

The Research Progress of Preservatives against Mildew and Corrosion in Aquatic

DOI: 10.25177/JFST.5.1.RA.10626

Review

Accepted Date: 16th Mar 2020; Published Date: 19th Mar 2020

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CITATION

Zeng Yayun, Shang Zhuang zhuang, Zhang Rui, Wang Run Lian, Cheng Weng Jie, Du Hui, Liao Yan, Zhang HongLian, The Research Progress of Preservatives against Mildew and Corrosion in Aquatic (2020) Journal of Food Science & Technology 5(1) pp:40-48

ABSTRACT

At present, aquatic dried products are severely corrupted and moldy. Anticorrosive pollution has always been a hot issue in the research of dried products. Among them, Penicillium, Aspergillus, Shewanella, and Pseudomonas are the dominant species of dried meat products. At present, there are many types of research on chemical antifungals of dry products, but natural biological preservatives have not been widely used due to high prices, narrow antibacterial spectrum, and inconvenience in the application. Because the preservation of aquatic dry products should not only maintain its freshness, but also its nutritional value. It is of great significance to study safe and efficient biological preservatives. The article summarizes the effects, advantages, and disadvantages of various types of biological preservatives on the anti-mildew and anti-corrosion of aquatic dry products.

Keywords: biological preservatives, dried aquatic products, antiseptic and mildew

1. INTRODUCTION

Chemical preservatives, such as synthetic phenolic compounds, butylated hydroxyanisole (BHA), butylated hydroxytoluene (BHT), and dodecyl gallate (DG), which have been widely used as antioxidants and antimicrobials in fish and other seafood. However, chemical preservatives, due to their single component, will make organisms develop drug resistance and lose their inhibitory effect. Secondly, chemical preservatives can only inhibit the growth of mold, but cannot kill mold and remove existing mycotoxin in raw materials. Thirdly, although limited use is adopted, each chemical preservative has a certain safety index and time limit. Excessive use of time or excessive use can cause cumulative toxicity to human and livestock because of the enrichment effect. Natural biological preservatives have the advantages of being natural, efficient, low or non-toxic, and do not damage the original flavor of food. In the current trend of pursuing green, the search for anti-mildew agents from natural antibacterial substances has become the mainstream and hot spot in the research on food and agricultural products (Dai Xiangrong, 2007). This review provides the single substances that have been found at the present stage and have low toxicity and good anti-mildew effect, and the development of new safety and environmental protection compound anti-mildew agent.

2. Definition and mechanism of biological preservatives

The biological preservatives are a safe and non-toxic food preservative that is obtained directly or artificially by extraction from animals and plants or microorganisms. Rich in antibacterial activity of biological resources in the nature, substance, for example, the sources of antibacterial peptide (Lu Yang et al., 2020) are very wide range and its biological preservatives mechanism mainly include the following: firstly, the substances that have antibacterial activity in the biological preservative can inhibit or kill putrid bacteria and mold in seafood, reduce volatile base nitrogen value, to realize the purpose of maintaining freshness seafood, Secondly, strong antioxidant effect can effectively prevent

the oxidation of unsaturated fatty acids and other substances resulting in poor product quality; Thirdly, the activity of enzyme can be effectively inhibited to prolong the time of color change of aquatic products. Finally, a layer of biofilm can be formed to prevent the pollution of foreign microorganisms, to reduce the loss of water content of aquatic products, and to maintain the quality of aquatic products (Zeng Fengxian et al., 2018).

3. Plant biological preservatives

Biological preservatives of plant origin refer to pure natural preservatives obtained directly from the purification of plants. They are widely used in multiple areas. propolis, tea polyphenols in tea, etc., are mainly used as biological preservatives, and have apparent effects on food preservatives (Pezeshk, S et al., 2016). However, the plant extract extraction of plant preservatives has not been widely used due to its high technical requirements, complex operation, high extraction cost and uncertain active components (Maqsood, S et al., 2014). And in nature, there are many plants such as houttuynia, Tsao, onion, ginger, and garlic containing bactericidal groups. Zhao Ruihua et al. (2019) discovered use different solvents extraction Huang Wa, houttuynia, Tsao, onion, ginger and garlic plant active substances have increased inhibition effect to seven kinds of mold, so the plant extracts not only in the applications of biological preservatives, seek anti-fungal substances from plants there is also a huge potential development space.

