

ELECTROCHEMICAL METHODS FOR THE PRESERVATION OF CRUSTACEOUS WASTES FROM SHELLFISH PROCESSING

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Abstract

The developed environmentally safe electrochemical methods for the preservation of crustaceous wastes from shellfish processing can be used both at sea and ashore. This technology makes possible long-term storage of crustaceous waste at unnormalized positive temperatures with simultaneous shell deproteinization. Due to the mild exposure conditions the electrochemical methods allow to preserve the high quality of valuable components (chitin, proteins, lipids, carotinoids and others) and to carry out comprehensive processing. The preservation of expired crustaceous waste with increased original bacterial content was found possible.

Key words: *preservation of crustaceous wastes, crustaceans, electrolyzer, cathode fraction, anode fraction.*

1. Introduction

During processing of sea (crab, shrimp, krill) and freshwater (crawfish, gammarus) crustaceous shellfish for food purposes the yield of wastes can vary from 50 to 80%. The valuable biochemical composition of the crustaceous wastes (CW) makes it possible to manufacture a wide range of value-added products [1].

Besides polysaccharide chitin (up to 25% on the dry basis) the CW contain:

- protein (up to 50%), containing all the essential amino acids;
- lipids (up to 15%), containing more than 30% of phospholipids and consisting mostly out of polyunsaturated fatty acids (PNFA) (with PNFA/SFA ratio 3:1);
- astaxanthin carotenoid colourant in the concentration from 80 to 130 mg per g of crab and shrimp CW respectively.
- Enzymes, hormones and other bioactive substances.

Unfortunately until now the majority of CW is practically not used at all – valuable substances being lost in vein and aquatic area and shore-line polluted by dumped wastes which in general aggravate the pollution load on the environment.

The high enzyme activity of CW, especially elevated by the presence of hepatopancreas in the cephalothorax of shellfish, may cause certain difficulties in its preservation. The action of proteolytic, chitinolytic and lipolytic enzymes limits the time period for collection and storage of CW yielded from crab and shrimp processing by 6 hours and from krill and gammarus by 2 hours at standard ambient conditions. The following well known methods as washing in sea water, cooking in water or in water with sodium chloride and sulphuric acid with further centrifugal separation and others [2] are used to reduce enzyme activity.

Freezing and storage in blocks at temperatures not higher than -18 °C within 12 months or drying with further storage in paper bags inside dry and properly ventilated premises represent the most widely used methods of CW preservation. The both methods are extremely energy consuming. Besides, drying of CW deteriorates the quality of its components, in particular, chitin molecular weight decreases and lipids and proteins oxidize, and freezing of CW requires large refrigeration facilities.

The preservation of CW can be performed by chemical reagents and alkali, acid or sodium chloride are mostly used for the purpose. The method has certain advantages: possibility to store CW on deck at ambient conditions for more than one year, low energy consumption, besides, not only preservation of CW but its deproteinization and demineralization take place during transportation under alkali or acid action. As a result, not merely CW but a semi-finished product ready to obtain chitin according to facilitated method is delivered a shore-based factory.

The chemical preservation method can be used for the preservation of CW from crabs, large shrimp and other shellfish being caught and processed by small-scale fishing vessels having a raw material flow limited by several tones per hour.

In case of crustaceous wastes processing onboard Antaktida type krill-catching factories with capacity of 100 - 120 tones of krill per day and 50 - 65 tones of CW per day the chemical reagent method can be only a supplement to the traditional drying and freezing methods.

The shortcomings of the chemical preservation method are as follows: limited productive capacity – several tones per day, aggressive chemical liquids kept onboard the vessel, protein quality deterioration due to destruction and β -elimination reactions and amini-acid racemization as affected by reasonably concentrated (2,5%) chemical agents.

Obviously, the development of a production method helping to store CW and to maintain quality of its components would make it possible to arrange comprehensive, low-waste processing of CW and to obtain chitin, protein concentrate or isolate, phospholipids, PNFA, astaxanthin and other products with high added value as well as to increase the profitability of crustaceous shellfish catching and processing in general.

The purpose of the research is to develop reagent-free methods for the preservation and storage of crustaceous wastes at normal conditions making possible and reasonable their complex processing at shore ensuring good quality of all the CW components, determination of storage life and quality of CW during and after its storage. The possibility to preserve “overaged” crustaceous raw material (OCRM) with enhanced bacterization of 1×10^6 - 1×10^7 CFU/g was a separate task of the research.

2. Materials and methods

The method foresees the OCRM treatment with low-mineralized (1 - 2%) water solutions of neutral salts treated unipolarly in membrane electrolyzers (by catolytes or anolytes).

