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## Halloysite Nanotube-Stabilized Natural Oil Pickering Emulsions: A Bio-Safe and Sustainable Platform for Pesticide Applications

Sandeep S. Palkhe<sup>1,\*</sup>, Gunvant H. Sonawane<sup>2</sup>

<sup>1</sup>Department of Chemistry, Arts, Commerce and Science College, Dharangaon, Jalgaon – 425 105, Maharashtra, India.

<sup>2</sup>Department of Chemistry, KVPS Arts, Commerce and Science College, Parola, Jalgaon – 425 111, Maharashtra, India.



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### ABSTRACT

Preparation of eco-friendly formulation is very essential for reducing the dependency on traditional pesticides. In this work, Pickering emulsions were prepared by using neem, corn and coconut oil. Halloysites nanotubes are added as an emulsifying or stabilizing agent and acephate is incorporated to evaluate its pesticidal activity. Microscopic images show that the interfacial tension and droplet size decrease with increasing HNT concentration. The contact angle affects the pesticide formulations' adhesion, wetting, and spreading behavior on plant leaves. The majority of prepared emulsions exhibit good wettability with contact angles less than 60°. FTIR, SEM, and EDS confirmed effective adsorption of HNTs at droplet interfaces, ensuring emulsion stability. *Staphylococcus aureus* and *Pseudomonas aeruginosa* were used as bacterial strains to test the biosafety. It facilitates their secure use. Using *Spodoptera frugiperda* as a pest model and maize as a plant model, insecticidal tests were conducted. Neem oil-based emulsions exhibit the highest mortality rate, while corn and coconut oil emulsions show moderate effects. These results show that HNT-stabilized natural oil emulsions provide a reliable, biosafe, and efficient platform for environmentally friendly pest control.

### 1. Introduction

Globally, crop yields were comparatively low in the recent past. Numerous factors, such as inefficient cultivation techniques, erratic weather patterns, pests, and diseases, contributed to the low crop production [1, 2]. It becomes very difficult to supply the population with enough grain. The climate conditions are beyond human control. However, by employing cutting-edge farming techniques like the use of agrochemicals, we can raise crop productivity. Agrochemicals are substances that can be safely sprayed on crops to boost yields, enhance quality, and shield them from environmental stresses. Pesticides, insecticides, herbicides, fungicides, fertilizers, and soil enhancers are the primary categories of agrochemicals [3]. However, overuse of agrochemicals can have the following adverse effects: Reduces soil quality, can change the nature of the soil by making it either too acidic or too alkaline, can damage the microbes present in the soil, fertilizers can easily be washed away by water, and cause pollution cause [1, 4]. To minimize the harmful effects of fertilizers and pesticides, the development of new formulations such as Sustained or controlled release formulations (CRFs) is essential [5, 6]. An important application of CRFs system is that it reduces the location of pests in the field by optimizing the required doses compared to the traditional method of administration. In addition, CRFs demonstrate reliable and reproducible delivery of the drug to the target area over the required length of time with prolonged effects [7-10].

Pickering emulsions, which have been extensively studied and implemented in numerous applications during the last century. It can be effectively used as CRFs. Pickering emulsion is an emulsion stabilized by solid particles that adsorb at the interface of the water and oil phases. Emulsions are usually either water-in-oil or oil-in-water [11-15]. Pickering emulsions are surfactant free [16], biodegradable and ecofriendly. They offer slow and sustained release of active ingredient which ensures longer-lasting protection. Similarly, it reduces pesticide leaching and wastage and improves field efficiency.

In recent years, Pickering emulsions stabilized by rod-like nanoparticles have attracted significant attention due to the advantages of low cost, few environmental pollution and toxic effects, and high emulsion stability [17-20]. Halloysite nanotubes (HNTs) have a large length:

diameter ratio and a tubular structure, while their surfaces possess active hydroxyl groups. Therefore, HNTs can be used as an anchor point for molecular adsorption and grafting reactions [21-25].

In most of the studies Pickering emulsions are prepared by using hazardous organic solvents. These organic solvents are harmful to the environment, human health, and crops. Instead of that, natural solvents, like essential oils, are safer and more ecofriendly in their place. Azadirachtin, a bioactive compound found in some essential oils like neem oil, has insecticidal, antibacterial, antifungal, and antioxidant properties<sup>17</sup>. Lauric acid, which is present in coconut oil breaks down microbial cell membranes and exhibits potent antibacterial and antifungal effects. Likewise, corn oil contains linoleic acid, which has anti-inflammatory and antioxidant qualities.

The two most important crops in India are maize and cotton. They have a major impact on the agricultural economy. However, insects like bollworms, aphids, thrips, leafhoppers, and whiteflies have a big influence on their productivity. 50–60% of cotton can be lost, particularly as a result of pink bollworm and whiteflies. Aphid infestation and *Helicoverpa* can cause a 20–30% decrease in maize yield.

Acephate is an organophosphate insecticide which is known for its systemic, contact, and stomach action against various insect pests, especially against sap-sucking and chewing insects. It plays important role in agricultural pest management, particularly for cotton, maize, and vegetable crops.

This work involved the preparation of O/W emulsions using a variety of natural oils, including coconut, corn, and neem. Emulsion stability was examined after HNT was added as an emulsifying agent. The stability of the water-natural oil emulsion increases as the concentration of HNT increases. Following that, acephate was mixed with HNT aqueous dispersions to create HNTs-Acephate O/W emulsions. The adsorption and aggregation of HNTs at the oil droplet interface results in a three-dimensional network structure that inhibits emulsion aggregation, giving the HNTs-Acephate O/W emulsions good stability. Insecticidal activity of HNTs-Acephate emulsions were evaluated using cotton and maize as the plant model and *S. frugiperda* as the pest model. The effects of different concentrations of HNTs-acephate on the bacteria *Pseudomonas aeruginosa* and *Staphylococcus aureus* were examined in order to evaluate the biosafety of these emulsions [26].

