GSC Advanced Research and Reviews
eISSN: 2582-4597 CODEN (USA): GARRC2
Cross Ref DOI: 10.30574/gscarr
Journal homepage: https://gsconlinepress.com/journals/gscarr/

(Research Article)

From mechanisms to application: Exploring Pickering emulsions stabilized by nanocellulose with eucalyptus oil for enhanced seed germination

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GSC Advanced Research and Reviews, 2024, 21(03), 163–183

Publication history: Received on 29 September 2024; revised on 04 Octobre 2024; accepted on 06 December 2024

Article DOI: https://doi.org/10.30574/gscarr.2024.21.3.0475

Abstract

This study comprehensively explores Pickering emulsions, their stabilization mechanisms, and the potential of nanocellulose in agricultural applications. Initially, the fundamental principles and mechanisms of Pickering emulsions are reviewed, highlighting their ability to form stable, particle-stabilized emulsions. The focus then shifts to cellulose nanocrystals (CNCs), extracted from sugarcane bagasse, as stabilizing agents in emulsions containing eucalyptus oil, with the aim of enhancing seed germination in mung beans. CNCs were characterized using X-ray diffraction (XRD), infrared spectroscopy (IR), and scanning electron microscopy (SEM), confirming their suitability for forming stable emulsions. Results demonstrate that CNC-stabilized Pickering emulsions with eucalyptus oil create a conducive microenvironment for seed germination, offering an eco-friendly and sustainable agricultural innovation. The utilization of sugarcane bagasse-derived CNCs emphasizes the valorization of agricultural waste, aligning with principles of circular economy and sustainability. While the findings are promising, further research is needed to elucidate the mechanisms by which CNC-stabilized emulsions enhance germination, evaluate their broader applicability to other crops, and examine long-term effects on plant growth and development. This work bridges fundamental research on Pickering emulsions and practical applications, showcasing the potential of nanotechnology and agricultural waste valorization in driving sustainable agricultural practices.

Keywords: Pickering emulsions; Cellulose nanocrystals (CNCs); Eucalyptus oil; Seed germination enhancement; Sustainable agriculture

1. Introduction

Originating from the leaves of the eucalyptus tree, eucalyptus oil has a long and illustrious history spanning several centuries. The commercial extraction of eucalyptus oil traces back to the indigenous people of Australia who first utilized the leaves of Eucalyptus tree for their medicinal properties[1]. Its numerous uses have caused a rise in demand throughout time in a number of industries, including pharmaceuticals, cosmetics, and more. Nevertheless, eucalyptus oil has intrinsic drawbacks that prevent it from being widely used, despite its popularity. Its hydrophobicity, photosensitivity, brittleness, and deterioration have made it difficult to formulate stable and efficient products[2]. These characteristics, which were before thought to be disadvantages, are now driving advancements in emulsion technology[3].

1.1. Emulsions

An emulsion is a biphasic system consisting of two immiscible liquids, one finely and uniformly dispersed phase as globules throughout the second continuous phase.

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1.1.1. Types of Emulsions

Based on the nature of continuous and dispersed phase, emulsions are categorized as oil in water (O/W) emulsions (Figure.1), where oil droplets are dispersed throughout the aqueous phase, water in oil (W/O) emulsions, with water droplets as the dispersed phase in the flow of oil as the continuous phase, and more complex configurations of emulsions such as oil in water in oil (O/W/O) emulsions and water in oil in water emulsions (W/O/W)[4].

Fats or oils are always formulated as O/W emulsions for oral administration, either as medications or as delivery vehicles for oil soluble pharmaceuticals. Water soluble drugs and oil soluble drugs are more quickly released from O/W and W/O emulsions respectively. Multiple emulsions are known for their excellent control over prolonged release[5]. Examples of food O/W emulsions include milk, cream, dairy drinks, infant formula, soups, salad dressings, mayonnaise, ice cream, and chocolate ganache; examples of W/O emulsions are butter, margarine, and spreads. Also, based on droplet size, emulsions are classified as those with a droplet size of macrons, which are thermodynamically unstable and micro-emulsions with a droplet size of microns, which are stable thermodynamically[6].

Food emulsions are kinetically stabilized by various types of emulsifiers. Depending upon the type of emulsifier used, emulsions are classified as Conventional emulsions and Pickering emulsions[7].

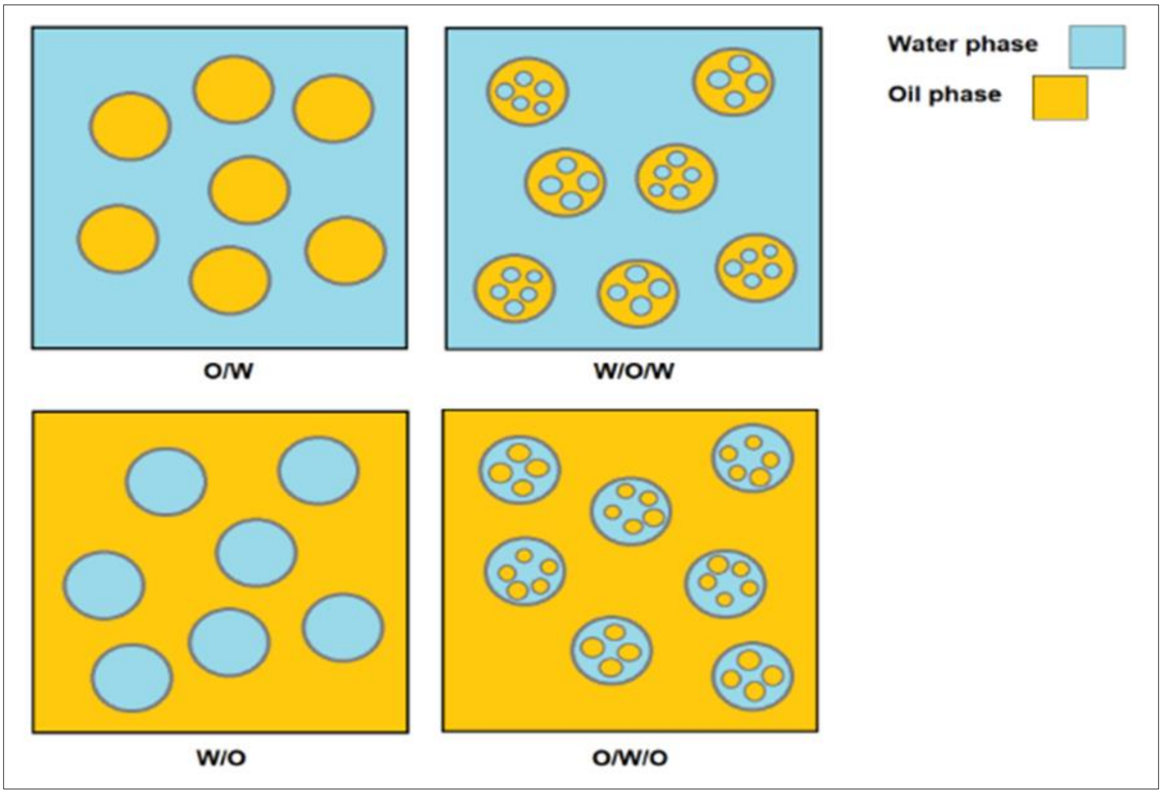

Figure 1 Schematic diagram of the different types of emulsions formed between water and oil[8]

1.1.2. Conventional emulsions

In conventional emulsions, low molecular weight emulsifiers (LMWE), also called as surfactants, or amphiphilic biopolymers are used as stabilizers. LMWEs can be either natural or synthetic in origin, consisting of a hydrophilic head (which can be non-ionic yet polar, or fully charged) and a hydrophobic tail usually comprising of at least one acyl chain.

Amphiphilic biopolymers are mostly associated with proteins like dairy products (caseins, β-lactoglobulin, etc.)[9], [10] and plant derived products like soy proteins[11]. Surface-active polysaccharides like gum Arabic, galactomannans and modified starches have also been used as emulsifiers[12].

The properties and characteristics of surfactant- and biopolymer-based interfaces have been discussed in detail and compared in previous studies[13], [14]. Surfactants are described to be more tightly packed at the interface, providing with greater lateral homogeneity in interface film[15]. Protein films are comparatively more porous.

1.1.3. Pickering emulsions

Pickering emulsions refer to the emulsions stabilized by solid colloidal particles which are partly wetted by oil and by water and act as emulsifiers. Such particles position themselves at the oil-water interface based on their relative affinity for both the phases, which is characterized by the contact angle. As a result, particles make the interface bend toward the phase for which their affinity is lower, implying that particles which are preferentially wetted by water will be suitable for forming O/W emulsions and vice versa as shown in Figure.2.

