ХОЛОДИЛЬНІ ТА СУПУТНІ ТЕХНОЛОГІЇ

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Influence of Biologically Inert Protective Coating Based on Pectin Substances on PUFA Quality and Shelf-Life of Frozen Fish

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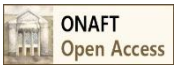
The influence of a biologically inert protective coating on the basis of low-esterified pectin substances (LEPS) on the qualitative indicators of frozen fish and its lipids is studied in this paper: organoleptic, physico-chemical, structural-mechanical and biochemical changes in fish of various methods of freezing during 240 days of cold storage. The limiting periods of storage of a silver carp (Hypophthalmichthys molitrix) of different ways of freezing are established. The prolongation of the shelf life of refrigeration and the higher quality indices of frozen fish with the use of a protective coating based on low-esterified pectin substances is due to the reduction of shrinkage and inhibition of hydrolytic decomposition and oxidative damage of lipids by preventing the contact of the surface of frozen fish with oxygen in the air. In addition, when freezing fish in a calcium chloride solution, the LEPS-based coatings exhibit barrier properties, preventing the diffusion of calcium ions into the muscle tissue of the product. Such a mechanism of influence on the duration of fish storage of various methods of freezing during prolonged cold storage allows to obtain frozen fish with high quality indices and to substantially reduce losses during refrigerated storage.

Keywords: *Protective coating, Low-esterified pectin, Freezing, Refrigerated storage, Lipids, PUFA, Hydrolytic decomposition, Oxidative damage, Hypophthalmichthys molitrix*



1. Introduction

Freezing is one of the most reliable and widely used methods of conservation, both onshore enterprises and on ships, which allows the maximum preservation of the nutritional and biological value of raw materials, flavor characteristics and significantly extend the storage time [1].

The quality of frozen fish and the period of cold storage depend on many factors and, first of all, on the degree of freshness of the raw material, the method of freezing, the temperature of cold storage, the degree of protection of the product from drying and oxidation of lipids, and also from the type of fish. It is known that slow air freezing degrades the quality of fish and shortens the duration of its cold storage. However, this method of freezing is universal and allows to freeze a large mass of fish simultaneously, which differs significantly in size-mass characteristics [1].

Studies of recent years have shown the economic and energy efficiency of freezing fish in cryogenic liquids, however, these methods require special equipment and large material costs. Today much attention is paid to the most accessible methods of freezing, for example, contact freezing in salt solutions (mainly sodium and calcium chlorides) [2, 3].

The processes of storing frozen fish are also improved in the direction of the use of glazing, packaging, and the application of various coatings. In the process of refrigeration, the fish undergoes a number of biochemical and physical changes associated with enzymatic and biochemical processes and the evaporation of part of the moisture contained in the muscle tissue. The main changes leading to a deterioration in the quality of the product are lipids oxidation and fish dehydration (shrinkage). One of the most common ways to prevent dehydration and oxidative deterioration of lipids in frozen fish is glazing, which is used for fish and fillet blocks or for large fish frozen in undivided form. The application of the glaze layer is carried out by immersion in water or watering the frozen product with water. Glaze is formed in the form of ice crust, which should evenly cover the surface of the block or fish. The amount of ice formed on the fish during glazing depends on the temperature of the block or the individual frozen fish, the duration of glazing, the number of dives and other factors. With a long dive and repetition of diving, the mass of the glaze on the fish can reach 10% of fish mass. However, in industrial conditions, the glaze weight is usually varies from 2 to 7%. The crust of ice formed in different places of the surface of the block or fish has a different thickness, which leads to different sublimation of water in different parts of the product. Water glazing is effective only for a short period of time, since glaze can be sublimated up to 1% monthly. Losses of glaze significantly increase, and protective properties deteriorate with temperature fluctuations during storage and transportation of frozen fish [1].

The use of only glazing with water only without packing the product into a polymer film and without the addition of antioxidants allows to obtain an insignificant protective effect only [1].

Recently, the researches are conducting in many countries aimed at creating biologically inert protective coatings formed directly on the product. It was found that using of acetoglycerides for glazing provides a better protective effect for frozen fish due to reducing shrinkage and fat oxidation than when glazed with water.