3.1 Wild blueberry extract

In addition to sugar, organic acids, and vitamin C, wild blueberries also contain many other nutrients, such as organic germanium, organic selenium, arbutin, amino acids, acids, etc., which is incomparable to other plants. What's more, anthocyanin pigments (anthocyanin, cyanidin, and methyl anthocyanin) in wild blueberries are up to 3.3 ~ 33.8 mg/kg; anthocyanin is a kind of biological flavonoids, internationally recognized as the most effective natural antioxidant scavenging free radicals in the human body. Its bacteriostatic mechanism in-

cludes the destruction of the stability of the cytoplasmic membrane, the increase of the permeability of the cell membrane, the inhibition of the extracellular enzymes of bacteria, the direct effect on the metabolism of microorganisms and the deprivation of nutrients for microbial growth, etc.(Yao Yuemei et al.,2002: Cote et al.,2011). However, due to the poor taste of wild blueberries and the lack of people's understanding of their nutritional value, it has not been paid much attention. Jiang Wenjie et al. (2013)once studied that the extract of wild blueberry had a certain inhibitory effect on four pathogenic bacteria, including *Pseudomonas aeruginosa*, *Listeria monocytogenes*, *Staphylococcus aureus*, and *Vibrio parahaemolyticus*. According to the research of Olumide a. Odeyemi(2018) and Xu Defeng et al.,(2015) , *Shewanella*, *Pseudomonas* and *Vibrio parahaemolyticus* are the main bacteria in all kinds of shrimp, while *staphylococcus* has a relatively high reproduction rate at 0 °C, which is a significant control bacteria in freezing. Dried shrimps and cooked shrimps may have repeated spoilage bacteria, so dried prawn with wild blueberry extract may also have a preservative effect. Current studies have shown that blueberry juice combined with natural extracts can significantly inhibit the growth of *E. coli* at 20°C. At a low temperature of 4 ° c, the addition of natural extracts resulted in greater lethal levels of *e. coli* than the treatment without blueberry juice. With the prolonging of culture time, the bacteriostatic effect also increased. That said, combined with temperature and time controls, natural extracts can be used as a fence to prevent food spoilage and contamination(Ban Zhaojun et al.,2015). But raspberries ellagic acid extract of subjects mold *Aspergillus oryzae*, *Aspergillus Niger* and Yeast subjects showed weaker inhibition, probably because the crude extract contains the chemical composition of mold and yeast growth, has weakened the antibacterial active ingredients on the inhibitory effect of mold and yeast, if the bacteriostatic, isolation and purification of active ingredients or join other antifungal, it could enhance the inhibition effect of mold and yeast(Xin Xiulan et al.,2019).

3.2 Terminalia ferdinandiana Extracts

Terminalia ferdinandiana also known as Kakadu plum, which is a deciduous tree plant that grows in tropical Australian woodlands. It is rich in vitamin C and has higher levels of water-soluble and oil-soluble oxidant (Ying Xiaoman et al.,2016). Recent studies have shown that phenolic ellagic acid (EA) has received increasing attention for its nutritional and pharmacological potential as an antioxidant and antimicrobial agent. The native Australian Kakadu plum (*Terminalia Ferdinandiana*) is a rich source of this phytochemical(Williams et al.,2016), so Kakadu plum extract has powerful antibacterial and antifungal effects. David et al(2014).have disclosed a topical skin care composition containing Kakadu plum extract or Acai berry extract or a combination of the two. The composition may include a high oxygen free radical absorbability (ORAC) value and may be capable of inhibiting microorganisms through preservatives such as various antimicrobials and antifungal agents. Cooked shrimp usually requires a shelf life of 14 days, but in his experiments, Kakadu plum extended the shelf life of shrimp to 21 days. Matthew J(2019) used metabolomics fingerprint analysis to identify the diversity and relative richness of tannins, flavonoids and terpenoids in Kakadu plum, some of which have been reported to inhibit the growth of methicillin-resistant *Staphylococcus aureus* alone. In *Artemisia annua* and HDF toxicity tests, all extracts were non-toxic, further indicating their edible and medicinal potential. Mitchell Henry Wrigh et al(2019).studied the inhibitory effect of Kakadu plum extract on the growth of *Shewanella*, and found that leaf and fruit extract showed a strong inhibitory effect on the growth of all *Shewanella*, but the mechanism of its action was not clear. However, there are few studies on the application of Kakadu plum extract in the antiseptics of dried shrimp, so it can be known that Kakadu plum has great potential value in the antiseptics of dried shrimp.

