# ***Review Article***

# **Pickering Emulsions and their Applications in the Food Industry**

**ABSTRACT:**

Pickering emulsions, stabilized by solid particles instead of traditional surfactants, have garnered significant attention for their potential applications in the food industry. This review explores the fundamental principles, mechanisms, major parameters affecting the stability of emulsion**,** preparation methodologies and advantages of Pickering emulsions, particularly their role in creating stable, natural, and clean-label food products. Key food applications such as beverages, dairy products, sauces, dressings, confectionery, and fat replacers are examined, highlighting how Pickering emulsions enhance texture, stability, and product performance.

**Keywords**: *Pickering emulsions, colloidal particles, wettability, food industry*

1. **INTRODUCTION**

Emulsion is a dispersion system made of two immiscible liquids, where one phase gets dispersed as microscopic droplets in another phase. When emulsion droplets collide with neighbouring droplets on Brownian movement, they tend to merge, which results destruction of dispersion system. Because of molecular incompatibility, they rapidly undergo phase separation (Zhang *et al*., 2023).On mechanical agitation, the two distinct phases can form a dispersion system but which is unstable. So, they essentially need an emulsifying agent to attain long-term stability to form a thermodynamically stable system (Chen *et al*., 2020).

Creating emulsions is easy but making them stable for longer period is difficult task. Thickening agents, stabilizers, and commonly emulsifiers are employed to prevent, or at least postpone, the separation which may eventually cause emulsions to break down thus making emulsions kinetically unstable. (Berton-Carabin & Schroën, 2015). Emulsifying agent comes board range of Surface-active agents. Ionic surfactants, non-ionic surfactants and amphiphilic biopolymers are included in molecular surfactants usually used as conventional emulsifiers. But they may be harmful to health causing irritation to skin *etc*. thus limiting their application (Chen *et al*., 2020)

There are new requirements on food industries as consumer awareness increases about healthy products, safety, and sustainability. The major demands are

1. Safe products
2. Reduction of artificial additives or ingredients
3. Nutrient foods rich in bioactive compounds

Pickering emulsions are one such solution to meet the demands, which provide stability devoid of surfactants (Øye *et al*., 2023).

1. **DEFINITION**

Pickering emulsion is a form of emulsion where emulsifiers are colloidal particles or solid particles (Pickering particles) instead of surfactants that adhere at the oil-water interface. It has the capacity to withstand flocculation, coagulation, droplet aggregation, and Ostwald ripening. The proper interaction of the droplets and particles at the interface ensures irreversible physical barrier formed by particles results in these properties. They have a ‘Surfactant-free’ character which sets them apart from conventional emulsions. The current world strives for a type of emulsion system which is stabilized by food grade and organic particles over surfactants stabilized conventional emulsions due to good recovery qualities, low toxicity, and cost (Rayees *et* *al*., 2024).

# **BACKGROUND**

Actually, Pickering emulsions have been known since the pioneering work of Ramsden (1903) and Pickering (1907). Emulsions stabilized by solid particles wetted by both liquids are known as Pickering emulsions, named after Pickering, who noted that oil droplets in emulsions coated with a film of solid particles smaller than oil droplets might prevent them from destabilizing. But they have been widely ignored since their disclosure. There exists a renewed interest bit recently (Berton-Carabin & Schroën, 2015). Hence, in the discipline of food emulsions Pickering emulsions have drawn substantial interest and related publications have been rising over the past few decades compared to Food nano emulsions and Food double emulsions (Øye *et al*., 2023).

**4. MECHANISM**

Surfactants adsorb at two-phase interface in a thermal equilibrium state between desorption and adsorption in case of conventional emulsions. Very rapid adsorption of molecular emulsifiers during the homogenization process, i.e. they actively adsorb and desorb from interface under the drive of thermal motion which results in destabilisation of emulsions. Whereas in the case of Pickering emulsions though solid particles adsorb slowly but irreversibly at interface resulting in greater requirement of thermal energy for undergoing Brownian movement by particles and high desorption energy. But Target emulsion droplets must have a minimum size of one order of magnitude higher than the colloidal particles. (Zhao *et al*., 2024). Stability mechanism of Pickering emulsions can be explained through theory of solid particle interface film and three-dimensional viscoelastic particle network mechanism (Chen *et al*., 2020).

**4.1.** **Theory of solid particle interface film:**

Through both steric hindrance and mechanical barrier property they strongly prevent the Coalescence and Ostwald ripening as particles encircle oil droplets forming a densely packed layer (either single or multiple layers) (Zhao *et al.*, 2024). Thicker the adsorbed particle layer, higher the coalescence stability and lower the coalescence rate. As the size of the colloidal particles decreases the specific surface area of emulsion droplets increases ensuring more stability of emulsion. Hence, emulsion with smaller droplets are frequently more stable form (Liang & Tang, 2013). The rheology and shear properties of the interface film improves as particle creates a physical barrier film that can prevent droplets from touching and aggregating each other (Chen *et al*., 2020). Furthermore, an electrostatic repulsion between the droplets created by charged colloidal particles can also prevent the droplets from aggregating and compared to larger ones, smaller droplets are more resistant to gravitational separation and aggregation (Yan *et al*., 2020).