Works are carried out in two directions. In the first direction, types of protective films based on synthetic polymers are sought, coatings of which are formed in the cold conditions from aqueous dispersions of polymers. Before use, this coating should be removed from the surface by consumers. Works on the second direction are associated with the creation of edible films based on natural polymers. Work is underway to create protective coatings of two types - soluble in cold or hot water and insoluble, but non-harmful and easily absorbed by the human body.

Thus, not only the intensification of freezing processes, but also the use of inexpensive moisture-, vapor-, gas-tight protective coatings is a promising direction of improving the quality and prolonging the shelf life of frozen fish. The use of protective coatings based on natural biopolymers not only makes it possible to prevent a decrease in the quality of the product, but also creates a number of amenities for its culinary processing. The introduction of protective edible and inedible films applied directly to the product, is important for improving the methods of preserving the quality of frozen fish products. In this case, it is possible to combine individual methods (glazing with packaging in a film, cardboard packaging, etc.) to select the most economically feasible method [1].

2. Main part

The procedure for carrying out the experiments was as follows: freezing was carried out by air and by contact brine process with preliminary deposition of a protective coating on the surface of fish. As a biologically inert protective coating, a film based on a natural biopolymer - low esterified pectin was used [2-4]. The applied protective coating does not affect the color, smell and taste of the product, it can be easily removed from the surface of the frozen fish during defrosting.

Control samples were the fish of air and brine freezing without applying a protective coating. The freezing temperature is minus 25°C, the final temperature in the fish body is minus 18°C. After freezing, the fish was packed in cardboard boxes and stored at minus 18°C for 240 days. Determination of changes in the quality of fish was carried out every 30 days of storage after thawing in water at a temperature of 20 ± 2 ° C to a temperature in the product 0 ° C at a fish-water ratio of 1: 3.

It has been established that samples of fish frozen in calcium chloride solution using a protective coating on the basis of LEPS have received the highest quality rating for organoleptic parameters at all duration of cold storage (Fig. 1).

The highest ball score for organoleptic characteristics was obtained by samples of fish frozen with using a protective coating based on LEPS with all methods of freezing and all duration of cold storage.

With prolonged refrigerated storage of fish in a frozen form, there is a decrease in the mass of the product, i.e. shrinkage. The amount of shrinkage depends on a variety of factors, such as the type, condition and size of the product, the kind of packaging, the way of packing and the location of the product in the refrigerator.

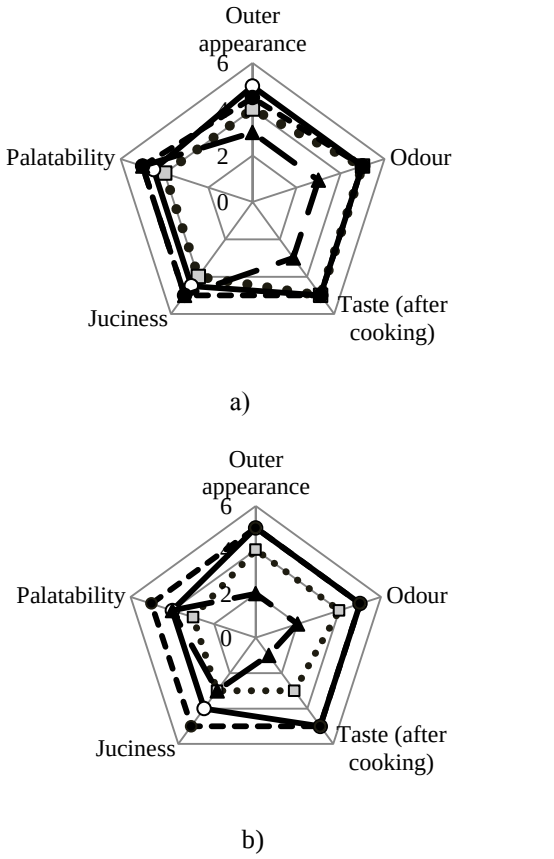


Figure 1 – Organoleptic evaluation of silver carp of brine and air freezing: a) after 180 days of cold storage; b) after 240 days of cold storage

The amount of shrinkage during refrigeration storage is also significantly affected by the freezing method and the temperature at which the freezing process is carried out. As studies have shown, the amount of shrinkage is significantly affected by the method of freezing, and the dependence is found at all times of cold storage.

