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PROCÉDE D'OBTENTION DE L'ALGINATE DE SODIUM DE L'ALGUE CYTOSEIRA BARBATA DE LA MER NOIRE

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A b s t r a c t

The paper presents a technological scheme for obtaining the sodium alginate and some comments about the stages which were resolved by means relatively different from those generally used in the alginate fabrication.

L'activité de recherches dans le but de l'établissement des procédés de séparation des substances utiles des algues marines est de date très récente dans notre pays. Le début de cette activité a été inauguré en 1970 par l'Institut de Recherches et d'Elaboration des Projets dans l'Industrie Alimentaire - Bucarest, avec une algue brune, Cystoseira barbata répandue sur le littoral roumain de la mer Noire. Les travaux ont été repris et amplifiés en 1971 par les auteurs dans le cadre de l'Institut Roumain de Recherches Maritimes.

À la suite de nombreuses expériences de laboratoire et à l'échelle semi-industrielle, on a élaboré un procédé d'extraction qui tient compte des particularités remarquables de comportement de l'algue Cystoseira barbata au cours du processus de traitement, en comparaison avec d'autres espèces d'emploi courant (OKAZAKI, 1970, CHAPMAN, 1953).

De la totalité des phases technologiques (fig.1), on insistera seulement sur les opérations qui se sont avérées plus difficiles par rapport à la technologie classique d'extraction et de séparation de l'acide