**4.3. Theory of network mechanism by three-dimensional viscoelastic particle**

The 3D network structure of particle aggregation may be formed around the droplets coated by particles in the continuous phase, thereby hindering their mobility This mechanism is based on sufficient interparticle attraction and adequate high concentration of solid particles that are not adsorbed (Zhao *et al*., 2024). A depletion process that relies on the existence of non-adsorbing polymers in the continuous phase can also sustain Pickering emulsions. When non-adsorbing polymer molecules are present in high enough concentrations to promote the flocculation of the emulsion droplets and colloidal particles in the Pickering emulsion, an osmotic stress is produced (Yan *et al.*, 2020). Rate of migration of particles and merger of droplets as the viscosity of the emulsion of emulsion increases with 3D structure thus avoiding the destabilization of emulsion and aggregation of droplets(Chen *et al*., 2020).

1. **MAJOR PARAMETERS WHICH DETERMINE THE STABILITY OF EMULSION**

"Emulsion stability" refers to an emulsion's capacity to tolerate variations in its physicochemical properties over time. Emulsions may exhibit instability processes such as phase separation, flocculation, coalescence, and gravitational separation (sedimentation). The stability of its physical characteristics, including size, structure, morphology, rheology, and others over a period defines the emulsion's ability to maintain stability (Rayees *et al*., 2024). In the food sector, Pickering emulsions are probably complicated colloidal dispersions made up of polymers, solid particles, and emulsion droplets. The stability and functional performance of the colloidal particles are expected to be affected by their size, concentration, and wettability as well as the properties of the water and oil phases and the oil-water ratio. Additionally, environmental and emulsification conditions will have a major impact on the production and stability of Pickering emulsions (Yu *et al*., 2023). Some of the important parameters which determine the stability are

**5.1. Wettability**

To preserve structural integrity and provide efficient attachment of particles at the interface, particle solubility is essential (Cheng *et al.*, 2024).Dual wettability, or partial wetting of solid particles by both phases, is necessary for the solid particles to be adsorbed at the oil–water interface during the production of a Pickering emulsion. Adsorption of solid particles reduces the driving force for particle transfer by increasing the oil–water interfacial area and decreasing energy of particles for Brownian movement (De Carvalho-Guimarães *et al.*, 2022). A particle needs to be wettable in order to function at the oil-water interface. The contact angle between the particle and the interface can be utilized to determine how wettable the solid particles employed in Pickering emulsion (Rayees *et al*., 2024).

Wettability affects the type of emulsion that is created and is measured by the contact angle, whereas hydrophobicity, which is dependent on the oil–water interface contact angle, has a significant impact on the adsorption of a particle at the interface. Direct measurement of contact angle ,captive drop method, gel trapping technique (GTT) etc are used for measuring contact angle (Low *et al.*, 2020). But generally, Young's equation can be used to determine θ where θ is the three-phase contact angle of solid particles which is an essential characteristic for describing their wettability (Zhao *et al.*, 2024).

Cosθ = (γso- γsw) / γow

γso issolid particle-oil interfacial tension

γsw  is solid particle-water interfacial tension

γow is oil-water interfacial tension, respectively

Particle-stabilized emulsions can be categorized as,

1. Oil-in-water (O/W) emulsions: hydrophilic particles stabilizers (e.g., silica, clay) with a contact angle in the range of 15° < θ <90° (measured through the water phase).
2. Water-in-oil (W/O) emulsions: hydrophobic particles are stabilizers (e.g., carbon black) with a contact angle in the range of 90° < θ < 165° (Dickinson, 2010).

If the wetting contact angle is between 30 and 150 degrees, where the particle desorption energy is many orders of magnitude more than the thermal energy of Brownian motion, the Pickering emulsion will exhibit irreversible adsorption features (Xiao *et al.*, 2016).Ideally, particles with a θ around 90◦ have a near neutral wettability at the O/W interface and are more appropriate for the fabrication of stable Pickering emulsions (Dickinson, 2010).When two phases completely moisten the particles, they stay scattered in one phase and are unable to form an emulsion. The wettability of the particles may be fine-tuned in a number of ways by altering their topology or surface functional groups (chemical anchoring or physical adsorption) (Gonzalez Ortiz *et al.,* 2020).



Fig 1: Schematic representation of oil/water and water /oil Pickering emulsion

**5.2. Particle concentration**

The particle concentration has a significant impact on the emulsion stability and average droplet size. Since solid particles cannot function as emulsifiers until they are adsorbed at the oil–water interface, the stability of the emulsion tends to grow proportionately with the concentration of the particle. The existence of too many particles inhibits coalescence because they adhere to and stabilize the liquid–liquid interface. It's interesting that particles that escape from a droplet can adsorb to another surface at the same time, linking two droplets with a shared particle monolayer. Coalescence is avoided because this arrangement maintains the equilibrium contact angle on both sides of the bridging particles. But in certain situations, rise particles concentration only results in a excess particle in one phase, therefore this is not a general principle for emulsion stability (Gonzalez Ortiz *et al*., 2020).

**5.3. Solid particle**

The characteristics of solid particles greatly influence the Pickering emulsions' stability, type (O/W or W/O), shape, and characteristics (Yang *et al.*, 2017). The preparation begins with choosing the right solid particles, which need to have suitable wettability properties so that they efficiently adsorb at the oil-water interface and can stabilize the interface by decreasing the interfacial tension b/w two phases as there exists the balance of hydrophobicity and hydrophilicity. These colloidal substances, which can range from inorganic materials to organic compounds act as a barrier to avoid the coalescence of oil droplets (Cheng *et al.*, 2024). Shape, stability, categorization, and attributes of Pickering emulsions are all majorly influenced by the qualities of solid particles (Rayees *et al.*, 2024).

