Research Article

The Feasibility of Using Agarophyte Processing Waste

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Dates

Published 13 January 2022

Publishing services provided by Knowledge E

Selection and Peer-review under the responsibility of the 8th Scientific and Practical Conference Conference Committee.

Abstract. When agarophytes are processed, 16-89% algal waste (AW) is formed. Due to the high content of minerals in this waste and the presence of proteins that are resistant to the action of proteolytic enzymes, such AW is mainly used in the production of feed for farm animals. The significant content of polysaccharides in dry AW indicates that it could be used as a raw material for the production of dietary fiber (DF). Due to the difference in the chemical composition of AW depending on the type of red algae, different approaches for its deproteinization have been used. Thus, a 3% alkali solution should be used for the deproteinization of algal waste from the red algae *Gracilaria*, a 0.5% alkali solution for *Gelidium*AW, and a 1% sodium carbonate solution for *A. plicata*AW.The duration of the deproteinization process is 30 min at a temperature of 97±2°C for all types of AW. In this study, functional and technological solutions of DF from AW were developed. The results showed that their water binding capacity was 6-22 g of water per 1 g of the preparation, the fat binding capacity was 1.6-3.3 g of fat per 1 g of the preparation, and the swelling capacity was 46-312% depending on the type of red algae.The obtained DF was used in the production of minced fish food products of the 'fish sticks' type, based on minced fish and consisting of cod and pink salmon. The study of the chemical composition and calorie content of the developed food product showed the possibility of its use in dietary nutrition.

Keywords: red algae, algal waste, deproteinization, dietary fiber

1. Results and discussion

When receiving agar from red algae, algal waste (AW) is formed, the wet weight of which makes from 295% to 663% to the weight of the dried raw material, depending on the type of algae (Table 1).

The limited use of algal waste is connected with a high content of mineral substances in them (20-25%), which is caused by the use of alkali solutions in agar production technology and the presence of proteins that are resistant to the action of proteolytic enzymes [5,8,7,14].Therefore, algal waste was often used for the production of various feeds (powders, hydrolyzates) for farm animals and fish, the use of which in animal farming made it possible to improve the quality of milk, increase the productivity of

TABLE 1: The amount of algal waste (AW) produced when receiving agar from different types of agarophyte and their chemical composition.

The type of red algae from which AW is obtained	Raw AW, % to air-dried algae	Dried AW, % to air-dried algae	Water content, %	Content, % dry matter		
				Ash	Protein (Ntotal*6,25)	Polysaccharide
G.amansii [1]	365	33,3	90,8	5,2	26,1	68,7
A.tobuchiensis [1]	380	88,8	76,6	7,2	41,5	51,3
A. plicata[1]	295	46,2	82,3	7,7	15,1	77,2
G. tenuistipitata[1]	663	15,9	95,3	6,6	27,7	65,7
A.tobuchiensis [2]	314	78,4	75,0	25,0	19,1	50,0

Notice [1]The yield of agar according to technology developed by FGBNU'VNIRO'[11] [2]The yield of agar according to technology, using calcium oxide[14]

animals by 9% and increase the weight gain of animals by 18-20%, when they were added to the diet of young cattle and pigs [1,4,6].

The agar production technology developed at FGBNU 'VNIRO' does not stipulate for using of alkali [11], which has led to a decrease in the content of minerals in algae waste from 25% to 7,2%. About 51,3-68,7% of dry matter of algal waste are polysaccharides, the main part of which is represented by low-hydrolyzablepolysaccharides (LHP), and proteins from 26,1 to 41,5% of dry AW (Table 1). Due to the significant content of polysaccharides in dry algal waste, there is a good reason to consider them as raw materials for obtaining dietary fiber (DF).

It is known that the lack of dietary fiber in the diet contributes to the occurrence of cardiovascular, gastrointestinal and metabolic disorders in humans. Regular consumption of dietary fiber in diets improves intestinal motor functions, lowers cholesterol level and regulates blood glucose[15,16]. Also, DF is used in food industry as water binding ingredient, which leads to increase in yield and decrease in defects by product manufacturing. The fat binding capacity (FBC) of dietary fiber is not high[9].

The main task by development of technology for obtaining dietary fiber from algal waste is obtaining of preparation with high functional and technological solutions (FTS). The contributions of Russian scientists have shown that the most effective disbonding of the carbohydrate-protein AW is achieved as a result of the use of alkali solutions[2,8,10].

The high fiber content in the red alga *Ahnfeltia* (14-17%) causes a rigid structure of its thalli, compared to*Gracilaria*, which contains from 3 to 10% fiber, that leads to the need of using different approaches for AW processing depending on the type of algae.

When studying the effect of alkali of various concentrations (from 3 to 7%) byprocessing the algae waste *Gracilaria* on the extraction of protein and FTS of dietary fiber, it

TABLE 2: Changes in the chemical composition, the yield and FTS of dietary fiber from *Gracilaria*depending on the concentration of alkali.