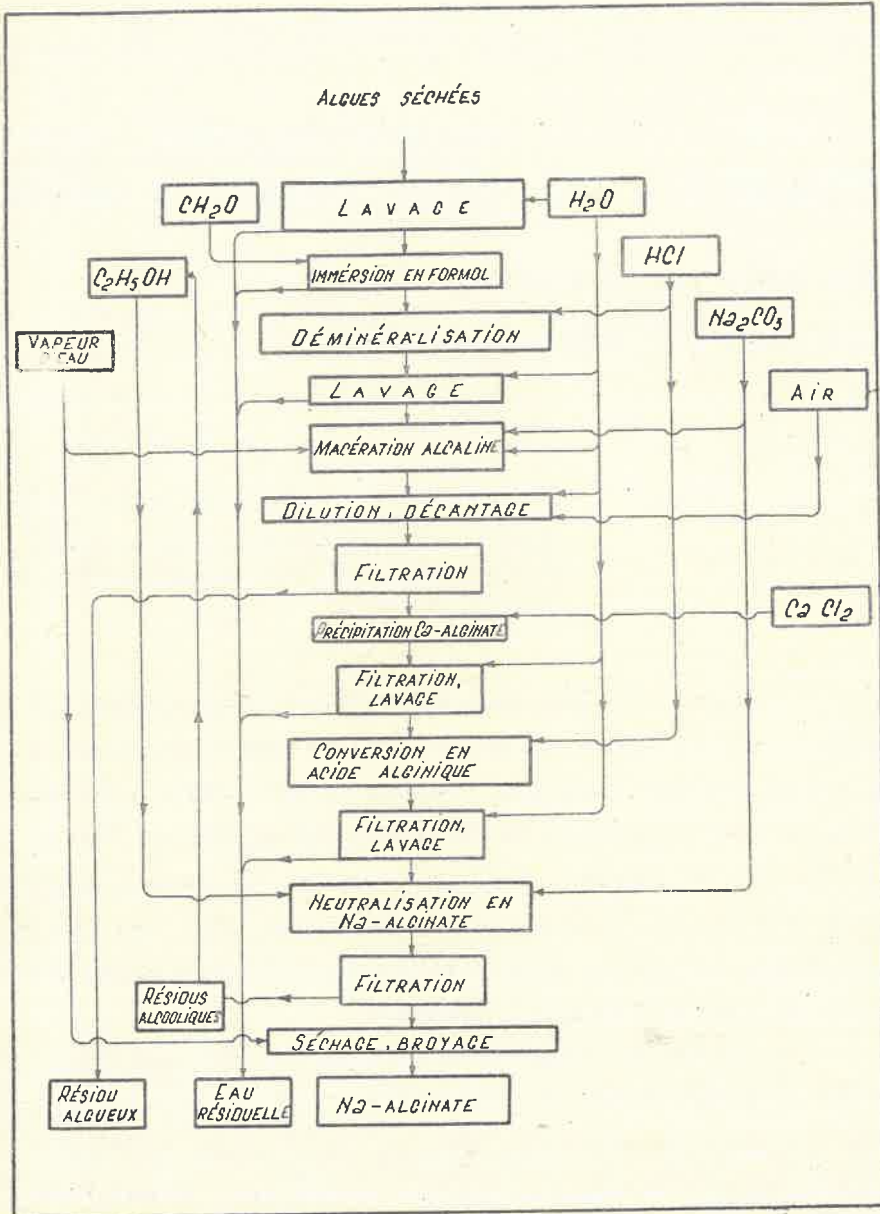


Fig.1. Schéma technologique d'obtention de l'alginate de sodium à partir de l'algue Cystoseira barbata

alginique (OKAZAKI, 1970; CHAPMAN, 1953; KIZEVETTER, 1967), notamment: fixation des pigments, macération alcaline des algues et récupération de l'acide alginique dans les solutions brutes d'alginate. Ces opérations sont déterminantes dans l'établissement de la durée du traitement, de la qualité du produit fini et du rendement - en un mot, de la rentabilité du processus dans son ensemble.

La première particularité du procédé établi consiste dans l'immersion des algues, après lavage, pour un intervalle de temps limité dans une solution diluée d'aldéhyde formique, à l'ébullition. Cette opération a un but multiple: l'insolubilisation des protéines et la fixation des pigments sous forme d'un complexe protéine-cellulose-aldéhyde formique, abaissement de la résistance mécanique du tissu cellulosique, préservation ultérieure de l'action des bactéries (BARASKOV, 1963). L'immersion des algues dans le formol substitue totalement, ou partiellement, en concordance avec la destination du produit, l'opération de décoloration par hypochlorites, pratiquée couramment dans la technologie des alginate et qui détériore l'acide alginique par dépolymérisation (OKAZAKI, 1970; CHAPMAN, 1953; KIZEVETTER, 1967).

La macération alcaline de la Cystoseira barbata s'effectue plus difficilement que celle de la Laminaria ou Fucus (OKAZAKI, 1970), grâce à la rigidité des rameaux et à la résistance des parois cellulaires aux agents chimiques.

En employant un agent de macération fortement alcalin, comme l'hydroxide de sodium, on a obtenu un produit de couleur foncée et à viscosité réduite (sous 50 cp). Les meilleurs résultats ont été fournis par le carbonate de sodium en excès par rapport à la proportion stoechiométrique pour l'accroissement de la vitesse de réaction et du rendement de l'extraction. La réaction découle sans dégradation du polymère, l'alcalinité de la solution restant dans les limites du pH 9 - 11. On a eu soin, de même, que la température ne dépasse pas pendant la macération la valeur de 60°C, étant donné qu'il existe une tendance de dépolymérisation de l'acide alginique aux températures plus élevées (CHAPMAN, 1953; BARASKOV, 1963). La durée de l'opération est influencée dans une

mesure importante aussi par le système mécanique d'homogénéisation. Un malaxeur commun, à palettes, ne peut pas fonctionner dans la première phase de la macération, quand les algues sont entières. En expérimentant divers systèmes on a constaté que l'homogénéisation accompagnée de l'écrasement est la plus convenable. L'utilisation d'un tambour rotatif à billes et à vitesse réglable a conduit à de bons résultats quant à la durée et à la qualité de pastification. Toutefois, la durée de macération n'a pas pu être diminuée au dessous de 4 heures.

La séparation de l'acide alginique de la solution diluée d'alginate, résultée de la dilution du macérat par précipitation directe avec un acide minéral - méthode fréquemment appliquée à l'échelle mondiale (OKAZAKI, 1970; KIZEVETTER, 1967) - se trouve être dans le cas de l'algue Cystoseira barbata une opération malaisée, donnant un précipité très fin, difficile à laver et à séparer. Par précipitation intermédiaire de l'alginate de calcium, volumineux et facilement séparable, le traitement ultérieur ne pose plus de problèmes spéciaux.