The idea of using electrochemically obtained solutions for OCRM preservation is based on the experimentally shown [3] possibility of bio-based raw material preservation at relatively lower than used in traditional production methods concentrations (0.1 - 0.2%) of electrochemically synthesized OH^- or H^+ ions that ensure the high quality life of chitin, proteins and other easily oxidized nutrients. The high quality indicators stem from the expressed recovery properties of catolytes.

The obvious advantage of the method is the absence of relatively concentrated (10%) alkali and acid solutions on board. The extractive power of catolytes, similar to the use of alkali, makes it possible to deproteinize crustateous raw material during its transportation and to deliver a semi-finished product for obtaining chitin – deproteinized carapace - to a shore-based factory.

Recent numerous scientific publications describe in detail disinfecting, sterilizing and deterring properties of neutral and acid type anolytes, neutral and alkali catolytes, the safety of which has been proved by toxicity and safe standard studies. According to classification they belong to toxicity class IV. Such plants as STEL, IZUMRUD, ENOSTERIL, REDOX,

STERILOX, OXI-1A have been specially designed and are widely used to generate the above mentioned electrolytes. Electrolyzers with various capacities have been widely used onboard vessels to purify pot water as well as drain and bilge waters. One of the examples of such equipment is H6-ИЭУ-1 plant having capacity of 3 - 6 m³ per hour and consuming 5 - 6 kW per hour. The review of publications shows that anolytes possess bactericidal properties due to acid pH and presence of oxidizers. However, while contacting with proteins their preservation capacities have short-term effect, besides, they rapidly lose their acid properties when interacting with highly mineralized CW [4].

During the development of CW preservation production methods the possibility to use acid and alkali anolyte, alkali catolyte, neutral anolyte obtained in membrane-free electrolyzer as well as raw material treatment directly inside the electrolyzer was studied. Different ratios of CW/preserving agent and electrolyte compositions were used in experiments. The best result was achieved in case of catolyte preservation according to the process operational diagram shown in **Figure 1**.

In the course of CW preservation methods development the possibility of using acid and alkali anolyte, alkali catolyte prepared in a membrane electrolyzer, and of neutral anolyte prepared in membrane-free electrolyzer. Different ratios of CW/preserving agent and electrolyte compositions were used in experiments. The raw material was treated not only with catolyte (**Figure 2**), but with anolyte and catolyte successively (**Figure 3**) with the purpose to study the possibility of reducing its microbial number.

3. Results and discussions

Our earlier studies proved that catolytes also possess preserving properties and are able to provide satisfactory storage life at normal conditions within three and more months for protein solutions produced out of wastes from fish and gammarus processing [5], hence our interest to find out if it could be possible to use catolytes for CW preservation. Another important task was to provide the deproteinization of CW during its storage and to obtain

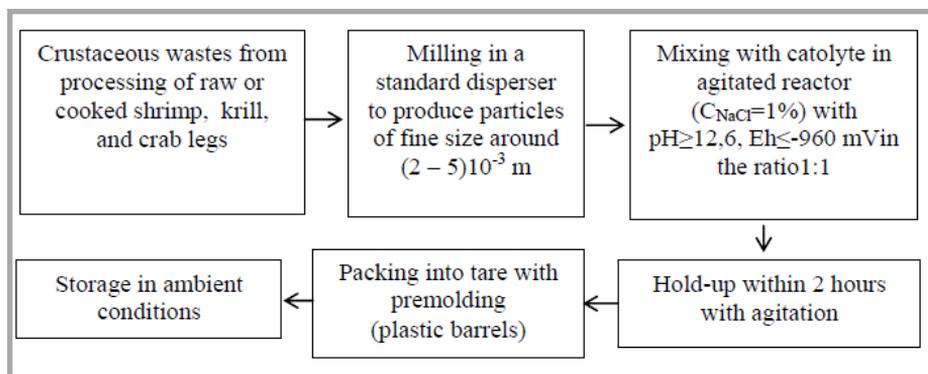


Figure 1. Process operational diagram demonstrating stages of electrochemical treatment of raw crustacean material.

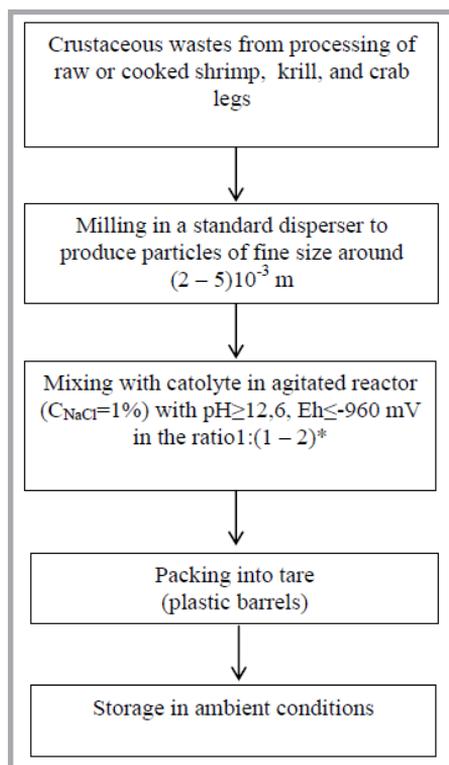


Figure 2. Raw CW electrochemical preservation operational diagram (* - hydromodulus 1:1 – for low-protein CW, hydromodulus 1:2 – for high-protein CW).