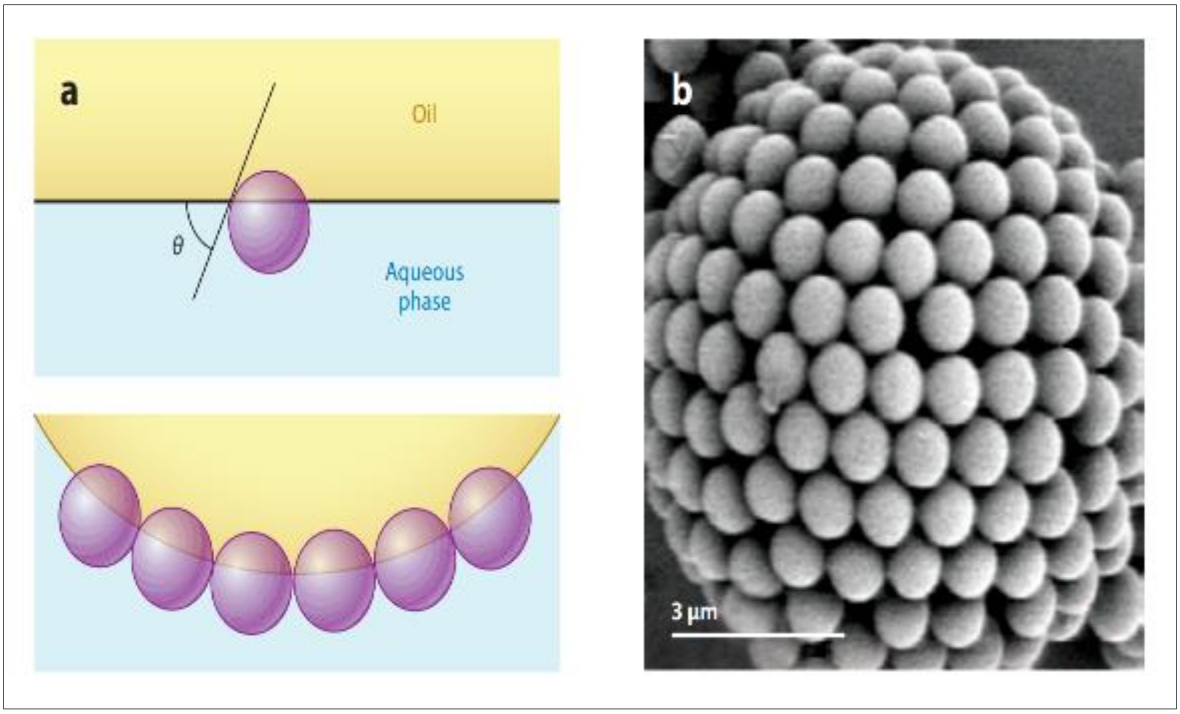

Figure 2 (a) Position of a small spherical particle at a planar oil-water interface for a contact angle less than 90 ∘ , and corresponding positioning of particles at a curved interface of an oil-in-water emulsion[16]. (b) Polystyrene particles assembled on an oil droplet in water[13].

Emulsions, which are colloidal systems of immiscible liquids, provide a way to maximize the advantages of eucalyptus oil while reducing its drawbacks[17]. Eucalyptus oil's photosensitivity, hydrophobicity, volatility, and instability[2] can all be successfully handled by adding it to emulsion compositions. By wrapping the oil droplets and protecting them from external elements that may otherwise harm their integrity, the emulsion serves as a protective vehicle[17]. The characteristics of eucalyptus oil that formerly made it difficult to use now work to its advantage. Its hydrophobicity permits targeted distribution and extended release, while its volatility amplifies the scent and therapeutic efficacy[2]. Eucalyptus oil becomes a powerful element through emulsification, enabling it to reach its maximum potential in a range of applications. For emulsions to be successfully applied in these various domains, their stability and characteristics are essential. Surfactants and emulsifiers, which adsorb at the oil-water interface to avoid coalescence and preserve stability, stabilize conventional emulsions[17]. These surfactant-based emulsions do, however, frequently encounter issues such as poor stability, environmental problems, and control issues during formulation[18].

1.2. Pickering Emulsions

A promising approach to stabilizing emulsions involves utilizing nanoparticles to create a colloidal system known as Pickering emulsions, which offer superior stability and application convenience[19].

1.2.1. Types of Pickering emulsions

Based on the nature of the solid particles used for stabilization and type of dispersed phase, Pickering emulsions are classified into the following types.

Table 1 Types of Pickering emulsions.

Types of Pickering emulsions based on	
Type of stabilizer used	Type of dispersed phase
Inorganic particle-stabilized emulsions Organic particle-stabilized emulsions Janus particle-stabilized emulsions Hybrid particle-stabilized emulsions Microgel-stabilized emulsions	Oil in water emulsions (O/W) Water in oil emulsions (W/O) Multiple emulsions (Like water in oil in water and oil in water in oil emulsions, W/O/W and O/W/O)

1.2.2. Stabilization mechanism of Pickering emulsions

The Irreversible Adsorption and Robust Physical Barriers of Particles at the Oil-Water Interface

To understand the difference between Pickering and traditional emulsions, the irreversible adsorption and robust physical barriers of particles at the oil-water interface are necessarily explained. Firm steric hindrance in Pickering emulsions is resulted from the strong adsorption driven by the partial wettability of certain spherical hard solid particles, hence preventing the emulsion droplets from flocculation and coalescence. Adsorption of particles at the oil-water interface requires partial wetting by both the oil and water phases. And the wettability is measured by contact angles (θ), specifying that O/W emulsions ($\theta < 90^\circ$) can be formed by particles easily wetted by water, otherwise, W/O emulsions ($90^\circ < \theta < 180^\circ$) are fabricated as discussed in Figure 3. An intact space barrier can be generated at the oil-water interface to stop droplet coalescence as the desorption of particles from the oil-water interface involves overcoming high interfacial energy. Pickering emulsions are therefore equipped with superior stability as compared to conventional surfactant-stabilized emulsions. This is a matter of interfacial energies of the three interfaces: solid-oil, solid-water, and water-oil[20].

The Capillary Pressure between Particles

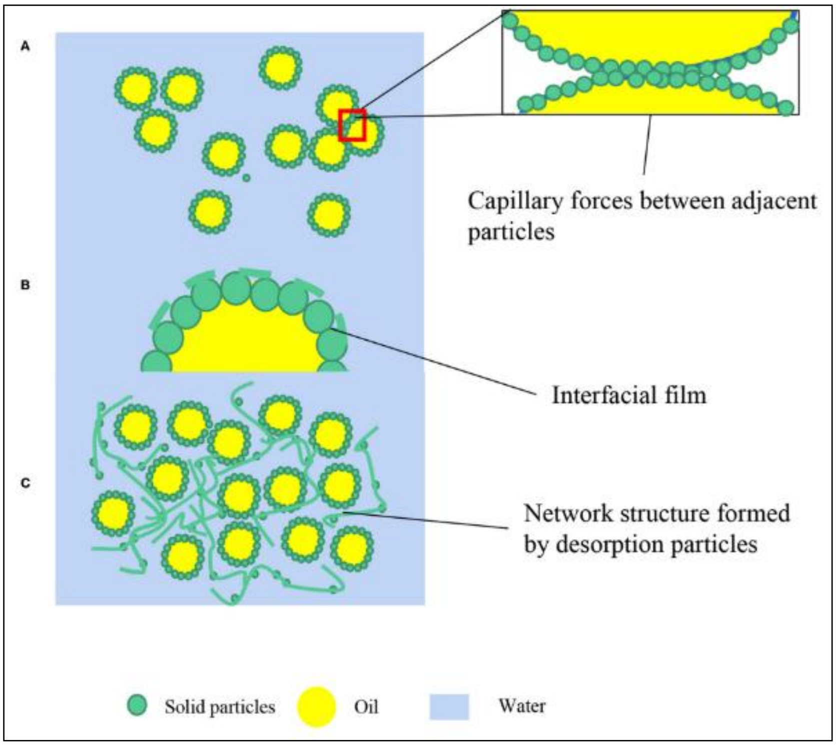

Figure 3 Different stabilization mechanisms of Pickering emulsions. (A) Capillary forces between adjacent particles; (B) Dense interfacial film; (C) Network structure in a continuous phase.[20]

The capillary pressure between adjacent interfacial particles prevents thin film formed by particles degradation. The non-spherical particles (rod-like, disk-like, fibers, etc.) fabricate more stable emulsion systems. One of the reasons revealed is that anisotropic particles with different geometrical shapes can generate stronger capillary pressure between adjacent particles at the interface.