\*Corresponding Author: [palkhess@rediffmail.com](mailto:palkhess@rediffmail.com) (Sandeep S. Palkhe)



## 2. Experimental Methods

### 2.1 Materials and Instruments

Halloysite nanotubes (HNTs) were purchased from Sigma-Aldrich India. Neem oil, corn oil and coconut oil were obtained by cold press method. Acephate obtained from Rallies India Pvt.ltd. The fresh leaves of cotton (scientific name *Gossypium*) and Maize (*Zea mays*) were collected from Jalgaon district, Maharashtra, India. Deionized water was used in all the experiments. Fourier transform infrared (FT-IR) spectra were recorded on FT-FTIR affinity model No. 1 with  $2.0\text{ cm}^{-1}$  resolution in the range of  $4000\text{--}400\text{ cm}^{-1}$  Digital Microscope (Bio Mini IS 4381) using 40 X magnification is used to capture the microscopic images of Pickering emulsions. The contact angle analyzer (DSA 100, Data Physics, OCA-25, Germany) was used to test the size of the droplet contact angle on the leaf surface. Vacuum Freez dryer FDL2-10N -2-60 B was used setting temperature at  $-55^\circ$  High Speed homogenizer (Remi RQ-127 A/D) was used for homogenization [27].

### 2.2 Preparation of HNTs–Natural Oil Emulsion

Pickering emulsions were created by homogenizing and sonicating an aqueous solution of natural oils (Corn/Coconut/Neem) for 20 minutes at 2:8, oil/water volume ratios. To stabilize Pickering emulsions, different amounts of HNTs (0, 0.5, 1, 2, and 5 weight percent) were added in it.

### 2.3 Preparation of HNTs–Acephate–Natural Oil Emulsion

A Pickering emulsion of insecticide was created by adding 0.5 g of acephate to 2 mL of natural oils (corn/coconut/neem) and 8 mL of aqueous solutions at various concentrations (0, 0.5, 1, 2, and 5 wt%) of HNTs, followed by homogenization and sonication for 20 minutes (Fig. 1).

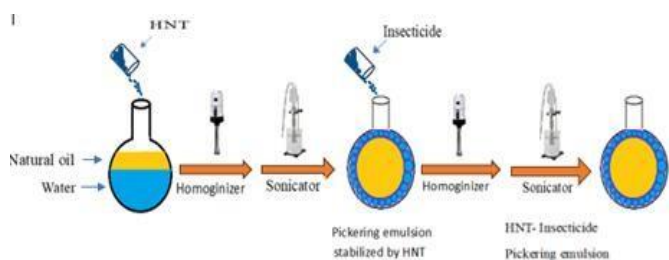


Fig. 1 Preparation of natural oil based Pickering emulsion

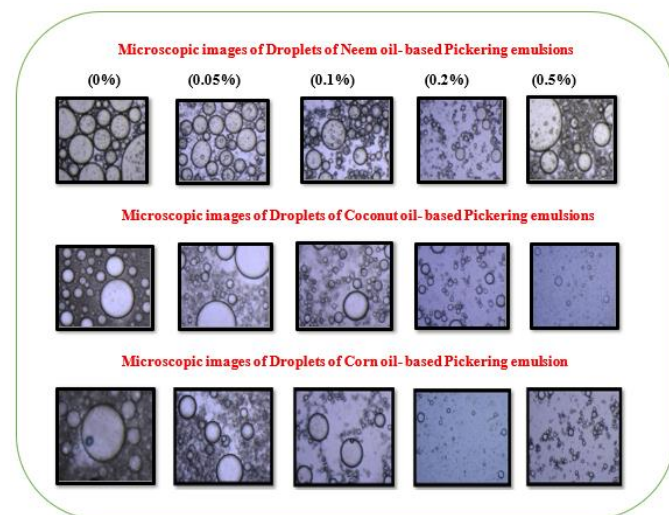


Fig. 2 Microscopic images of droplets of various natural oil based Pickering emulsion

## 3. Results and Discussion

### 3.1 Microscopic Images of Droplets of Various Natural Oil -Based Pickering Emulsion

Emulsifiers reduce droplet size by reducing the interfacial tension. An extremely high droplet size will rapidly trigger the de-emulsification process [1,6]. Kinetic stability is more prevalent in emulsions with smaller droplets. Smaller droplet sizes often provide greater stability. Smaller droplets have a higher surface area to volume ratio, which allows stabilizing particles to be adsorbed at the interface more effectively. In the preceding Pickering emulsions, halloysite nanotubes adsorb at the oil-water contact, generating a stiff barrier. This barrier suppresses droplet

coalescence far more efficiently than surfactants. Pickering emulsion based on neem oil had higher stability and smaller droplet size at 0.2% (Fig. 2). In a similar vein, Pickering emulsion based on coconut oil has lower droplet size and higher stability at 0.5%, whereas Pickering emulsion based on corn oil has smaller droplet size and greater stability at 0.2%. Droplet images of these emulsions were examined using a Digital Binocular Microscope (Micron optic) at magnifications ranging from 4x to 100x.

### 3.2 Contact Angle of HNTs–Acephate Emulsion on the Leaf Surface

The spreading, wetting, and adhesion behaviour of pesticide formulations on plant leaves are all influenced by the contact angle. The contact angle plays a major role in determining the droplet wettability of a leaf surface. The droplet's wettability can be classified as good ( $\theta < 60^\circ$ ), moderate ( $60^\circ \leq \theta < 80^\circ$ ), poor ( $80^\circ \leq \theta < 100^\circ$ ), or very poor ( $\theta \geq 100^\circ$ ). The higher the contact angle of the droplet on the leaf surface, the less wet the liquid will be on that surface. The surface of Maize and cotton leaves was coated with  $8\ \mu\text{L}$  of a Acephate emulsion containing 0, 0.5, 1, 2, and 5 weight percent HNTs in water in order to assess the wetting properties of the emulsions on the crop leaves [28]; Figs. 3-8 explains its properties individually. The contact angle of a coconut oil-based emulsion on cotton leaves varies slightly. As the concentration of HNT increases, the contact angle decreases slightly, from  $72.9^\circ$  to  $48.43^\circ$ , indicating good wettability. On the other hand, the same emulsion shows different results on maize leaves; as the concentration of HNT increases, the contact angle increases from  $56.17^\circ$  to  $59.37^\circ$ , indicating moderate wettability.

The same trend can be seen in corn oil-based emulsions. For cotton leaves, when the concentration of HNT increases, the contact angle decreases from  $61.86^\circ$  to  $57^\circ$ , but for 0.1% concentration, it is at least  $54.79^\circ$ , indicating strong wettability. Similarly, uneven contact angles in maize leaves have been reported. However, the 0.2% emulsion has a minimum contact angle of  $41^\circ$ , indicating significant wettability.

