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Article

A Comprehensive Review of Natural Polymer-Based Emulsifying Agents: Industrial Applications and Computational Perspectives

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Abstract: Emulsions are used a lot in the food, pharmaceutical and cosmetic industries. But they have a Emulsions are extensively utilized in the food, pharmaceutical, and cosmetic sectors; yet, their intrinsic instability poses a significant constraint. Natural polymers have arisen as sustainable substitutes for synthetic emulsifiers owing to their biodegradability, biocompatibility, and functional flexibility. This review emphasizes the categorization of natural polymers and their function in emulsion stabilization. Critical instability mechanisms, including as creaming, flocculation, and coalescence, are examined in conjunction with stabilization strategies. The efficacy of natural polymers is assessed through interfacial adsorption, steric hindrance, electrostatic interactions, and viscosity augmentation. Polysaccharides and proteins exhibit considerable promise as emulsifying agents, enhancing stability while minimizing environmental effect. In contrast to synthetic emulsifiers, natural alternatives have benefits including non-toxicity and regulatory approval. Their utilization in pharmaceutical delivery, food systems, and environmental cleanup is also examined. Nonetheless, issues including unpredictability, restricted stability under harsh conditions, and scaling limitations endure. Subsequent study ought to concentrate on functional modification and sophisticated formulation techniques to improve performance and broaden industrial applications.
Keywords: Natural polymers, Emulsion stability, Biopolymers, Interfacial adsorption, Steric stabilization, Sustainable emulsifiers, Drug delivery, Food systems

1.INTRODUCTION

Biopolymers have been utilized historically; however, their application has diminished over the past two centuries due to the rapid emergence of affordable, mass-produced materials derived from petrochemical feedstocks, which have proven more suitable for societal demands. In recent years, elevated petroleum prices and societal concerns regarding the adoption of environmentally friendly products have resulted in heightened interest in bio renewable polymers and the implementation of sustainable technologies for their production.

Customers are more interested in commercial products that are more environmentally friendly, sustainable, and natural. Foodstuffs beauty products, cleaning products, and other personal hygiene items are examples of these things. The industry has made an effort to replace the synthetic functional components of these goods with organic alternatives. . Numerous techniques for producing these renewable materials have been the subject of both academic and commercial study. Products made from biomass that have had fewer chemical treatments or modifications and use less energy are becoming more and more popular among consumers who want "clean" labeling to ensure that these products are sustainable, safe, and readily available.[1]

To reduce the growing pollution of the environment brought on by chemical-based dyes, metallic heavy metal ions, and additional dangerous materials, effective and long-lasting remediation methods are required. In this perspective, natural polymers including chitosan, cellulose, lignin, and pectin have become quite interesting due to their availability, chemical functionalisation potential, and biodegradability. Crosslinking and interface stimulation can improve the intrinsic adsorption capabilities of natural polymers.

Biopolymers, which are polymers derived from organic materials that are either chemically produced from biological components or biosynthesised by living organisms, include protein (polymers comprised of amino acids), hereditary material (polymers comprised of nucleic acids), and glycoform [2].

Because of their biocompatibility, biodegradability, and functional flexibility, natural polymers are essential parts of pharmacological formulations. Natural polymers are favoured over their synthetic counterparts because of their inherent benefits, which include non-toxicity, sustainability, and renewability, in keeping with the global trend toward ecologically benign pharmaceutical excipients. Depending on their characteristics, they carry out a variety of tasks, including coatings, packing, as well as a number of other mechanical tasks. Unlike many other synthetic polymers, such waste plastics, they are biodegradable and do not accumulate [3].

Depending on whether these polymers are inert on the surface (most polysaccharides) or active on the surface (most proteins), they can be incorporated in two different ways [4]. Depending on their characteristics, they carry out a variety of tasks, including coating, packing, and other mechanical work. in contrast to waste plastics and a variety of other synthetic polymers [5]. They do not build up and are biodegradable.