The interfacial rheological responses

The interfacial adsorption and the interaction amongst particles carry the potential to affect film (Figure) drainage. The interfacial structure may be transformed into the multilayer arrangement, with one or more extra layers of ordered monodisperse hard spheres accommodated in the interdroplet region, where a substantial excess of particles exists in the continuous phase. The additional particle layering can lead to an oscillatory potential of mean force and an associated kinetic structural barrier, preventing coalescence. This layering formed by particles that are not adsorbed at the oil-water interface is common, especially in a host of colloidal particles, such as self-assembling entities which are neither fully monodispersed nor closely resembling hard spherical particles.[20]

The Formation of Particles' Network in the Space between Droplets

Another important stabilization principle is the intrinsic ability of microgels to act as a versatile thickener agent and colloid stabilizer in an aqueous medium. The more stable and highly viscous structure can stabilize biopolymer based HIPEs due to a self-supporting gel network (Figure 2C). This way, HIPEs are able to have resistance to good freeze-thaw reversibility and drastic heating. The particles predominantly play the role of a "structure agent" rather than necessarily being adsorbed at the oil-water interface. Xu et al. used bovine serum albumin glycated with galactose possessing much structural integrity and higher refolding ability that can improve the stability of HIPEs compared to native bovine serum albumin. Additionally, Rayner et al.[21] further found that some adsorbed layers of biopolymer particles at the oil-water interface can be made to fuse together into a coherent gel-like lipid-encapsulating layer through post-emulsification thermal processing[20].

1.2.3. Factors affecting stability of Pickering emulsion

The effectiveness of particle emulsifiers' ability is strongly influenced by the hydrophobicity of particles, therefore affecting the type of Pickering emulsion. In most cases, changing the surface chemistry with small molecules or polymers through chemical anchoring and physical adsorption can alter the wettability of particles. Nevertheless, the interaction between particles and amphiphiles renders particles' wettability and tunability in in situ modification. In addition to the wettability of particles, external factors also have a critical influence on the stability of emulsions, such as the pH of the emulsion, particle concentration, ionic strength, the corresponding particle size, droplet size of emulsion, the type and fraction of oil phase as shown in Figure 4.[22]

pH

The pH of the system alters the surface charge of particles, hence affecting the electrostatic interaction among them, regulating the adsorption behaviour as well as the space barrier formed at the oil-water interface. Therefore, the emulsion droplets exhibit dispersion or flocculation with the different adsorption behaviours and space barriers of particles. Xiao et al.[22]stabilized Pickering emulsions with grafted carboxymethyl maize starch (CMS) nanoparticles showing pH responsive properties. Under acidic conditions, a significant decrease in electrostatic interactions, hydrogen bonding, covalent bonding, and van der Waals forces resulted in particles separating from the two-phase interface into the oil phase making emulsions unstable. On the contrary, the nanoparticles can stabilize emulsions at pH 10. Li et al[23]. explored the influence of pH on the edible mayonnaise-like Pickering emulsions. Liu et al.[25] applied chitosan interaction to prepare pH-responsive Pickering emulsion. At $pH > 6$, chitosan nanoparticles or micro-metersized floccular precipitates were formed and adsorbed on the interface to stabilize the emulsion. While at $pH < 6$, chitosan dissolved in water, and demulsification occurred.

The Size of Solid Particles and Emulsion Droplets

The particle size of solid particles also influences the stability of the emulsions. Theoretically, a harder space obstacle can be formed with a decrease in particle size. So, it can make the solid particles adsorbed pretty closely at the water-oil interface[26], preventing the coalescence among droplets and the instability of emulsion. However, some studies have shown that particle size kept too large or too small may have an adverse effect on the stability of the emulsion[27] found that the wettability of particles may be changed with the change in particle size. The Pickering emulsions stabilized by sweet potato and corn starch with a diameter ranging from 100–220 nm had much better stability than the particles with a diameter either less than 100 nm or larger than 220 nm. Additionally, the decrease in the size of droplets caused by increasing gel particles strength leads to maintain the stability of emulsions.

Oil Type and Volume Fraction

The type of oil used for the preparation of Pickering emulsion and the radio of the dispersed and continuous phase play important roles in the stability of the emulsion. The oil type determines the interfacial tension of the droplets and the interactions among the particles on the two-phase interface can also be influenced. Zhang et al.[16] stabilized O/W Pickering emulsions, hexadecane/H2O, and decane/H2O Pickering emulsions, with poly (sodiump-styrenesulfonate) bush (PS@PSS), by ultrasonic power. The microscope images showed that droplets were significantly bigger and more homogeneous in hexadecane than in decane. When the oil fraction increased from 0.2 to 0.6, the emulsions type changed from O/W to W/O which was stabilized by the water-insoluble phytosterols[28].

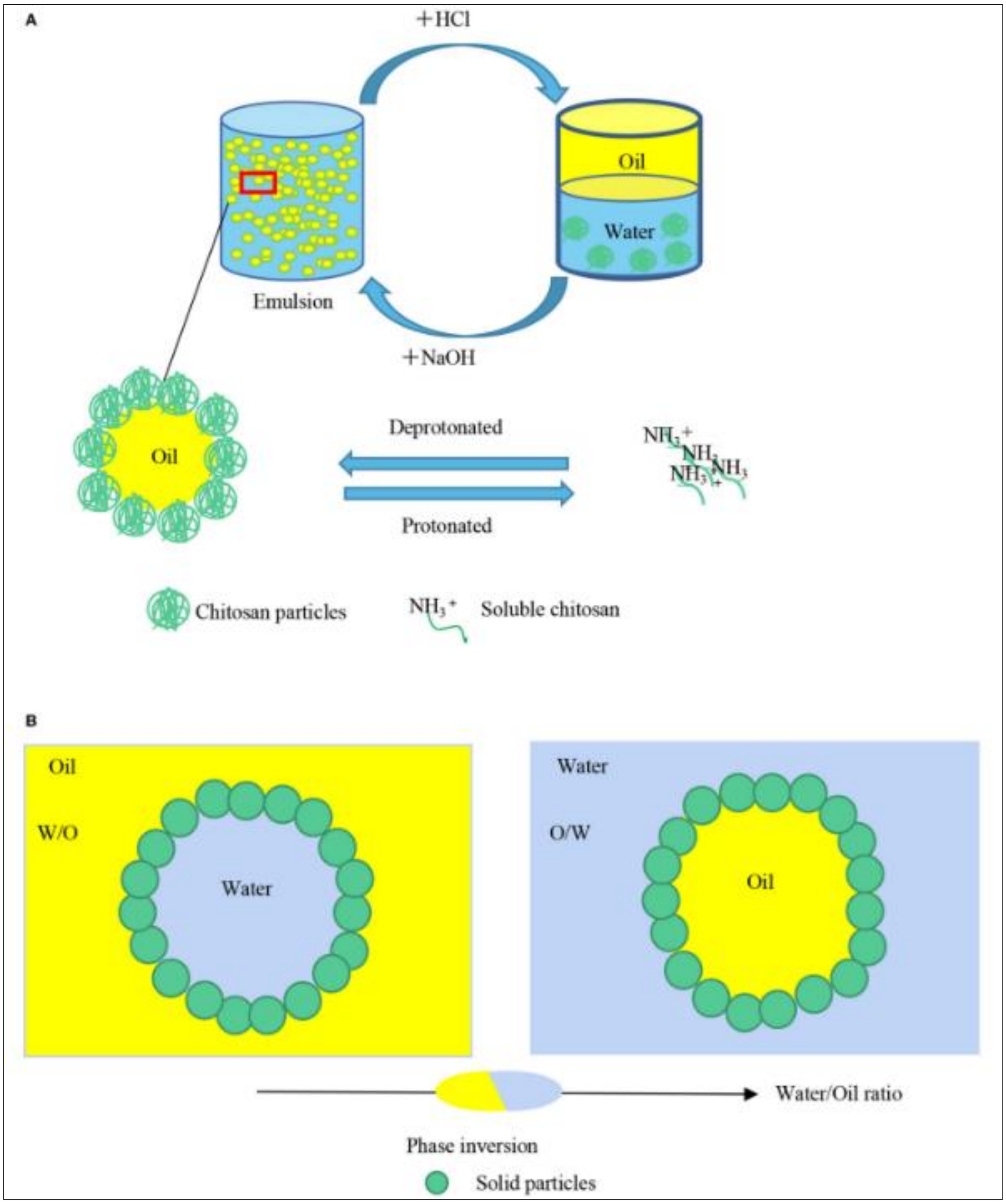

Figure 4 (A) External factors affect the stability of Pickering emulsions pH affects the electrostatic interaction among solid particles, causing to regulate the adsorption behaviour of solid particles. The emulsion droplets will exhibit dispersion or flocculation with the different adsorption behaviours. (B) Phase inversion will happen when the oil radio increase from 0.2 to 0.6.[29], [30]