Good wettability is indicated by the neem oil-based emulsion's contact angle of  $48^\circ$  to  $44^\circ$  on maize leaves. At concentrations of 0.1 and 0.5%, the contact angle is at its minimum. Likewise, for cotton leaves, the contact angle increases in tandem with the HNT content. It ranges from  $56.38^\circ$  to  $64.76^\circ$  indicating moderate wettability [29].

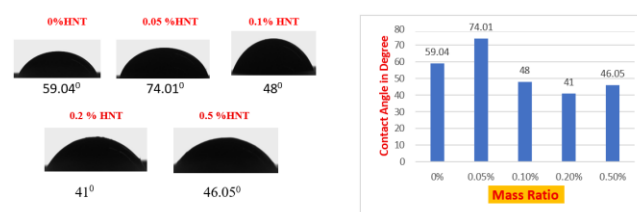


Fig. 3 Contact angle of corn oil based pickering emulsion on maize leaf

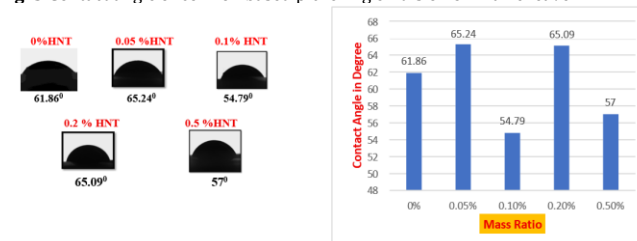


Fig. 4 Contact angle of corn oil based pickering emulsion on cotton leaves

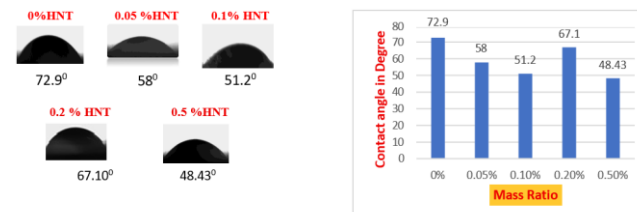


Fig. 5 Contact angle of coconut oil based pickering emulsion on cotton leaves

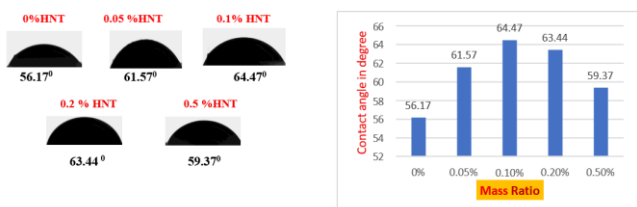


Fig. 6 Contact angle of coconut oil based pickering emulsion on maize leaves

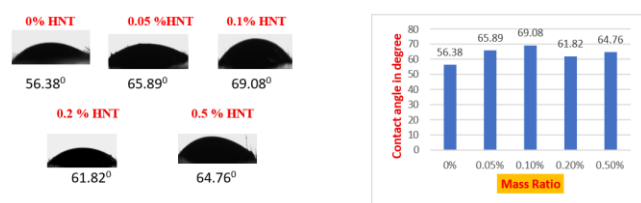


Fig. 7 Contact angle of neem oil based pickering emulsion on cotton leaves

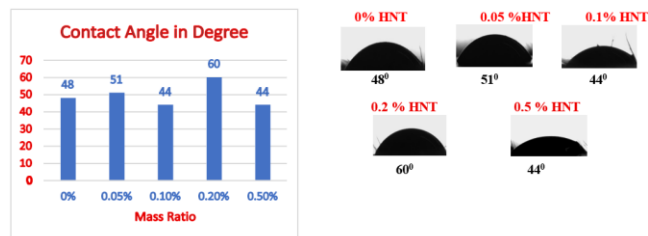


Fig. 8 Contact angle of neem oil based pickering emulsion on maize leaves

### 3.3 FTIR Analysis

#### 3.3.1 FTIR Analysis for Coconut Oil-Based Pickering Emulsion

Presence of Acephate can be identified by peaks at 1250–1020  $\text{cm}^{-1}$  which occurs due to P=O and P–O–C stretching, a broad signal at 3300–3400  $\text{cm}^{-1}$  arises for N–H stretching, and 1600  $\text{cm}^{-1}$  arises due to N–H bending (Fig. 9). Similarly, signals at 1030  $\text{cm}^{-1}$  for Si–O stretching, 910  $\text{cm}^{-1}$  for Al–OH, and 530–470  $\text{cm}^{-1}$  for Al–O–Si bending confirms the presence of HNT. Characteristic peaks at 1740  $\text{cm}^{-1}$  for C=O stretching, another signal at 2920 and 2850  $\text{cm}^{-1}$  due to C–H stretching while peaks at 1150–1050  $\text{cm}^{-1}$  due to C–O stretching confirms the presence of coconut oil with 0% HNT. Final emulsion which contains 0.2 % HNT retains the coconut oil peaks at 2920, 2850, and 1740  $\text{cm}^{-1}$ . Broad peaks in the range 3300–3400  $\text{cm}^{-1}$  indicates O–H interactions and H-bonding due to HNTs. Minor changes in the signals at about 1050–1030  $\text{cm}^{-1}$  shows a relationship between HNT and coconut oil or phosphate. Above spectrum reflects a stable Pickering emulsion where the coconut oil–water interface is effectively stabilized by Halloysite nanotubes (HNTs) through physical interactions with both coconut oil and Acephate [30].