deproteinated carapace – a half-stock for obtaining chitin and valuable protein products. Unlike traditional preservation agents such as acids and alkali, catholytes and anolytes demonstrate rather unstable properties and rapid decomposition outside the electrolyzer. As soon as there is a certain time period between the production of preserving agents and treatment of CW with their use, it was necessary to study the time-history of the agent's acid-base and redox properties. The **Figure 4** demonstrates that the reducing capacities of catholytes are mostly unstable and they should be used not later than 1.5 hours after having left the electrolyzer.

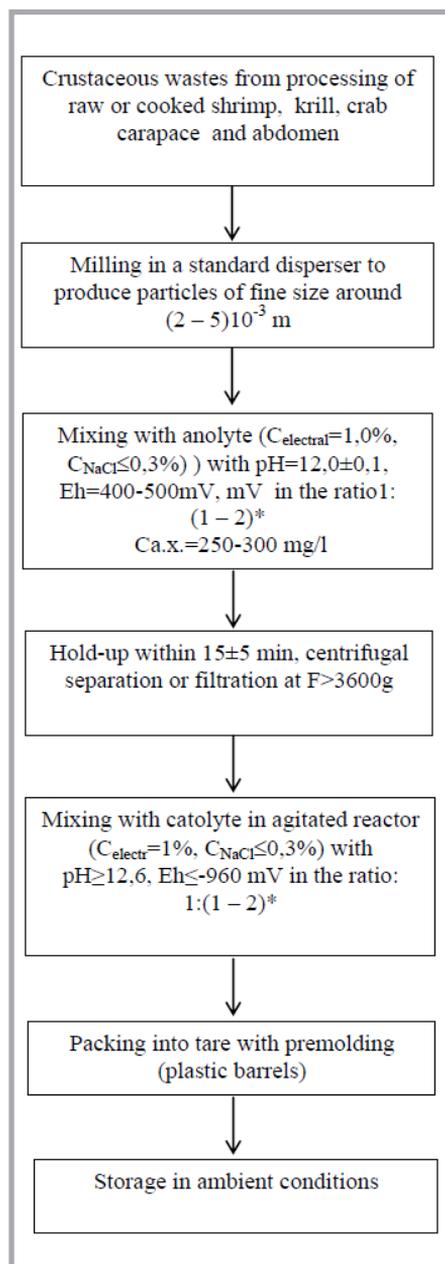


Figure 3. Process diagram for the electrochemical treatment of “overhold” crustacean raw material (autolysis in progress) (* - hydromodulus 1:1 – for low-protein CW, hydromodulus 1:2 – for high-protein CW).

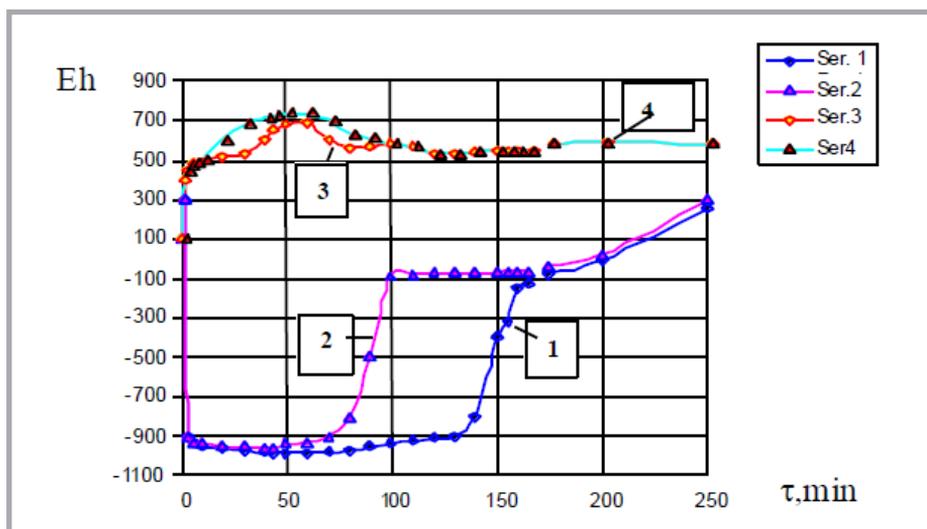


Figure 4. The redox-potential profile (E_h , mB) of catolyte (1, 2) and anolyte (3, 4) depending on time (t) of electrolysis treatment (45 min) and Na_2SO_4 solution relaxation.