Comme agent de précipitation on a utilisé le chlorure de calcium en excès qui présente l'avantage de pouvoir être facilement éliminé par simple lavage, après la conversion de l'alginate de calcium en acide alginique à l'aide de l'acide chlorhydrique.

L'alginate de sodium obtenu présente des caractéristiques supérieures (viscosité au moins 200 cp, pouvant atteindre jusqu'à 2000 cp), ce qui lui confère un large champ d'application.

Le rendement de l'extraction dans une installation-pilote, avec des algues récoltées dans la période optimale de l'accumulation de l'acide alginique (octobre), a été de 18,7% par rapport à la substance sèche (MIRZA, 1972).

On a démontré ainsi que l'algue Cystoseira barbata du littoral roumain de la mer Noire se prête avec de bons résultats au traitement industriel, en vue de l'obtention des alginates.

En même temps, le fait que les préoccupations dans ce domaine ne sont pour nous que dans une phase primaire, laisse entrevoir de multiples possibilités d'amélioration du procédé présenté.

R é s u m é

Les auteurs présentent un schéma technologique de fabrication de l'alginate de sodium à partir de l'algue Cystoseira barbata de la mer Noire ainsi que quelques particularités de ce processus.

Les problèmes dont la résolution a été plus ardue, se rattachent au virage intense des pigments dans les solutions brutes d'alginate, à la résistance mécanique et chimique particulièrement élevée de l'algue aux agents de macération ainsi qu'à la nécessité de séparation avec rendement appréciable et dans des conditions techniques avantageuses des composés alginiques dans les solutions diluées.

Pour l'insolubilisation des pigments et des protéines, on immerge les algues dans une solution diluée de formaldéhyde.

La macération s'effectue dans un tambour rotatif et comme agent de macération on utilise le carbonate de sodium.

La récupération de l'acide alginique dans les solutions diluées d'alginate comprend la précipitation intermédiaire de l'alginate de calcium.

Les recherches effectuées ont conduit à une technologie relativement simple qui permet de réaliser un produit de qualité supérieure.

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CERTAIN ASPECTS REGARDING THE USE OF MARINE ALGAE FOR POULTRY FOOD

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A b s t r a c t

By investigating the effect of administering seaweed to the poultry food, the authors found that marine algae possess a quite significant nutritive value and that such algae may substitute up to 20% of the normal daily ratio. It has also been found that algae, particularly green algae, when consumed fresh or frozen, show a favourable action on the colour of the yolk. For poultry fed with 5-7% fresh algae (*Cladophora*), the yolk showed a colour twice to three times more intense than the witness yolk. The same amount of green algae caused a more pleasant aspect of the chicken meat and a darker coloration of the legs. The taste and smell of the meat and of the eggs was not affected at all by the algae.

The considerable nutritive value of microphyte and macrophyte algae resulted in recent years in an increasing interest for their use for zootechnical purposes. The results of the research work carried out in this direction on various species of animals and fowl, are very promising, and in many countries an actual industry of collecting and preparing algae for fodder was developed.

The nutritive principles entering in the constitution of algae caused these plants to become a source of fodder able to substitute a significant percentage of the animal food. But at least of the same importance

are certain substances contained in algae with a large physiological activity in the organism of animals. These substances - microelements and vitamins - acting in the direction of stimulating metabolic processes, result in an increase of the production, an increase of the quality of the products, and in a general improvement of the health condition of the respective animals.

For poultry, the supplementation of the daily ration with algaemeal, which is a complex natural product, proved to have a positive influence on the brilliancy of the feathers, on the improvement of the general health condition and on the increase of weight. (McINNES, A. A., 1956). In some cases, marine algae meal may be used for poultry food in order to make-up for deficiencies of some essential components in the nutritive mixtures (HØIE, Y. and SANDVIK, Ø., 1956). Some investigators found that important amounts of iodine are accumulated in the eggs as a result of the use of brown algae for feeding poultry. (SUNDE, L. 1956 ; HØIE, Y. and SANDVIK, Ø., 1956). The authors quoted found that the iodine content of eggs increased from 6 gamma/egg (witness without algae) to 910 gamma/egg for hens the food of which included 7% Laminaria meal.