The lowest losses in refrigerated storage for 240 days are observed in samples of fish frozen in a solution of calcium chloride with coating – 0.95% (Fig. 2b), while shrinkage of fish samples frozen in air reaches 5.2% (Fig. 2a).

The use of a biologically inert protective coating on the basis of LEPS allows to reduce the amount of shrinkage by 2.3 and 2.8% with air and brine freezing respectively for the same period of cold storage. The analysis of the obtained data showed that the shrinkage increases with the increase in the duration of the refrigerating storage with all freezing methods, the main part of the moisture (up to 70% of the evaporated moisture) sublimates in the first 120 days of storage.

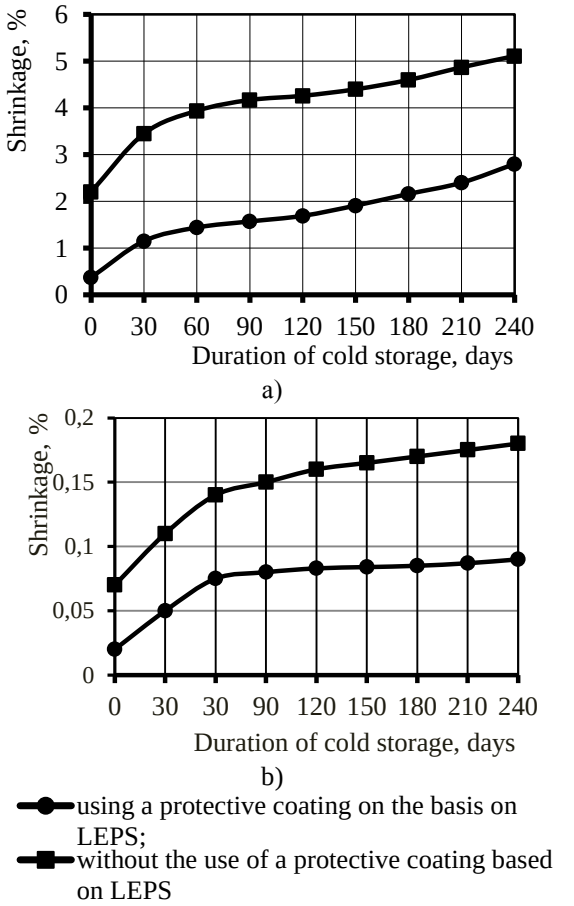


Figure 2 – Influence of the freezing method on the shrinkage of silver carp as a function of the duration of cold storage: a) air freezing; b) brine freezing

The data obtained are consistent with the organoleptic evaluation, as well as with the data on moisture determination in the muscle tissue of samples of silver carp frozen with different methods of freezing (Table 1).

Table 1 – Changes in the moisture content in muscle tissue of frozen silver carp

Duration of sstor-age, days	Method of freezing			
	air	brine	Using protective coating	
			air	brine
30	73,2	75,0	75,3	75,3
90	71,3	74,3	75,3	75,3
180	70,6	73,4	75,2	75,2
240	70,2	72,5	75,2	75,2

The initial moisture content in the muscle tissue of silver carp is 75.4%.

Such differences are explained by the fact that the pectin substances on the basis of which the coating is obtained have the ability to hold a large amount of moisture and, forming a film on the surface of the fish, reliably protects the samples from contact with oxygen in the process of refrigeration, thereby reducing the loss of moisture during the storage process.

Significant reduction in mass loss during storage of fish samples frozen in a solution of calcium chloride without the use of a protective coating compared with fish of air freezing is due to a minimum dryness of 0.045% during freezing, whereas in samples of fish in air freezing, the mass loss during freezing is more than 2, 0%.

Cold storage of frozen fish is accompanied by hydrolysis and oxidation of lipids of muscle tissue.

The greatest changes were noted in lipid samples of fish frozen in a solution of calcium chloride without the use of protective coating, as evidenced by an increase in the values of acid numbers, which is explained by the predominant hydrolysis of phospholipids (Fig. 3).