Polymers are utilized in various industries, including food, pharmaceuticals, cosmetics, pesticides, and fertilizers, according to their fundamental properties, with their emulsification capabilities determined by their monomer units. The utilization of biopolymer alternatives to synthetic emulsion stabilizers is increasing due to consumer demand for organic food products. Emulsion stabilisers are naturally occurring polymers generated from bacteria, microbes, and various biological components that include amino acids, nucleic acids, carbohydrates, and other things. Proteins from plants and animals serve as vital natural emulsion stabilisers.In the pharmaceutical industry, phospholipids such as phosphatidyl choline (PC), phosphatidyl ethanolamine (PE), and phosphatidyl glycerol (PG) are very effective emulsion stabilisers.The food and cosmetics industries use lecithin, a compound of phospholipids.

It is believed that proteins connected to non-surface-active polysaccharides are responsible for emulsifying academic abilities. This can be produced naturally, since many gums and mucilages contain polysaccharides that are naturally coupled with proteins, or by combining polysaccharides and proteins to form precipitated complex coacervates or surface-active connections [6]. Based mostly on experimental research on emulsion stabilisation, it is thought that the protein component of plant-derived polysaccharides serves as an emulsion stabiliser. This has been verified by recent experiments on Acacia gum, which show that the gum fraction with higher molar mass and protein content preferentially adsorbs on oil/water emulsion droplets [7]. By combining the emulsifying qualities of amphiphilic proteins with the physicochemical characteristics and environmental stability of polysaccharides, bioemulsifiers that are both safe and efficient can be created [8, 9].

Foods-based emulsifiers, which come from natural or edible sources such as corn, soybeans, oatmeal, eggs, milk, and fruits, are becoming more and more popular in the food business because of their clean label appeal, natural ingredient identification, and capacity to satisfy customer demand for fewer artificial chemicals.

The innovative and dynamic cosmetics sector is always doing research, which is frequently influenced by market trends. Emulsifiers have had a significant influence on its evolution, despite the fact that it encompasses several different areas. These components are essential to many products, and ongoing research has produced ever-better products. Consumers are getting more aware about cosmetic items and their desired attributes, as evidenced by several studies. Mintel's 2024 global consumer trends study [10] found that consumers are willing to spend for cosmetics with natural ingredients. Additionally, they advocate for the beauty sector to prioritize sustainability.

2.NATURAL POLYMERS & ITS CLASSIFICATION

A macromolecule made up of repeating structural units linked by covalent bonds is called a polymer. Polymers of natural origin are biopolymers produced by bacteria, plants, and animals during metabolism, growth, development, and reproduction [11,12]. Natural polymers that are connected to Biopolymers, which are monomeric molecules that employ covalent bonds to create macromolecular structures, are the result of living creatures' metabolism [13–15]. They provide vital functions in nature, including storing cellular energy and preserving and conveying genetic information. Their biodegradability, which enables CO2 to be liberated and quickly absorbed by soil and crops, is their primary benefit. The majority of these biopolymers, including cellulose (which makes up around 33% of all plant components), lignin, starch, and chitin/chitosan, are categorised as polysaccharides [14,16]. Because of their accessibility, biodegradability, and potential for chemical functionalisation, polymers that are natural such as chitosan, cellulose, lignin, and pectin have been demonstrated to be highly promising. Cross-linking and surface activation can increase the intrinsic adsorption capacity of natural polymers.

Despite the availability of both polymers that are both synthetic and natural the utilisation of natural polymers in medical applications is preferred due to their accessibility, cost, and lack of toxicity.

They can undergo chemical changes, are generally biocompatible, and may be biodegradable.[17]. Primary natural polymers include polysaccharides, polynucleotides, and polypeptides. Because of their attributes, they can be used in a variety of ways. Polymers are utilised in many industries, such as food, pharmaceuticals, cosmetics, fertilisers, and insecticides, based on their fundamental characteristics. The ability of polymers to emulsify is determined by their monomer units.The classification of natural polymers is shown in Figure 1.

