

## Chitosan A Natural Alternative Preservative to Chemical Preservative for Seafood

Ulaganathan Arisekar

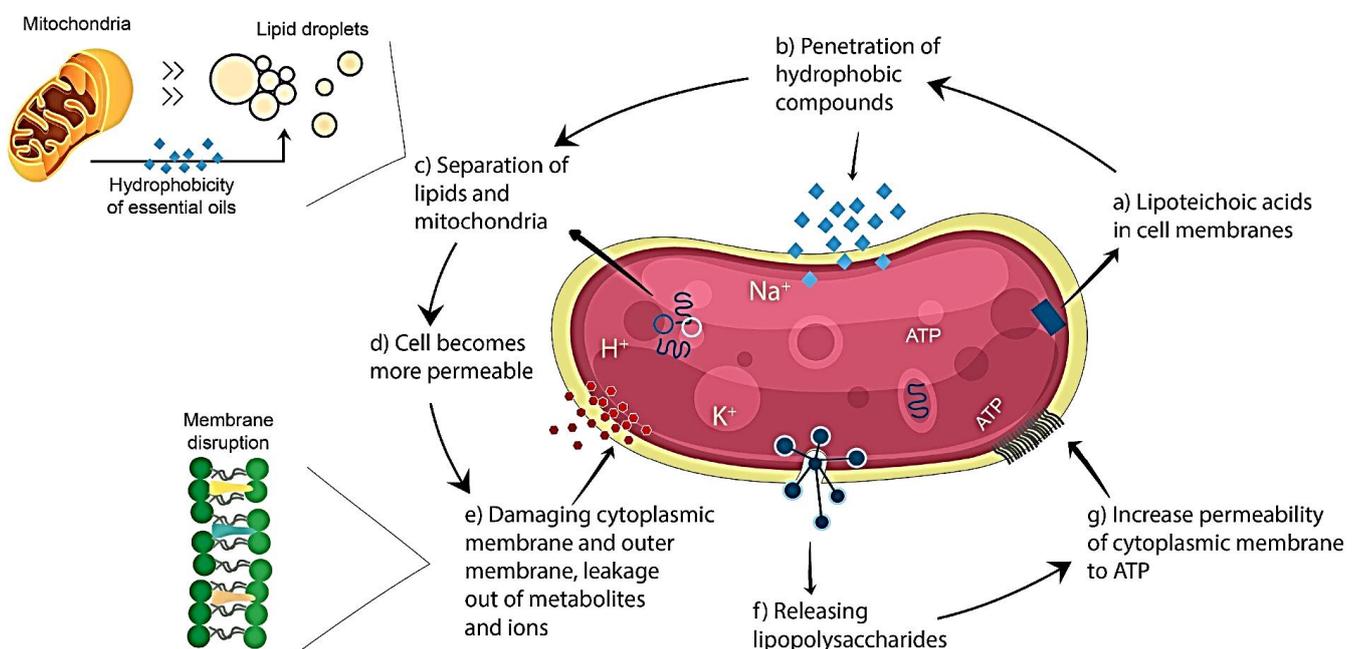
Ph. D Research Scholar, Department of Fish Quality Assurance and Management, Fisheries College and Research Institute, Tamil Nadu Fisheries University, Thoothukudi, Tamil Nadu