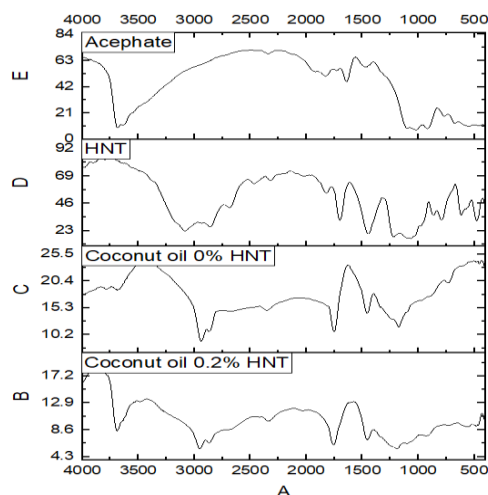


Fig. 9 FTIR spectra for coconut oil based Pickering emulsion

#### 3.3.2 FTIR Analysis for Corn Oil-Based Pickering Emulsion

There is no change in signals for acephate and HNT. Peaks are same as that in coconut oil spectra. The stability of corn oil-based Pickering emulsion can be checked by examining the impact of HNT on corn oil system and how this affects the emulsion's stability and molecular interactions. Corn oil without emulsifier exhibits typical triglyceride peaks, including 1740  $\text{cm}^{-1}$  for C=O ester stretching, 2850–2920  $\text{cm}^{-1}$  for C–H stretching, and 1000–1200  $\text{cm}^{-1}$  for C–O stretching (Fig. 10). For this emulsion, no significant interactions are evident in the O–H or Si–O regions, indicating a pure oil phase with no stabilizing ingredient. Emulsion is likely to have low physical stability, with coalescence or phase separation over time due to a lack of solid stabilizers. Corn oil-based emulsion containing 0.2% HNT (emulsifier). Retains key oil-related bands, but displays changes in intensity and small shifts, especially broadening near 3400  $\text{cm}^{-1}$  (O–H stretching). Due to possible hydrogen bonding between HNT surface and

oil component minor spectral changes occur from 1000 to 1100  $\text{cm}^{-1}$ . It indicates Si–O interactions. These characteristic peaks indicate physical interaction between HNT and oil molecules, which improve interfacial stabilization. Corn oil containing 0.2% HNT improves emulsion stability through interfacial adsorption, which improves resistance to coalescence and sedimentation [31].

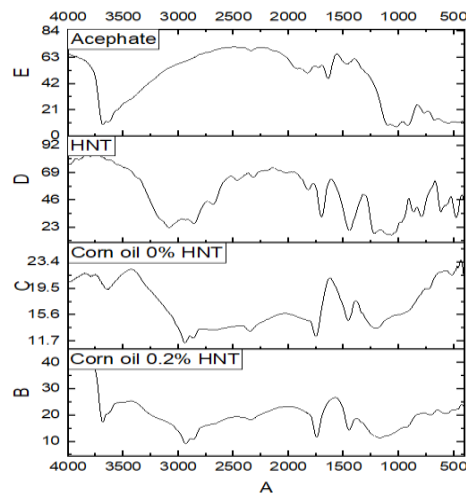


Fig. 10 FTIR spectra for corn oil based Pickering emulsion

#### 3.3.3 FTIR Analysis for Neem Oil-Based Pickering Emulsion

Acephate, HNT, and neem oil with 0% and 0.2% HNT are all present in the Neem oil-based emulsion. Each spectrum was analyzed for key functional group vibrations indicative of molecular interactions relevant to emulsion stability. Presence of acephate can be confirmed by the broad peak at 3300–3400  $\text{cm}^{-1}$ , which arises due to N–H/O–H band (Fig. 11). Similarly, 1250–1020  $\text{cm}^{-1}$  occurs due to P=O and P–O–C vibrations. However, the presence of HNT can be confirmed by prominent peaks at 3690–3400  $\text{cm}^{-1}$  for O–H stretching and 1000–1100  $\text{cm}^{-1}$  due to Al–O–Si bending. Normal triglyceride peaks related to fatty acids and esters, such as C=O (1740  $\text{cm}^{-1}$ ), C–H (2920 & 2850  $\text{cm}^{-1}$ ), and C–O (1000–1150  $\text{cm}^{-1}$ ) confirms the presence of neem oil.

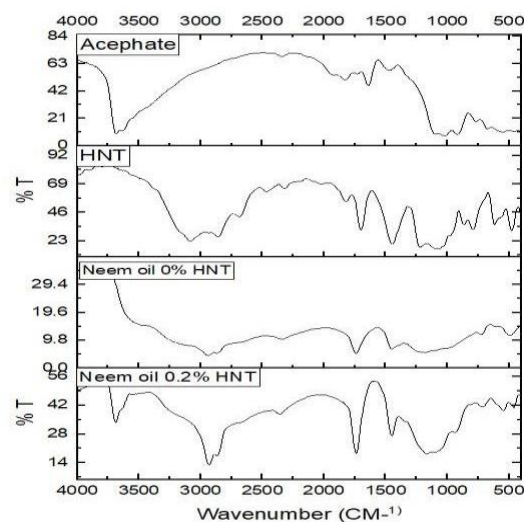


Fig. 11 FTIR spectra for neem oil based Pickering emulsion

Similar peaks for neem oil with 0.2% HNT appears with slight shifts and intensity changes in the 1000–1100  $\text{cm}^{-1}$  and 1700  $\text{cm}^{-1}$  regions [32]. This suggests interactions between neem oil and HNT, potentially via hydrogen bonding or physical adsorption. New or intensified peaks at 900–1100  $\text{cm}^{-1}$  could indicate the presence of Si–O from HNT in the blend. Peak broadening and shifts in the 3400  $\text{cm}^{-1}$  (O–H) indicating physical interactions between neem oil and HNT.

### 3.4 SEM and EDS Analysis

#### 3.4.1 For Coconut Oil-Based Pickering Emulsion

The surface morphology of the coconut oil–water Pickering emulsion stabilized by halloysite nanotubes (HNTs) was investigated using SEM at different magnifications and shown in Fig. 12. At lower magnification

(35,000×) nature of particles appears to be elongated and film like. Which indicates the formation of continuous particle layer at the oil-water interface, confirming that HNTs are successfully adsorbed on the droplet interface. It forms a physical barrier and prevents from droplets coalescence. Whereas, higher magnification images (50,000X) shows that particles are closely packed and uniformly distributed across the surface. This dense packing of particles provides mechanical rigidity and reduces the chances of droplets deformation or merging [33]. The existence of smaller and evenly dispersed particles within smoother interfacial regions clearly supports the complete droplet coverage. Overall, the SEM images confirm the effective adsorption of HNTs on to the droplet interface, which distinguishes stable Pickering emulsions. It is anticipated that these structural features will give the system excellent morphological stability.