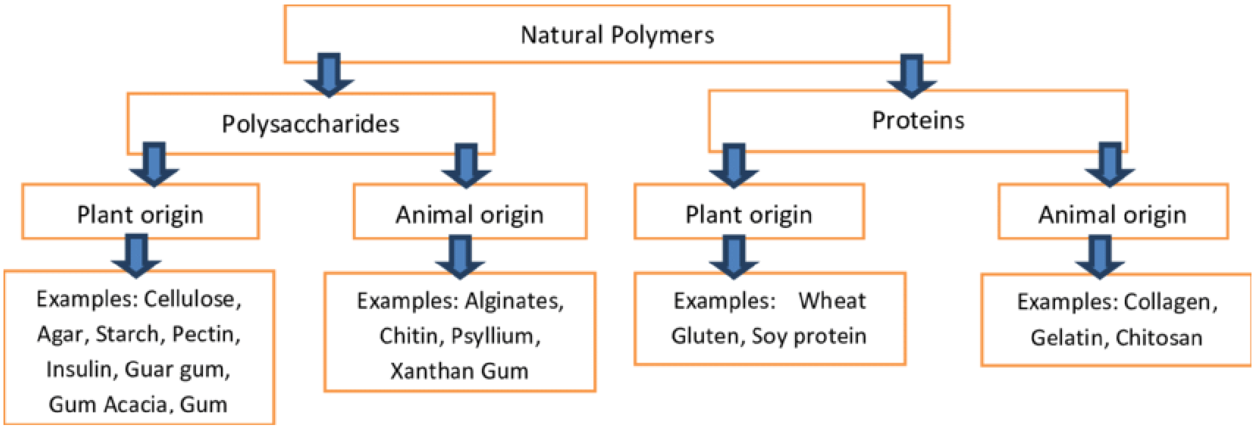

Figure1 Classification of Natural Polymers

3.EMULSION AND EMULSION STABILIZERS

Emulsions are colloidal systems consisting of more than one immiscible liquid in which one is dispersed finely in the other utilising homogenisation techniques and surfactants. The other liquid is referred to as the continuous phase, whereas the dispersed liquid is called the dispersed phase [18]. The two main varieties of emulsions are water-in-oil emulsions (W/O), where water is the dispersed phase, and oil-in-water emulsions (O/W), where oil is the dispersed phase, since both water and oil are the most often utilised liquids to make nutrient-grade emulsions. The most prevalent kinds of colloidal dispersions are O/W and W/O emulsions.These systems exhibit thermodynamic instability due to the unfavourable interaction between water and oil, which ultimately results in separation and adversely impacts the emulsions' shelf life and protective effectiveness [19, 20]. The most common processes that might cause an emulsion to become unstable are creaming, flocculation, and coalescence [21].

The food business can employ a variety of manufactured and natural emulsifiers, including proteins, polysaccharides, phospholipids, and surfactants. Emulsifiers are surface-active compounds that are crucial to the production of emulsions in two ways: first, they assist emulsion formation, and second, they enhance emulsion stability [22].

3.1 Instability of emulsions

Due to their thermodynamic unstability emulsions are vulnerable to phase separation, flocculation, Ostwald ripening, and coalescence [23]. Different levels of phase separation result from the oil phase quickly leaking from the interfacial layer and emulsification becomes less effective over time.