Solid particles must have the following characteristics to be used as a stabilizer for Pickering emulsion: (i) they must be partially wettable by both the continuous and dispersed phases of the system while maintaining their insoluble nature in either phase; (ii) their surface charge must not be excessively high to the point where they repel one another rather than firmly adhering to the interfaces between the two immiscible liquids; and (iii) their size must be significantly smaller than the intended emulsion size (Low *et al.*, 2020).

Commonly the solid particles used are silica, clay, hap, magnetic nanoparticles, chitosan (CS), cyclodextrin (CD), nanotubes, and some food-grade stabilizers such as starch, soy protein, and zein protein, etc. The nanomaterials used to create Pickering emulsion fall into three categories: Janus Colloidal Particles (JCPs), Microspheres, and Microcapsules (Yang *et al.*, 2017). Because of the higher aspect ratio of anisotropic particles, several researchers believed that the desorption energy value, capillary force, and interfacial layer may all be increased to produce more stable emulsion systems. Various asymmetrical structures, such as ellipsoids, nanofibrils, nanocages, plated forms, nanotubes, and others, can exhibit distinct Pickering emulsion stability mechanisms (Rayees *et al.*, 2024).Nanoparticle-stabilized Pickering emulsions have become highly adaptable due to their exceptional stability. The emulsion droplet is more stable under a range of experimental settings, and the emulsion can be readily demulsified after extraction methods, especially if the nanoparticles are magnetic based on the requirement (De Carvalho-Guimarães *et al.,* 2022).

Numerous studies have demonstrated that complexing with other substances can modify particles to increase their hydrophobicity, which gives PEs additional stability, especially against a range of biochemical and environmental conditions where a single-moiety particle (such as a protein-based particle) might degrade (Nimaming *et al.*, 2023).

**5.4. Surface charge, pH and salt concentration**

The adsorption of charged particles on the emulsion surfaces is usually because of the droplet charge in Pickering emulsions. Several environmental conditions, including pH, ionic strength, and chemical interactions, can affect these particles' surface charge (McClements, 2015).The stability of a colloidal dispersion, which is heavily reliant on the quantity of surface charge, can be investigated by measuring the zeta potential (Zp) of the particle suspension. It is essential for both the colloidal properties of solid particles and the adsorption of solid particles onto the interfaces between two immiscible liquids. Solid particles with a high Zp have a tendency to separate from one another rather than firmly adhere to the o/w surfaces. When Zp is reduced to a low-charged zone, the colloidal particles aggregate, strengthening the particles’ network in the continuous phase and enhancing emulsion stability (Low *et al.*, 2020). Stability improvement was seen with the surface charge reduction (Ridel *et al*., 2016).In many studies to regulate the stability of Pickering emulsions, changes in pH or salt concentration are employed (Albert et al., 2019). It was found that CNC could stabilize Oil/water emulsions at 0.1 wt% concentration with as little as 3 mM NaCl concentration. Similarly, CNC could stabilize C (Varanasi *et al.*, 2018). Oil/water emulsions at 0.1 wt% concentration with CaCl2 concentration as low as 1 mM or even lower. High pH levels encourage strong electrostatic repulsive forces between droplets, preventing coalescence and thereby enhancing the emulsio ’s stability (Zhang *et al.*, 2024).

**5.5. Dimensions of Pickering particles**

In essence, the Pickering particulate's dimensions determine two important characteristics of the final emulsion that will be generated: (i) the emulsion's stability and (ii) the size of the emulsion droplets (Low *et al*., 2020).The detachment energy is provided by

ΔE = γOW πR2 sphere(1− |cosθ|)2 (Binks & Lumsdon, 2000)

It can be inferred that the detachment energy varies linearly with 1-|cosθ| for discs and rods and quadratically with 1-|cos θ| for spheres. This indicates that, in comparison to spherical particles, more energy would be needed to desorb disc and rod-like Pickering particles from a liquid-liquid interface (Vis *et al.,* 2015).It depicts that even non-spherical particles have better emulsification properties. The size of the particles also influences the size of the droplets that are created during emulsification; the size of the droplets reduces as the size of the stabilizing particles increases (Low *et al.*, 2020). The relationship between the diameter of emulsion droplet and Pickering particles as follows: re=4φdrp/φp where re and rp are the radius of emulsion droplets and Pickering particles respectively whereas φd and φp are the volume fraction of dispersed phase and particles respectively. This relationship states that, for a constant volume fraction of dispersed phase and Pickering particles, the emulsion droplets should enlarge in proportion to the Pickering particle radius (Binks & Lumsdon, 2001). Generally, the size of the particle selected for Pickering stabilization should be at least one order of magnitude smaller than the droplet size required to create a stable emulsion (Varanasi *et al.*, 2018).

**6.CLASSIFICATION**

It comprises the kind of stabilizing particles that are used, which affect the emulsion's characteristics; the volume fraction of the dispersed phase, which determines the emulsion's structure and uses; and particular functional characteristics that establish its interactions and appropriateness for sectors like food, medicine, and cosmetics (Cheng *et al.*, 2024).



Fig 2: Classification of Pickering emulsions

**7.DEGRADATION OF PICKERING EMULSION**

Pickering emulsion degradation processes are essential for designing them with long-term stability and productivity

**7.1. Physical degradation:**

Despite the fact that the solid particles in Pickering emulsions usually create a steric barrier that inhibits this merging, insufficient particle coverage or poor adhesion can undermine this barrier, making the droplets susceptible to coalescence and emulsion instability (Cheng *et al*., 2024). Additionally, when the same amount of water and oil is mixed, an emulsion for long-term stability will be preferentially created; but, if the ratio is too high, the emulsion will suffer "catastrophic phase inversion" and become unstable against coalescence due to its non-preferred nature (Gonzalez Ortiz *et al*., 2020).Differences in internal pressure cause Ostwald ripening. Though it is less frequent in Pickering emulsions, it can nevertheless happen if the continuous phase can partially dissolve the dispersed phase. The stability and homogeneity of the emulsion may be affected over time by the formation of larger droplets at the expense of smaller ones due to the slow diffusion of molecules (Cheng *et al*., 2024).