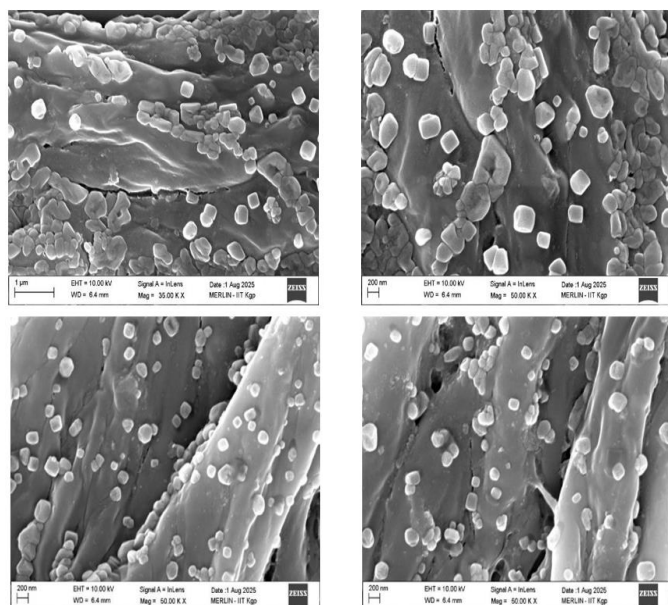


Fig. 12 SEM images for coconut oil based emulsion

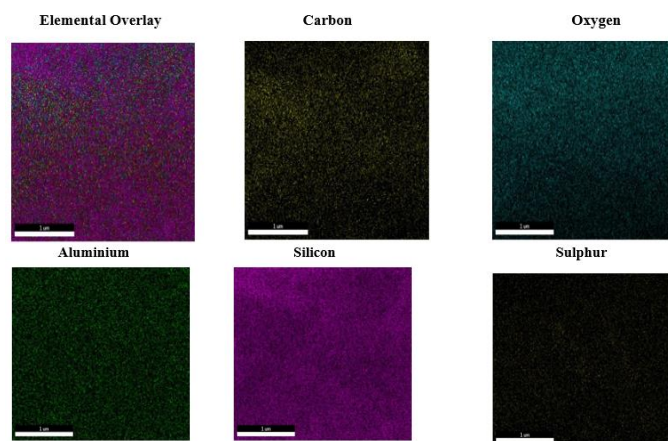


Fig. 13 EDS analysis of coconut oil based emulsion

Table 1 Elemental analysis for coconut oil based emulsion

	Wt. %	At. %	Net Int.	Error %	Kratio	Z	R	A	F
C K	23.47	33.09	327	10.06	0.04	1.07	0.97	0.17	1.00
N K	14.84	17.94	183	10.60	0.03	1.04	0.98	0.17	1.00
O K	26.44	27.99	897.6	9.32	0.06	1.02	0.99	0.23	1.00
Al K	1.81	1.14	300	4.25	0.01	0.90	1.03	0.85	1.03
Si K	28.32	17.08	4737.9	2.42	0.24	0.92	1.03	0.91	1.00
P K	2.84	1.55	314.4	4.41	0.02	0.88	1.04	0.78	1.00
S K	2.28	1.21	262	3.92	0.02	0.90	1.04	0.83	1.00

The compositional information obtained from EDS spectrum (Figs. 13-14 and Table 1) confirms the morphological interpretation from the SEM micrographs. The spectrum shows strong and dominant peaks for the presence of silicon, along with significant amounts of carbon, oxygen, and smaller but notable quantities of phosphorus, aluminium, sulphur, and nitrogen. The two main components of halloysite nanotubes are silicon and aluminium; the presence of halloysite is confirmed by a strong silicon

peak and a notable aluminium peak. Carbon is the major component for coconut oil, and acephate. Similarly, oxygen is a common element for Halloysites nanotubes and coconut oil. Large signals for carbon and oxygen confirm the presence of coconut oil. Peaks for phosphorus, sulphur and nitrogen clearly indicate the presence of acephate. This elemental analysis clearly indicates that halloysites nanotubes have special emulsifying qualities that help in creation of a stable Pickering emulsion.

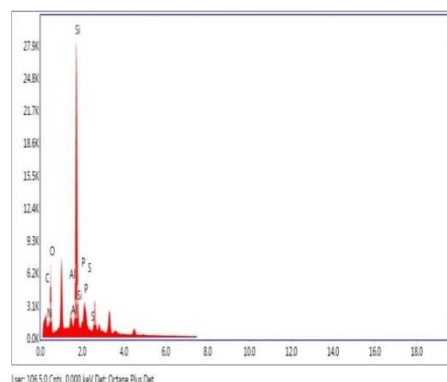


Fig. 14 EDS elemental analysis for coconut oil based emulsion

### 3.4.2 For Corn Oil-Based Pickering Emulsion

SEM images of Corn oil-based Pickering emulsion from Fig. 15 show densely packed, rod-like and short- elongated plate morphologies. It confirms that tubular nature of HNTs have aggregated or partially broken-down during emulsification. HNTs have amphiphilic nature so, they show good wettability at oil-water interface [34]. The strong particle adsorption reduces droplet coalescence and enhances stability. At lower magnification (35,000 X) we can observe that HNTs have nearly covered all the droplets interface and create a continuous layer of particle matter. While images at higher magnification (50,000 X) reveals that size of individual particle ranges approximately from 130 to 300 nm. The observed morphology demonstrates high interfacial stability and ensures long term emulsions stability.