An oil-in-water emulsion experiences flocculation, a kind of instability, when a sizable portion of dispersed droplets condense into flocs. It happens when droplets are more drawn to one other than they are repulsed [24]. During flocculation, the droplet radius remains constant, but droplets cluster together, accelerating gravity separation and endangering the stability of emulsions [25]. Coalescence is the process by which oil droplets in an emulsion progressively come together to form bigger droplets or cluster; this is an indication of instability. An imbalance between the attraction and repulsive forces between droplets is the main factor influencing it. Droplet coalescence is also influenced by the interfacial film's thickness and viscoelasticity [26]. The phenomena wherein smaller droplets in an emulsion diffuse into larger ones due to variations in Laplace pressure between different sized droplets is ostwald ripening. Delamination or settling is directly caused by this process, which broadens the emulsion's particle size distribution [27]. An oil-based phase with elevated water dissolution, such as shorter-chain triglycerides, can significantly accelerate the Ostwald maturation process by enhancing molecular movement between droplets. Additionally, during storage, emulsions may undergo chemical changes such lipid oxidation, triglyceride hydrolysis, and unsaturated fatty acid polymerisation that impact their stability. For instance, lipid oxidation may proceed more rapidly in the bulk or continuous phase than in the dispersion phase. O/W is more resistant to oxidation because it encapsulates oil [28].

3.2 Emulsions stabilized by Natural Polymer

The term "emulsifier" refers to amphiphilic substances that adsorb on the surfaces of oil droplets in oil-in-water emulsions that reduce interfacial tension and stop aggregation. The most widely used food-grade Proteins, polysaccharides, phospholipids, and small molecule surfactants are examples of emulsifiers [29]. Lately, finding food-grade colloidal particles to stabilize food emulsions has attracted a lot of attention through a Pickering process [30]. Food emulsifiers' distinct structural and chemical characteristics determine their capacity to create and maintain oil-in-water emulsions.In order to promote droplet breakup, the optimal natural emulsifier must quickly bind to the surfaces of oil droplets formed in homogenisation, significantly reduce the interfacial tension between oil and water, and provide a barrier to prevent droplets from consolidating inside the homogeniser.

4.FACTORS AFFECTING EMULSION STABILITY

4.1 Interfacial Adsorption

The thermodynamically unstable mixtures having at least two immiscible phases and an emulsifier that can maintain stability over time with enough mixing energy are known as emulsions [31]. In order to provide consistent long-term qualities, the emulsifier is essential. Emulsifiers are typically active surface materials that can be applied at the interface between oil and water to minimise tension at the interface and stop or slow aggregation processes [32]. The hydrophilic portion of the emulsifier is usually found in the watery phase, while the hydrophobic tail is still contained in the oil phase [33, 34]. Because of their adsorption kinetics, the surfactant molecules need time to migrate to the interface and form a layer in order to reach the interfacial tension equilibrium during emulsion formation [33]. In addition to being influenced by environmental factors like pH and temperature, as figure 2 shows, this pattern changes depending on the type of emulsifier, taking anywhere from minutes (for some saponins) to hours (for other proteins).

