types of extra framework cations available, which contribute to its various applications. Due to the variety of pore dimensions in the structure, and the adsorption capacity, zeolites are extensively used as molecular sieves and as catalysts (Auerbach et al., 2003).

Zeolite comprises with an XO_4 tetrahedral structure where X=Al, Si in which O atoms connect the neighbouring tetrahedra (Auerbach et al., 2003). The silica framework, when incorporated with Al, gives a negative charge to the network, which is counterbalanced by the extra framework cations in the network. Presence of these extra framework cations makes zeolite rich in ion-exchange properties as well (Auerbach et al., 2003).

Adsorption properties of zeolite are acquired due to the presence of channels and cages in the internal structure, that are formed because of the intracrystalline voids that are formed according to the way atoms are arranged in the three-dimensional network. The internal volume of zeolite containing channels and cages with different pore sizes allows a better selectivity of the molecules through the pore system (Auerbach et al., 2003).

Li et al. (2020) have used Y-type faujasite (FAU) zeolites containing Na^{+}, Ca^{2+}, La^{3+} to develop a fragrance carrier using linalool and limonene as model fragrance compounds to study the potential effect of non-framework cations of different valence states contributing to the adsorption and releasing characteristics of the composites. Utilization of Y-type FAU zeolite has been of particular interest in the adsorption of fragrant molecules, due to the presence of two independent, interconnected cages with different pore characteristics that allow selective adsorption (Li et al., 2020). After the encapsulation of the compounds into the matrix, fragrance composites have displayed higher thermal stability, exhibiting characteristics of slow and steady release of the volatile compounds (Li et al., 2020). Using experimental and computational calculations, they have shown that there is a higher correlation of the non-framework

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cation (NaY>CaY>LaY) with the releasing profile, and it was supported by the computational chemistry calculations of Density Functional Theory, showing that the releasing rate followed the opposite trend of the electrostatic attractions of non-framework cations with the guest molecules (Li et al., 2020).

Kaya et al. (2013) have studied thermal properties and release properties of oregano essential oil, after adsorbing on to two different types of natural zeolites of clinoptilolite type. Using thermogravimetric analysis, they have shown that the essential oil is slowly released once adsorbed onto zeolite, and vacuum drying of the zeolite samples prior to oil adsorption does not significantly improve adsorption properties of the matrix, though it could favour the adsorption process (Kaya et al., 2013).

Perera et al. (2022) have studied the potential effectiveness of two minerals, zeolite and Cloisite-20A nanoclay, in prolonged odour driven repellent activity against *Sitophilus zeamais*, after the adsorption of *Ruta graveolens* L. essential oil. Using IR analysis, they have shown that there exists a 90-day long persistence of the essential oil in both zeolite and Cloisite-20A, and hence exhibit a (50-100) % repellent activity against *S. zeamais*, during the 90 days duration (Perera et al., 2022). In their study, they have exhibited the higher thermal stability of the bio-composites than the neat minerals, and the slow-releasing property of the bio-composites having the ability to overcome the limited applications of essential oils as insect repellents in the neat form (Perera et al., 2022).

3.1.2 Montmorillonite

Montmorillonite nanoclay is extensively used for various applications such as in the synthesis of active packaging films, as a drug carrier system, in the production of scaffolds for biomedical functions, and as an adsorbent.

Montmorillonite is a phyllosilicate nanoclay that has a layered structure, with two tetrahedral sheets of O-Si-O sandwiching an octahedral sheet of O-Al(Mg)-O (Guo et al., 2020). Isomorphous substitution adds an overall positive charge to the layers of the layered clay, in which the cations are distributed in the interlayer spaces (Guo et al., 2020). In the primary clay structure, van der Waals forces and electrostatic forces hold the neighbouring layers together to form primary particles that aggregate to form secondary particles (Guo et al., 2020). Due to the presence of inorganic cations, montmorillonite exhibits hydrophilic properties, that limit the applications of the nanoclay associating hydrophobic compounds. However, by substituting the interlayer inorganic cations with organic cations, such as quaternary alkylammonium ions, organically modified montmorillonite with a hydrophobic surface can be obtained (Lagaly et al., 2013, Song et al., 2020, Xi et al., 2010). In an organic medium, organically modified montmorillonite has a good ability to swell, to form colloids and to delaminate (Xi et al., 2005, Zawrah et al., 2014). Due to these properties, organically modified montmorillonites are used in synthesizing clay/polymer nanocomposites, in wastewater treatment as an organic adsorbent, and in cosmetic and paint industries (Zhou et al., 2019). Montmorillonites, and organically modified montmorillonites are used to develop slow-release formulations due to the availability of adsorption sites in the interlayer spaces and on the surface and the edges of the layered clay structure (Jayrajsinh et al., 2017).