3.3 Sodium alginate

Sodium alginate (SA), is a byproduct of extracting iodine and mannitol from the kelp of brown algae

or sargasso. Sodium alginate is a salt of alginate, which is a polymer of D-manuronic acid and L-guluronic acid and is produced by brown algae or sargasso(George et al.,2006). Because of its unique colloids, alginate has its advantages. Sodium alginate is anionic polymers, which can be combined with cationic by ionic bonds, for example combined with Ca^{2+} , Fe^{2+} plasma, the current through crosslinking with calcium to form strong gel or insoluble polymer (Zhang Jing et al.,2019;Rhim et al.,2004), has been used to enhance the antioxidant activity of sweet cherry(Diaz-Mula et al.,2011). Ren Banglai's study(Ren Banglai et al.,2013) showed that sodium alginate treatment delayed the weight loss and pepper of the fruit and had a better antiseptic effect on the pepper. A new self-repairing silane/alginate anticorrosive coating developed by Gao Xueli et al. can delay the corrosion of metal(Gao xueli et al.,2019). Although sodium alginate alone has obvious antiseptic effect, it still has limitations in some aspects. Xing Xiaoliang et al.(2019) also found that sodium alginate coating could effectively delay the decline of sensory quality, significantly improve the texture of color, and inhibit the growth of bacteria. However, at present, it is generally used in the application of fruits, vegetables and aquatic products, but not in the application of preservatives in dry products(Gao Cuili.,2013). Sodium alginate molecule contains a large number of -COOH groups, which dissociates to form a lot of -COO⁻ groups with non-polyanion behavior in aqueous solution, plus its relatively high viscosity, so it is a better drug carrier(Moebus et al.,2012). If some substances with particular properties, antibacterial property and hydrophilic property are added to sodium alginate to form composite film, and then the moisture content of aquatic products may be effectively maintained, wilting is delayed and the better appearance quality of dried products is maintained. For instance, Wu Di (2017)invented the use of sodium alginate and chitosan to prepare microsphere preservatives to adsorb glycyrrhizae and other preservatives, and the antiseptic components adsorb on the surface of microsphere could be well maintained.

4. Biopreservatives of animal origin

Animal-derived biological preservatives refer to natural preservatives obtained by purification from animals, such as chitosan, antimicrobial peptides and other active substances.

4.1 Antibacterial peptides

Antibacterial peptide is a kind of polypeptide animal encoded by plant cell specific genes, and induced by the external conditions, having killing effect on bacteria, fungi and viruses and other microorganisms(Xi Jin et al.,2019).Antimicrobial peptides are characterized by small molecular weight, strong alkalinity, thermal stability and broad spectrum resistance to exogenous organisms such as bacteria and mold, and also have systematic research to its action mechanism at present. After a series of studies, Dekker N believed that the mechanism of action of antimicrobial peptides was to break down the bacterial plasma membrane, leading to the formation of permeability difference between inside and outside the cell and resulting in cell lysis(Dekker N et al.,2001).Through more systematic studies, Fehlbaum P et al. confirmed that Thanatin ACTS on bacteria though inhibiting cellular respiration to kill microorganism (Fehlbaum et al.,1996).Because of its special mechanism of action, antimicrobial peptides have broad-spectrum bactericidal properties and have strong killing effect on gram-negative bacteria and positive bacteria, drug-resistant bacteria and molds. So Antimicrobial peptides have great potential to be used as raw materials for anti-mildew preservatives. However, due to the low content of antimicrobial peptides in animals and plants, it is difficult and costly to extract them directly, so there is no large-scale production of antimicrobial peptides in animals and plants at the present stage, and the amount of antimicrobial peptides produced is relatively small, which cannot meet the demand for extensive application in the medical field, let alone in other industries. However, with the development and progress of bioengineering technology in recent years, mass production of antimicrobial peptides has become possible.