Indicatorname		Concentration of alkali, %		
		3	5	7
The yield, % dry matter		29,2	24,4	17,5
WBC	22±3°C	11,1	10,9	10,1
	87±3°C	23,3	22,3	21,7
FBC	22±3°C	1,5	1,8	1,5
	87±3°C	1,6	1,3	1,3
Swelling	22±3°C	298	209	200
	87±3°C	354	333	317
Water content, %		6,9	6,8	5,9
Content, % dry matter				
Ash		7,2	6,9	6,0
Protein (Ntotal*6,25)		3,3	2,8	3,2
Carbohydrate	Glucose	9,9	4,7	6,9
	Mannose	1,3	0,9	1,1
	Agar	47,8	34,7	22,4
	LHP	30,5	50,4	60,4

was found that an increase of the concentration of alkali by more than 3% is not rational, since it does not lead to an increase in these indicators (Table 2).

With an increase of the concentration of alkali (from 3% to 7%) when processing algal waste from *Gracilaria*, the extraction of residual agar occurs, which leads to a decrease in yield of dietary fiber (Table 2).

To select a rational method for removing alkali solution from dietary fibers *Gracilaria*, there were studied two methods of washing them, which are boiling dietary fibers for an hour at pH 5,5±0,5 and 6,5±0,5, followed by hot water rinsing. When boiling dietary fiber from *Gracilaria*at pH 5,5±0,5 a decrease in the residual content of agar by 8% occurs, which leads to a decrease in water binding capacity (WBC) and swelling of the preparation (Table 3).

FBC with the considered methods of washing dietary fiber remained practically unchanged and made 1,6-2,0 g of fat per 1 g of the preparation (Table 3). Thus, the algal waste of *Gracilaria* should be processed with the 3% alkali solution for 30 minutes at a temperature of 97±2 °C(duty of water 1:4), followed by boiling it in water at a pH of 6,5±0,5, at a temperature 97±2 °C (1±0,1 hour) and rinsing with hot water.

When processing AW *A. plicata* in order to obtain a DF preparation, the deproteinization of AW with sodium carbonate, calcium oxide, and potassium hydroxide for 0,5, 1,0,

TABLE 3: Changes in the chemical composition and FTS of dietary fiber from *Gracilaria*, depending on the method of washing.

Indicatorname		The type of washing AW from*Gracilaria*	
		1[1]	2[2]
WBC	22±3°C	21,8	16,5
	87±3°C	30,0	24,9
FBC	22±3°C	1,8	2,0
	87±3°C	1,6	1,9
Swelling	22±3°C	200	250
	87±3°C	175	190
Water content, %		8,6	5,0
Content, % dry matter			
Ash		6,5	5,2
Protein (Ntotal *6,25)		3,5	4,2
Carbohydrate	Glucose	4,8	4,3
	Mannose	0,9	1,0
	Agar	35,4	27,4
	LHP	48,9	57,9

Notice [1]Dietaryfiber from AW*Gracilaria,*obtained after boiling atpH6,5±0,5 [2]Dietaryfiber from AW*Gracilaria,*obtained after boiling atpH 5,5±0,5

and 1,5h, with the concentration of reagents being 1, 3, and 6% was carried out (Table 4).

To select rational parameters for obtaining DF, statistical processing of the experimental results was carried out, as a result of which Fisher's criterion was calculated (Table 5).

When comparing the obtained Fisher criterion (Fex) with the tabular value of this criterion (Ftab=19, with α=0,05; f1=2; f2=2), it was found that the main factor affecting the deproteinization process is the type of applied reagent. This variable factor has a statistically significant effect on such indicators as the content of protein, carbohydrates in DF, as well as their yield. All other variable factors do not have a statistically significant effect on the process of AW deproteinization. Thus, to obtain DF, it is necessary to process the algal waste for 0,5h at a reagent concentration of 1% (Table 5).

Comparison of the average yield rate, content of protein and carbohydrate of DF using Duncan's range test for different types of reagents showed that there were no statistically significant differences between the use of potassium hydroxide and sodium carbonate when carrying out a processing of algal waste. Based on a comparison of the cost, safety and technical and economic indicators of potassium hydroxide and sodium carbonate, the expediency of using sodium carbonate for the processing of algal waste was established.

TABLE 4: Changes of physicochemical parameters and DF yield depending on the conditions of deproteinization of AW *A. plicata*.

Conditions of deproteinization of AW	Content					Yield of DF, %	Swelling%	Water binding capacity, g of water/ гof DF
	water, %	protein, % dry matter	ash, % dry matter	Carbohydrate, % dry matter				
				total	fibres, % dry matter			
1% Na_2CO_3, 1h	10,2	30,70	7,56	61,7	43,8	12,4	242	5,7
3% Na_2CO_3, 0,5h	11,1	26,16	6,62	67,2	33,7	15,4	382	6,3
6% Na_2CO_3, 1,5h	11,1	27,64	5,41	66,9	36,0	14,9	380	5,8
1% CaO, 0,5h	11,1	28,50	8,22	63,3	39,4	16,4	250	5,5
3% CaO, 1,5h	10,7	26,52	9,59	63,9	40,5	15,8	350	5,9
6% CaO, 1h	10,7	28,25	10,58	61,2	43,5	13,7	309	5,4
1% KOH, 1,5h	9,9	22,31	10,48	67,2	57,7	7,6	244	6,2
3% KOH, 1h	13,7	20,56	9,75	69,7	48,6	9,1	277	6,0
6% KOH, 0,5h	13,1	14,68	12,64	72,7	53,5	7,6	245	6,5

TABLE 5: Values of the calculated Fisher's criterion (Fex) for test items.