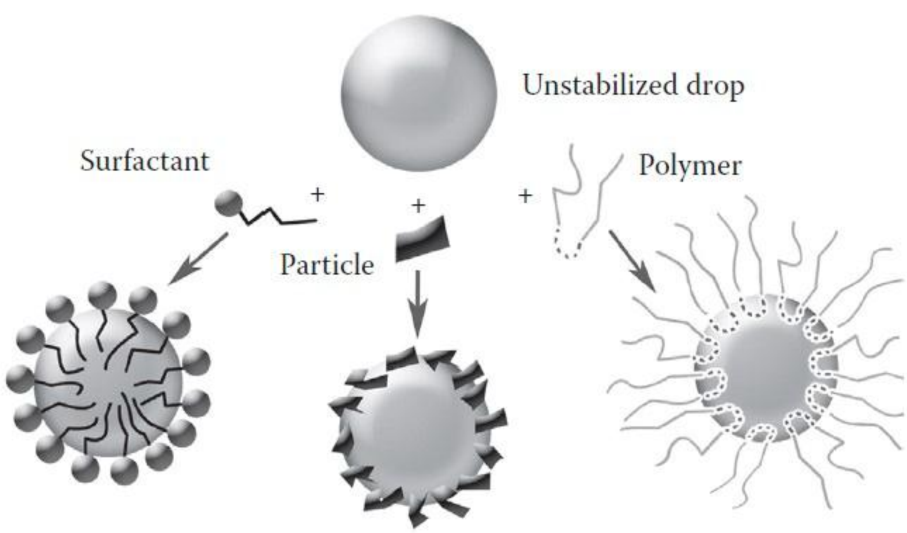

Figure 2. Interfacial Stabilizing Layers Formed by Surfactants.Particles & Polymers

4.2Steric Stabilization

Adsorbed emulsifiers should produce strong repulsive interactions, such as steric or electrostatic repulsion, to prevent droplets from aggregating during droplet-droplet contacts.

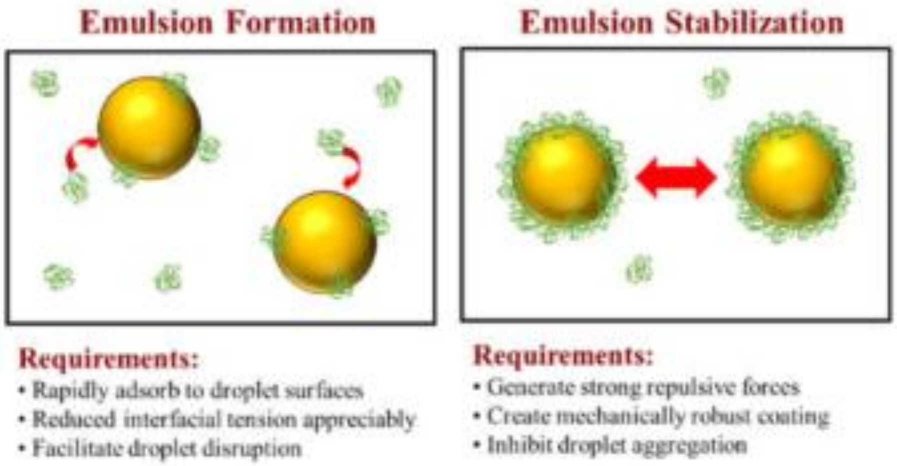

Figure 3: Image depicts the formation and stabilization of emulsions.

4.3. Electrostatic Interactions

Although structures with multiple layers can also emerge, the emulsion are often stabilised with a single-layer architecture enclosing the droplets. The multilayer structure increases stability and offers further protection for the interior phase by encouraging the droplets' electrostatic and steric repulsion [35]. To provide a strong stabilising layer, a variety of emulsifiers must be used [36, 37]. To avoid phase change and droplet agglomeration separation, the emulsifiers must produce strong steric repulsive forces, electrostatic forces, or an electrosteric stabilisation process that may oppose the attractive interactions among the oil droplets [38].

4.4. Viscosity Enhancement

Proteins can bind to and emulsify hydrophilic polysaccharides because they are essentially surface-active. This changes the viscosity of the water phase, thereby delaying droplet migration. At lower polymer concentrations, proteins and polysaccharides have superior stabilizing properties.