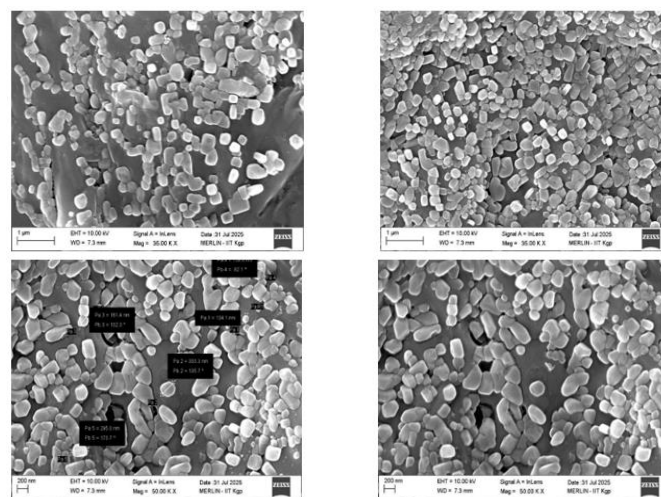


Fig. 15 SEM images for corn oil based emulsion

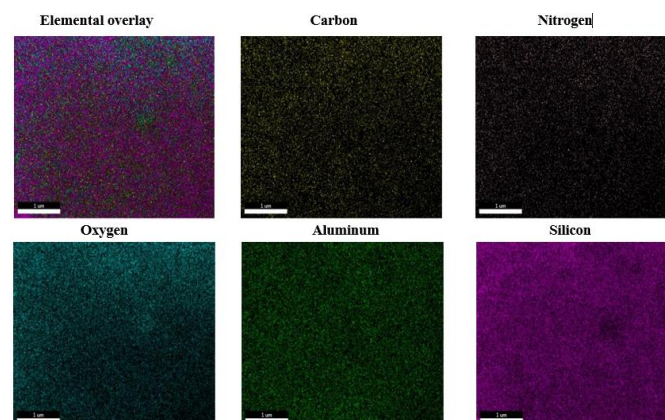
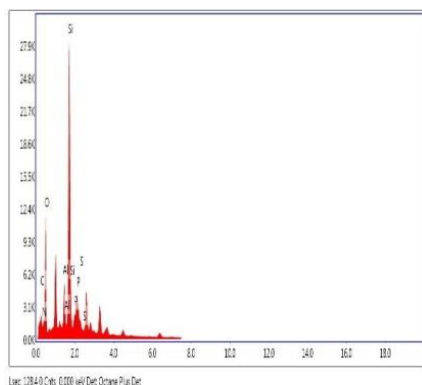


Fig. 16 EDS analysis of corn oil based emulsion

The EDS spectrum is well resolved with K $\alpha$  peaks of C, N, O, Al, Si, P, and S (Figs. 16-17 and Table 2). The dominant Si and Al signals, together with oxygen, confirm the presence of aluminosilicate halloysite, which acts as an emulsifier. Corn oil and acephate contains carbon as a major constituent and intense peak for carbon confirms its presence. while the simultaneous appearance of N, P, and S is a diagnostic sign of the insecticide (acephate) at the interface. Overall, the elemental fingerprint supports a halloysite-rich interfacial layer embedded in an organic matrix containing acephate, consistent with the formulation and stable Pickering stabilization of the emulsion droplets.

**Table 2** Elemental analysis for corn oil based emulsion

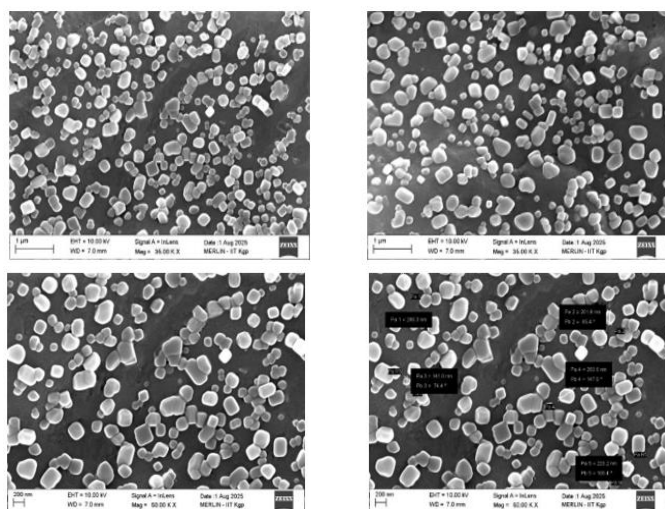
	Wt.%	At. %	Net Int.	Error %	Kratio	Z	R	A	F
C K	23.47	33.09	327	10.06	0.04	1.07	0.97	0.17	1.00
N K	14.84	17.94	183	10.60	0.03	1.04	0.98	0.17	1.00
O K	26.44	27.99	897.6	9.32	0.06	1.02	0.99	0.23	1.00
AlK	1.81	1.14	300	4.25	0.01	0.90	1.03	0.85	1.03
SiK	28.32	17.08	4737	2.42	0.24	0.92	1.03	0.91	1.00
P K	2.84	1.55	314.4	4.41	0.02	0.88	1.04	0.78	1.00
S K	2.28	1.21	262	3.92	0.02	0.90	1.04	0.83	1.00



**Fig. 17** Graphical representation of elemental analysis for corn oil- based emulsion

### 3.4.3 Neem Oil-Based Pickering Emulsion

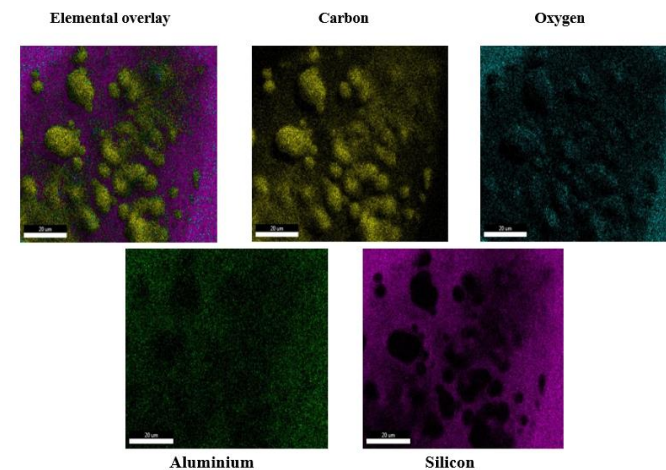
The SEM images from Fig. 18 reveals that neem oil-based Pickering emulsion stabilized by HNTs has well- dispersed, non-coalesced, and morphologically uniform particles. These particles are uniformly distributed throughout the field. The droplets maintain discrete boundaries without deformation, which indicates that HNT particles are strongly adsorbed at the oil-water interface, preventing coalescence [27]. Strong HNT adsorption at the oil-water interface gives the emulsion system improved colloidal and kinetic stability. The morphological description shows that this nanostructured emulsion will show controlled and prolonged release of acephate and bioactive components of neem oil.