### SUMMARY

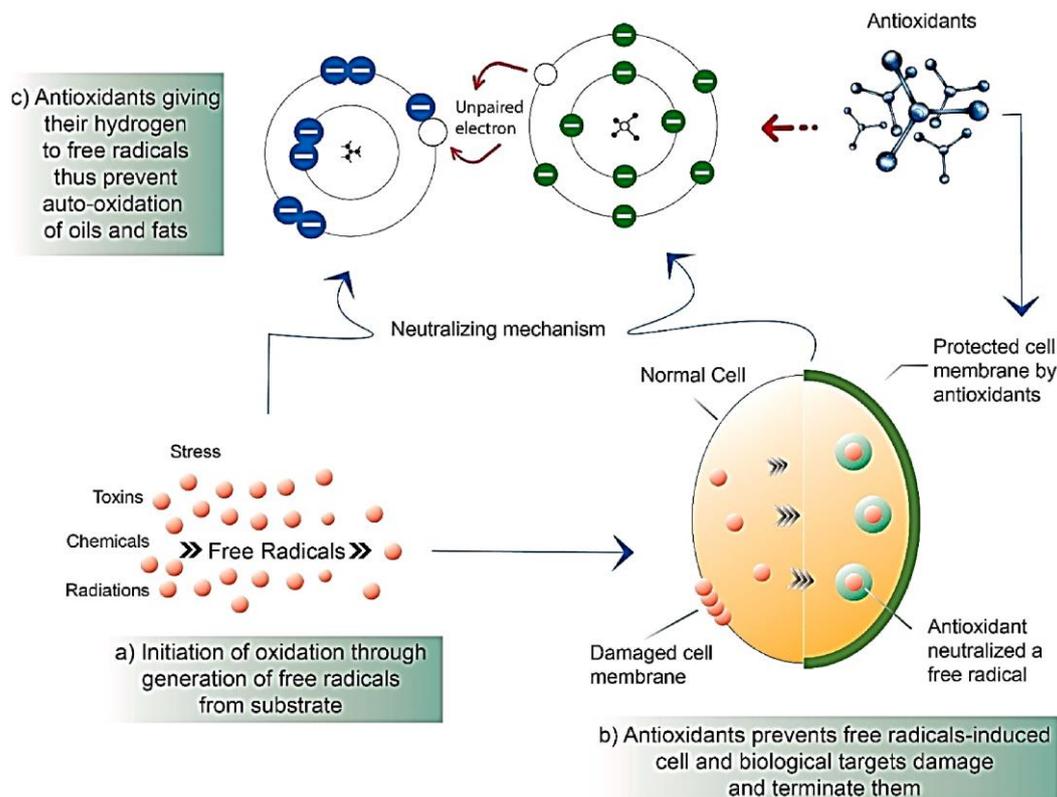
Fish and other aquatic organisms quickly lose most of their quality after being caught. The growth of foodborne pathogens and spoilage microorganisms is directly correlated with temperature, making temperature the most influential factor in reducing the shelf life of seafood. The aqua-food business faces difficulty in satisfying customer demand for fisheries products that are both fresh and safely processed, without the use of chemical or synthetic preservatives. Therefore, natural preservatives such as chitosan, essential oils (EOs), plant extracts, and lactic acid bacteria have become increasingly popular. The antimicrobial and antioxidant qualities of these preservatives allow for prolonged preservation of fish and seafood without loss of quality or safety. Use of chitosan with essential oils (EOs) in edible coatings, film wrapping, and dipping solutions has proven to be fruitful. The purpose of this review is to assess the efficacy of chitosan, essential oils (EOs), and other natural preservatives in extending the freshness and quality of fisheries products. The current state of aquatic food preservation in Southeast Asian countries is also discussed, along with the mechanisms of action of natural additives, the detrimental effects of chemical preservatives, and the noted research gaps in this area. Overall, the findings of this study contribute to the progress made in the field of natural preservatives for the aqua-food industry.

### INTRODUCTION

The delicate flavor and high nutritional value of seafood have contributed to its spectacular rise in popularity (Yu et al., 2020). The FDA and EPA have steadily raised the daily intake recommendations for seafood, especially for pregnant women and children. In 2018, fish production was estimated at 179 million tonnes worldwide, making up 17 percent of the world's total animal protein supply (FAO, 2020). However, fish is notoriously difficult to store because its high moisture content, the abundance of low molecular weight compounds, and neutral pH make it an ideal breeding ground for microorganisms and biochemical deterioration. Shortly after death, fish undergo endogenous enzymatic processes, oxidation, and microbial activity, which alter the fish's sensory and nutritional characteristics and shorten its shelf life. Lipid oxidation has notable impacts on fish, including the formation of off smells and aromas, the generation of toxic compounds, and changes in color, all of which have detrimental health and economic consequences (Gharsallaoui et al., 2016; Tongnuanchan and Benjakul, 2014).



**Fig. 1.** Antimicrobial mechanisms of natural preservatives, which act mainly on the cell membrane and cytoplasm. Due to the presence of lipoteichoic acids (a) in Gram-positive bacterial cell walls, hydrophobic compounds enter the cell (b) and separating the lipids from mitochondria (c) and making the cell permeable (d). As a result, the cytoplasmic membrane and outer membrane become damaged and the internal metabolites and ions leaked out (e). As for Gram-negative bacteria, due to the release of lipopolysaccharides (f), the cytoplasmic membrane becomes disintegrated to ATP (g) (Hossain et al., 2021).