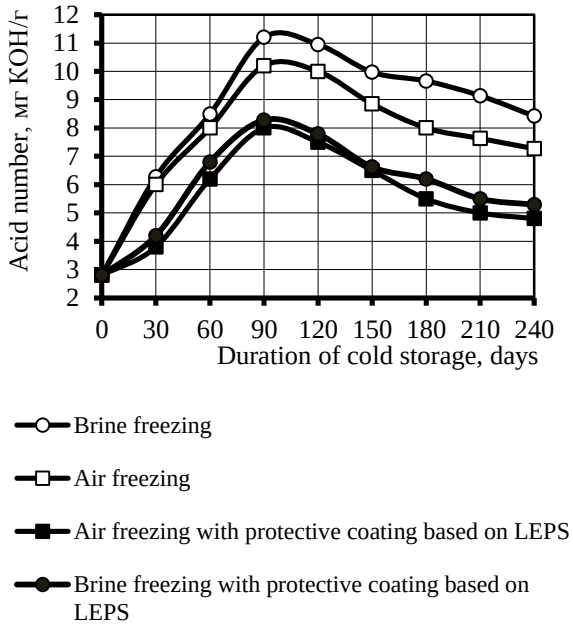


Figure 3 – Influence of the freezing method and the duration of cold storage on the accumulation of free fatty acids in the silver carp muscle tissue

The initial value of the acid number of silver carp lipids was about 2.8 mg KOH / 1 g of fat, peroxide number - 0.0191% iodine / 100 g of fat, and aldehyde number 0.57 mg cinnamaldehyde / 100 g of fat.

The highest value of acid numbers is observed in lipids of silver carp frozen in calcium chloride solution without using a protective coating after 90 days of cold storage - 11.6 mg KOH / 1 g of fat, which is 1.3 mg KOH / 1 g of fat more than after freezing in the air. The use of a protective coating on the basis of LEPS for all methods of freezing makes it possible to reduce the values of the acid number by 26.7 and 21.2% in both air and brine freezing respectively.

It was found that the greatest changes were observed in lipids of silver carp frozen in calcium chloride solution without the use of protective coating, and the smallest - when freezing in calcium chloride solution using a protective coating based on LEPS 0.277 and 0.145% iodine/100 g of fat (fig. 4).

For samples frozen in air using a protective coating on the basis of LEPS, a reduction in the peroxide value was observed in comparison with the samples of air freezing without the use of a protective coating on average by 25.0% during the whole period of cold storage.

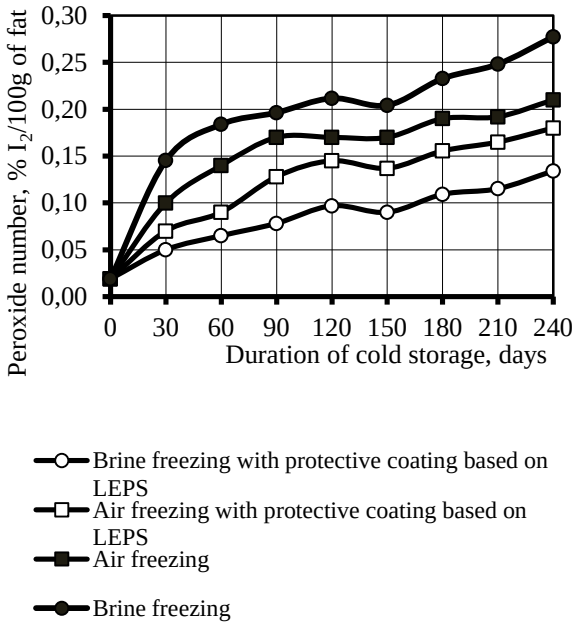


Figure 4 – Changes in the peroxide number of lipids of silver carp muscle tissue, depending on the duration of cold storage and the method of freezing

Values of aldehyde numbers steadily increased during the entire storage period and were 0.304, 0.40; 0.491; 0.627 mg cinnamaldehyde / 100 g of fat, respectively, when frozen in a solution of calcium chloride and in air using a protective coating based on LEPS, freezing in air and brine freezing without the use of a protective coating.

The nature of changes in the degree of oxidation and the stability of lipids to the development of oxidative damage processes are determined by the type of fish, as well as by the temperature and duration of refrigeration.

Analyzing the data obtained, it should be noted that the nature of changes of the lipid quality indices during refrigeration is similar at all stages, but a wave-like changes in values are observed. Thus, for example, the peroxide number of fish of all methods of freezing changes little during the first 60 days of storage, after reaching the end of 90 days storage reaches its maximum values, then there is a rapid decrease after 120 days of storage, and after 180 days of storage the value of the peroxide number increases again. The question of the existence of rhythmic vibrations in physical, chemical and biological processes is widely discussed in modern literature. In relation to frozen fish, one should speak of tissues in the transitional state, because the processes which are characteristic to a living organism continue for a long time and low temperatures do not stop them, but only reduce the rate of these reactions.