At present, antimicrobial peptides are rarely used in the antiseptics of aquatic products. They are mainly used as a small peptide with good antiseptic effect and other biological preservatives to maintain the quality of aquatic products and extend the shelf life. Due to the excellent properties of antimicrobial peptides, there are also applications of antimicrobial peptides in the preservation of aquatic products. For example, the antimicrobial peptide APNT-6 is being developed by Sun Lijun from Guangdong Ocean University as a new preservative for aquatic products (Sun Lijun et al., 2011). It is believed that with more and more in-depth application research on antimicrobial peptides, antimicrobial peptides will be widely used in the field of antiseptics and preservation of aquatic products in the future.

4.2 Chitosan

Chitosan is the product of deacetylation of chitin, which is a kind of cationic polysaccharide. Chitin can be extracted from the carapace of shrimps, crabs and other crustaceans, and is a kind of natural polymer (Park et al., 2008; Wang Kang., 2017). A large number of studies have shown that chitosan has inhibitory effects on a variety of microorganisms such as bacteria and fungi, and its antimicrobial properties have attracted extensive attention and research. In recent years, the antimicrobial properties of chitosan have been playing a role in more and more fields (Coma et al., 2002; Xia Wenshui et al., 1998; Qin Caiqin et al., 2005; TSAI et al., 2004). Mohan (Mohan et al., 2011) etc. Through the study of chitosan to the surface coating of frozen Indian sardine, the formation of volatile alkali and the formation of oxidation products is significantly reduced, and the water retention, titer and structural properties of the samples significantly improved, it also extends sardines edible period for 3 ~ 5 days. Due to the good modularity of chitosan, making it difficult for the protein in the meat of aquatic products to be decomposed, thus the hardness and elasticity of aquatic products and meat products can also be improved. Water-soluble chitosan as an improved chitosan, its solubility is greatly improved on the basis of still having poly-

mer properties. Moreover, under the frozen storage condition of -18°C, tuna meat soaked with 15 g/L chitosan has the best anti-corrosion effect, and it can also improve the luster surface and the hardness of fish (Li Renwei et al., 2013). J. Gómez-Estaca et al. (2010) found that chitosan combined with essential oil has an anti-bacterial effect on the surface of cod and prolonged its shelf life well under refrigeration conditions.

At present, research on chitosan as a composite preservative is quite popular, because chitosan is a natural product, safe and non-toxic, has bactericidal and bacteriostatic effects in specific food, is resistant to high temperature and high pressure, and can be used as a broad spectrum of natural preservative. In addition, chitosan can also be used as a compound anti-mildew agent. Through experiments, Wang Kang proved that chitosan nanometer silver compound anti-mildew agent can effectively prevent mildew and corrosion on animal specimens (Wang Kang., 2017). Chouljenko et al. (2016) found that after 120 days of storage, compared with the control group, shrimp treated with water-soluble chitosan had lower aerobic plate number, yeast number, mold number and lipid oxidation rate, and no significant changes in color, texture and moisture content of shrimp during refrigeration. At present, there is no unified understanding of the bacteriostatic mechanism of chitosan (Liu Hui et al., 2004; Lim et al., 2004), but the concentration of chitosan also has a certain effect on the bacteriostatic property, and is not the higher the concentration, the better the bacteriostatic effect. Studies have shown that chitosan can only be dissolved in acidic solution and is insoluble in water, which makes the use of chitosan as a biological preservative limited. Therefore, at present, chitosan is mostly used in the use of composite preservatives, and there are more researches on fish antiseptics, while the researches and applications of shrimp and other aquatic products in composite antimildew agents are less.

5. Biopreservatives of microbial origin

Microbial biological preservatives are preservative microorganisms that produce bacteriostatic substances to inhibit the growth of putrid bacteria, such as natamycin etc. natamycin is an active cyclic tetracene compound produced by *Streptomyces natalis*, which is a good fungal inhibitor and is mostly used in food surface antiseptics (Lu Jian et al., 2005; Li Bo et al., 2011).