Temperature

The emulsifying temperature alsoaffects the stability of food-grade Pickering emulsions. The nanoparticles had poor thermal stability, however, the thermal stability of Pickering emulsions got enhanced with the application of the triple emulsifier.[29] In the actual preparation process, the final stability of the emulsion is the result of the interaction of various factors

1.2.4. Interface stabilizers in Pickering emulsions

Different shapes of food grade particles stabilizing Pickering emulsions

In recent years, food grade nanoparticles of different shapes have caught researchers' attention. Various kinds of protein nanoparticles are reviewed by Zhang et al[30] along with their preparation processes. Particles with different shapes have different densities, desorption energy and capillary forces between adjacent particles[31], [32], [33]. This leads to large variations in extent of stabilization. The variety in solid particle shapes is related to their sources, properties, structures, and particle preparation methods. The morphological shape also modifies the wettability behavior of particles and interactions between adjacent particles, therefore, critically impacting the emulsion stability.[30], [34]

Spherical solid particles

Mostly formed by protein, polysaccharide, and other macromolecules crimped by intramolecular forces. Spherical particles formed by a single natural molecule are not regular enough. To get anti-aggregation properties improved, extra substances are required to form complexes.

Rod-like solid particles

Regular rod, prolate ellipsoid, and spindle rod shapes are often prepared using CNCs rod-shaped particles, cellulosic colloidal nanorods, etc[35]. These have relatively sufficient aspect ratios, effectively stabilizing Pickering emulsions[36], [37]. Such emulsions are more stable ascompared to those with spherical particles, supportive conditions provided by specific surface area, high strength, low density, and amphiphilic ability of CNC. Madivala et al. formed W/O emulsions stabilized by hydrophobic prolate ellipsoids (obtained by stretching polystyrene latex particles) and O/W emulsions stabilized by hydrophilic spindle type hematite particles. His study highlighted the major influence of particle aspect ratio on emulsion stability.[38]

Nanofibrils

A much larger aspect ratio, forming strong, entangled and disordered network structures is the significant cause of higher stability of emulsions stabilized by nanofibrils than those stabilized by rod-shaped particles.[39] Nanofibrils tend to form three-dimensional networks on the surface of oil droplets and improve the mechanical properties of the emulsion. Besides, an elastic monolayer structure will be produced [35].

Nanocages

Presently, cage-like food grade stabilizers are new type of emulsifiers as nanocages with hollow interiors and porous wall surfaces prepared with protein. The stability mechanism of nanocages is similar to that of spherical particles. [30]

Layered double hydroxides

Young et al.[40] investigated how layered double hydroxides (LDH) particle concentration, salt concentration and oil phase volume fraction influence emulsion type and stability. It was found that the droplet size increased with higher oil phase volume fraction and decreased with increasing salt and particle concentrations. Also, hydrophobic behavior of LDH leads to the formation of W/O emulsion preferably.

Other irregular shapes

Other than the commonly mentioned shapes, particles also exist as spores, scaly, and so on. The spore particles with rough surface structure and the presence of Y-shaped marking of Lycopodium clavatum solely stabilized Pickering emulsion with oils varying polarity, forming clusters and chains at the interface. Liu et al. prepared phytosterol colloidal particles which can prove to be a novel candidate to deliver active substances.[28] In conclusion, in addition to wettability, particle morphology also plays a crucial role in determining the type, stability and behavior of Pickering emulsions. Experimental studies have demonstrated that particle shape has an influence over the packing and can induce capillary interactions[41].

1.2.5. Categories of interface stabilizers

Hydroxyapatite

Hydroxyapatite [$Ca_{10}(PO_4)_6(OH)_2$] is an important component in human bodies, especially in bones and teeth, as the main mineral. As per a study, HAp nanoparticles could help form O/W Pickering emulsions when the oil contained an ester group or the oil phase contained other polymers with ester groups, whereas HAp nanoparticles alone could not work as an emulsifier for Pickering emulsions. HAp nanoparticles have already been extensively used in the formation of Pickering emulsions applied to a variety of applications such as biomaterials, adsorbents, and catalysts.[42]

Silica

Silica is one of the most extensively studied Pickering emulsifiers because they are easily obtained and modified. Massive experiments have indicated that unmodified silica tends to stabilize O/W Pickering emulsions due to the hydrophilicity resulting from Si-OH groups on particle surface, whereas hydrophobically modified silica preferentially stabilizes W/O Pickering emulsions[43], [44]. Many studies have produced various kinds of modified silica, in order to get different properties for better application through Pickering emulsions, such as polymerization. Factors influencing silica-stabilized Pickering emulsions, such as pH and salt concentration, have been investigated systematically.[22]

Magnetic Nanoparticles

In recent years, magnetic Fe_3O_4 nanoparticles have attracted great research attention, especially in biomedical field, due to the negligible toxicity and useful magnetic property. The unmodified Fe_3O_4 nanoparticles are hydrophilic owing to the many hydroxyl groups on the particle surface, while they can be turned into hydrophobic through appropriate surface decoration. There have been a number of studies using modified Fe_3O_4 to form Pickering systems[41], [45]. One of the most unique advantages of Pickering emulsions stabilized by magnetic particles is that they can be easily demulsified and reused by simply apply an external magnetic field. A study has efficiently proposed a convenient system for the extraction of wastes from water. They employed hydrophobic oleic acid coated nano-Fe_3O_4 particles to firstly form W/O Pickering emulsion, and then W1/O/W2 came into being after adding the aqueous feed phase with organic waste. [46]

Chitosan

Chitosan, the second abundant polymer in the world, is a linear polysaccharide produced by deacetylation of chitin. The most outstanding and irreplaceable properties of CS are its biodegradability and biocompatibility due to the free amino and hydroxyl groups along its backbone, which makes it very useful in the field of biomedicine and pharmaceutics. Moreover, CS is a particularly green polymer owing to its excellent solubility in dilute acid aqueous solutions[47]. In research, bare CS nanoparticles were used as the emulsifier to establish Pickering emulsion, and MCs were formed through evaporation of CH_2Cl_2.[48]

Carbon Nanotube

Carbon nanotubes (CNTs) have appealed great interests in recent years due to their unique properties, like large surface area and more exposed active sites. Nevertheless, because of the hydrophobicity of CNTs, it is hard to disperse them well in aqueous solutions, thus most of former studies focused on preparation of W/O emulsions, whereas more useful researches about O/W emulsions were far less. To increase the hydrophilicity of CNTs through an easier and higher-yielding method, an attractive approach was made to treat CNTs with oxygen plasma to introduce hydrophilic functional groups, like hydroxyl and carboxyl groups, while no noticeable damage arose after the treatment; besides, it was notable in the experimental results that sonication time, CNTs concentration, and plasma treatment period had crucial influences on the size as well as size distribution of droplets.[49]

Natural Stabilizers

Some biological and food-grade particles have been increasingly employed in formulation of Pickering emulsions due to their excellent biocompatibility, biodegradability, as well as attractive potential applications in food and drug delivery fields. Fabrication methods and interfacial attachment efficiency tuning of these edible particles, research trend and challenges of employing them as Pickering emulsifiers have been well-reviewed by another article[50]. Some highly efficient Pickering emulsifiers have been discussed here in detail[31], [36], [43].

Starch

A natural material obtained from various botanic resources, being biodegradable and non-toxic, starch granule is an excellent candidate with potential uses in food industry, biomedicine, and so on. However, as a kind of native material from different resources, starch particles have broad size range, affecting its performance as an emulsifier. In addition, considering the poor hydrophobicity of starch granules, specific modifications successfully stabilize O/W Pickering emulsions[51]. A study has compared four kinds of native starch granules from different resources in several aspects, such as particle size and configuration, surface charge, contact angle, emulsion stability, and surface morphology, to investigate factors determining emulsion-stabilizing ability of starch granules[52]. It concluded that the size of particles rather than morphology or surface chemistry affected the ability of starch granules to stabilize Pickering emulsions. Researchers have also found that proper heat treatment could make monolayer barrier formed by starch particles denser due to the swelling of starch particles, thus providing products with more promising applications in drug-release and molecule protection[53]. It has already been verified that native starch granules could be tuned more hydrophobic after modification by octenyl succinic anhydride (OSA) while keeping its vital properties unaffected[54].