Perera et al. (2022), have developed a bio-composite by adsorbing *R. graveolens* L. essential oil onto zeolite, and Cloisite-20A nanoclay, which is an organically modified montmorillonite, and presented the ability of zeolite and Cloisite-20A minerals to act as odour-barriers by slowing down the release of volatile compounds in the essential oil. Prolonged release of the essential oil for a 90-day period was observed for the bio-composite, and within that period, repellent activity of the essential oil accounting

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for (50-100) % against *S. zeamais* persisted (Perera et al., 2022). In their study it is further mentioned that, compared to the zeolite-essential oil bio-composite, the Cloiste 20A-essential oil bio-composite has a better repulsive action against *S. zeamais* over the time, due to the comparatively higher adsorption of the essential oil on Cloisite 20A matrix (Perera et al., 2022).

In addition to the insect repellent properties, insecticidal properties of essential oil are studied regarding the development of controlled release formulations. In a previous study by Nguemtchouin et al. (2013), the persistent insecticidal activity of the *O. gratissimum* essential oil, after adsorbing on to modified and non-modified montmorillonite was tested against *S. zeamais*. Further in their study, they have compared the activity of the formulations developed using non-modified and organically modified montmorillonites to show that, the higher retention of the essential oil was observed in the organically modified montmorillonite compared to the non-modified nanoclay, due to the ability of forming hydrogen bonds between the clay and Thymol, which is the major constituent of *O. gratissimum* essential oil (Nguemtchouin et al., 2013).

3.1.3 β-cyclodextrin

Beta-cyclodextrin (BCD), which is a cyclic oligosaccharide that contains seven monomeric D-glucopyranose units linked by α-(1,4)-glycosidic bonds, is significantly used to modify releasing properties of volatile compounds. A truncated conical shaped structure is obtained by BCD, by the chair conformation arrangement of the monomers (Del Valle, 2004, Martins et al., 2020). Due to the molecular arrangement, BCD consists of a hydrophobic interior surface and a hydrophilic exterior surface in its cone shaped structure. The presence of a hydrophobic surface inside the cone shaped structure supports the inclusion of volatile compounds due to their hydrophobicity (Hădărugă et al., 2019, Herrera et al., 2019).

In BCD, the cavity diameter is a significant parameter in the formation of inclusive complexes. The interior diameter of BCD is around 0.78 nm, and it typically can include aromatic compounds in the formation of inclusive complexes (Shin et al., 2018). Due to its non-toxicity, BCD is used for a range of applications (Feng et al., 2021).

In the formation of inclusion complexes, a ‘Guest’ molecule is entrapped inside the cavity of the ‘Host’ molecule, which is BCD, by forming weak secondary interactions such as hydrophobic interactions. To form an inclusion complex, it is important that both the ‘Guest’ and the ‘Host’ molecules fulfil some essential criteria that determine the better fit of the ‘Guest’ molecule within the ‘Host’ molecule (Das et al., 2019, Giri et al., 2021). Size, geometry, polarity of the ‘Guest’ molecule, and the ability of forming secondary interactions with the ‘Host’ molecule are such imperative properties that a ‘Guest’ molecule should possess to form an inclusion complex. Upon the formation of an inclusion complex with BCD, physicochemical properties of the ‘Guest’ molecule are altered. When an inclusion complex is formed with highly volatile compounds as ‘guest’ molecules, it enables the slow and gradual release of the volatile compounds, due to which BCD has been used in a variety of applications such as in the formation of inclusion complexes of BCD and citronella oil that perform successful repellent activity against *A. aegypti*, and the inclusion of permethrin in BCD molecules that are grafted in cotton fabric, to obtain effective residual insect repellent activity against *A. aegypti* and *Anopheles stephensi* (Songkro et al., 2012).