At present, dried aquatic products are seriously mildew, and anti-mildew pollution has been a popular spot in the research of dried products, among which *penicillium* and *aspergillus* are the dominant strains of dried meat products. In the article of Yan Yongzhen et al. (2010), the antifungal mechanism of natamycin was explained. It is through the combination of ergosterol on the membrane of the fungus that causes the membrane distortion and causes the exudation of cell contents to achieve the effect of inhibiting the growth of or killing the fungus. Zhang Xuan et al. (2013) showed that natamycin showed very significant inhibitory effect on molds and yeast, and its minimum inhibitory concentration was 1 mg/L. Some experimental results showed that (Tian Qiong et al., 2002), the majority of molds were inhibited at the concentration of natamycin 0.5 ~ 6 PPM, very few strains were inhibited at the concentration of natamycin 10 ~ 25 PPM, and most yeasts were inhibited at the concentration of natamycin 1.0 ~ 5.0 PPM. Huang Wei et al. (2007) also found that glutinous rice snacks were preserved at room temperature (25°C), with a humectant content of 0.6% ~ 0.8%, and 10 ~ 25 mg/kg of natamycin could significantly inhibit the growth of mold and yeast. Natamycin, when added in the right amount, will not only keep original flavor of the product, but also prevent food spoilage caused by the fungus, thus extending the shelf life. Natamycin is widely used, highly efficient, antibacterial for a long time, and will not be absorbed by the digestive tract of the human body, so it is a natural and safe food preservative, which is usually suitable for antiseptic and mildew on the surface of food, but its production cost is high. and the bacteriostatic property of natamycin

is easily affected by high temperature, so it is not suitable to be added before high temperature sterilization. When the concentration of natamycin was lower than 12 mg/L, and sterilized at 115 °C for 20 min, the inhibitory effect of yeast strain was lost (Yan Yongzhen et al., 2010), so more attention should be paid to the application of anti-mildew agent. At present, natamycin is rarely used in the antiseptic research of aquatic products, so there is a lot of potential research space in improving the ability of natamycin producing bacteria and its application in aquatic products.

At present, microbial biological preservatives are mainly used in mildew and antiseptics of dairy products, beverages, pork and beef, but rarely in aquatic products.

As a biological natural preservative, natamycin has great potential and development space in the research of anti-mildew and antiseptic inhibitors for aquatic products.

6. Compound biological preservative

Compound biological preservatives are based on the fence theory. According to the different characteristics of biological preservatives, the advantages of multiple biological preservatives can be exerted on one compound preservative, so as to achieve the effect of "1+1 > 2".

For example, nisin can effectively inhibit Gram-positive bacteria and has a long-term antiseptic effect, but the disadvantage is that it has a poor inhibitory effect on Gram-negative bacteria, while lysozyme happens to have an inhibitory effect on Gram-negative bacteria. the antiseptic effect is more significant in the initial antiseptic stage of aquatic products, combining the above characteristics of lysozyme and *Streptococcus lactis*. The combination of the two accelerates the penetration (depolarization) of the cell membrane of *Staphylococcus aureus*. This also reflects the action mechanism of nisin. Therefore, nisin and lysozyme showed a synergistic effect on Gram-positive bacteria because they strengthened the killing mecha-

nism of bacteria(Wilfred et al.,2000), and it was verified in many experiments that the effect of lysozyme / *Streptococcus lactis* compound biological preservative was better than that of single biological preservative. In addition, Li Hui et al.(2018) studied the changes of the quality characteristics of white shrimp soaked in natamycin / ϵ -polylysine compound preservatives during low temperature storage at 0 °C. It can also be found that the effect of compound preservatives is much better than that of ϵ -polylysine and natamycin single preservative. Otherwise, Xiao-lei HAO et al.(2017) found that chitosan is separately used can delay the physiological senescence of hairy acid berries, but it is difficult to inhibit pathogenic microorganisms (mainly fungi) during storage; as a fungal inhibitor, natamycin has low water-solubility and is difficult to use alone.