5.ADVANTAGES AND CHALLENGES OF BIOPOLYMERS COMPARED TO SYNTHETIC POLYMERS

Plastic is a major rival of biopolymers because it was one of the very first artificial polymers ever made. Most of the feedstocks used in the production of plastic come from the fossil fuel sector. While the use of petroleum and fossil fuels is decreasing, the use of plastics has grown throughout time. Furthermore, because petroleum-based plastics include carbon, which has been buried in the ground for millions of years, they have a detrimental effect on the environment. Therefore, there are more greenhouse gas emissions in the atmosphere when these carbons are released by burning or other activities [39, 40]. Polyethylene terephthalate (PET), high-density polyethylene (HDPE), packaging plastics, and other synthetic polymers can linger in the environment for extended periods of time; as of 2018, the rate of recycling were 29.1%, 29.3%, and 8.7%, respectively (USEPA, 2021). abuse, nevertheless, and the difficulty of handling and disposing them appropriately. The damage these items bring to the environment and the earth's ecosystem, which exacerbates their dreadful repercussions, makes these figures negligible. Therefore, finding polymers is more important than ever in the search for a superior substitute for synthetic materials, and biopolymers might be good options [41]. Over the past 10 years, there has been a rise in demand for products that are environmentally friendly that contain biopolymers such proteins, lipids, and polysaccharides due to the public's growing awareness of environmental deterioration.

These include inexpensive renewable raw materials that potentially replace petroleum-based, nonbiodegradable plastic products [42]. They can be built using feedstocks like food waste or algae, as well as a range of crops for agriculture like maize or soybeans. Biopolymers can be produced from non-traditional sources like algae and food waste in addition to regular ones like maize and soybeans [44, 43]. Biopolymers are generally cost-effective and environmentally friendly; processing their waste is an alternative. They lessen the possibility and impact of global warming brought on by the depletion of fossil resources in addition to being biodegradable, compostable, sustainable, highly recyclable, and less eco-toxic [44]. These unique characteristics distinguish them from synthetic polymers, especially in fields where compatibility and biodegradability are essential, such as textiles, engineering, agriculture, and medicine. Furthermore, the cost of biopolymer products should be taken into account from an economic perspective as, despite their benefits, their ability to compete on price with synthetic polymers will determine their future.

Industries have embraced petroleum-based polymers without taking environmental concerns into account since they tend to be less costly than the majority of biopolymers [45, 46]. Therefore, the usage of biopolymers may increase quickly and have a positive effect on the environment and general health if this one economic barrier is removed. This will lessen degradation and give time to address the root causes of major environmental disasters like global warming. Traditional polymers are not biodegradable. However, natural resources like wheat or flaxseed are used to make fibre reinforcements and polymer matrixes.

The microbes that consume these elements produce carbon dioxide and water as byproducts. In this instance, biopolymers can be gathered and mixed with biowaste for composting. The different breakdown properties of synthetic and biopolymers are shown in Table 4.

Table 4: Comparison of synthetic and biopolymers.

Polymer	**Type**	**Degradation Time**	**Mechanism of Degradation**	**References**
PHB/PHA	Synthetic	>24 months	Microbial fermentation	[47]
Collagen with cross-links	Semi-synthetic	>6 weeks	Collagenase is an enzymatic	[48]
Films made of hyaluronan	Biopolymer	1 week to 4 months	Enzyme: hyaluronidase	[49]
Chitosan that is cross-linked	Semi-synthetic	>20 weeks	Lysosome and chitosanase	[50]
Types I, II, and III collagen	Bio/ Semi-synthetic	12 h	Enzyme: collagenase	[51]
Alginate	Semi-synthetic	~80 days	Hydrolytic breakdown	[52]

For some biopolymers, such as polyhydroxybutyrate (PHB), poly (butylene adipate-co-terephthalate), potato starch, PLA, cornflour, and solanyl (starch-based resin), the adoption of cost-benefit analysis based on the flash pyrolysis of waste biopolymers might be economically advantageous [53]. The pyrolysis of biomass and waste biopolymers was thought to be the only practical way to incorporate biopolymers into the plastics industry in the near future.

6. APPLICATION OF NATURAL POLYMERS

Biopolymers work well as test stabilisers either by themselves or in combination. Because of their durability, low toxicity, low immunogenicity, bio-adaptability, fine reactivity to chemicals, relative economic stability, nutritional benefits, and biodegradability [8], polymerised composites are preferred in food [54,55]. They have also been proven to be secure for use. Using a variety of compounds, such as flavours, preservatives, and emulsifying agents, to improve the taste, texture, or appearance of food has long been a popular practice worldwide.