Pujiastuti et al. (2017) have encapsulated citronellal, which is an active repellent compound, in BCD using the emulsion-based method followed by freeze drying of the complex. The best controlled release properties were exhibited by the complex consisting of 1:1 weight-based ratio of the active

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compound and BCD (Pujiastuti et al., 2017). Compared to the unencapsulated active compound, encapsulated compound exhibited 84.67% percentage repellence against *A. aegypti* (Pujiastuti et al., 2017).

Songkro et al. (2012) have encapsulated citronella oil, citronellal and citronellol active compounds in BCD in the ratios of 1:1 and 1:2, following a kneading method. To compare the efficacy of the inclusion complexes, lotions were prepared using the neat citronella oil and the inclusion complexes of the citronella oil, and it was shown that the rate of release of the citronella oil was slower in the lotions containing the inclusion complexes in the ratios 1:1, and 1:2 respectively (0.6532 ± 0.0233 mg cm^{-2} h^{-1} 0.5705 ± 0.0314 mg cm^{-2} h^{-1}), compared to the lotion prepared using the neat citronella oil (0.7463 ± 0.0050 mg cm^{-2} h^{-1}), and hence could act as a repellent against *A. aegypti* for a comparatively longer time than the unencapsulated oil (Songkro et al., 2012).

3.1.4 Polymeric microcapsules

Polymeric microcapsules are natural or synthetic polymers, that are used as insect repellents by microencapsulating essential oils and other bio active compounds. Presence of a cavity in polymeric microcapsules aids in the encapsulation of active compounds within it, facilitating the slow release of the active compound through the wall of the microcapsule (Mamusa et al., 2021). Microencapsulation of the active compounds reduces the unfavourable side effects that may result from the direct permeation of repellent active compounds on to the skin (Tavares et al., 2018).

Chung et al. (2013) have synthesized microcapsules encapsulated with thyme oil by *in situ* polymerization method, using melamine-formaldehyde prepolymer and three different emulsifying agents. Characteristics of the synthesized microcapsules, their releasing behaviour and the insect repellent activity were tested after synthesis (Chung et al., 2013). Thermal degradation of the microcapsules was shown at 150 ^{o}C, and it was further shown that both the storage temperature and the type of emulsifier used play a significant role in the sustained release of thyme oil (Chung et al., 2013). Repellent efficacy over 90% was observed for a prolonged period as 4 weeks, upon testing with the insect larvae of *Plodia interpunctella* (Chung et al., 2013).

Ogilvie-Battersby et al. (2022) have synthesized microcapsules by encapsulating geraniol, which is an excellent insect repellent compound, in the natural polymer gelatin/arabic gum following complex-coacervation. Releasing properties of the encapsulated geraniol were studied to show that the retention ability and the prolonging release of the repellent active compound were enabled after encapsulation (Ogilvie-Battersby et al., 2022).

3.1.5 Electrospun nanomaterials

Electrospun nanomaterials are identified as efficient, and advanced matrices that can be utilized to develop slow-release formulations incorporating volatile, organic compounds such as essential oils. Electrospun nanomaterials are developed using ‘Electrospinning’, which is a versatile nanofabrication technique, that operates at high electric voltages to eject polymeric materials downscaled to nanosize.

Presence of a fibrous morphology with high porosity, large surface to volume ratio, and fibre diameters of the nano range facilitates the sustained release of the active compounds in an essential oil, reducing its volatilization, thus enhancing the length of activity (Neo et al., 2013).

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Munoz et al. (2019), have developed Citriodiol (CD) loaded nanofibrous mats to depict the prolonged repellent activity of the bio repellent CD, against *Aedes aegypti*. In their study, CD loaded nanofiber mats were prepared using monolithic nanofibers, and core-enriched nanofibers. In the repellency test against *Aedes aegypti*, the CD-loaded electrospun nanofiber mats (monolithic and core-enriched nanofiber mats) were kept as an active layer between two polyester fabric layers. It was observed that the repellent activity of the CD- loaded monolithic nanofiber mats decreased immediately to reach 0% in less than 10 days, while the CD-loaded core-enriched nanofiber mats depicted 100% repellent activity for 13 days. Thus, it suggested that the loaded core-enriched nanofiber mats possessed prolonged repellent activity once loaded with CD, than the monolithic nanofiber mats (Muñoz et al., 2019).