**7.2. Chemical degradation**

Lipid hydroperoxides and transition metal ions interacting close to the droplet surfaces is the primary source of lipid oxidation in many foods based on emulsions (Mcclements & Decker, 2000).Emulsions containing chemically sensitive substances, such as bioactive chemicals or polymer stabilizers, may undergo hydrolysis. Some emulsifiers can be turned into sulphates and fatty alcohols after base or acid hydrolysis, which are harmful which is more seen in case of conventional emulsions (Tercki *et al*., 2023). Another degradation process is oxidation, which makes emulsion constituents like the oil phase or stabilizing particles susceptible to chemical alterations (Chen *et al*., 2024).

**7.3. Biological Degradation:**

Since emulsions can provide a suitable habitat for bacteria, yeast, or mold, particularly if they include nutrients and are maintained in circumstances that are favorable to these microorganisms, microbial spoilage is a serious issue. Such microbial development may change the emulsion's physical stability, jeopardizing its efficacy and safety and possibly rendering it inappropriate for its intended use (Wang *et al*., 2024).

**8.CRITERIA:**

Emulsion having desired stability can achieved only when these two main criteria are successfully fulfilled:

1. Formulation
2. Efficient emulsification process

Though formulation mainly affects the long-term stability of emulsion, but the process also matters since the shear rate of the emulsification process often governs the droplet size of solid particles (Pickering particles) (Chevalier & Bolzinger, 2013).

**9.PREPARATION OF PICKERING EMULSION**

Methods for preparation of PE can be categorised into High energy and Low energy methods. Where High energy methods are more suitable for industrial application which produces emulsion from using high shear rate. Whereas in low energy methods physical-chemical ,raw materials’ properties plays significant role in droplet formation (Gauthier & Capron, 2021).Steric repulsion is a frequent barrier that prevents particle adsorption when polymer-functionalized particles are used as stabilizers. Mechanical forces like high shear mixing, high-pressure homogenization, or sonication can be used to overcome it (Köhler *et al*., 2010; Larson-Smith & Pozzo, 2012)

**9.1. High-energy processes**:

Because of their poor binding kinetics, particles at surfaces typically take a long time to equilibrate when little or no external energy is supplied (Wu & Ma, 2016).To create stable Pickering emulsions, particle emulsifiers must often be driven to the interfaces using a lot of external energy. Rotor-stator homogenization, high-pressure homogenization, ultrasonic emulsification, microfluidic emulsification, and membrane emulsification are among the many emulsification techniques that can be used for preparing Pickering emulsions (Gauthier & Capron, 2021).

**9.1.1. Ultrasonication**: It is a green technology which uses low-frequency sound waves, commonly above 16 kHz (ranging between 20 and 80 kHz) for diffusing one phase into another using (Pandita *et* al., 2024).Because it can both emulsify and force particle adsorption onto droplet interfaces, sonication is a useful technique in Pickering emulsion formation (Lee *et al*., 2008)

The ultrasonic probe is most frequently used to form Pickering emulsions. By transferring sonication energy to the surrounding sample, the probe primarily uses cavitation and ultrasonic forces to induce emulsification. The primary factors affecting the droplet size are the emulsification time, ultrasonic frequency, and amplitude (Albert *et al.*, 2019).Lee et al( examined oil-in-water emulsions that were insonated with polymer-coated amphiphilic gold nanoparticles (GNP) (Lee et al., 2019). The investigations showed that cavitation has to occur as a result of the application of acoustic fields in order to generate Pickering emulsions utilizing sterically stabilized particles. Since cavitation was not produced in the presence of weak acoustic fields, there was no particle adsorption. The dense coating of gold nanoparticles, which is close to the tight-packing limit, allowed for high surface coverage in the study.



Fig 3: Schematic representation of Ultrasonicator

**9.1.2. High-pressure homogenization**: It involves high-pressure pumps (ranging from 3 to 500 MPa) and specified nozzles for carrying out the emulsification process continuously. Even though most widely used continuous emulsifying method in industry is high-pressure homogenization. It is advised to do a pre-emulsification phase to produce an initial coarse emulsion in order to produce a fine emulsion at the homogenizer's outlet later on (Albert *et* al., 2019).

In a service duration of no more than a few minutes, nanoparticles frequently greatly enhance abrasion, particularly when high pressure is applied, which is inappropriate for a commercial operation. However, issue was resolved by using a mixing stream right behind the mixing and homogenizing valve (SHM-valve) i.e. an operation without passing the nano-particles through the high pressure area (pump and orifice) (Köhler *et al.*, 2010).Thus the risk of damage caused by highly abrasive particles to the high-pressure homogenizer that can be solved by the adding particles just after the nozzle with the mixing stream (Albert *et* al., 2019).

To refine coarse emulsions, the high-pressure homogenizer and the microfluidizer are frequently employed. The geometry of the two processes is different, yet they work similarly. Usually, multiple runs through the homogenizer or microfluidizer are required to produce a nanoemulsion (Gauthier and Capron 2021). 

