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INCREASING THE EFFICIENCY OF POULTRY AND FISH FREEZING USING PROTECTIVE PECTIN COATINGS

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Abstract. Maintaining the quality of poultry and pond fish as much as possible is important. Freezing poultry immediately after slaughter and fish after catching allows you to solve this problem. Freezing in liquid media leads to an increase in the speed of the process and, accordingly, a better preservation of the quality indicators of products. At the same time, in the process of freezing in brines containing calcium chloride, it leads to the diffusion of calcium ions into the muscle tissue of poultry or fish and the appearance of a bitter taste. To prevent salting out of raw materials, we have proposed the use of biologically inert coatings based on pectin.

The purpose of this study is to study the possibility of using low methoxylated pectin substances to improve product quality. The influence of a number of technological factors on the protective properties of the coating is studied. These factors include the concentration of pectin substances, the pH of the medium, the presence or absence of pretreatment of the surface of a poultry or fish carcass with citric acid. The strength of the coating and its barrier properties with respect to the diffusion of calcium ions have been studied. It is recommended to use a concentration of pectin substances of 3% with preliminary treatment of the carcass surface with 1% citric acid solution, followed by fixing the formed pectin film with 1% calcium chloride solution. Such processing allows to achieve a maximum concentration of calcium chloride in the muscle tissue of poultry or fish of no more than 0.5% – the value allowed by the standard.

It is shown that the use of freezing in brine leads to a significant decrease in the weight loss of the product during storage compared to freezing in air – three times. The use of a coating based on pectin can reduce weight loss by a factor of eight. The quality indicators of products are also much better preserved – water retention capacity, acid number of fat and peroxide value of fat. The organoleptic properties of poultry and fish processed according to the proposed technology are noticeably superior to those of raw materials frozen both in air and in brine without applying a protective coating.

Key words: poultry, pond fish, brine, freezing, pectin, coating

ПІДВИЩЕННЯ ЕФЕКТИВНОСТІ ЗАМОРОЖУВАННЯ ПТИЦІ ТА РИБИЗ ВИКОРИСТАННЯМ ЗАХИСНИХ ПОКРИТТІВ

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Анотація. Збереження якості сільськогосподарської птиці та риби в процесі переробки є актуальною проблемою. Цю проблему дозволяє вирішити максимально швидке заморожування сировини: птиці після забою, а риби – після вилову. Для збільшення швидкості процесу, а, отже, кращого збереження якісних показників продукції, доцільно використовувати заморожування у рідких середовищах. Оскільки ці середовища являють собою розчин хлористого кальцію, це призводить до дифузії іонів кальцію до м'язової тканини та появи гіркотого смаку.

Для запобігання просолюванню сировини нами запропоновано використовувати біологічно інертні покриття на основі пектину.

Метою даного дослідження є вивчення можливості використання низькометоксильованих пектинових речовин для підвищення якості продукції. Вивчено вплив ряду технологічних факторів на захисні

властивості покриття. Ці фактори включають концентрацію пектинових речовин, рН середовища, наявність або відсутність попередньої обробки поверхні тушок птиці або риби лимонною кислотою.

Вивчено вплив вказаних факторів на міцність покриття та його бар'єрні властивості по відношенню до дифузії іонів кальція. Рекомендується використовувати пектинові речовини концентрацією 3% з попередньою обробкою поверхні тушок 1% розчином лимонної кислоти та подальшою фіксацією пектинової плівки 1% розчином хлориду кальцію. Така обробка дозволяє запобігти накопиченню хлориду кальцію у м'язовій тканині птиці та риби вище 0,5% – значення, яке припустимо згідно стандарту.

Показано, що розсільне заморожування призводить до значного зниження втрат маси продуктів при зберіганні у порівнянні з повітряним заморожуванням – в три рази. Використання покриття на основі пектину дозволяє знизити втрати маси у вісім разів. Значимо краще зберігаються якісні показники продукції – водоутримуюча здатність, кислотне число жиру та перекісне число жиру. Органолептичними властивостями продукції, обробленої за запропонованою технологією, перевищує контрольні зразки.

Ключові слова: птиця, ставкова риба, розсіл, заморожування, пектин, покриття, водоутримуюча здатність, кислотне число жиру та перекісне число жиру

Introduction. Formulation of the problem. Currently, in Ukraine, as well as throughout the world, pond fish farming is becoming widespread [6]. Farming poultry, usually broiler chickens, are often raised at the same locations as freshwater fish. These farms are located at a considerable distance from the place of consumption of food products, therefore, the problem of maximum preservation of the quality of poultry and fish during storage and transportation is becoming increasingly important [5; 25]. The best way to preserve the quality of these raw materials is to freeze them [12; 13; 40; 44; 45]. At the same time, the higher the freezing rate, the slower the processes of oxidation and deterioration of the labile components of raw materials, the less the likelihood of the development of microorganisms, the better the organoleptic and technological properties are preserved [19; 28; 31; 43].