What's more, when selecting the main components of composite preservatives, we should also pay attention to the influence of various components on the main indexes. For example, tea polyphenols and chitosan have antibacterial complementarity. TVB-N is a very important chemical index of shrimp freshness. If chitosan is selected as one of the main components of composite preservatives, which is also the main factor affecting TVB-N. At the same time, the concentration and content proportion of chitosan are selected according to the different concentration of Chitosan film-forming property; Tea polyphenol is the secondary factor that affecting TVB-N and the total number of colonies. The higher the content of tea polyphenol is, the worse the sensory quality is. It may be that the yellow color of tea polyphenol affects the appearance of the food, while nisin is the main factor affecting product quality and microorganism, etc. (Xing Xiaoliang et al.,2019).Combined with response surface methodology (RSM) and TVB-N of dried aquatic products as response value, it can truly achieve the effect of "1 + 1 > 2" after each single natural anti-mildew active substance is compounded(Tian Feng et al.,2013).

In addition, the combination of hydroxyl group

and amino group in chitosan with water molecules can make it have high water-retention and moisture-retention, which is very suitable for the application of aquatic products to prevent water loss. Chitosan is more obvious in inhibiting the melanosis of crustaceans, which may be due to the fact that chitosan polymer can be used as a cationic surfactant, which can absorb the negatively charged oxidized polyphenolase derivatives and their substrates, and reduce the probability of the combination of the multi-component oxidase and the substrates. Therefore, chitosan has significant works in inhibiting the melanosis of shrimp, this characteristic can play an important role in the preservation of crustaceans. However, because it can only dissolve in some dilute acid solutions, and its solubility is easily affected by the pH cause its stability is poor. In addition, due to its poor oxidation resistance and stability, chitosan is rarely used for the preservatives alone, so it is necessary to find another corresponding substance to remedy its defects. Tingting et al(2013), Studied the anti-septic effect of grape seed extract and tea polyphenol as natural preservative combined with chitosan on the slices of *sciaenos ocellatus* during cold storage. The results showed that compared with the cold storage control group, the shelf life of the cold storage experimental group could be prolonged by 6-8 days. In a similar research, Cao (2009)developed a compound preservative without sulfite which solve the problems of shrimp Melanosis, sulfite abuse and short shelf life, and confirmed the preservation and anti-Melanosis effect of trachoma. According to the results of L9 (34) orthogonal test, the best combination of chitosan 0.5g / L, phytic acid 0.5g / L, EDTA 0.5g / L and 4 -HR 0.01g / L was determined. This is an effect that can't be compared by any single substance.

7. Conclusion

Compared with chemical preservatives, biological preservatives as natural preservatives have more environmentally friendly, efficient and safe advantages. Biological preservatives can be used in aquatic products, and according to many research experiments, they can inhibit the growth of spoil-

age bacteria and molds in aquatic products and prevent the occurrence of spoilage molds. Through the extensive study on the fluctuation of various biological preservatives in aquatic products, such as base nitrogen, total number of bacteria, weight loss rate and other related indexes, it is found that at present, many active substances basically have antibacterial and antiseptic effects, and to a certain extent have reached the purpose of product anti-sepsis and prolonged shelf life. In addition, the current study only for a single anti-corrosive effect have been relatively few, most of which are on the compound biological preservative, Nowadays, chitosan has become a popular material for the preparation of compound preservatives. Most of the studies show that chitosan compounded with other active substances have good effect on the antiseptis of aquatic products, such as plant-derived biological preservative tea polyphenols. It may be that fish has a lower purchase price and a longer spoilage period than shrimp and crab. At present, there are more biological preservatives for fish preservatives, while there are fewer biological preservatives for shrimp and crab preservatives. In addition, preservatives are mainly used on fresh or ready-to-eat aquatic products in the market, while there are few preservatives specially used for aquatic dried products. However, there are some phenomena that aquatic dried products are corrupted and spoiled due to mold and spoilage bacteria. Therefore, the research and development of biological preservatives for aquatic dried products is more difficult and has more research and practical value. This review discusses the application of several natural biological preservatives in aquatic products and the advantages of natural compound preservatives, which provides a theoretical basis for the development of the preservatives for dried aquatic products.

Competing interests

The authors declare that they have no competing interests.

Acknowledgements

This research was supported by Industrial development special fund project of Shenzhen Dapeng New District (KY20180204)

Guangdong provincial innovation and entrepreneurship training program for college students (CXXL2017039)

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