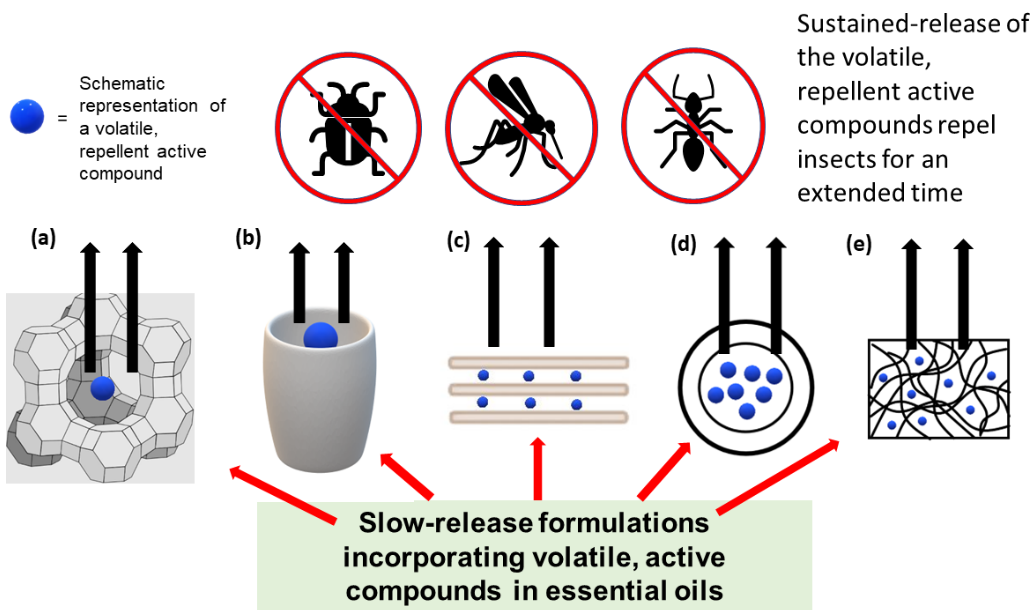

Figure 4: Schematic representation of the slow-release formulations incorporating volatile, active compounds in essential oils (EO); (a) Faujasite-EO (b) β-cyclodextrin-EO (c) Montmorillonite-EO (d) Polymeric microcapsules-EO (e) Electrospun nanofiber-EO formulations

4 Conclusion

Pervasive arthropod-borne diseases such as dengue and malaria are among the reasons to proceed with scientific advancements in insect repellent formulations. Synthetic repellents tend to be high in efficacy, providing rapid results compared to natural insect repellents. Still the high toxicity and the reduced biocompatibility of the synthetic repellents encourage the development of biocompatible and safe natural insect repellent formulations. Essential oils being biocompatible and non-toxic to mammals, are a better and a safer alternative to synthetic repellents, addressing the issue of 'high-volatility'. Development of slow-release formulations using inorganic and polymeric materials enables the prolonged release of essential oil, increasing the longevity of application. Polymeric microcapsules and BCD are commonly used in making slow-release insect repellent formulations compared to zeolite and montmorillonite.

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Testing the developed formulations against test insects should be an imperative part in developing slow-release formulations containing insect repellent active compounds to get a proper understanding about the efficacy. Future research should be further conducted to study the contribution of nanotechnology in developing insect repellent formulations with higher efficacy and better performance. Also, further research can be conducted to develop sustained-release systems ensuring targeted delivery of repellent active compounds triggered by external stimuli, to optimize their release efficiency. Furthermore, it is imperative to transition advanced, eco-friendly insect repellent formulations, incorporating sustained-release technology, that have thus far been limited to laboratory scale testing, into the marketplace with high accessibility and affordability to a wider population.

List of Abbreviations

BCD β-Cyclodextrin

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