A high rate of freezing provides brine freezing in a solution of calcium chloride, which is due to a much higher coefficient of heat transfer from the object to the brine in comparison with air [2; 35]. However, there is a risk of diffusion of calcium chloride in the tissues of poultry or fish. This substance, although is beneficial for human's health, has a bitter taste, which can lead to a decrease in consumer value. Thus, the search for a coating that would prevent the diffusion of calcium salts into poultry or fish carcasses is becoming increasingly important [34].

Analysis of recent research and publications. Due to the highly efficient thermal process between the product and the liquid low-temperature medium, freezing of poultry and large fish carcasses in aqueous solutions of sodium and calcium chlorides provides a high freezing rate and the formation of a fine-crystalline structure in the tissues of the product, which allows better preservation of high quality [3; 38; 41]. High freezing speed allows to extend the shelf life of products by 1.5–2 times compared to the standard freezing speed [20; 26].

To prevent the penetration of salts from the brine into the muscle tissue, various coatings are used. Traditionally, to prevent salting of fish during brine freezing, packaging in plastic films is used [8, 4]. The product is wrapped in an impermeable film and then kept in a saline solution at a temperature of minus 35 °C, which allows for 30 minutes or less to bring the temperature in the center of the product to minus 18 °C [39]. A number of works have shown the economic and energy efficiency of the method for freezing poultry packed in a film in a calcium chloride solution [22; 48; 49].

However, then there is the problem of removing the inedible polymer film. The most promising is the use of films based on natural biopolymers, which are applied directly to a poultry carcass or fish. Such coatings allow not only to prevent the penetration of calcium salts into muscle tissue, but also to significantly reduce shrinkage and inhibit oxidative deterioration of lipids, thereby preserving the original properties of the product for a longer time. Films are obtained from natural compounds: agar, alginic acids, cellulose ethers (CMC, MC) and pectin substances [33; 37; 46].

Of particular interest is the use of a coating based on low methoxylated pectin substances. Such a film not only reduces shrinkage and the rate of oxidative deterioration of lipids both during storage and during freezing, but also prevents salting (diffusion of calcium ions) during brine freezing of the product [15; 18; 23].

The purpose of the research

The aim of this work is to improve the technology of freezing poultry and fish by using protective coatings based on low methoxylated pectin substances (LMPS).

To achieve this goal, it was necessary to solve the following tasks:

- to substantiate the advisability of using protective coatings based on LMPS;
- to study the protective properties and quality characteristics of coatings;
- to develop technological parameters for obtaining a protective coating;

- to study the physicochemical and organoleptic properties of poultry and fish frozen in a solution of calcium chloride using protective coatings based on LMPS;
- to develop a technological scheme for brine freezing of poultry and fish using protective coatings based on LMPS;
- to study the effect of the proposed freezing method on the change in quality characteristics and the duration of refrigerated storage of poultry and fish

Research materials and methods. In this work, specimens of grass carp and broiler chicken of the COBB-500 cross raised in the Odessa region were used. The grass carp (*Ctenopharyngodon idella*) is a large herbivorous species of the family *Cyprinidae* native to eastern Asia, with an original range from northern Vietnam to the Amur River on the China border. Historically it was cultivated in China for food, but was introduced in Europe and the United States for aquatic weed control, becoming the species of fish with the largest reported production in aquaculture globally, over five million tonnes per year [10]. A broiler is a chicken of *Gallus gallus domesticus*, that is bred and raised specifically for meat production. Broiler is used to refer specifically to younger chickens under 2 kg, as compared with the larger roasters.

In our work, we used both industrial pectin and an extract from apple pomace isolated by alkaline hydrolysis [17; 18].

In order to study the qualitative characteristics of raw materials, semi-finished products, auxiliary materials and finished products, modern conventional and special physical, chemical, biochemical, physicochemical, microbiological, mathematical and analytical methods were used with the use of modern devices and equipment [9; 21].

The barrier properties of the films were investigated in model experiments using a dialysis glass [14; 31].