**Fig. 18** SEM images for neem oil based emulsion

A dominant carbon (C) peak in the EDS spectrum clearly indicates the presence of neem oil and acephate as shown in Figs. 19-20 and Table 3. As both the compounds are carbon rich species. Oxygen is a major constituent present both in oil phase (e.g., ester, hydroxyl, or phosphate groups) and the aluminosilicate structure of halloysite. A moderate oxygen (O) peak

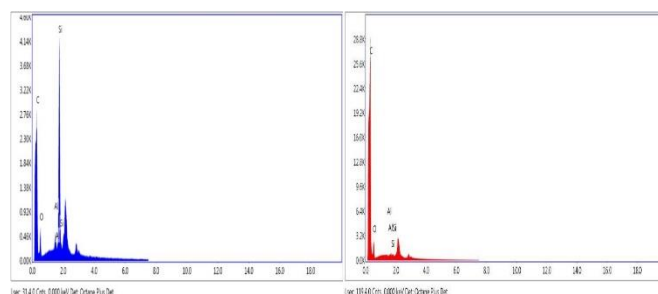
confirms the presence of both oil phase and halloysite nanotubes. Similarly, distinct aluminium (Al) and silicon (Si) peaks gives clear relevance of halloysites nanotubes. The relative intensity and clarity of the Al and Si peaks suggest a good dispersion and interfacial localization of the nanotubes. Similarly, observed elemental distribution also gives supportive evidence to EDS spectrum. It confirms that halloysites nanotubes improve emulsion stability. Overall EDS spectrum confirms that emulsion contains carbon based organic material which is effectively stabilized by halloysites nanotubes, indicating successful formulation of neem oil-based Pickering emulsion containing acephate.



**Fig. 19** EDS analysis of neem oil based emulsion

**Table 3** Elemental analysis for Neem oil- based emulsion

Element	Weight %	Atomic %	Net Int.	Error %	Kratio	Z	R	A	F
C K	74.31	84.24	2003.9	8.20	0.27	1.03	0.99	0.35	1.00
O K	8.94	7.61	224.1	12.81	0.02	0.98	1.01	0.18	1.00
AlK	1.49	0.75	248.1	4.98	0.01	0.86	1.04	0.90	1.02
SiK	15.25	7.40	2537.4	2.41	0.13	0.88	1.04	0.95	1.00



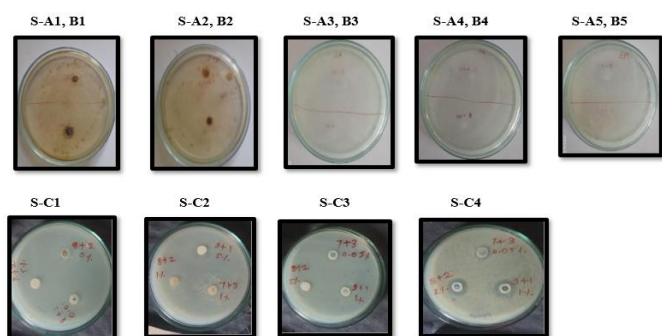
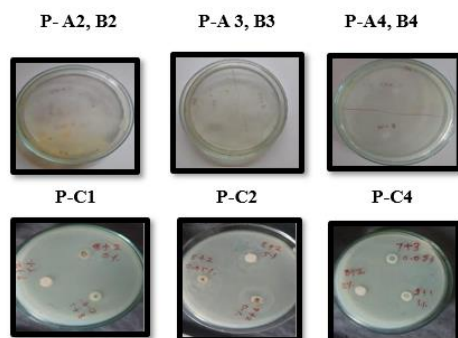
**Fig. 20** Graphical representation of elemental analysis for neem oil based emulsion

### 3.5 Antibacterial Activity

The Biosafety of HNTs- acephate emulsions was passed by examining the impact of various concentration of these emulsions on the bacteria *Staphylococcus aureus* (Fig. 21) and *Pseudomonas aeruginosa* (Fig. 22). The cultures *Staphylococcus aureus* and *Pseudomonas aeruginosa* were grown in nutrient broth medium. The make of the nutrient broth medium was- HI Media Laboratories, Mumbai. The nutrient broth composition was (g/l) Peptone 10.0 Beef extract 10.0, Sodium chloride 5.0, pH after sterilization 7.3±0.1]. It was grown at 37 °C for its accelerated growth. Freshly grown culture was spread on the nutrient agar plate. A well 0.7 mm diameter with sterile borer was prepared in the medium. Each sample having varied concentration each 100  $\mu$ L (microliter) was loaded to well in plate. Plates were incubated at 37 °C and observed for growth of that respective microorganism on plate. After incubation, the zone of inhibition was checked around the colony and its diameter were measured and tabulated in Table 4. A Pickering emulsion containing neem oil shown high antibacterial action against *S. aureus* at doses of 0.05, 1%, and 2%. Pickering emulsions based on corn oil had substantial action only at doses of 0.05 and 0.2%. However, at doses of 0.1, 0.2, and 0.5, the coconut oil-based Pickering emulsion showed increased effectiveness against *S. aureus*. In contrast, all samples demonstrated extremely limited antibacterial activity against *P. aeruginosa*, indicating innate resistance. The findings suggest that the antibacterial effectiveness of samples at varying doses against certain bacterial strains varies. It is worth noting that samples with higher concentrations had limited activity against *P. aeruginosa* but stronger inhibitory effects against *Staphylococcus aureus*.