**Fig. 2.** Antioxidant mechanisms of natural preservatives. Free radicals from stressors, toxins, chemicals, and radiations induce oxidation (a), and antioxidants prevent those radicals from tissue damage by scavenging and terminating/neutralizing them (b). Auto-oxidation is prevented by antioxidants, which provide hydrogen ions to bind with the unpaired electron of the free radicals (c) (Hossain et al., 2021).

Fish must be preserved properly to keep their quality and extend their shelf life. In addition to more conventional preservation techniques like chilling, freezing, salting, and drying, the fish processing industry makes extensive use of more modern preservation strategies like super chilling, modified atmosphere packaging (MAP), vacuum packaging, irradiation, and high-pressure processing (HPP). These preservation strategies are not yet adequate to totally stop microbial responses and lipid oxidation (Gharsallaoui et al., 2016). Several synthetic or chemical preservatives have shown promise in preventing texture and color changes, unpleasant taste and rancid odor, and the loss of nutrients in fish during storage. These include sodium benzoates, sodium nitrite, butylated hydroxyanisole (BHA), and butylated hydroxytoluene (BHT).

In recent years, there has been a global uptick in attention paid to food quality and safety on the part of consumers, producers, the food business, and government authorities. Natural alternatives to artificial preservatives are being sought out by the food industry as an increasing number of customers express concern over the potential negative health impacts of these substances (Tongnuanchan and Benjakul, 2014). To support the expanding food trade and satisfy the preferences of modern consumers, businesses must provide more natural, minimally processed, and synthetic preservative-free meals. Numerous studies have been conducted recently on the topic of natural preservatives for fishery products, and new natural preservatives are being discovered on a regular basis. These organic compounds are typically derived from microorganisms, animals, or plants (Tongnuanchan and Benjakul, 2014). Natural preservatives like these contain antibacterial and antioxidant characteristics that keep the fish fresh for a longer period of time.

A variety of additional substances with powerful antibacterial and antioxidant capabilities, such as lysozyme, lactoperoxidase, plant extract, and bioactive peptides, have been discovered to be useful in fish and shellfish (Baptista et al., 2020; Tongnuanchan and Benjakul, 2014). The use of these natural preservatives has the potential to aid in meeting the rising market demand for "clean label," or chemical-free, fish products. This article provides an up-to-date look into the use of essential oils, chitosan, and other natural preservatives to maintain quality and extend the shelf life of fish and fisheries products, along with some commentary on the antibacterial and antioxidant mechanisms underlying their efficacy. In addition, the process of food spoiling, seafood preservation methods, the health impact of chemical preservatives, and the advantages and disadvantages of mixing essential oils and chitosan as food preservatives are briefly explored (Tongnuanchan and Benjakul, 2014).

### **Spoilage mechanisms**

Spoilage occurs when fish undergoes any alteration from its original condition that alters its aroma, flavor, visual appearance, or textural quality. In general, there are three distinct processes that lead to fish spoilage: There are three types of spoiling: (i) autolytic deterioration, (ii) oxidative spoilage, and (iii) microbiological spoilage.

### **Preservatives used in Southeast Asian countries**

Fresh fish consumption in Southeast Asian countries like Bangladesh, India, and Pakistan is lower than predicted despite the region's abundant rivers, canals, reservoirs, lakes, and floodplains. It's mostly because of the subcontinent's limited supply, high price, low preservation quality, and insufficient marketing infrastructure. Fresh fish, dried and salted fish, fish in a sauce or paste, and other forms of fish are always present on the dinner tables of rice-eating cultures. Fish preservation methods such as canning, freezing, and icing using LAB, sodium alginate, or calcium chloride are quite inexpensive in other Asian and European countries, such as Japan and South Korea, but quite pricey in Southeast Asian countries. The expense of current preservation technologies is one factor, but the culinary preferences of consumers in these countries are also significant. Canned or frozen fish is unsellable in regions where consumers like spicy fish taste due to the lack of distinct tastes. For this reason, the most frequent methods of preserving fish in Southeast Asian countries are drying, salting, and turning it into pastes and sauces.