Results of the research and their discussion. Of particular importance in the formation of a film is the degree of esterification (DE) of pectin substances. In the studies, the SE value was 35%, since a decrease in the DE below 35% leads to instant clot formation, disruption of homogeneity. In addition, with a further decrease in SE, the destruction of pectin substances and a decrease in molecular weight, on which the jelly-forming ability of pectin depends, is observed. An increase in the DE above 40% leads to a decrease in the strength of the film, and upon reaching more than 55%, no gel is formed [16; 27].

The barrier properties of films with a pectin substances (PS) concentration of 1–4% were investigated in model experiments using a dialysis glass.

It was found that a minimum of calcium penetrates when using coatings with a PS concentration of 3 and 4%, and the amount of diffusing calcium differs insignificantly. The tendency to gelation noticeably increases with a decrease in the pH of the system due to an increase in the hydrophilicity of the molecule [16; 47]. Therefore, when treating the contact surface of the dialysis glass with 1% citric acid solution, the amount of diffusing calcium was 3,6–4%.

Further investigation of the films revealed that, in addition to DE, the strength characteristics are influenced by the concentration of pectin substances and the pH of the medium (Fig. 1).

Treatment with citric acid significantly increases the strength of the coating (Fig. 2).

An increase in the strength of pectin coatings upon acidification with citric acid is explained by a higher calcium content and, accordingly, a more dense “crosslinking” of pectin molecules at the site of free carboxylic groups.

The higher calcium content in protective coatings with the use of citric acid is apparently explained by the ability of acid cations to knock out monovalent metal ions from bonds, at the place of which calcium is added [16; 47].

However, an increase in the concentration of calcium ions in the protective coating leads to a decrease in the cryoscopic temperature. It has been established that films with the addition of citric acid are characterized by a lower cryoscopic temperature, which is explained by the ability of acid cations to knock out monovalent metal ions from bonds, at the place of which calcium is added [16]. This correlates with the data on the saturation of the films.

The dependence of cryoscopic and cryohydrate temperatures on the concentration of pectin and calcium content has been established.

A decrease in cryoscopic temperature by 4–6 °C compared to pure pectin was noted [30; 46; 50]. This causes, on the one hand, greater strength due to calcium compounds and, on the other hand, increases the linear rate of crystal formation throughout the volume of the film, which provides a fine-crystalline structure during ice formation and its uniform distribution [1; 32; 42].