Fig 4: Advantages and disadvantages of High Pressure processing (Albert *et* al., 2019).

**9.1.3. Rotor-stator homogenization**: Generally regarded as a relatively low-efficiency homogenization technique, several Pickering emulsions are obtained using rotor-stator mixers such as the Ultra-Turrax (Gauthier and Capron 2021). Rotor-stator homogenizer one of the most popular devices for mixing and emulsifying highly viscous liquids, it consists of a perforated stator screen closure with one or more rows of rotor blades mounted on an impeller shaft(Pang *et al.*, 2021). Effective dispersion and/or emulsification can be obtained when the liquids are drawn axially towards the rotor-stator head as the rotor rotates, accelerated tangentially, and then released radially through the slots in the stator screen (Mortensen *et al.,* 2017). High amounts of hydraulic cutting are produced, rapid homogenization is encouraged, and tiny droplets are produced within the Pickering emulsions when the difference speed between the rotor and stator is nearly equal to the tolerance (De Carvalho-Guimarães *et al*., 2022). In the case of Pickering emulsions, the emulsification times range from 30 seconds to a few minutes, and the rotation rates are primarily between 5,000 and 30,000 rpm with a velocity of 5 to 20 m/s (Albert *et al*., 2019).



Fig 5: Schematic representation of Rotar -stator homogenizer

**9.1.4. Microfluidic technology:** A micrometre-sized channel with a specific geometry in which fluids circulate makes up a microfluidic device(Albert *et al.,* 2019). The continuous phase flows vertically, while dispersed phase in parallel and when these two phases intersect, there is formation of spherical droplets by dispersed phase takes place in continuous phase (Yao *et* al., 2018). With this "bottom-up" method of emulsification, even with low fluid volumes, excellent multiple emulsions with total control over the quantity and move of encapsulated inner droplets can be created (Engl *et al*., 2008). The resulting emulsions are far more stable than those produced with conventional homogenizers and have a number of benefits, including simple preparation and accurate droplet control. A thick layer forms around the droplets to stabilize the emulsion since microfluidic technology is a gentle and promising technique that does not destroy the stabilizer's agglomerates due to its low shear pressure application (Chen *et al*., 2020). This process divides the emulsion into two streams, which collide to reduce droplet size. Nano-emulsions often require multiple passes through the microfluidizer or homogenizer. Several microfluidic devices with various types of junctions to date have been designed for the generation of Pickering emulsion droplets including T-junction, cross-junction and Y-junction (Pandita *et al.*, 2024). A sharp edge is made available by the T-junction microchannel device to create micro-droplets from biomaterial solutions. The scattered phase is introduced from the perpendicular channel in the T-junction design, whereas the continuous phase flows in the main channel. When the pressure gradient and the shear forces applied by the continuous phase combine, the scattered phase's tip elongates into the main channel until it fragments into a droplet (Jamalabadi *et al.,* 2017). Two opposing streams of the continuous phase focus the dispersed phase flow in a cross-junction configuration, and droplets form when the dispersed phase jet becomes too thin to endure inside the continuous phase. The balance between the interfacial tension and shear forces determines how the droplets are generated in a Y-junction shape (Pandita *et al.*, 2024).

**9.1.5. Membrane emulsification**: it involves the formulation of PEs by precisely controlling the shearing conditions and injection rate through microporous membranes (Manga *et* al., 2012). Direct membrane emulsification (DME) and Premix membrane emulsification (PEM) are two methods of membrane emulsification (ME) that primarily create emulsion droplets by forcing a pure dispersed phase or a pre-mix emulsion into a continuous phase through a microporous membrane (Piacentini *et al*., 2014). The phase parameters like density and viscosity of the dispersed and continuous phase, interfacial tension and the membrane parameters including geometry and distance, pore size, porosity and surface wettability have major impact on membrane emulsification process along with various process parameters ranging from shear stress, temperature to transmembrane pressure (Pandita *et al.*, 2024). To boost productivity, several methods have been developed, such as rotating/vibrating membrane emulsification, stirred-cell membrane emulsification, and cross-flow membrane emulsification (Holdich *et al.*, 2020). Although it is an eco-friendly process that uses low energy to create an emulsion with the same particle size, maintaining particle size consistency and homogeneity, this approach takes a more time, results in low yields, and works best with low-viscosity systems (Yuan *et al*., 2009).

**9.2. Low energy methods:** Phase inversion is an alternative PE production option that optimizes components for concentrated PEs with thin droplets and minimal energy consumption, even when viscous oils are used. There is little study on low-energy Pickering nano-emulsions, including steam condensation or spontaneous emulsification.

**9.2.1. Spontaneous** **emulsification (Ouzo effect):** Here stabilisation of emulsion brought by employing stabilizing particles during constant stirring of aqueous phase which involves mixing water-insoluble oil with a water-soluble co-solvent. Co-solvents which are soluble in water destabilize the oil, leading to nanodrop production via nanoprecipitation. Stabilizing particles sustain these droplets, resulting in an oil-in-water emulsion following co-solvent evaporation. Oil content can be raised via solvent shifts (Song & Kovscek, 2019). Komaika *et* *al* examined the potential to use a low-energy technique (spontaneous emulsification) with a natural surfactant (sunflower phospholipids) to create oil-in-water emulsions (Komaiko et al., 2015). The emulsions were unstable to gravitational separation because the droplets created by spontaneous emulsification were comparatively large (d > 10 μm. At low SOR (surfactant-to-oil ratio) values of 0.1 and 0.5, phospholipid-based emulsions exhibited lower particle sizes than those prepared using synthetic surfactants (Tween 80). At a higher SOR (1.0), however, this trend reversed, indicating that low-energy methods could be employed with natural surfactants for applications that do not require tiny droplets. For purposes where tiny droplets are not necessary, natural emulsifiers can be added to SE emulsions. Low-energy techniques, however, might only work with particular oils and emulsifiers and frequently call for large quantities of surfactants, making them unsuitable for different of food applications (McClements & Rao, 2011).

