ESSENTIAL OIL ENCAPSULATED IN ZEOLITE STRUCTURES AS A MOSQUITO REPELLENT SYSTEM

K.C. Madhusanka[1], Sanjeewa K. Rodrigo[1*], Lakmal Jayarathna[2], W. M. S. H. Wijesundara[3], T. C. Weeraratne[3] and W. A. P. P. De Silva[3]

[1]Department of Chemistry, The Open University of Sri Lanka,
[2]National Institute of Fundamental Studies, Sri Lanka,
[3]Department of Zoology, University of Peradeniya, Sri Lanka

The study explores the use of essential oils encapsulated in zeolite structures as a novel mosquito-repellent system. Given the persistent global challenges of mosquito-borne diseases and the inadequacies of traditional control methods, including the drawbacks of synthetic repellents like DEET, there is a growing interest in natural alternatives due to their lower toxicity and effectiveness. This research aims to develop a portable mosquito repellent kit utilizing essential oils such as cinnamon and citronella as bio-derived repellents. Essential oils evaporate rapidly, which diminishes their effectiveness. The study objectives include loading essential oils into zeolite matrices using both the mixing and vacuum methods, assessing the loading capacity and encapsulation efficiency, and evaluating the mosquito-repellent properties of the resulting formulations. Commercial-grade zeolite, activated at 450 °C, was used for this purpose. Encapsulation properties of cinnamon oil-zeolite composites were investigated through FTIR and Raman spectroscopy, while morphological characteristics were analyzed using SEM. The mosquito repellent efficacy against *Aedes aegypti* was tested using a three-chamber method, with neat cinnamon oil as the control. Encapsulation of cinnamon oil in zeolite successfully extended its repellent activity against *Aedes aegypti*. Raman and FTIR data confirmed the incorporation of cinnamon oil into the zeolite structures. Despite the minimal use of essential oil (100 µL), the repellent activity was notably high. This approach effectively reduces rapid evaporation by facilitating the slow release of cinnamon oil from zeolite. Consequently, zeolite-encapsulated essential oils proved more effective than neat essential oils in terms of slow release and sustained repellency. This innovative method shows promise for meeting market needs for mosquito protection, effectiveness, and user convenience, while also contributing to global disease prevention efforts.

Keywords: Mosquitoes, Essential oils, Zeolites, Encapsulation, Extract, Repellent, Slow release.

[*]*Corresponding Author: srodr@ou.ac.lk*

ESSENTIAL OIL ENCAPSULATED IN ZEOLITE STRUCTURES AS A MOSQUITO REPELLENT SYSTEM

K.C. Madhusanka[1], Sanjeewa K. Rodrigo[1*], Lakmal Jayarathna[2], W. M. S. H. Wijesundara[3], T. C. Weeraratne[3] and W. A. P. P. De Silva[3]
[1]Department of Chemistry, The Open University of Sri Lanka,
[2]National Institute of Fundamental Studies, Sri Lanka,
[3]Department of Zoology, University of Peradeniya,
Sri Lanka

INTRODUCTION

Despite centuries of control efforts, the global challenge of mosquito-borne diseases continues. Mosquitoes act as vectors and transmit diseases such as dengue, malaria, yellow fever, and Japanese encephalitis. Therefore, using insecticides is crucial for preventing mosquito-borne diseases. However, DEET, a widely used synthetic repellent, can have negative effects on human health. (D. L. Sudakin, 2003). The use of bio-derived repellents such as essential oils is desirable due to their low toxicity, spatial activity, and natural origin (D. Setyaningsih, 2020). However, the inherent instability and high volatility of essential oils limit their effectiveness in prolonging the repellency over a sufficient period. Microporous structures, especially activated zeolites, are highlighted as attractive host materials to encapsulate essential oils owing to their cost-effectiveness and non-toxicity in biological environments. Encapsulation of essential oils in zeolite structures offers several advantages over other encapsulation methods, including stability, controlled release, tunable acidity, prevention of agglomeration and sintering, and versatility (Ferreira *et al*., 2022). The repellent nature of essential oils results in volatile mixtures of hydrocarbons with different functional groups. The monoterpenes and sesquiterpenes associated with these oils can enhance each other's beneficial effects. Essential oils such as cinnamon, citrus, and holy basil are often known to have mosquito-repellent properties. This research explored the efficacy of essential oil loaded zeolite as sustained release mosquito repellent system, which involved activation of zeolite, preparation of essential oil-loaded zeolite, determination of encapsulation efficiency, and determination of mosquito-repellent activity of nanocomposites. We envisage the essential oil encapsulated-zeolite based sustained release system has the potential to be developed as a portable mosquito repellent kit.