In this country, the first experiments in using marine algae for poultry food were carried out by TIMARIU, S. and his co-workers (1963). On this occasion it has been found that Phyllophore-meal is eaten with much pleasure, when mixed with the basal ration, and that it may be mixed in amounts ranging between 10 and 20% of the total amount of food without negative consequences to the consumers.

In the present paper we propose to determine the influence of algae on the egg and meat production of poultry, on the colour of the yolk, the nutritive value of algae and the amounts eaten with pleasure.

Materials and methods of investigation

The tests were carried out on 15 months old battery-raised New Hampshire hens. The witness lot was fed with rations composed of the following mixture : 72% corn, 4% peas, 6% sun flower groats, 8% soya groats, 6% meat and bone meal, 4% chalk powder. The nutritive value of

the basal ration amounted to 71.88 % total digestible substance, of which 18.23 % was digestible proteins. The experimental lots composed of 12 hens each, received a food where algae substituted the original nutritive mixture in percentages ranging between 3 g and 20 g %. Two different alga ingredients were used : alga-meal in amounts ranging between 5 and 20%, and fresh green algae, in amounts representing 3 g, 5 g and 7 g % of dry food substance. The alga meal obtained from the Agigea (Constanța) food - meal factory was prepared from a mixture of various species of green, red and brown algae deposited ashore by the waves. The amounts of fresh green algae which were given to the hens, were constituted only of various species of Cladophora. They were collected by hand from the underwater fields of algae and were given with the food either fresh or frozen, and well macerated. The amounts of fresh algae added to the rations were converted into units of dried substance and expressed in percentages of the nutritive mixture, as in the case of alga meal.

The tests were carried out over a period of 45 days in June-July 1969. During this period, the eggs were collected from all lots fed with algae, as well as from the witness lot, and the colour of the yolk was determined by comparison, using the La Roche scale. Observations were also carried out on the general health condition and behaviour of the fowl and the egg production was observed.

Simultaneous with these experiments, the 3, 5 and 7 g % green algae diet was administered to three lots of 30-60 days old hybrid meat chickens, each, which were destined to put on weight. During the test which lasted also 45 days, the increase in weight and the colour of the legs of the test chickens was compared with the witness lot. At the end of the experiments, when a number of chickens were sacrificed, appreciations on the taste, the smell and the general aspect of the chicken meat were made.

Results

In order to obtain a general edification on the organic and mineral composition of the algae used during the test, their chemical

analysis presented in table 1 was made^{x)}, As it may be observed, this sort of food contains significant amounts of substances which may be utilized by the organism of animals. At the same time, also the nutritive value of the alga meal was investigated through digestibility tests. Thus

Table 1

Chemical composition of seaweed used as addition to poultry food

Designation of substance	Composition expressed in percentages of dry substance of :	
	<u>Cladophora</u> sp.	Seaweed meal
Organic matter	51,46	37,91
Proteins	23,71	16,24
Albumins (% of proteins)	14,47	13,53
Fats	1,03	0,78
Extractive, non-nitrated substances	15,48	11,73
Cellulose	11,24	9,16
Carotene	0,52	0,92
Ash	48,54	54,05
Macro-elements (g)		
Calcium	2,93	4,76
Magnesium	0,48	1,57
Phosphorus	0,214	0,214
Sulphur	1,21	1,14
Micro-elements (mg)		
Iron	16,2	13,6
Manganese	6,6	3,25
Cobalt	0,247	0,127

It was found that the meal prepared from various species of algae, possesses a nutritive value comparable to that of the meal prepared from

^{x)} The authors wish to express their thanks to Mrs. Despina Turcu, of the Institute for Zootechnic Research of Bucharest, for her kindness on accomplishing the chemical analysis of the algae

lucerne, currently used for poultry food. The total amount of digestible substance of algae is 24.18%, of which 15% are proteins, while the digestible substance of lucerne amounts to 28% and 11 % respectively. By comparing the nutritive value of alga meal with the value of the usual diet used during this test, it was found that under the aspect of richness in digestible proteins, the algae are very close to the artificial mixture; they contain 15% digestible proteins as compared to 18.23% of the base ration.