**9.2.2. Vapor condensation**

Water-in-oil Pickering emulsions can be obtained through water-vapor condensation on the oil surface. At an appropriate temperature and humidity nanodroplets of water are formed by condensation on oil surfaces by utilizing the unique properties of water (Gauthier & Capron, 2021). Kang *et al*. studied that even at very low nanoparticle loadings (approximately 0.2 % silica by weight), Pickering nanoemulsions can be produced with droplet diameters below 500 nm in a single-step process by condensing water vapor on a subcooled oil infused with nanoparticles that spread on water (Kang et al., 2018). Highly monodisperse nanoemulsions can be created by adjusting variables including nanoparticle size, concentration, and condensation duration. Condensation-based emulsion production is a quick, scalable, and energy-efficient method that may be modified for a broad range of emulsion-based applications. Initially silica is blended with oil and the combination is thereafter kept at 2 °C and steady humidity in a thermostatic chamber. The air in the chamber is kept below its dew point by regulation. Water droplets are formed by condensation on the oil The pictorial representation of process is shown in figure

Fig 6: Formation of Water-in-oil emulsion by Vapor condensation

 **10.ADVANTAGES OVER CONVENTIONAL/TRADITIONAL EMULSIONS**

 Pickering emulsions offer the following numerous special benefits:

1. It uses solid particles as emulsifiers to stabilize the emulsion. These particles produce a coating that stops oil droplets from aggregating by getting anchored at the oil-water interface constantly.
2. They afford higher stability, less toxicity, and stimuli-responsiveness compared to surfactants’ stabilized conventional emulsions (Wu & Ma, 2016).
3. Many low-molecular-weight surfactants have various kinds of biological adverse effects, the commonly described of which include peripheral neurotoxicity, acute hypersensitivity reactions, and membrane-damaging effects. In contrast, Pickering nanoparticles are removed by splenic and liver macrophages during systemic circulation (Wu & Ma, 2016).
4. It uses biodegradable compounds making it completely safe for usage in food sector. Additionally, many essential oils (EOs), which are functional components, are conveyed by it, serving as fantastic carrier. Addition of these compounds into the coating or packaging film composition greatly extends the of the food products’ shelf life that is packaged (Pandita *et* al., 2024).
5. Even though its preparation is easy and simple, this emulsion system is not prone to Ostwald ripening, coalescence and demulsification resulting in superior emulsion stability (Yang *et* al., 2017).
6. By altering the coating or functionalizing the surfaces of solid particles, the wettability of the particles at the oil-water interface can be changed. As a result, their inherent adaptability makes them appropriate for creating both easy as well as complicated formulations (Rayees *et* al., 2024).

 **11.POTENTIAL APPLICATIONS IN FOOD INDUSTRY**

**11.1. Low-fat products:** Animal fats and vegetable hydrogenated oils widely used in foods such as cream, ice cream, and butter and products are loved by consumers because these fats and oils are having delicate and dense taste. Animal fats are expensive and have a high carbon footprint. Whereas The trans fatty acids formed during the hydrogenation process of vegetable hydrogenated oils have negative effects on the cardiovascular system when ingested by the human body (Tian *et al.,* 2024a).Chronic excess intake of trans and saturated fats are the major cause of cardiovascular disease, type 2 diabetes, ischemic stroke and low-density lipoprotein cholesterol(De Souza et al., 2015).Since chronic illnesses account for almost 80% of all deaths globally, the World Health Organization notes their prevalence as a significant obstacle to sustainable development. The food industry is encountering that its tricky to find healthier alternatives that don't alter the final products' physical and sensory qualities due to the obligation to remove partly hydrogenated oils (PHOs) from food items (Wang *et al*., 2016).Hence Scientists and manufacturers are actively searching for fat substitutes that do not affect the organoleptic properties of food and are acceptable to consumers. Obesity and excessive fat consumption are the most common issues in developed nations. It is feasible to reduce fat content by using food-grade multiple w/o/w Pickering emulsions because an internal water phase partially replaces the oil phase. Lipid oxidation can be effectively reduced and the oil digestion process can be delayed by the microstructure of solid particles at the oil-water interface (Klojdová & Stathopoulos, 2022). Ex: Cream in the preparation of frozen yogurt and ice cream can be replaced by Pickering emulsions stabilized by ethyl cellulose (Zhang *et al*., 2023). Butter was replaced in cakes resulting in reduced calories and longer shelf life without changing the colour and texture (Feng *et al*., 2020).