Zein

Zein is an abundant material extracted from corn, which has been extensively studied in many fields[55]. As a kind of water-insoluble food-grade protein, zein bears high proportion of hydrophobic amino acids, while the degree of hydrophobicity can be tuned by pH (Pomes, 1971). It was proposed by that zein colloidal particles could directly serve as Pickering emulsifiers without surface-modification, because the three phase contact angle θ was close to 90 ∘ when pH deviated from zein isoelectric point.[56]

Soy Protein

Soy protein is commercially available and non-toxic, even well nutritious, making it a promising food-grade material to establish Pickering emulsion systems[57], [58]. Besides, their compatibility under high pressure emulsifying condition results in much finer droplets. In recent few years, great attention has been paid for the application of soy proteins like soy protein isolate (SPI) or its major component glycinin, especially the serial works done by the group[58].

1.3. Cellulose

Cellulose, a widespread plant-derived polysaccharide, serves as an effective emulsifier in Pickering emulsions, where solid particles stabilize the interface between immiscible liquids. Whether in nanoparticle or microfiber form, cellulose's amphiphilic properties enable it to adsorb at the oil-water interface, creating a robust barrier against coalescence. Its customizable size and surface properties offer control over emulsion stability and rheological behavior. Moreover, cellulose's biocompatibility and sustainability make it an appealing choice, aligning with the demand for eco-friendly products. Chemically modifiable cellulose derivatives further enhance its emulsification capabilities and suitability for diverse applications, spanning food, cosmetics, pharmaceuticals, and materials science, establishing cellulose as a versatile and environmentally friendly emulsifier in Pickering emulsions.

Nanocellulose, a common polysaccharide present in plant cell walls, can be derived from cellulose through degradation processes, resulting in distinctive structural and surface features. These nanocellulose particles are highly beneficial as Pickering emulsion stabilizers due to their high aspect ratios, large surface areas, and amphiphilic properties. In contrast to conventional emulsifiers, nanocellulose exhibits improved interfacial adsorption and barrier qualities, enhancing emulsion stability and preventing coalescence. Furthermore, the exceptional adaptability of nanocellulose allows for fine-grained control over encapsulation effectiveness, rheological behavior, and emulsion droplet size. Their compatibility with various oil phases, such as eucalyptus oil, underscores their suitability for diverse formulation contexts. Additionally, the biocompatible and reusable nature of nanocellulose aligns with the growing demand for environmentally acceptable and sustainable emulsion systems, making it a preferred choice over conventional emulsifiers.[59]

1.3.1. Types of Nanocellulose

There are three primary forms of nanocellulose, which are generated from cellulose present in plant cell walls: bacterial cellulose nanofibers (BCNFs), cellulose nanocrystals (CNCs), and cellulose nanofibrils (CNFs)[59]. CNCs are rod-shaped nanoparticles with high aspect ratios and crystalline structures that are made by enzymatic or acid hydrolysis. They are perfect for stabilizing emulsions and reinforcing materials[22]. The mechanical disintegration process yields CNFs with a fibrillar shape and flexibility that make them ideal for use in barrier films and biological applications. Biogenically produced by bacteria, BCNFs have high crystallinity and are ultrafine, well-defined nanofibers that are perfect for tissue scaffolds, wound dressings, and functional materials[60]. Because these nanocellulose variations are renewable, biocompatible, and biodegradable, they may be tuned for a variety of applications and offer varied features that support breakthrough materials and sustainable technology. However cellulose nanocrystals (CNCs) are preferable to cellulose nanofibrils (CNFs) and bacterial cellulose nanofibers (BCNFs) for a variety of applications due to their superior characteristics. CNCs have a larger surface area and aspect ratio, which improves stability and allows for effective adsorption at interfaces. They are excellent reinforcements in composites because of their extremely crystalline structure, which confers remarkable mechanical capabilities. The surface chemistry of CNCs makes it simple to functionalize for desired qualities, and they provide uniformity and accurate size control, enabling customized application. Furthermore, CNCs are easily accessible for industrial and research purposes because of their wide commercial availability. While both CNFs and BCNFs have advantages, CNCs are the favoured option in a variety of applications requiring sophisticated materials because of their superior performance and versatility[59]. Through a process known as Pickering stabilization, cellulose nanocrystals (CNCs) adsorb at the oil-water interface and self-assemble into a monolayer over scattered oil droplets to stabilize emulsions. Due to their hydrophilic characteristics, CNCs are able to preferentially orient near the interface, resulting in the formation of a physical barrier that stops phase separation and droplet coalescence[42]. By preventing droplet movement and deformation, this barrier improves emulsion stability and prolongs shelf life by preventing creaming or phase separation. Because of their special qualities, which include their high aspect ratio and surface chemistry, CNCs work well as emulsion stabilizers and are appropriate for a wide range of industrial uses[61].

In this study CNCs were prepared from Microcrystalline Cellulose (MCC) by Acid Hydrolysis method which does act as an emulsifier for preparation of emulsion. To the best of our knowledge Eucalyptus Oil Pickering Emulsion (EOPE) stabilized by CNCs have not been studied yet. Therefore it is much important to evaluate whether EOPE is more or less effective than the Eucalyptus Oil itself. Thus the present research focuses on the characterization and Antimicrobial effects of EOPEs stabilised by CNCs. EOPEs were prepared by sonicating Eucalyptus Oil and CNC aqueous dispersion and their characterizations were carried out.

2. Materials and Methods

2.1. Chemicals and Materials

Sugarcane Bagasse, Eucalyptus Oil, Sodium Hydroxide, Sulphuric Acid. Throughout the process, distilled water was used as a solvent and for formation of aqueous phase of the emulsions.

2.2. Preparation of Cellulose Nanocrystal

1) Acid Hydrolysis: At 45˚C, 2 g of cellulose was mixed with 64 weight percent sulphuric acid solutions and magnetically agitated for a reaction period of 15 to 60 minutes. The hydrolysis was subsequently stopped by diluting the liquid ten times with cold distilled water. In order to achieve a pH of neutrality, the suspension was centrifuged for 10 minutes at 5000 rpm and then repeatedly rinsed with distilled water. During washing, the suspension was also reduced to 50 millilitres. After that, the suspension was neutralized and homogenized using ultrasonication.

2) Ultrasonication: The cellulose suspension that had been hydrolyzed by acid and subsequently neutralized was subjected to ultrasonication for one minute in an ice bath to prevent overheating. This process resulted in the formation of crystalline nanocellulose.

2.3. Preparation of CNC-Stabilized Pickering Emulsions

Eucalyptus Oil was added, specifically, to the 10 ml of the ultrasonicated CNC suspension, having approximately 0.1 gm of nanocellulose synthesized from sugarcane bagasse. The combinations as listed in Table 1 were sonicated for 1 min to obtain the PEs. These emulsions were then stored in plastic vials at room temperature

After preparing a set of Pickering emulsions (PEs) as shown in Figure.5 , it was kept for several days under observation. The next step involves selecting the most suitable PE formulation based on various parameters and performance characteristics. A systematic evaluation was conducted, considering key factors such as stability, droplet size distribution, and emulsion morphology.