Sourceofvariance	The name of process reaction					
	protein	carbohydrat (total)	fibres	yield	swelling	water binding capacity
Concentration of reagent	4,2186	5,2195	1,5553	0,8990	7,8073	0,9423
Processingtime	3,5336	5,9478	0,4632	0,7981	2,1668	2,1539
Type of reagent	30,0248	24,5109	11,2279	22,8648	5,6330	5,2115

As a result of the studies, it was found that the rational parameters of processing of algalwastefromtheWhiteSeaAhnfeltia*A. plicata*are: 1% sodium carbonate solution, duty of water 1: 4, temperature 97±2 °C, duration 0,5h.

For algal waste *Gelidium*, it is rational to carry out deproteinization with 0,5% alkali. Due to the rigidity of the structure of the thalli of AW*A.tobuchiensis*, before the stage of their deproteinization it is necessary to apply acid treatment (5% sulfuric acid, temperature 97±2°C and duration 30 min,duty of water 1:5) to destroy the structure of its tissue. It is rational to carry out alkaline treatment of AW *A. tobuchiensis* in the same way as for AW *Gracilaria*.

Analysis of microbiological indicators of the quality and content of heavy metals in the developed preparations of dietary fiber from algal waste showed their full compliance with the requirements of Technical Regulations (TR) EAEU 040/2016 'On the safety of

Table 6: Chemical composition and functional and technological properties of dietary fiber.

The name of dietary fibre	Content						WBC, gwater/g DF	Swelling,%
	Water, %	Ash, % dry matter	Protein, % dry matter	carbohydrates, % dry matter				
				total	including			
					fibres	EHP[1]		
A.plicata	11,0	7,1	28,4	64,5	38,8	25,7	6,0	312,0
A.tobuchiensis	7,8	2,5	14,9	82,6	78,7	3,9	6,2	46,0
Gelidium	8,0	2,5	21,7	75,8	70,7	5,1	5,9	177,0
Gracilaria 1	6,9	7,2	3,3	89,5	30,5	59,0	11,1	298,0
Gracilaria 2	8,6	6,5	3,5	90,0	48,9	41,1	21,8	200,0
wheaten 1	4,9	1,0	0,5	98,5	96,0	2,5	5,3	145,0
wheaten 2	3,8	5,3	17,1	77,6	12,8	64,8	4,4	173,0
potato	11,5	3,5	5,1	91,4	26,0	65,4	6,7	223,0
pease 1	7,1	3,2	6,9	89,9	70,1	19,8	6,7	229,0
pease 2	8,7	1,8	4,7	93,5	49,6	43,9	11,5	350,0
carrot	9,3	6,0	2,4	91,6	71,4	20,2	13,4	374,0
orange	6,0	3,1	9,0	88,0	44,0	44,0	17,4	981,0
bamboo	5,1	0,3	0,1	99,6	97,0	2,6	4,7	149,0

Notice 1 Easyhydrolysablecarbohydrates

fish and fish products'and Technical Regulations of Custom Union(TR CU) 021/2011 'On the food safety'. Based on the studies carried out, technical conditions (TC) 9284-127-0072124-12 'Dietary fiber from algae' and technology guidelines (TG) for production were developed, as well as patent RF 2445780 'A method of obtaining dietary fiber from algal raw materials' was obtained.

The developed dietary fibers from algae are equal to commercial DF preparations in terms of such indicators as fiber content, swelling and water binding capacity(Table 6).

According to the classification proposed by M.S. Dudkin and L.F. Shchelkunov[3], the obtained DF in terms of fiber content can be counted as semiconcentrates, and according to the total content of carbohydrates, which include fiber and agar, to DF concentrates.

Dietary fibers from agarophytes were used by obtaining minced fish food products, the 'fish sticks' type based on minced fish, which consists of 60% cod and 40% pink salmon. Low fat content (5%) and insignificant energy value (116 kcal / 100 g of product) of 'fish sticks' allow them to be classified as a medium in calories product and used in dietary nutrition.

On the basis of the studies carried out, the possibility of using dietary fibers from algae in the technology of minced fish food has been shown. Technical documentation for 'Diet fish sticks with dietary fiber' (TC 9266-006-00472124 and their TG) was developed and RF patent No. 2459456 'Diet product' was received.

2. Conclusion

Thus, rational regimes for processing algal waste of various types of agarophytes and technical documentation for their production have been developed, as well as recommendations for the use of dietary fibers in the manufacture of minced fish food products.

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