**11.2. Encapsulation and controlled release:** Pickering emulsions have gained lot of interest for this purpose because of their high loading capacities, good stability characteristics, and tunable properties (Cui *et al*., 2021). These properties make them a promising tool for improving active substance delivery as they function as excellent carriers for active ingredients that are sensitive to environmental conditions(Tian *et al*., 2024b). Pickering nanoemulsions generally have good stability and more efficient on bacteria and biofilms as they have good encapsulation efficiency for antibacterial and antibiofilm components. (Gauthier & Capron, 2021). High internal phase Pickering emulsions (HIPPE) can deliver bioactive components, protecting them against light exposure and heat treatment due to their structural and functional properties. Serve as drug delivery carriers without any negative side effects (Ji & Luo, 2023). Using gel-like Pickering emulsions stabilized by pea protein isolate (PPI), a lipophilic bioactive β-carotene release in the colon may be delivered sustainably (Cheon *et* al., 2023). Stability and loss of encapsulated curcumin was investigated in starch granule (quinoa starch) stabilized Pickering emulsions was studied by Marefati *et al* where results indicated that heat-treated emulsions (HT) retained more curcumin even when exposed to environmental and physiological conditions simulated in vitro digestions (Marefati et al., 2017). The PE technique has become a viable strategy for safeguarding active compounds from evaporation and oxidation, helping to solve the stability problems associated with bioactive compounds (Pandita *et al*., 2024).Thus, as an active carrier for the delivery of bioactive compounds, Pickering emulsions have a promising future.

**11.3. 3-D Food printing technology and porous design**: 3D printing technology is based on computer-aided design, which allows small quantities of customized goods to be manufactured at comparatively low costs by stacking printing inks layer by layer using a numerical control system and software (Berman, 2012).It is an innovative food manufacturing process that has multiple benefits, such as low waste, time savings, high precision, and high efficiency (Tian *et al.*, 2024b). Personalized nutritional profiles are developed along with complex edible-shaped products by 3D printing technology. 3D food products which are having good appeal and can be made healthy with Pickering emulsion formulated by natural ingredients making them nutritionally superior. The kind and concentration of emulsifiers, the emulsion's pH and temperature, the mixing speed and duration, and other emulsion parameters can all be changed to create porous materials with a variety of pore sizes and shapes (Ji & Luo, 2023). Ex: Plant protein-based edible pickering emulsions (PEs) and high internal phase PEs (HIPPEs) for 3D printing and delivering flavoring substances was investigated by (Feng *et al*., 2022) opening possibilities for food grade particle usage in Pickering emulsion and its potential application in 3D printing with enhanced flavor retention. Wan *et al* worked on protein-polysaccharide complexes created by structuring rice proteins (RPs) and carboxymethyl cellulose (CMC) using synergistic interactions as stabilizers for high internal phase Pickering emulsions (HIPPEs) for fabricating food-grade three-dimensional printing (Wan *et al*., 2021). The complexes were fabricated by a simple pH-cycle method, which displayed outstanding colloidal stability during heat treatment and long-term storage.

**11.4. Formulation of plant-based food products:** Researchers in the food industry are constantly motivated to create plant-based products due to customers' demand for vegan food products. For example, plant-based mayonnaise was created using Pickering emulsions stabilized by gum nanoparticles (Sharkawy & Rodrigues, 2024). Similarly in a study when the chickpea protein content is 5%, and the oil phase is 69%, or when the oil phase is 65% with a homogenization pressure of 40 Bar, the emulsion demonstrates an optimal appearance and rheological characteristics that are fairly similar to those of commercial mayonnaise products (Bi *et al*., 2024). Polysaccharide(rice flour)-based Pickering emulsions/foams were used in the preparation of gluten-free rice bread without additives to retain the gas produced by fermentation and to promote the swelling ability of the batter/bread (Yano *et al*., 2017). The Pickering emulsions produced using soybean isolate (SPI) which were heated and crosslinked with transglutaminase (TG) enzyme had the lowest temperature for ice crystal formation and they had better freeze-thaw stability. Plant-based ice cream was stabilized using Pickering emulsion prepared using these modified soy protein particles (Hei *et al.*, 2024).

**11.5. Food preservation and packaging:** Active packaging film can be developed having antioxidant or antibacterial property because of incorporation of substances having such properties ,through encapsulation by Pickering emulsions (Gauthier & Capron, 2021). Surfactant-free Pickering emulsion has been regarded as an active carrier to load oil-soluble active agents for the preparation of active edible films to keep food quality and safety. A study reveals that there was delayed decay of strawberries when coated with -konjac glucomannan composite films stabilised by Pickering emulsion than plastic wrap (Zhao *et* al., 2024). Hemmatkhah *et al*. was successfully in preparing WPI/inulin-stabilized PE microcapsules which had increased encapsulation efficiency for cumin seed essential oil using ultrasonication method. The cellulosic papers impregnated with encapsulated CSEO (Cumin seed essential oil) exhibited good antioxidant and antimicrobial activities (Hemmatkhah *et al*., 2020). Hamburgers' shelf life was extended when packed with these fabricated active papers without changes in sensorial attributes. Dihydromyricetin were loaded into Dialdehyde cellulose nanocrystals (DCNC). These nanocrystals were used as stabilizers for Pickering emulsion and incorporated into the gelatin matrix to fabricate gelatin-based active edible films. Films had strong UV barrier ability, high transparency, good water resistance, favourable mechanical property, effective antioxidant activity and stability during storage (Xu *et al*., 2021).