In addition, the wave-like changes in the content of various compounds can be explained both by the features of the interaction of various oxidation-reduction systems, and by the peculiarities of the course of the various chemical reactions that make up this system. The rate and direction of the reaction, all other conditions being equal, are determined by the concentration ratios of the reacting substances and the products formed. In view of the foregoing, it is quite natural that the reduced or oxidized forms of the constituent elements of different oxidation-reduction systems will be formed and accumulate unevenly.

Signs of oxidative damage to lipids are felt organoleptically at peroxide values greater than 0.19-0.20% iodine/100 g of fat, and aldehyde numbers more than 0.56 mg cinnamaldehyde / 100 g of fat.

The first signs of lipid oxidation were organoleptically detected in samples of brine frozen fish after storage at a temperature of minus 18 ° C for 120 days, for fish frozen in air using a protective coating on the basis of LEPS after 240 days; for samples of air freezing - after 210 days of storage and in fish frozen in a solution of calcium chloride using a protective coating on the basis of LEPS after 240 days of storage. The results of the organoleptic evaluation are consistent with the results of determination of peroxide and aldehyde numbers of lipids of silver carp.

Comparison of the peroxide and aldehyde numbers of the silver carp freezed with different methods of freezing shows that the degree of oxidation of lipids in muscle tissue of fish samples frozen in a calcium chloride solution is greater than when frozen in air or brine frozen using a protective coating based on LEPS.

This can be explained by the penetration of calcium ions into the muscle tissue of fish during freezing, leveling the beneficial effect of high-speed freezing. In addition, diffusing into muscle tissue, calcium ions activate the action of endogenous enzymes, lipases and lipoxygenases in particular, which promote acceleration of hydrolytic decomposition and oxidative damage to fats. The smallest changes associated with hydrolytic decomposition and oxidative deterioration undergo lipids of fish samples frozen in calcium chloride solution using a protective coating based on LEPS during the whole period of cold storage (Table 2).

This is apparently due to a decrease in the rate of hydrolysis of lipids as a result of minimal disruption of the histological structure due to the high rate of freezing and the protective properties of the coating, which prevents both diffusion of calcium ions during the freezing process and eliminates the contact of the surface of the fish sample with air oxygen during refrigeration.

Table 2 – Influence of the freezing method on the changes in muscle tissue lipids of silver carp after 240 days of cold storage

Index	Method of freezing			
	air	brine	Using protective coating	
			air	air
Acid number, mg KOH / 1g of fat	7,27	8,42	-	-
Peroxide number, % iodine / 100g of fat	0,21	0,28	0,145	0,134
Aldehyde number, mg cinnamaldehyde / 100 g of fat	0,49	0,63	0,40	0,304

The carried out researches have shown that the quality characteristics of a silver carp in the case of freezing in calcium chloride solution using a protective coating on the basis of LEPS is higher in comparison with the qualitative characteristics of fish of the traditional method of freezing,

as well as brine frozen without the use of protective coating at all duration of cold storage.

As a result the use of a protective coating during brine freezing inhibits the development of lipid oxidation and promotes better preservation of its nutritional value, since it slows the breakdown of biologically active polyunsaturated fatty acids.

The results of microbiological studies have shown that trends in changes in the total bacterial contamination of silver carp for 240 days of cold storage are similar. Microbial count of fish samples of all freezing methods is reduced by an average of 0.8% of the initial value. The decrease in the number of bacteria in the cold storage of silver carp is explained by the death of microorganisms at negative temperatures.

Conclusions

The conducted studies show that for such an unstable system as a fish, technologies that allow preserving aroma and flavor components, microstructure, hydrophilic properties, as well as reduce their bacterial contamination, the degree of denaturation and aggregation of proteins, the intensity of proteolytic transformations of proteins, hydrolytic decomposition and oxidation of lipids. The use of new biologically inert coatings on the basis of natural biopolymers applied directly from water solutions to products closely adhering to the surface and filling all cavities capable of significantly reducing shrinkage and inhibiting oxidative damage of lipids during refrigeration is a promising direction for improving the refrigerated storage of frozen fish.