These biopolymer substitutes for synthetic emulsion stabilisers are expanding due to customer desire for natural food items.

These biopolymer substitutes for synthetic emulsion stabilisers are expanding due to customer desire for natural food items. Proteins and polysaccharides are the most often used biopolymers, frequently in colloidal diffusion synthesis forms such emulsions or froths [56]. It is astounding how well biopolymers have been mechanically applied in a variety of fields, such as mining, microbiology, nutrition, medicine, and cosmetics technology [57]. The creation of recyclable plastics is one of the most significant uses of biopolymers. Plastics constitutes one of the most widely utilised materials nowadays. The majority of polymers made chemically are not biodegradable. In the foreseeable future, this might lead to serious issues. Consequently, non-biodegradable synthetic plastic can be replaced by biodegradable plastic. Plastics are made from around 0.5% of biocompatible polymers, including cellulose, polylactic acid (PLA), polyhydroxyalkanoate (PHA), and polyhydroxybutyrate-valerate (PHBV) [58].

When employed as stabilisers for emulsions, , biopolymers serve as emulsifying substances (polypeptides), viscosity modifiers (polysaccharides), and weight agents (polysaccharides and polypeptides). By covering individual droplets, they help lessen coalescence.

Food stability and structure have been greatly enhanced by biopolymers [59]. raising the density of the oil globules to reduce creaming, coating each oil globule with a soft layer to prevent coalescence, and raising the viscosity of the regular phase to reduce globule movement are some of their techniques [60].

All of these techniques increase the product's longevity while also enhancing emulsion stability.

Biopolymers can improve the stability of emulsions as well as their nutritional value, texture, oral consistency, and shelf life. Nutrient distribution in food products and bioactive compounds are only two of the many uses for biopolymers.

7.CHALLENGES AND FUTURE ASPECTS

Consuming more natural, plant-based, bioresource, and ecologically friendly meals, beverages, and cosmetics has been identified as a current trend. In order to create, separate, and utilize natural substances such biopolymers as natural emulsifiers, industries, researchers, and chemists are focusing on fulfill this request. This list includes polysaccharide-based biological surfactants and other bio-derived polymers, in contrast to their synthetic counterparts. Many of these emulsifiers have been shown to be appropriate for use in the manufacturing of foods and beauty products because they can produce stable droplets of oil-in-water emulsions [61]. The expense of producing these biopolymers is the primary obstacle in this industry. Currently, the cost of production and purification is too high for biopolymers to be widely used in industry. Additionally, better techniques and equipment are needed. Another barrier is funding for biopolymer research [62].

8.CONCLUSION

Certain biopolymer stabilizers have been found to perform better than synthetic emulsion stabilizers in a number of industries, such as food, medicine, and cosmetics. This is because the biopolymer emulsion stabilizer has reduced levels of immunogenicity, toxicity, biodegradability, and affordability. nutritional benefits and simplicity of handling, transfer, and use. Biopolymers with smaller diameters and lower concentrations have better stabilizing properties. In general, a variety of parameters, such as temperature variation, preserving duration, pH level, ion strength, methods of processing, etc., affect a biopolymer's capacity to stabilise a nanoemulsion. Biopolymers are also utilised in food items to improve texture and nutrient distribution, boost nutritional value, and improve self-life.

Further research on plant protein emulsion will be helpful for biopolymer and emulsion stability since it is the best substitute for synthetic nanoemulsion and animal protein emulsion.

These extremely useful characteristics demonstrate the enormous potential of biopolymers as emulsifiers in a range of innovative food and pharmaceutical technologies, as well as in several other industries including the manufacture of biofuel, biochemical fertiliser, biodegradable plastics, etc. Therefore, employing biopolymer-based goods will be highly effective in preserving the carbon cycle and contributing to the preservation of the ecosystem and the world.

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