Southeast Asian countries like Bangladesh and India have long relied on cost-effective traditional preservation methods. The knowledge of the fishermen and the fish vendors are still confined to the sun-drying process, along with certain additional methods like salting, which is the oldest way of fish preservation in the world. Sun drying destroys vital elements such as fibers, carbs, and amino acids. While economically appealing, traditional drying methods of fish preservation can only meet demand in their home regions. Furthermore, the types of microorganisms present, the nutritional content of the fish, and so on cannot be guaranteed by using such unsanitary methods. Some of the modern processing procedures, such as super chilling, MAP, and HPP, should be implemented in these regions to guarantee the quality of the fish product and make them appealing to consumers. Supercooling has been proven to be an effective modern preservation method by preventing autolysis and microbiological action. In addition, MAP and HPP have gained popularity because of their long storage life, capacity to suppress microbial action, and ability to retard enzymatic activities at low temperatures. Therefore, Southeast Asian countries should think about adopting these cutting-edge preservation technologies as an alternative to more conventional preservation methods in order to satisfy customer demand and compete with their counterparts in the industrialized world.

### **Over view of chitosan**

Natural chitosan can be found in the exoskeletons of insects and crustaceans. Chitosan is a polycation biopolymer. Chitosan is a linear polysaccharide with a high percentage of N-deacetylated chitin and a low percentage of N-acetylated chitin, made of more than 80%  $\beta$ -(1,4)-2-amino-d-glucopyranose and less than 20%  $\beta$ -(1,4)-2-acetamido-d-glucopyranose. Chitosan and its derivatives are useful molecules for medicinal, food, agricultural, and wastewater treatment because of their biodegradability, biocompatibility, bioadhesion, and nontoxicity. The antimicrobial action of chitosan is fundamentally influenced by chitosan type, polymerization degree, natural nutritional constituency, host, nutrient or chemical composition of the substrates or both, and ambient factors, which include temperature, pH, and oxidative stress (e.g., substrate water activity, moisture or both). Furthermore, chitosan has a novel application in the form of edible biopolymer-based films for bioactive

substances to enhance the shelf life of fish due to their capacity to delay oxygen, moisture, solute transport, and odors. Chitosan has been reported in recent years to be employed as a bioactive film in food, specifically for the preservation of fish.

### Chitosan treatment and Mechanisms of action

Spoilage occurs when fish undergoes any alteration from its original condition that alters its aroma, flavor, visual appearance, or textural quality. In general, there are three distinct processes that lead to fish spoilage: There are three types of spoiling: (i) autolytic deterioration, (ii) oxidative spoilage, and (iii) microbiological spoilage. The commercialization of fisheries products requires novel approaches to packaging as well as new technologies. In recent years, many different active packaging technologies have been created to extend the life of products and improve their safety. The benefits of these materials include their biodegradability, edibility, biocompatibility, and aesthetics, as well as their barrier qualities against oxygen and physical stresses (Dehghani et al., 2018). Chitosan coatings have been shown to improve the chemical quality of fresh fish and fish fillets, hence extending their shelf life (Table 1). Products made from Atlantic salmon coated with chitosan at a concentration of 1.5 percent (w/v) were shown to be superior in terms of color retention and microbiological contamination control when frozen and thawed. Catfish fillets treated with a chitosan solution made by mixing 0.5% chitosan with 1% acetic acid solution had an extended shelf life of 8 days. Moreover, it was discovered that chitosan coatings of 2%, 0.5 %, and 1.0 % on fish fillets significantly reduced lipid and protein oxidation. There was a considerable decrease in the numbers of *Shewanella putrefaciens*, *Pseudomonas fluorescens*, and psychrotrophic and mesophilic bacteria after coating the rainbow trout with a lactoperoxidase system (LPOS). Trout fillets treated with coatings were found to have a 4-day longer shelf life than their uncoated counterparts. Furthermore, the TVB-N and pH values of the *Nemipterus japonicus* fillet were improved in comparison to untreated samples, and the shelf-life of the *N. japonicus* fillet was extended by approximately >10 days.