Table 2 Emulsions of various Compositions

Sr. No	Volume Of Oil in ml	% Volume of oil	Vol. Of Water		% Volume Of Water	Amount of CNC	Total Volume of PE in ml
			With NC	Pure Water			
1	0.75	5	10	4.25	95	0.1	15
2	1.5	10	10	3.5	90	0.1	15
3	2.25	15	10	2.75	85	0.1	15
4	3	20	10	2	80	0.1	15
5	3.75	25	10	1.25	75	0.1	15

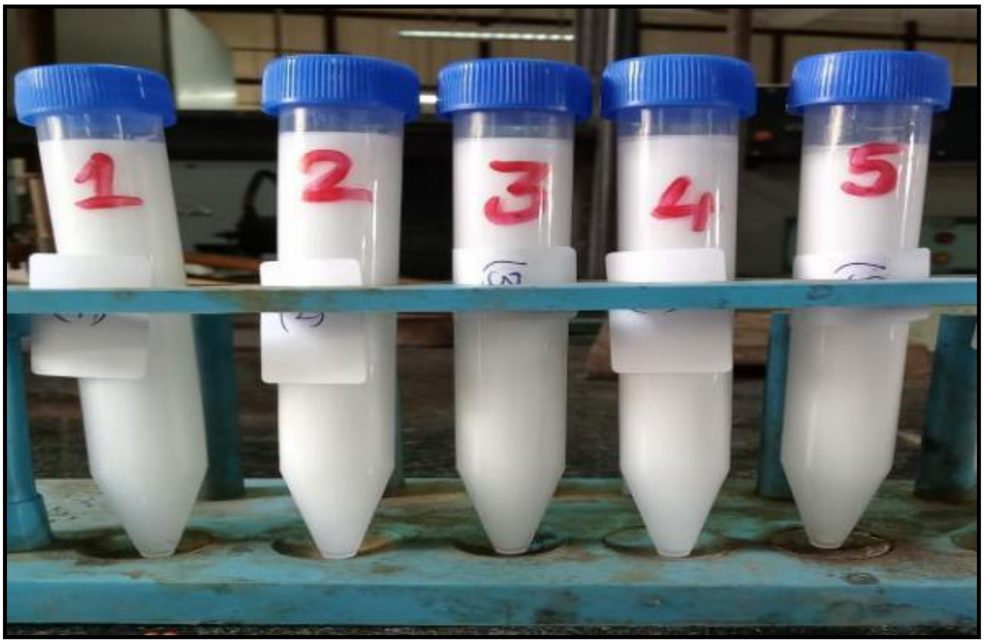

Figure 5 Set of Pickering Emulsion with water, Eucalyptus Oil and nanocellulose

2.4. Characterizations

2.4.1. Fourier transfer-infrared (FT-IR) Spectroscopic Analysis of CNC:

The IR spectra of CNC were determined by means of a Perkin Elmer FT-IR spectrometer to confirm the functional groups present in the synthesized material. The CNC synthesized from corn husk was analyzed within the range of 400–4000 cm-1 using the KBr palette method.

2.4.2. XRD Analysis of CNC

The crystallinity of the sugarcane baggage after different treatments was determined using an X-ray diffractometer (Bruker D-8 Discover) with CuKα radiation (λ = 0.1542 nm). The scanning range and the scanning speed were 5-40° and 5 deg/s, respectively.

2.4.3. SEM Micrographs of CNC

Scanning electron microscopy (SEM) analysis was performed using a Jeol JSM-6400 scanning electron microscope to observe the surface morphology of sugarcane basgasses at different stages of treatment. All samples were air-dried and coated with a gold to avoid charging. The images were taken with an accelerating voltage of 15 kV.

2.4.4. Morphological Analysis of Pickering emulsions

The storage stability of all kinds of PEs was checked by analyzing the optical images of the emulsions at regular intervals. The morphology of the oil-water interface between the droplets was observed, giving a clear idea of comparatively stable emulsions for the selection of oil and O/W concentration.

2.4.5. Shear stability of Pickering emulsions.

All the primary emulsions were subjected to centrifugation at 1000 rpm for 2 min so as to check for the effect of shear stress on stability.

2.4.6. Enhanced Microscopic Images of Pickering emulsions.

Enhanced Microscopic analysis was performed using an Olympus BX51 microscope to observe the Pickering Emulsion more accurately. TC Capture Software was used to get the images.

2.4.7. Antimicrobial Activity.

This study was carried out by the Agar Disk Diffusion Method (DDM). Circular discs of nanofiber membranes with the diameter of 6 mm circular discs were obtained by a puncher. The Gram-positive bacteria Staphylococcus aureus (S. aureus, ATCC 25923) were cultivated overnight in the Luria-Bertani nutrient medium, which was prepared by dissolving 15 g peptone, 5 g beef broth, and 5 g sodium chloride in 1 L distilled water at pH 7.0 followed by sterilization. The above bacteria suspension was diluted to the concentration of 108 colony-forming units (CFUs) per mL and spread onto an infusion agar plate. The circular samples were sterilized and then gently pasted on the inoculated plates. After incubation at 37 °C for 24 h, the diameters of inhibition zones around the discs were measured using a ruler.

3. Results and Discussion

3.1. IR Spectroscopic Analysis of CNC

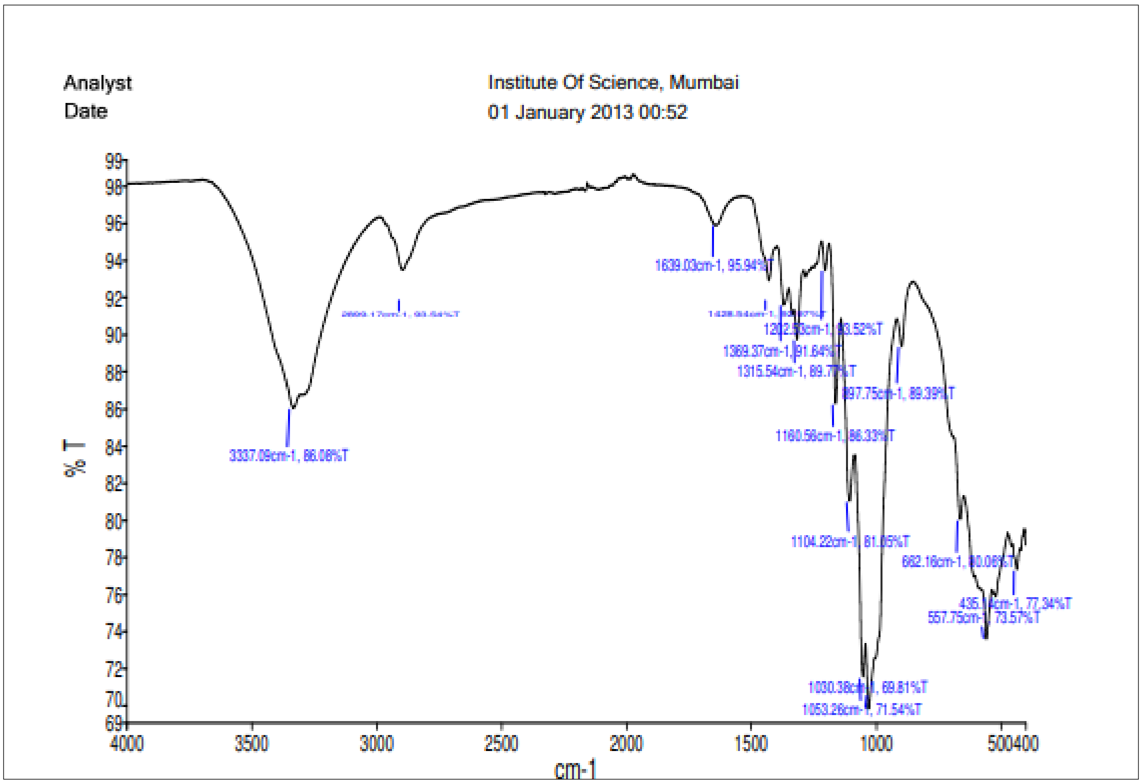

Figure 6 IR spectrum of synthesized CNC

The chemical structure of CNC synthesized from sugarcane bagasse was analysed using FTIR, as shown in Figure.6 The FTIR spectrum finally confirms the presence of cellulose functional groups only, specifying the successful removal of hemicellulose and lignin after successive treatments. The absorption band at 3339.92 cm-1 corresponds to the OH stretching of the cellulosic hydroxyl group. The CH stretching peak arose around 2900-2910 cm-1. The absorption peak at 570.72 cm-1 reflects C-O-C stretching at the β (1, 4) glycosidic linkage in cellulose. The absorption at 1000-1300 cm-1 refers to the presence of CO group of the cellulose component.

3.2. XRD analysis of CNC

X-ray diffraction pattern and the crystallinity index of CNCs obtained after hydrolysis time 45 minutes were studied and compared with untreated corn husk. The crystalline peaks around 2θ = 16°, 22°, and 35° were defined cellulose I exhibiting the hkl 110, 200, and 004 crystallographic planes, respectively as shown in Figure 7 . Upon removing the non-cellulosic constituents of the corn husk by chemical treatment, the intensity of peak become more defined. The crystallinity index was determined and summarized in Table 3. The cellulose nanocrystals show the highest crystallinity index value (68.33%) which displayed the strongest and sharpest peak at 2θ = 22°. The increased crystallinity of treated corn husk compared to untreated one was attributed to the progressive removal of amorphous non-cellulosic materials. The increased crystallinity is also expected to increase their stiffness and rigidity resulting in the increased mechanical properties and reinforcing capacity of composite reinforcement.