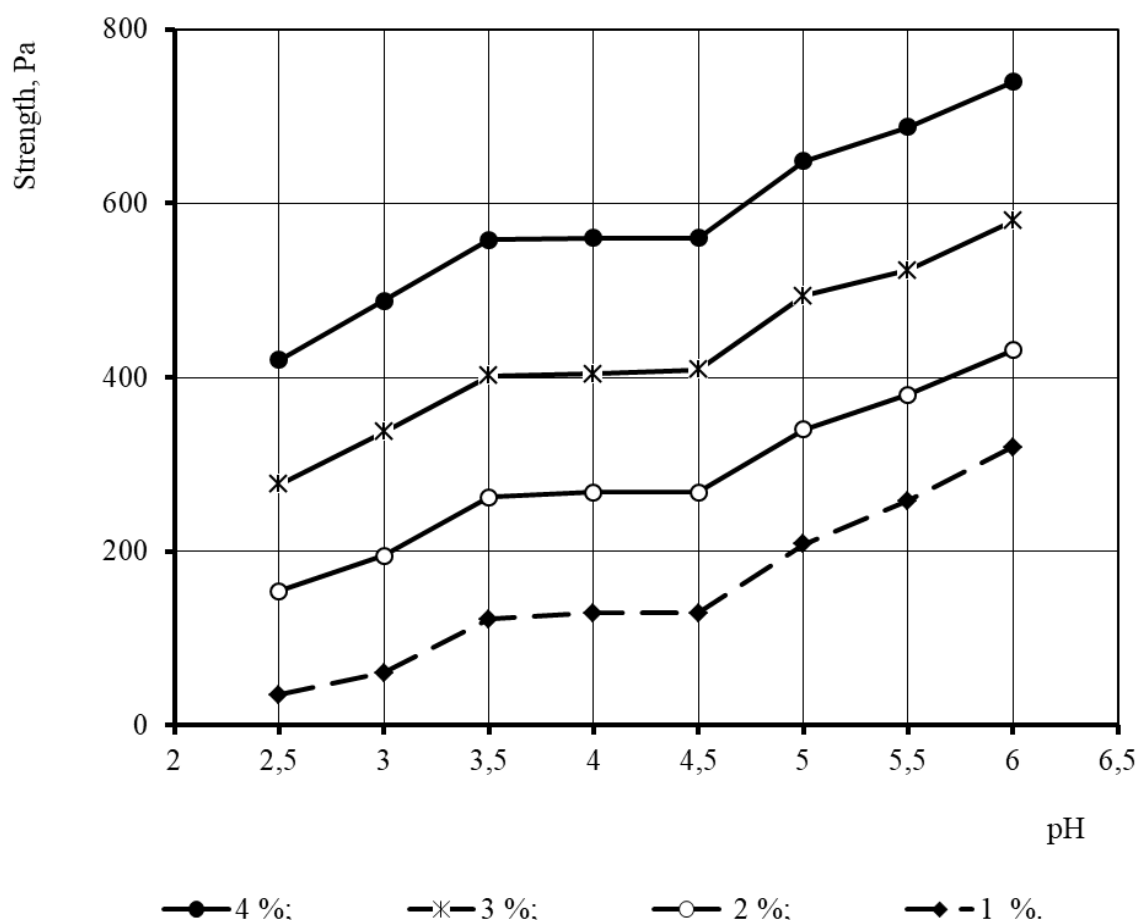


Figure 1 – Effect of pH on the strength of protective coatings

We also studied the behavior of protective coatings when applied directly to the surface of chicken and fish carcasses and the quality indicators of the product during storage [7; 11; 24; 29].

Freezing was carried out in a solution of calcium chloride (with the use of protective coatings and without coatings and in air. The density of the solution in the studies was 1250 kg / m^3 , the ratio of the amount of the product and the solution was 1:3, the temperature in all cases was maintained at minus 25°C . The frozen product was stored at minus 18°C for 8 months. The change in quality indicators was determined after storage (table 2).

During the study, it was found that the duration of broilers and grass carp freezing in a solution of calcium chloride ranged from 0,9 to 1,8 hours, which is 7–9 times less compared to the duration of freezing in air.

The freezing rate of products in a calcium chloride solution was 6–7 cm/hour, while in air it was 0,7–0,8 cm/hour. It has been shown that the application of a protective coating insignificantly affects the freezing rate and storage duration.

The results of the layer-by-layer determination of the mass fraction of calcium chloride showed that the greatest salting (when freezing the product without a protective coating) occurs in the first 20 minutes of freezing for fish and 25 minutes for broilers.

During this period, up to 80–90% of calcium penetrates into muscle tissue. The subsequent slowdown in salting is explained by the formation of ice crystals, which prevent further diffusion of calcium ions into muscle tissue [32; 42].

When frozen in a solution of calcium chloride using a protective pectin coating, the amount of diffusing calcium in the tissues of poultry and fish is reduced 5–6 times, respectively, compared to the uncoated product, and the use of citric acid allows to reduce the amount of diffusing calcium by another 3–4 times.

In a production environment, an important criterion for the effectiveness of the freezing process is product shrinkage. When frozen in a solution of calcium chloride, the shrinkage of poultry and fish is reduced 32–38 times compared to freezing in air. When using protective coatings, no shrinkage during freezing was observed (Table 1).