As a whole the fowl consumed well the diets supplemented with seaweed, exception of the lot which a 20% alga meal ration was given. This fact indicates that at least for the start, the alga percentages in the food must not exceed that value.

During our observations, the egg production, the corporeal weight and the general condition of the hens did not show any noticeable alteration which could have been credited to the feeding on seaweed. But, a very evident influence was remarked on the colour of the yolk. As may be gathered from table 2, the average colour ratings are much higher for eggs produced by hens fed with alga food. A very significant influence in this respect, showed the green algae (Cladophora), given fresh or frozen. An

Table 2

Colour of the yolk, depending on the food given

Type of food given	Amount of algae contained in the food (g %)	Average colour ratings
Basal diet	-	3,75
Basal diet supplemented with fresh <i>Cladophora</i> sp.	3 g	5,70
	5 g	10,20
	7 g	13,35
Basal diet supplemented with seaweed meal	5 g	6,90
	20 g	7,95

amount of 7 g % dried substance of these algae resulted in an intensification of the yolk colour by 3.5 times, as compared to the witness lot.

As among other properties, the quality of eggs is defined also through the colour of their yolk, a preoccupation and the development of

adequate means for improving its colour is not lacking interest. Together with the tests carried out on hens, the same amounts of fresh green algae (3, 5, 7 g %) were added also to the food given to the 30 - 60 days old chickens put to grow fat. An improvement of the general aspect of the meat and a darker colour of the legs, as compared with the witness lot, could be observed.

A similar effect was also reported by I. A. ABAKUNOVA, (quot. DINU, M., 1968) which used dried microphyte algae (Chlorella and Scenedesmus) in amounts of 14 % of the ration, and which after 70 days found that the test chickens had darker beaks, crests and legs.

Other investigators showed that the addition of microphyte algae in the poultry food is followed by an increase of the corporeal weight, by an increase of egg production and of the weight of the eggs, MALEK, I., TKACEV, I. F., ABAKUNOVA, I. A. (Quot. by DINU, M., 1968). These positive consequences are due to the increased protein content of unicellular algae, their nutritive value being similar to that of meat and bone meal (DINU, M., 1968).

Recently BURLACU, Gh. and his co-workers (1971) investigated the nutritive value of a diet where the proteins of animal origin were substituted by microphyte alga proteins. The authors reached at the conclusion that for 3-4 weeks old chicken, the nutritive value of the alga food is less than that of the food containing animal proteins. For 11-12 weeks old chicken, however, the difference between these two values becomes less, owing to the increased capacity of the chicken of this age to digest the alga proteins.

In agreement with other results and statements, our tests showed that the alga-treated food does not diminish the consumption quantities of the poultry products. The taste and smell of eggs and meat obtained from alga-fed poultry did not show any modifications.

Conclusions

Seaweed, particularly green algae of the genus Cladophora, added fresh to the poultry food showed a positive effect on the colour of

the yolk and on the pigmentation of the legs. An amount of 7 g % (dried substance) of fresh algae added to the food of the hens, caused an intensification of the coloration of the yolk by 3.5 times. as compared to the witness.

Moreover, green algae imparted a more pleasant aspect to the meat and a darker colour to the legs of the chicken.

The food products (eggs and meat) obtained from poultry nourished on alga treated food, maintained their un-altered characteristic taste and smell.

The egg production and the rate of increase of the corporal weight was not modified by the alga food.

Marine algae thrown ashore by storms or specially collected, may be used for poultry food in amounts not exceeding 20% of the ration. The superior quality of the poultry products obtained by this method and the savings of food materials achievable, are reasons in favour of using algae in this economic field.

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