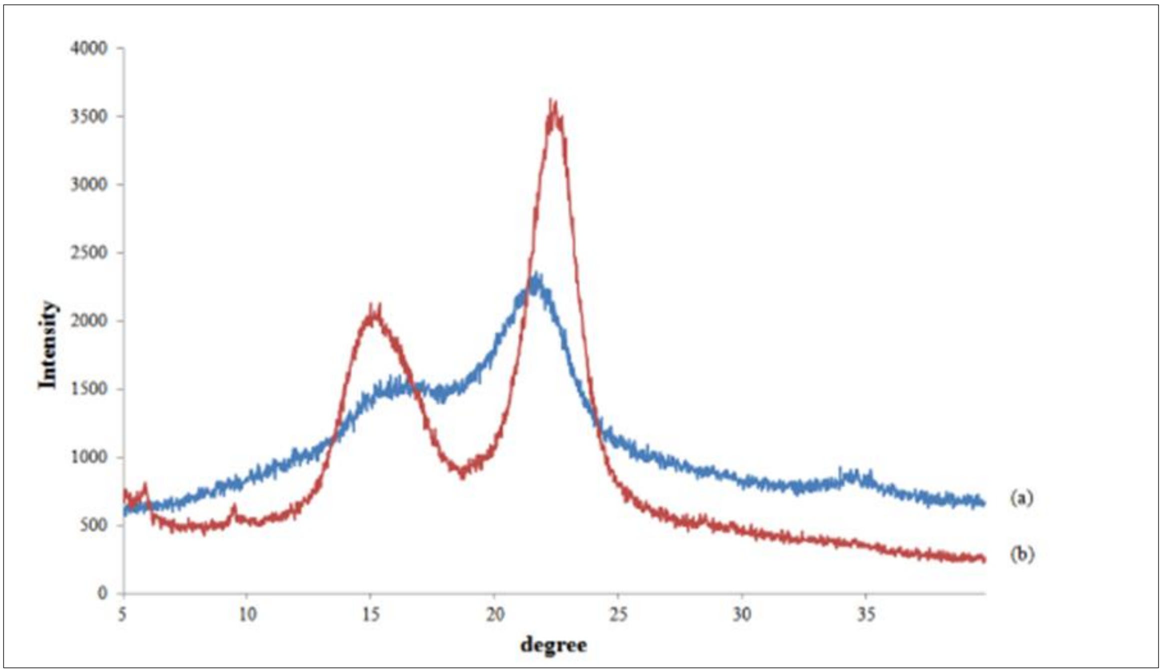

Figure 7 XRD analysis of CNC

3.3. SEM Micrographs of CNC.

From the SEM micrographs, it got clear that the morphology of the sugarcane bagasses changed with the chemical treatment. After alkali treatment, the fiber surface became rougher. This could indicate the partial removal of the outer non-cellulosic layer composed of material such as hemicellulose, lignin, pectin, wax, and other impurities contained in the corn husk. The alkali treatment helped defibrillation and the opening of the fiber bundles, and this trend increased along with the bleaching treatment. The breakdown of the fibers into nanocrystals indicates almost all the components that bind the fibril structure of the sugarcane bagasses were removed under the strong chemical treatment, and the cellulose got transformed into nanocrystalline structure, as expected.

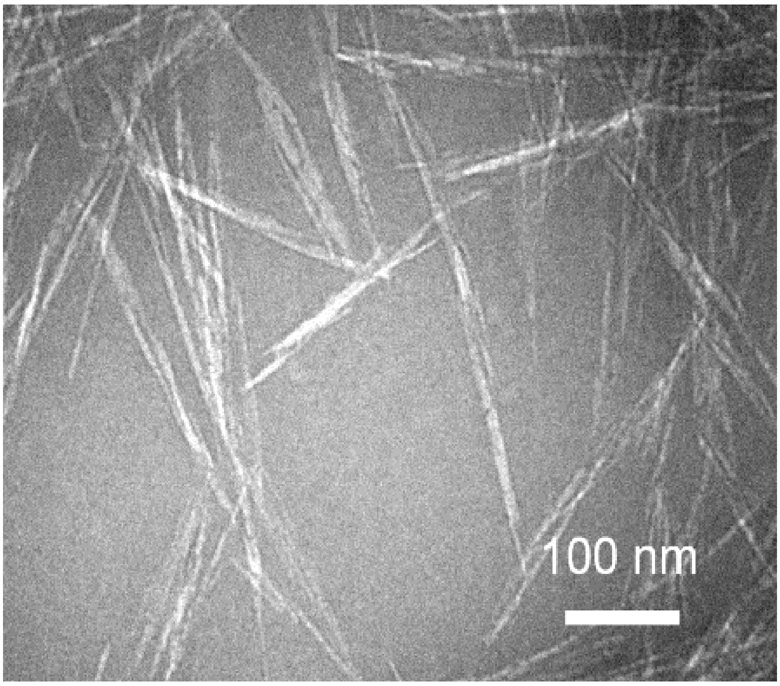

Figure 8 SEM Micrographs of CNC

3.4. Morphological Analysis of Pickering emulsions.

Pickering emulsions stabilized by 0.2 g CNC synthesized from sugarcane bagasses with Eucalyptus Oil were observed under the optical microscope. The images obtained are depicted below.

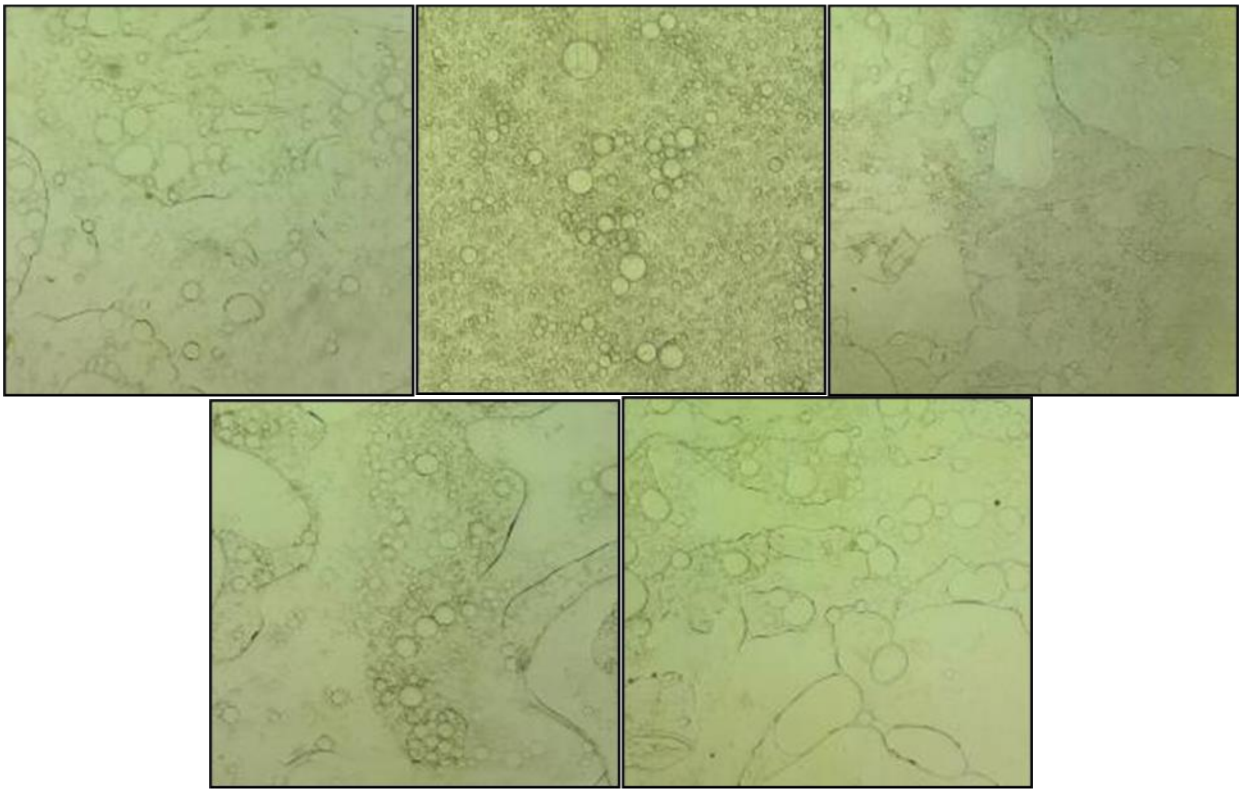

Figure 9 Optical microscopic images of CNC stabilized Pickering emulsions.