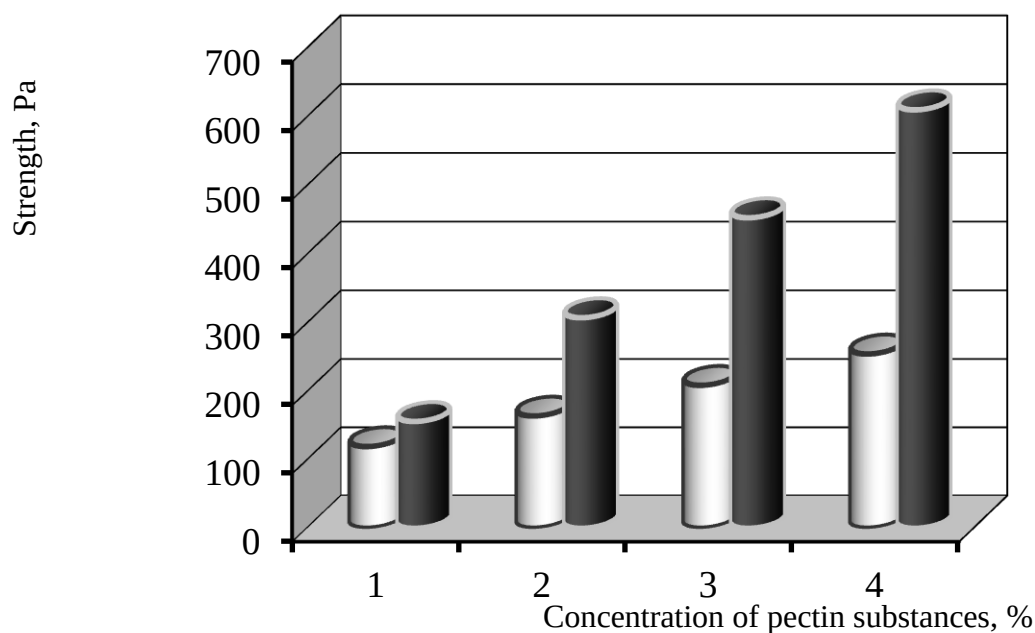


Fig. 2 – Influence of the concentration of pectin substances and the pH of the medium on the strength characteristics of the protective

■ without acid treatment; ■ with acid treatment

Figure 2 – Influence of concentration of pectin substances and the pH of the medium on the strenght characteristics of the protective coating

When stored for 8 months, the shrinkage of fish frozen in calcium chloride solution was 17 times lower than that of fish frozen in air.

An increase in storage time is accompanied by a decrease in water-holding capacity (WHC) and a shift in pH towards the alkaline side. The influence of the method of freezing on the WHC of muscle tissue is observed for all periods of refrigerated storage.

Table 1 – Influence of the method of freezing and protective coating on the shrinkage of poultry and fish

Index	Without the use of a protective coating		Using a protective coating	
	air freezing	brine freezing	air freezing	brine freezing
Poultry				
Before freezing, g	2245,2	2268,9	2275,1	3829
After freezing, g	2202,5	2227,1	2385,8	4069
Loss of weight, g	42,7	1,8	-	-
Loss of weight,%	1,9	0,043	-	-
Fish				
Before freezing, g	3589,3	4330,1	3525,7	3829,4
After freezing, g	3524,7	4328,4	3665,3	4069,2
Loss of weight, g	64,6	1,7	-	-
Loss of weight,%	1,8	0,039	-	-

A decrease in the WHC of products frozen in a solution of calcium chloride with the use of protective coatings can be explained by a slight decrease in the freezing rate.

To characterize the qualitative changes in the fish, a comparative assessment of the studied methods was carried out according to the following indicators: organoleptic assessment according to an 9-point system, water-holding capacity (WHC), peroxide and acid number of fat, shrinkage and calcium content (Table 2).

Samples frozen in a calcium chloride solution using a protective coating based on pectin substances had higher quality indicators and a higher organoleptic score. The presence of calcium ions in muscle tissue was

organoleptically not detected. Thus, the protective coating not only significantly slows down salting, but also lengthens the period of refrigerated storage by preventing shrinkage and inhibition of oxidative deterioration of lipids.

Technological research has led to the following **conclusions**:

- freezing in an aqueous solution of calcium chloride is the most effective way of preserving broilers and large fish species in order to maintain high quality for a long time;
- protective coatings based on pectin substances make it possible to control the diffusion of calcium ions into muscle tissue;
- the strength of protective coatings increases with a decrease in pH and an increase in the concentration of calcium ions in the protective coating;
- the use of protective coatings based on a 3% pectin solution with preliminary treatment of the product surface with a 1% solution of citric acid and subsequent fixation of the film with a 1% solution of calcium chloride allows achieving a minimum concentration of calcium ions during brine freezing, which is 0,5% – the value allowed by the standard 3 months.

Table 2 – Influence of the freezing method on the quality of frozen poultry and fish

Index	Fresh raw material	After freezing			Cold storage 3 months		
		I*	II	III	I	II	III
Poultry							
Loss of weight,%	-	1,9	-	-	3,7	1,4	0,16
WHS,%	71,8	56,3	62,9	67,2	50,4	59,6	65,1
Acid number, mg/g	0,4	1,3	0,6	0,4	2,2	1,4	0,8
Peroxide number, mg I ₂ /100 g	0,01	0,03	0,02	0,01	0,06	0,04	0,02
Organoleptic assessment, points	8,5	7,4	8,2	8,3	6,5	7,8	8,1
Fish							
Loss of weight,%	-	1,8	-	-	3,3	1,1	0,12
WHS,%	68,5	47,9	61,7	65,6	39,2	57,7	63,3
Acid number, mg/g	0,7	2,2	1,7	1,3	4,2	3,5	2,1
Peroxide number, mg I ₂ /100 g	0,02	0,04	0,03	0,02	0,08	0,06	0,04
Organoleptic assessment, points	18	17	16	17,8	16,5	15,5	17,6

*Note: I – air freezing; II – brine freezing; III – brine freezing using a protective coating

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