METHODOLOGY

Zeolite activation

This method was chosen based on preliminary studies to ensure optimal activation without structural degradation. First the zeolite (500 g) was subjected to pre-drying step at 100 °C to remove surface moisture, followed by controlled heating at a rate of 1–5 °C/min to the desired activation temperature, 450 °C using a muffle furnace (Achintya R. Sujan, 2018).

Cinnamon oil-encapsulation

The encapsulation of cinnamon oil (Purchased from New Lanka Cinnamon (pvt) Ltd) in zeolite was carried out using two different methods: the mixing method and the vacuum method. During the mixing process, the zeolite was first activated. The cinnamon oil was diluted in solvents such as ethanol (5:1:30 zeolite: essential oil: ethanol) to improve its flow and penetration into zeolite pores. The zeolite powder was then thoroughly mixed with the cinnamon oil solution for 20-24 hours. The solution was heated to remove ethanol. The sample was then sealed to ensure long-term stability.

In the vacuum method, the zeolite was placed in a vacuum chamber and the zeolite-pores were vacuumed and then the cinnamon oil was forced into the pores under vacuum. Ethanol was evaporated by heating the zeolite essential oil mixture. Then the zeolite material was sealed tightly.

Mosquito repellent activity of the cinnamon oil-zeolite composites

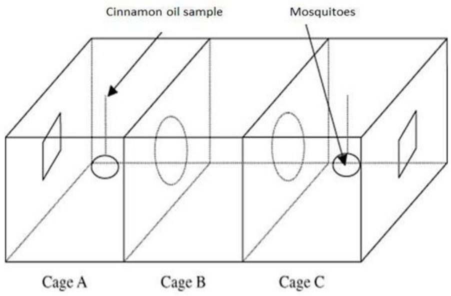

Figure 01: Cage A- Cinnamon sample, Cage B-Mosquitoes introduced here, Cage C-Free cage

Mosquito repellent activity of nanoencapsulated-cinnamon oil against *Aedes aegypti* was determined using the three-cage method with neat cinnamon oil as the control. Three test boxes, each with the same dimension (length, width, and height), were assembled (Fig. 01). These boxes were covered with nets. In the left box, a repellent sample and 10% Sucrose solution were placed. Mosquitoes of the species *Aedes aegypti* were released into the middle box. The third box was kept empty. The count of mosquitoes in each box was recorded every 30 minutes over a period of 4 hours. Mosquitoes were captured using an aspirator. For each experiment, thirty mosquitoes were introduced into the middle box. Experiment was conducted in triplicate.

Characterization

Cinnamon oil was characterized using FTIR spectroscopy and compared with the reference spectra. Zeolite was screened with FTIR and SEM images before and after activation. Micro-Raman spectroscopy was used to investigate the encapsulation of cinnamon oil in zeolite pores.

RESULTS AND DISCUSSION

Characterization of cinnamon oil

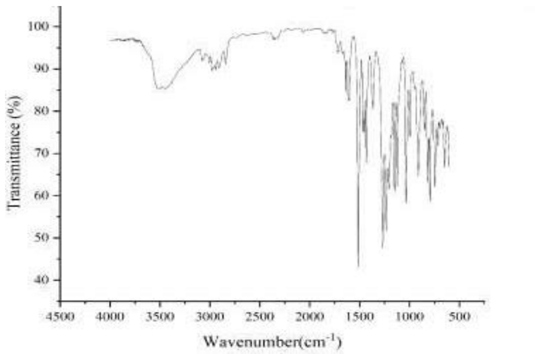

Figure 02: FTIR spectrum of neat Cinnamon oil

FTIR spectrum of neat cinnamon oil (Figure 02) shows a prominent peak for cinnamaldehyde, which can be identified in between 1511- 1463cm^{-1}, and this is characteristic of cinnamon oil.