3.5. Shear stability of Pickering emulsions.

After centrifugation at 1000 rpm for 2 min, to check the shear stability of the emulsions, it was observed that all emulsions were losing their intact interfacial morphology except Emulsion no. 2 and 5

Upon analyzing the microscopic images obtained from the emulsion set, a notable observation emerged: emulsion number 2 and 5 consistently demonstrated superior results compared to the remaining samples. While the images of the other emulsions exhibited various degrees of disturbance, emulsion number 2 and 6 stood out for its sustained clarity and integrity.

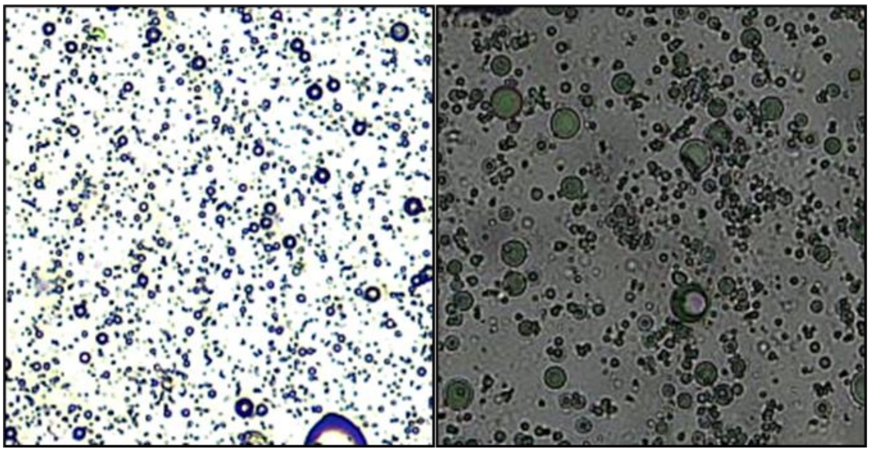

Figure 10 Enhanced Microscopic Images Emulsions3.7 Antimicrobial Activity of Pickering Emulsion**.**

3.6. Antimicrobial Activity of Emulsion

After formation of the of Pickering emulsions, antibacterial tests were carried out. It clearly indicates that the 15 ml of Pickering emulsions containing 10% of Eucalyptus Oil, i.e. 2 gave better antibacterial performance than others. The diameter of zone of inhibition for 2, i.e. 15 mm is high enough to prove that via PEs, antimicrobial activities of Eucalyptus oil can be enhanced to many folds. Hence 10% concentration of Eucalyptus oil was made in bulk for further observations and application purpose.

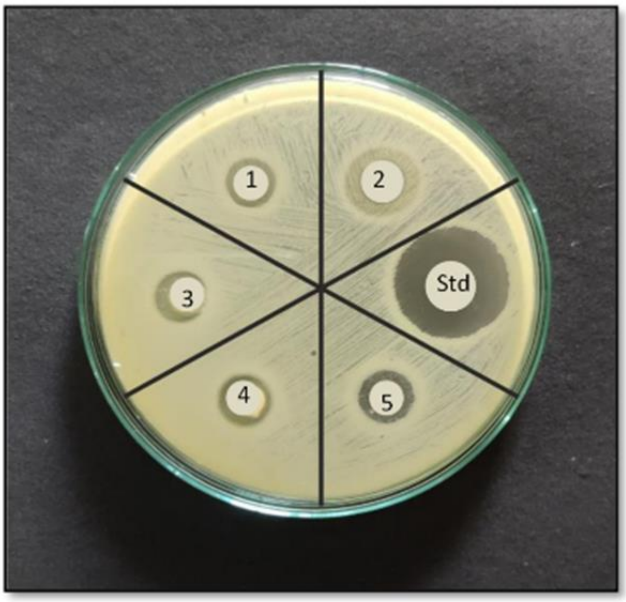

Figure 11 Antibacterial activity of Pickering Emulsion of Eucalyptus Oil

Table 3 Inhibition zone diameter of respective Pickering Emulsion.

Sample Label	Diameter of inhibition zone (in mm) Bacterial strain- Staphylococcus aureus	
	For Sample	For Standard
1	12	22
2	15	22
3	7	22
4	9	22
5	8	22

4. Application of Seed Germination of Mung Beans

Innovations in agricultural practices are crucial for enhancing crop yield and ensuring food security. The application of Pickering emulsions, such as the eucalyptus oil-coated emulsion developed in this study, presents a promising avenue for improving seed germination processes. By coating mung beans with this emulsion, a notable enhancement in germination rates was observed compared to untreated beans. This finding underscores the potential of utilizing emulsion coatings to optimize seed germination, thereby contributing to sustainable agriculture and addressing global food challenges.

Furthermore, the utilization of Pickering emulsions in seed germination holds significant implications for eco-friendly agricultural practices. By harnessing the natural properties of eucalyptus oil within the emulsion, not only do we witness improved germination rates, but also the potential for pest control and disease resistance. This environmentally conscious approach aligns with the growing demand for sustainable farming methods that minimize the use of synthetic chemicals. Thus, integrating emulsion coatings into seed germination processes offers a holistic solution for enhancing crop productivity while promoting ecological balance within agricultural ecosystems.

Figure 12 Germination of Mung Beans without and with application of pickering emulsion respectively

5. Conclusions

In conclusion, this study has explored the potential application of Pickering emulsion stabilized by cellulose nanocrystals (CNCs) extracted from sugarcane bagasse to enhance seed germination, specifically in mung beans. Prior to assessing their effectiveness in seed germination, the CNCs were thoroughly characterized through techniques such as X-ray diffraction (XRD), infrared spectroscopy (IR), and scanning electron microscopy (SEM), providing valuable insights into their structural and morphological properties.

The results obtained from this research suggest that the Pickering emulsion stabilized by CNCs holds promise as a novel and eco-friendly approach for promoting seed germination. By acting as stabilizing agents, CNCs facilitate the formation of stable emulsions, thus creating a favorable environment for seed germination. Furthermore, the utilization of CNCs derived from sugarcane bagasse underscores the potential of utilizing agricultural waste for sustainable applications in various fields.

While the findings of this study are promising, further research is warranted to fully elucidate the mechanisms underlying the enhancement of seed germination by CNC-stabilized Pickering emulsions. Additionally, exploring the applicability of this approach to other plant species and investigating its long-term effects on plant growth and development would contribute to a comprehensive understanding of its potential utility in agriculture.

Overall, this research sheds light on the multifaceted applications of cellulose nanocrystals and highlights their role in sustainable agricultural practices. By harnessing the potential of nanotechnology, we can innovate solutions that not only address current challenges but also contribute to a more sustainable and environmentally conscious future.

5.1. Future prospects

Looking ahead, the exploration of Pickering emulsions stabilized by cellulose nanocrystals (CNCs) extracted from agricultural waste presents a plethora of exciting possibilities for future research and applications. One avenue of interest lies in the further optimization and fine-tuning of the emulsion formulation to enhance its effectiveness in promoting seed germination across a broader range of plant species. This may involve exploring different sources of cellulose nanocrystals, refining the emulsion preparation methods, and investigating the incorporation of additional bioactive compounds to synergistically enhance seed germination and early plant growth.

Moreover, the potential applications of CNC-stabilized Pickering emulsions extend beyond seed germination to encompass various other areas of agriculture and beyond. For instance, these emulsions could be explored as delivery systems for agricultural inputs such as fertilizers, pesticides, and growth regulators, offering controlled release and targeted delivery to plants. Additionally, the biocompatible and environmentally friendly nature of CNCs makes them promising candidates for applications beyond agriculture, such as in the food industry, cosmetics, and pharmaceuticals. Further research in these areas could unlock new avenues for sustainable innovation and contribute to addressing global challenges related to food security, environmental sustainability, and human health.

Furthermore, seeds treated with CNC-stabilized Pickering emulsions may exhibit enhanced qualities compared to those treated with conventional methods. The emulsion coating provides a conducive microenvironment for seed germination and early seedling growth, potentially leading to plants with improved vigor, resilience, and yield. Enhanced nutrient uptake, increased drought tolerance, and protection against pathogens and environmental stresses are among the potential benefits conferred by the emulsion coating. This could result in crops with better quality attributes, contributing to improved agricultural productivity and sustainability in the long term.

Compliance with ethical standards

Acknowledgments

The authors gratefully acknowledge the Director, Institute of Science, Mumbai, for continuous support and encouragement.

Disclosure of conflict of interest

No potential conflict of interest was reported by the author(s)

Funding sources

This research received no specific grant from any funding agency in the public, commercial, or not-for-profit sectors.

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