**Table 4** Zone of inhibition against *S. aureus* and *P. aeruginosa*

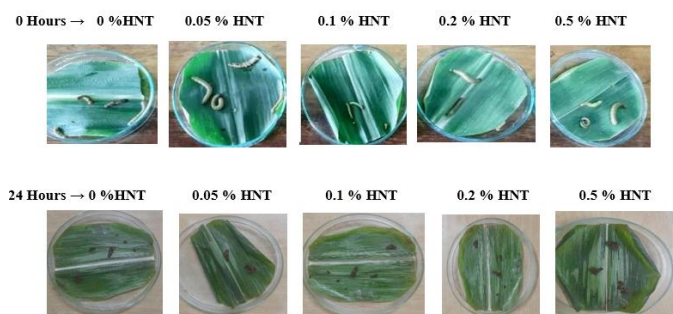
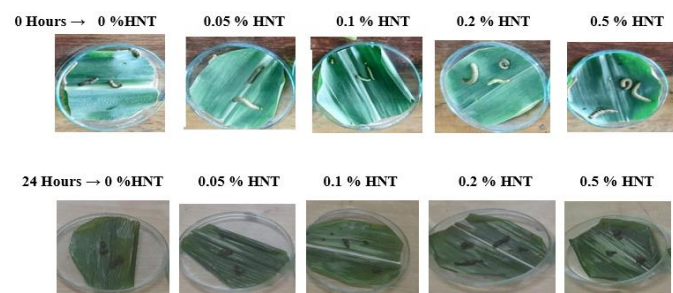
S. No.	Type of Emulsion used	Emulsion Percent	Zone of inhibition (in mm)	
			<i>S. aureus</i>	<i>P. aeruginosa</i>
01	Coconut oil-based Pickering Emulsion	A-1 (0%)	3	0
		A-2 (0.05%)	4	0
		A-3 (0.1%)	5	0
		A-4 (0.2%)	5	10
		A-5 (0.5%)	5	0
02	Corn oil-based Pickering Emulsion	B-1 (0%)	1	0
		B-2 (0.05%)	4	4
		B-3 (0.1%)	1	6
		B-4 (0.2%)	7	12
		B-5 (0.5%)	0	0
03	Neem oil-based Pickering Emulsion	C-1 (0%)	12	8
		C-2 (0.05%)	13.5	8
		C-3 (0.1%)	14	0
		C-4 (0.2%)	14	8
		C-5 (0.5%)	13	0

**Fig. 21** Antimicrobial test against *S. aureus***Fig. 22** Antimicrobial test against *P. aeruginosa*

### 3.6 Insecticidal Activity

The insect *Spodoptera frugiperda* which is commonly known as fall armyworm is a highly destructive pest, and it has become a global threat for maize producing countries [1,19]. Larvae of *S. frugiperda* consume leaves, whorls, tassels, which causes severe defoliation, hinders photosynthesis, and lowers grain yield. Production of maize can be directly or indirectly get affected by *S. frugiperda*. Direct effects may include sap loss and mechanical tissue damage which reduces the plants photosynthetic area and metabolic efficiency. Indirect effect may include feeding wounds facilitate pathogen entry. Therefore, to investigate biosafety and insecticidal activity, *S. frugiperda* was selected as a pest model and corn leaves were selected as a plant model. In order to evaluate the insecticidal effects of HNTs-Acephate emulsion, these leaves were first cleaned with DI water and then immersed in various oil-based emulsions for four hours. The insects began to die and mortality of all oil-based HNT-Acephate emulsions were investigated. The experimental result (Figs. 23-25) showed that mortality rates of all experimental treatment groups were completed after 24 h. The mortality rate for Corn oil-based emulsion is moderate. Mortality is highest in emulsions containing 0.5% HNT and lowest in emulsions containing 0.0% and 0.1% HNT. Similarly, with the exception of 0.1w% HNT, larval mortality increased with increasing HNT dispersion concentration in the coconut oil-based emulsion. The emulsions with 0.2w% HNT and 0.5w% HNT have the highest mortality. In contrast, Neem oil-based emulsion has the best mortality rate of any oil-based emulsion. For this emulsion, as the emulsifier percentage increases, so does the mortality rate. Again, it is greatest at 0.2 and 0.5 w% HNT.

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**Fig. 23** Insecticidal activity of corn oil based pickering emulsions**Fig. 24** Insecticidal activity of coconut oil based pickering emulsion**Fig. 25** Insecticidal activity of neem oil based pickering emulsion

## 4. Conclusion

In this study, various natural oils, including corn, coconut, and neem oils, are used to prepare Pickering emulsions with different concentrations. Halloysite nano clay was used as a stabilizing agent, and acephate was added to test its insecticidal properties. Microscopic images of the prepared emulsions reveal that the Pickering emulsion based on neem oil had smaller droplets at 0.2% concentration. Similar to this, Pickering emulsion prepared with coconut oil has smaller droplets and is more stable at 0.5%, whereas Pickering emulsion made with corn oil has smaller droplets and is more stable at 0.2%. Thus, as the HNT concentration increases, the interfacial tension and droplet size decrease. The contact angle was measured using maize and cotton leaves. A coconut oil-based emulsion's contact angle on cotton leaves ranges from 72.9° to 48.43°, which is a slight variation. On maize leaves, however, the same emulsion exhibits an uneven contact angle; as the HNT concentration rises, the contact angle rises from 56.17° to 59.37°, signifying moderate wettability. Emulsions based on corn oil exhibit the same pattern. Contact angle drops from 61.86° to 57° for cotton leaves, but it is at least 54.79° for concentrations of 0.1%, indicating strong wettability. On the other hand, a minimum contact angle of 41° for a 0.2% emulsion of maize leaves indicates significant wettability. The contact angle of emulsions based on neem oil on maize leaves ranges from 48° to 44°. The contact angle is at its lowest at concentrations of 0.1 and 0.5%. Similarly, for cotton leaves, the contact angle increases in tandem with the HNT content. It ranges from 56.38° to 64.76° indicating moderate wettability. Most of prepared emulsions shows contact angle < 60° which shows good wettability. The FTIR spectrum shows a stable Pickering emulsion in which Halloysite nanotubes (HNTs) successfully stabilize the natural oil-water interface through physical interactions, improving resistance to sedimentation and coalescence. The SEM images confirm the effective adsorption of HNTs on to the droplet interface, which distinguishes stable Pickering emulsions. It is anticipated that these structural features will give the system excellent morphological stability. To assess these emulsions' biosafety, the effects of varying HNTs-acephate emulsion concentrations on the bacteria *P.*

*aeruginosa* and *S. aureus* were investigated. The results imply that samples at different doses have different antibacterial efficacy against particular bacterial strains. Notably, samples with greater concentrations exhibited less activity against *P. aeruginosa*, but *Staphylococcus aureus* is more strongly inhibited. HNTs- Acephate emulsions were tested for insecticidal activity using *S. frugiperda* as the pest model and maize as the plant model. Emulsion made from corn oil has a moderate mortality rate. The emulsion with the highest mortality was the one with 0.5% HNT content. The maximum mortality was seen in coconut oil-based emulsions with 0.2 and 0.5 w% HNT. In contrast, neem oil-based emulsion had the best mortality rate among all oil-based emulsions. The mortality rate for this emulsion rises with the percentage of emulsifier used. Again, it peaks at 0.2 and 0.5 w% HNT.

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