Zeolite activation

Comparison of FTIR spectra before and after zeolite activation revealed significant differences. The region between 1600-3700 cm^{-1}, corresponding to zeolite-bound water (Iona M. McIntosh1, 2017), is significantly reduced after heating the zeolite to higher temperatures, as shown in Figure 03. This indicates that the water bound to the zeolite pores has been removed, hence the barrier of penetration of essential oils into the pores of zeolite is reduced.

As shown in Figure 04 and Figure 05, SEM analysis was used to study the surface morphology of zeolite before and after activation. The activated zeolite showed a slightly different structure compared to the pre-activated zeolite (Totok Eka Suharto, 2023). This suggests that the activation process opens up the zeolite pores, allowing essential oils to better penetrate the pores. Activation of zeolite using high temperatures led to the removal of water bound to the zeolite pores, as shown by FTIR spectroscopy. SEM analysis confirmed the changes in surface morphology, indicating that the zeolite pores opened-up after activation.

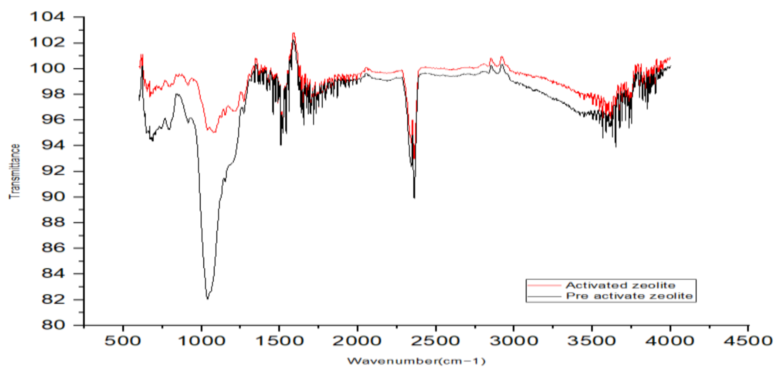

Figure 03: (Black) Before-activation of zeolite, (Red)Activated zeolite

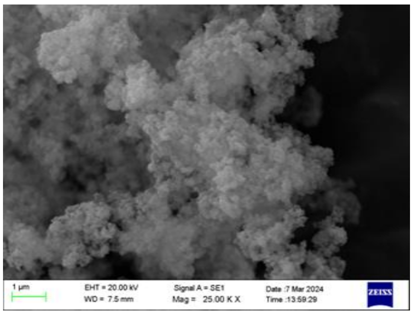

Figure 04: SEM image of Pre activated zeolite

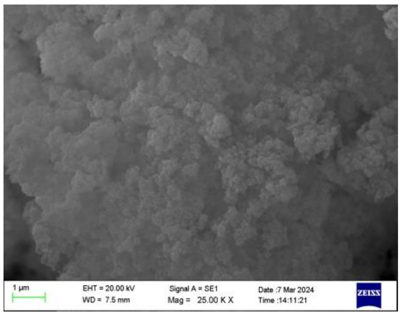

Figure 05: SEM image of activated zeolite

Encapsulation of cinnamon oil using mixing method

Raman spectroscopic analysis

Micro-Raman spectroscopy was used to investigate the encapsulation of cinnamon oil in zeolite. The Raman peaks of zeolite group minerals typically fall in the range of 379–538 cm^{-1}, with variations depending on the specific zeolite type. The presence of a characteristic peak at 1093 cm^{-1} in the Raman spectrum (Sekit, 1982) of the encapsulated zeolite sample indicated the successful incorporation of cinnamon oil. As shown in Figure 06, the peak at 1093 cm^{-1} corresponds to zeolite (Si-O-C) bonding, confirming the bonding of cinnamon oil. The intensity of the peak varied with the concentration of the essential oil, showing that increasing the concentration led to a more intense peak in the spectrum.