Chitosan has been shown to have antibacterial activity against a wide variety of bacteria, both gram-positive and gram-negative. The mechanism of action of chitosan involves either a change in the cell envelope or a disturbance of the integrity of the cytoplasmic membrane. Chitosan only engages in antimicrobial activity when its pH is between 6.2 and 7, and when it is used in food. It can be dissolved in 1-2% acetic acid concentration, or it can be used in packaging films made of chitosan. Chitosan is soluble only in acidic circumstances, therefore its antibacterial efficacy depends on a variety of parameters outside just pH, such as its molecular weight, degree of deacetylation, and degree of polymerization. Positively charged chitosan has a greater density, and this increases its electrostatic interaction with the cell surface, which in turn increases its antibacterial activity (Fig. 1). Chitosan may interact with molecules on the surface of microbes, cause the suppression of mRNA transcription. Chitosan can't enter the cytoplasm, so we don't know how it binds to DNA; it might also cross the bacterial barrier and disrupt it, but that's not apparent either (Ma et al., 2017). However, chitosan is too big to penetrate the cell membrane and engage in direct interactions due to its size. One possible method by which chitosan modifies cell membrane composition is its polycationic character. Since many microorganisms have negatively charged surface components and chitosan contains amine groups ( $\text{NH}_3^+$ ) of glucosamine, the interaction between these compounds causes extensive alteration of the cell surface, which in turn causes leakage of intracellular substances and, ultimately, cell death. Lipopolysaccharide and teichoic acid found in gram-positive and -negative bacteria play a crucial role in associating chitosan with cell membranes, altering, destabilizing, and ultimately disrupting cell wall dynamics.

Once released from the cell of fungal infections by plant host hydrolytic enzymes, chitosan has been hypothesized to reach into the nuclei and interfere with RNA and protein synthesis. The interaction between chitosan and the cell of the microorganism led to opportunistic fungal infection with significant swelling and cell wall lysis. Chitosan's powerful hydrogen-donating capacity makes it a potent antioxidant for extending the shelf life of food. Chitosan's antioxidant properties are enhanced by the presence of oxidation byproducts such as reactive oxygen species (ROS), superoxide anion radicals, hydroxyl radicals, and hydrogen peroxide. However, chitosan's antioxidant properties can also be attributed to its low molecular weight and a high degree of quaternization. Antioxidant experiments have been conducted on chitosan, and they have found that it is effective at preventing the oxidation of lipids such as phosphatidylcholine and linoleate liposomes (Fig. 2). The high chelating characteristic is useful as a food supplement of chitosan from crab shells with various degree of deacetylation demonstrated higher scavenging activity. Since chitosan significantly reduced lipid oxidation after

cooking, it may become more widely used in response to the growing demand for synthetic antioxidants-free marine.

## CONCLUSION

The food industry and scientists have been working to find natural products that can be used to preserve fish and fisheries products in response to consumer demand for all-natural ingredients. Many undiscovered unique natural products are possibly still waiting to be discovered. Natural food preservatives such as chitosan and essential oils (EOs) were among the topics covered in this review because of their usefulness in extending the storage life of fisheries products (Hossain et al., 2021). There is a wide variation in the effectiveness of natural preservatives at preventing the growth of spoilage microorganisms and slowing down specific enzymatic activities that contribute to deterioration. Nevertheless, some natural preservatives, including chitosan and essential oils, have been demonstrated to be more effective than chemical additives in getting rid of health hazards to human health. It's unfortunate that natural preservatives are so scarce in the marketplace despite their many applications (Hossain et al., 2021).

Traditional extraction methods are used to create this preservative from a wide variety of plants and organisms, but these processes are expensive, difficult to reproduce and yield uneven extraction rates when tested in the lab. We know surprisingly little about their massive-scale processing. The study of industrial extraction of these compounds is therefore warranted. It has been shown that chitosan can suppress lipid oxidation, decrease microbial growth, and enhance the sensory qualities of fish products (Hossain et al., 2021). It is still being researched whether chitosan can be combined with other natural ingredients to achieve greater effects than those of the individual preservatives alone (synergistic effects). More research is needed to find ways to mitigate the mildly undesirable side effects of natural preservatives such as darkening and off-putting odor. It is important to think about issues including uneven coating, prolonged draining, and flavor shifts when deciding to use preservatives. Finally, all-natural preservatives should be examined in the lab for their bacterial community, indigenous enzyme kinetics, and potential lipid oxidation before being used in the industry.

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