The samples of electrochemically preserved CW, with the purpose to define its optimal storage temperature modes and shelf-life, were packed into glass containers and stored at uncontrolled positive temperatures in ambient conditions and at elevated temperature (30 °C) within a thermostated enclosure for accelerated aging as well.

For comparative purposes a reference CW sample was prepared according to a traditional technology: it was treated with sodium hydroxide as a preservative agent. The physical- and-chemical characteristics of raw material – CW of cooked-and-frozen manually peeled shrimp and samples preserved electrochemically according to the production methods described in **Figures 1** and **2**, and treated with sodium hydroxide are given in **Table 1**.

The assessment of the CW preserved samples quality within the specified storage period was performed and the following spoilage indicators were checked and presented in the **Table 2**: microbiological (total viable aerobic count TVAC), biochemical (total volatile nitrogen - TVN) and sulfhydryl groups concentration – SH) and organoleptic.

The **Table 2** demonstrates that microbiological indicators of all the samples comply with the Sanitary Regulations and Standards requirements 2.3.2 1078-01 (п. 1.3.7.1) [6]. The best results were shown by the CW sample preserved by means of anolyte and catolyte solutions - immediately after treatment its TVAC reduced from $4,4 \cdot 10^6$ (in original raw material) down to $2,4 \cdot 10^2$.

During three month storage period a certain bacterial die-away in the samples due to enhanced (alkaline) pH values was noticed.

Table 1. Physical-and-chemical and organoleptic properties of the raw material – CW of cooked-and-frozen shrimp, preserved electrochemically by the solutions prepared according to the production methods described in **Figures 2 and 3**, and treated by traditional alkali method.

CW from cooked-and-frozen shrimp	CW yield, % from process weight	pH	Content, %	
			lipids	nitrogenous matter
Original raw material	38.0	7,5	4,8	17,0
Catolyte preserved raw material	76.0	12,0 - 12,3	4,0	14,2
Anolyte disinfected and catolyte preserved raw material	53.0	12,0 - 12,1	3,8	13,0
Alkali preserved raw material	75.0	12,6	4,1	14,0

Table 2. Microbiological, biochemical and organoleptic indicators of shrimp CW samples preserved by freezing, electrochemical and traditional alkali treatment methods, before and after storage at +30 °C temperature.

Name of shrimp CW sample	TVAC, UFC/g (GOST 100444.15)		TVN, mg/100 g (GOST 7636)	SH-group total content, mg-eq/g (ctf.№2423/60)	pH	Organoleptic properties
	Before storage	After 6 month storage				
Original raw material, cooked and frozen	4.4·10 ⁶	4.0·10 ⁶	3.38 ± 0.5	10.21 ± 1.5	7.0 ± 0.1	Satisfactory, without changes, pink colour, odour characteristic for cooked and frozen shrimp
Catolyte preserved raw material	1.3·10 ⁴	7.0·10 ²	0.69 ± 0.5	17.18 ± 2.5	11.0 ± 0.1	Similar
Anolyte disinfected and catolyte preserved raw material	2.4·10 ²	9.0·10 ¹	14.30 ± 0.5	16.65 ± 2.5	12.0 ± 0.1	Satisfactory, without changes, white-pink colour, odour characteristic for cooked and frozen shrimp
NaOH (2.5%) preserved raw material	2.1·10 ⁴	-	14.30 ± 0.5	16.63 ± 2.5	12.0 ± 0.1	Satisfactory, red-pink colour, strong ammonia odour

The positive influence of alkaline pH values has affected the SH-groups concentration as well – it increased for 60-70 % compared to concentration in frozen raw material samples.

The advantages of electrochemical preservation in respect of CW “protein spoilage” compared to alkaline preservation are worth mentioning as the TVAC of alkaline treated sample was four times as much as those taken from raw material and 20 times as much as catolyte preserved samples. The data was proved during the assessment of samples’ organoleptic properties.

4. Conclusion

It is possible to state that an environmentally friendly electrochemical production method for crustaceous wastes (CW) preservation has been developed. This acid and alkali-free method allows to store CW in non-controlled positive temperature conditions,

to deproteinize carapace during its storage and transportation, and to preserve the high quality of raw material components. The production method can be successfully applied both onboard fishing vessels and at shore-based processing factories.

Impact of the listed factors on pantsirsoderzhashchy raw materials allowed:

- to reach a deep deproteinirovaniye much softer conditions, than at acid-base technology and to receive chitin, proteins and lipids not only with a high exit, but also with the greatest possible preservation of their native structure and properties;
- to reach demanded extent of purification of chitin at single carrying out stages of a deproteinirovaniye;
- it is essential to simplify the technological scheme of conservation of pantsirsoderzhashchy waste of processing of crustaceans.

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