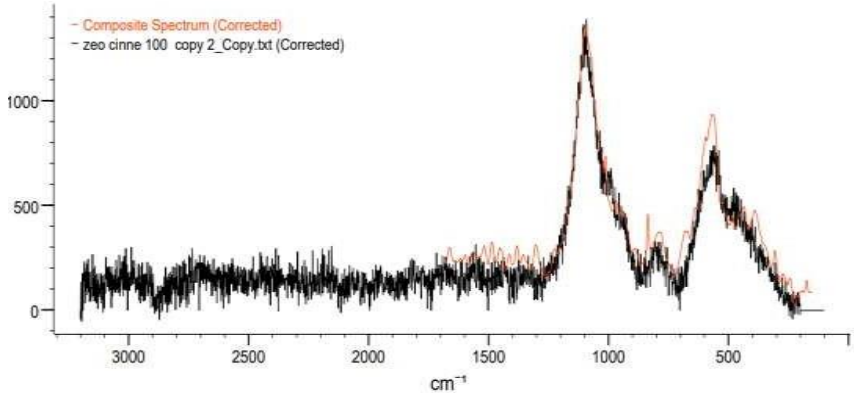

Figure 06: 100 µL-cinnamon encapsulated zeolite

Encapsulation of cinnamon oil using vacuum method

FTIR data provided insight into the binding of cinnamon oil in zeolite, highlighting specific binding patterns and structural changes as a result of the vacuum method. As shown in Figure 07, the clear peak at 1500 cm^{-1} further supported the successful encapsulation process. FTIR analysis of the vacuum method for encapsulation of cinnamon oil into zeolite showed distinct binding characteristics and structural changes, demonstrating the effectiveness of this encapsulation approach.

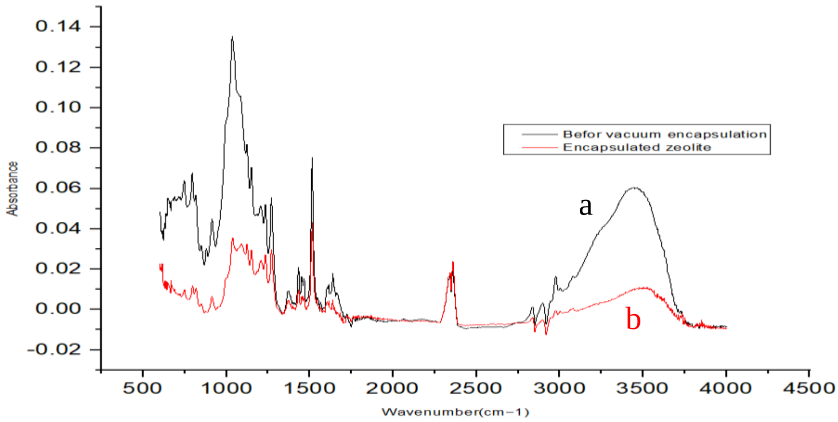

Figure 07: a-FTIR spectrum of zeolite before encapsulation of cinnamon oil, b-FTIR spectrum of zeolite with encapsulated cinnamon oil

Mosquito repellent test

The study involved testing the efficacy of zeolite-encapsulated cinnamon oil-as a sustained release mosquito repellent system with neat cinnamon oil as the control. When the repellent activity of Zeolite-cinnamon oil composite (Figure 08) and neat oil (Figure 09) compared the cinnamon encapsulated zeolite maintained more stable repellency levels over for 4 hours, while the neat cinnamon oil repellency gradually decreased over time due to rapid evaporation.

Both the neat oil and encapsulated zeolite samples initially exhibited repellency levels above 80%, while the cinnamon-coated zeolite seemed to maintain this efficiency for longer period of time. The slow-release properties of the zeolite encapsulation method were able to maintain the repellency over time. However, as pure oil evaporates quickly, its repellency decreases. Therefore, zeolite with cinnamon provides a good solution for mosquito control indicating its potential as a sustained release system