The advantage of using a biologically inert protective coating on the basis of LEPS with all methods of freezing is obvious at all times of cold storage of a silver carp. Analysis of the experimental data showed that the highest quality was achieved in fish samples frozen using a protective coating based on LEPS.

The use of protective coatings allows to implement a highly effective method of contact brine freezing, to lengthen the shelf life of fish by reducing the shrinkage and inhibition of hydrolytic decomposition of lipids and oxidative damage of PUFA and reducing the loss of food raw materials, as well as further preventing the growth of the microflora of silver carp due to the bactericidal properties of pectin substances.

References

1. **Artyuhova S.A.** (2001) *Tehnologiya produktov iz gidrobiontov: uchebnik dlya vuzov*. Ed. Safronova T.M., Shenderyuk V.I. Moskow, Kolos, 496 p.
2. **Bezusov A.T., Palamarchuk G.S., Babkov M.I.** (2001) Vplyv sposobu zamorozhuvannia na yakist morozhenoi ryby. *Obladnannia ta tehnologii harchovyh vyrobnytstv*, iss. 6. vol. 1, 52-58.
3. **Bezusov A.T., Palamarchuk A.S., Titlov A.S., Manoli T.A.** (2003) Razrabotka tehnologii rassolnogo zamorazhivaniia ryby s ispolzovaniem zaschitnykh pokrytii. *Vestnik Mezhdunarodnoi Akademii Holoda*, No.3, 29-33.
4. **Stankevich G.M., Gerasim G.S.** (2012) Vybir ratsionalnykh parametriv udoskonalennia tehnologii ropnogo zamorozhuvannia ryby. *Food Sciense and Technology*, No. 4 (21), 97-100.

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Вплив біологічно інертного захисного покриття на основі низькоетерифікованих пектинових речовин на якість поліненасичених жирних кислот і терміни зберігання мороженої риби

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В роботі досліджується вплив біологічно інертного захисного покриття на основі низькоетерифікованих пектинових речовин (НПР) на якісні показники мороженої риби: органолептичні, фізико-хімічні, біохімічні та мікробіологічні зміни риби різних способів заморожування протягом 240 діб холодильного зберігання. Встановлено граничні терміни зберігання білого товстолобика різних способів заморожування. Пролонгування термінів холодильного зберігання і більш високі якісні показники мороженої риби при використанні захисного покриття на основі низькоетерифікованих пектинових речовин обумовлено зниженням усушки та гальмуванням гідролітичного розпаду і окислювального псування ліпідів за рахунок запобігання контакту поверхні мороженої риби з киснем повітря. Крім того, при заморожуванні риби в розчині хлориду кальцію, покриття на основі НПР проявляють бар'єрні властивості, що запобігає дифузії іонів кальцію в м'язову тканину продукту. Такий механізм впливу на тривалість зберігання риби різних способів заморожування протягом тривалого холодильного зберігання дозволяє отримувати морожену рибу з високими якісними показниками та істотно знизити втрати і подовжити терміни холодильного зберігання.

Ключові слова: *Захисне покриття, Низькоетерифікований пектин, Заморожування, Холодильне зберігання, Органолептичні показники, Усушка, Гідролітичний розпад, Окислювальне псування.*

Література

1. **Артюхова С.А.** Технология продуктов из гидробионтов: учебник для вузов / С.А. Артюхова [и др.]; под ред. Т.М. Сафроновой и В.И. Шендерюка. – Москва: Колос, 2001. – 496 с.

2. **Безусов А.Т.** Вплив способу заморожування на якість мороженої риби / А.Т. Безусов, Г.С. Паламарчук, М.І. Бабков // Обладнання та технології харчових виробництв. Темат. зб. наук. праць. – Донецьк: ДонДУЕТ, 2001. – Вип. 6., Т. 1. – С. 52-58.

3. **Безусов А.Т.** Разработка технологии рассольного замораживания рыбы с использованием защитных покрытий / А.Т. Безусов, А.С. Паламарчук, А.С. Титлов, Т.А. Маноли // Вестник Международной академии холода. – М., 2003. – №3. – С. 29 – 33.

4. **Станкевич Г.М.** Вибір раціональних параметрів удосконалення технології ропного заморожування риби / Г.М. Станкевич, Г.С. Герасим // Харчова наука і технологія. – 2012. – Вип. № 4 (21). – С. 97-100.

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