**11.6. Modification of lipid digestion**: Pickering emulsions can be designed to control the digestion and absorption of lipids in the gastrointestinal tract, thereby increasing satiety and reducing appetite, which may be an effective strategy to tackle obesity. Polysaccharide-based particles as stabilizers for Pickering emulsions have gained lot of attention as they are able to regulate lipid absorption and digestion. For this, starch particles, chitosan, cellulose nanocrystals, and chitin nanocrystals have all been often employed (Cui *et al*., 2021). In an in-vitro lipid digestion study by Tzoumaki *et al*at the o/w contact, there was a significant and permanent adsorption of the chitin nanocrystals (Tzoumaki *et al.*, 2013). Pickering emulsion stopped lipase and bile salts from widely dislodging the solid particles, and the nanocrystals formed a network in the bulk (continuous) phase that slowed down the kinetics of lipid digestion and caused delayed lipid digestion. Sankar *et al* used complementary physicochemical and microstructural studies to examine the impact of composite particle-particle interactions on the gastrointestinal stability of emulsions (Sarkar et al., 2018). The protein nanogel particle (lactoferrin nanogel particles, or LFN) stabilized emulsion may be protected by the secondary interfacial layer of polysaccharide particles (inulin nanoparticles, or INP), which could also postpone stomach digestion. Nanochitin-supported Pickering emulsions were obtained and their characteristics were noted as they passed through a human GIT model. The adsorbed nanochitin layer hindered the ability of lipase to reach the lipid phase, which reduced the area of lipids accessible to the lipase; and, the cationic nanochitin bound to anionic bile acids, fatty acids, or lipase and resulting in lipid digestion which is helpful for for developing high-satiety foods but the nutritional adverse effect was reduces vitamin bioaccessibility (Zhou *et al*., 2020).

**11.7. As Catalyst:** Pickering emulsions are particle-stabilized surfactant-free dispersions whose droplets have a large specific surface area, and can be used as interface catalytic reactors that can greatly improve catalytic efficiency as they have the potential to trap the enzymes into the liquid phase with the particles at the water-oil interface as the solid barrier which protects enzymes from the organic medium. Excellent recovery of solid catalyst, vast interfacial area to boost reaction kinetics, selectively catalysing action, spontaneous separation of key products based on ‘phase transfer’ process and prohibiting pointless secondary reactions are major properties due to which Pickering interfacial catalysis (PIC), Pickering-assisted catalysis (PAC) and Pickering interfacial biocatalysis (PIB) have drawn great interest for research in field of Catalysis technology (Ni *et al.*, 2022). Xi et al. employed phosphorylated zein nanoparticles (ZCPOPs) mounted in gold nanoparticles (Au NCs) to stabilize the Pickering emulsion system for the biphasic cascade catalysis process in oil-in-water (o/w). With unpredictable catalytic activity and horseradish peroxidase-like characteristics, the combination of chemo- and bio-catalysis increased the catalytic yield by more than two times when compared to solitary metal catalysis (Xi *et al*., 2021). Pickering emulsions have unmatched qualities that lead to their bright application prospects in food catalysis, despite the fact that there have been few research conducted on their usage as biomimetic interfacial catalytic reactors in the current food sector (Tian *et al.*, 2024b).

**11.8. Prevent lipid oxidation:** Food lipid oxidation can be caused by irradiation, active oxygen species, transition metal ions, enzymes, etc., and can result in potentially harmful components that reduce the nutritional and sensory value of fatty foods (Kaderides *et al*., 2021).Pickering emulsion stabilizers can extend the shelf life of food items, improve their lipid oxidative stability, and raise their market appeal. The oil-water interface layer of plant-based protein Pickering emulsions is much thicker than that of surfactant emulsions. It can better prevent lipid peroxides in oil droplets from contacting transition metal ions in the phase to delay oxidation (Tian *et al*., 2024a).

**11.9. Detergents**: Companies that manufacture and prepare food inevitably generate a lot of oil and grease, and the key component in conventional detergents is surfactant. Extended usage of these detergents can have negative environmental effects. Therefore, detergents made from solid-particle (biodegradable Pickering particles) offer superior stain removal as well as being ecologically sound (Zhang *et al*., 2023).

**11.10. Bioimaging/ Biosensing**: Highly luminescent graphene quantum dots can be employed as stabilizers to produce Pickering emulsions and particles with controlled nanostructures and high luminescence, which would be useful for bioimaging, drug delivery, and optoelectronic devices. Colloidosome shells are usually composed of hundreds or thousands of nanoparticles. They have smooth surfaces with large surface areas, which facilitates the grafting of functional groups or makes possible other applications needing large surface areas, such as biosensing or bioimaging (Wu & Ma, 2016).

 **12. CONCLUSION:**

1. They find their applications in various industries like coatings, paints, adhesives, rubber, sealants, drug release systems, etc due their properties like high stability, low viscosity and transparent nature along with their ability to reduce surfactant. But, there are several challenges which need to be addressed before scaling up for industrial applications (Gauthier & Capron, 2021).
2. There is a need for systematic approach and more scientific research in packaging sector on the film-forming mechanism involving Pickering emulsions and those films which have controlled release mechanism of bioactive substances (Zhao *et al*., 2024).
3. Though lot of systems are patented, commercialization of product based on Pickering emulsions is yet to be done by overcoming some obstacles related to industrialization of Pickering emulsions. Preparation of the particle will need to be scaled up, which is not obvious for all the particle types(Albert *et al*., 2019).
4. Compared to molecular surfactants Pickering emulsions are a less developed and more expensive technology as natural particles need modification to have dual wettability and other properties to meet the criteria which indirectly adds to the cost.
5. Pickering emulsions will have a of rapid development with the advancement of material technology and an extensive understanding of their formation and action mechanisms (Wu & Ma, 2016).
6. There exists an increasing demand for emulsions with, low viscosity, high transparency, low toxicity or long shelf life which can be meet by nanosized particles and finally by Pickering emulsions which are surfactants free making them environmentally sustainable.

**COMPETING INTERESTS DISCLAIMER:**

Authors have declared that they have no known competing financial interests OR non-financial interests OR personal relationships that could have appeared to influence the work reported in this paper.

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