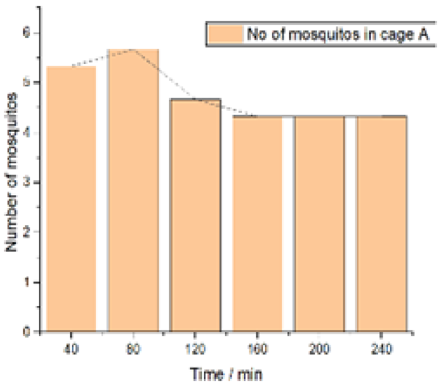

Figure 08: Cage A- Cinnamon oil encapsulated Zeolite sample test

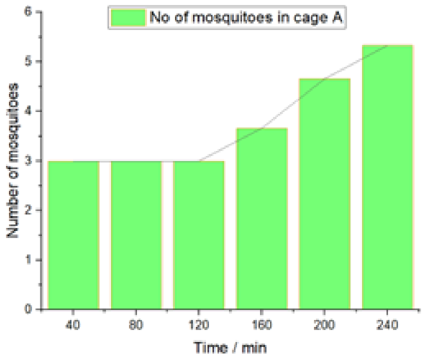

Figure 09: Cage A - Neat Cinnamon oil sample test

CONCLUSIONS

This study explored the development and potential of essential oils encapsulated in zeolite structures as a novel sustained release-mosquito-repellent system. Given the constant challenges posed by mosquito-borne diseases and the limitations of traditional repellents such as DEET, there is increasing interest in natural alternatives. The results of the study demonstrated the possibility of incorporating essential oils into zeolite structures as an effective sustained-release-mosquito-repellent system. Although the amount of essential oil used was as small as 100 µL, the repellent activity is as high as 80%-90% over 04 hours. The important factor in here is to minimize the rapid evaporation of cinnamon oil upon encapsulation in zeolite. This innovative approach offers a sustainable and bio-derived solution with low toxicity and broad repellent activity. Furthermore, it holds promise for meeting market demand for protection against mosquitoes while contributing to global disease prevention efforts.

REFERENCES

Ferreira, A. P., Almeida-Aguiar, C., Costa, S. P. G., & Neves, I. C. (2022). Essential Oils Encapsulated in Zeolite Structures as Delivery Systems (EODS): An Overview. *Molecules (Basel, Switzerland), 27*(23), 8525. https://doi.org/10.3390/molecules27238525.

McIntosh, Iona & Nichols, Alex & Tani, Kenichiro & Llewellin, Ed. (2017). Accounting for the species-dependence of the 3500 cm-1 H2Ot infrared molar absorptivity coefficient: Implications for hydrated volcanic glasses. American Mineralogist. 102. 1677-1689. 10.2138/am-2017-5952CCBY

Ohashi, Haruo & Sekita, Masami. (1982). Raman Spectroscopic Study of the Si-O-Si Stretching Vibration in Clinopyroxenes. 77. 455-459. 10.2465/ganko1941.77.455.

Setyaningsih, Dwi & Roselly, Fitriana & Muna, Neli. (2020). Formulation of Essential Oils as Mosquito Repellent. Journal of Tropical Pharmacy and Chemistry. 5. 71-79. 10.25026/jtpc.v5i2.231.

Soon-II Kim, Kyu-Sik Chang, Young-Cheol Yang, Byung-Seok Kim, Professor Dr Young-Joon Ahn (2004) Repellency of aerosol and cream products containing fennel oil to mosquitoes under laboratory and field conditions. *sci*, https://doi.org/10.1002/ps.921

Sudakin, D. L., & Trevathan, W. R. (2003). DEET: a review and update of safety and risk in the general population. *Journal of toxicology. Clinical toxicology*, *41*(6), 831–839. https://doi.org/10.1081/clt-120025348

Suharto, Totok & Salamah, Siti. (2023). Removal of Lead and Iron in Leachate Wastewater of The TPST Piyungan by Activated Natural Zeolite. Elkawnie. 9. 218. 10.22373/ekw.v9i2.16988.

Sujan, Achintya, Dong-Yeun & Zhu, Guanghui & Babu, Vinod & Stephenson, Neil & Rosinski, Andrew & Du, Hai & Luo, Yang & Koros, William & Lively, Ryan. (2018). High Temperature Activation of Zeolite-Loaded Fiber Sorbents. Industrial & Engineering Chemistry Research. 57. 10.1021/acs.iecr.8b02210.