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Short Communication

Armadora Pereira and the Usage of the Fishing Waste

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Abstract

This paper explains the continuous endeavor of a Fishing Company to reuse and place value on fishing wastes, whose possible benefits were unknown. We have considered the squid cuttlebone (endoskeleton) to generate B-Chitin and B-Chitosan, biopolymers with many properties and benefits.

Armadora Pereira is a fishing company based in Vigo (Spain) with agencies in many countries, specially devoted to the squid extractive fishing.

Committed to the use of sustainable and environment-friendly new measures, we opted for innovative approaches such as scientific investigation on the usage and placing value on sub-products generated from our captures industrial process.

Our B-Chitosan offers a great level of deacetylation - ultrapure level - and physicochemical characteristics. The unique characteristics of our B-Chitosan made it an splendid candidate for biomedical and pharmaceutic industries; production of bandages, use in material engineering and also an excellent material to create encapsulating structures to monitor releasing of drugs/nutrients, as well as utilization in high profile cosmetic and nutritional industries.

Keywords: Armadora Pereira; Fishing Waste

Patagonian squid marketing

By now, Armadora Pereira has sold Patagonian Squid wholesale, in supermarkets, own stores and it has been distributed for catering in different ways: whole and processed squid (clean and cut). The bulk of waste is the cuttlebone, which is going to be valued to be exploited and contribute to a better advantage beyond its elimination.

Introduction

Chitin and chitosan of marine origin

Chitin is, after the cellulose, the most abundant and ubiquitous material we find in Nature. This polysaccharide is compound by N-acetyl glucosamine units and glucosamine in different proportion, depending on its level of acetylation, and distribution patterns within the molecule. The chitin of marine origin is mainly found in the exoskeletons of shellfish and endoskeletons of some mollusks, more specifically, like in our case, in the squid endoskeletons – often known as "cuttlebone"- providing a structural function in the creature. In the first case, this polymer presents what we have called A-chitin and the second B-chitin. Both A-chitin and B-chitin are associated to proteins and are insoluble in water and in the major part of solvents; however, the B-chitin, subject of this study, shows conformational characteristics which will have a decisive influence in their features, effects and final uses.

The B-chitin is not associated to the typical pigments of the shells, that's why the demineralization phase may be avoided, commonly carried out with strong acid solutions (HC1), with the consequent reduction of environmental and economic costs. And what is most important, the B-Chitin presents a parallel conformation of its structural chains due to the weakness of its interlaminar hydrogen links. As a result, the B-Chitin has a more open structure which grants a better uptake, solubility and reactivity than that of the A-Chitin. This higher affinity with solvents means that the phase of deproteinization by chemical means will require less concentration and volume of solvents. Likewise, this particularly open structure offers a more available substrate for the action of alkaline solutions during the stage of deacetylation in order to obtain the most important and characteristic derivate of the chitin: the chitosan.

The chitosan is a partially deacetylated form of the chitin. It is compound of N-acetyl glucosamine and a 50% or more of its total content of units of glucosamine, depending on its level of deacetylation, in variable positions, inside the polymeric structure. The presence of this amino groups gives it solubility in mild acid solutions, behaving like an exclusive natural polysaccharide of cationic type. This important quality will condition at last the bioactivities that this material and its uses in the different industries offers. The chitosan is a biodegradable compound, biocompatible and no toxic. It offers, among others, great antiseptic capacities – antibacterial and antimycotic- antioxidants and chelating. Due to its solubility and its cationic natural charge, dependent on its level of deacetylation, can be modified and combined with natural and synthetic compounds in order to create polymers with improved features, special characteristics and custom usages. This is mainly the case of the B-Chitosan, which reaches better level of deacetylation than those which derive from the crustaceans.

Physicochemical description of the b-chitosan extricated from the *loligo* SPP

Its extraction is made by an alkaline procedure after the removal of the B-Chitin from the endoskeleton (cuttlebone) of the *Loligo* spp. The product is offered in the form of granulated powder (size particle < 1 mm) Neutral Ph. Biodegradable, biocompatible and no toxic.

Hereafter physicochemical characteristics of both extracts detailed:

Analysis Relation C/N (Elemental analysis; Combustion)

B-Chitin

- Relation C/N: 6.689+/-0.04 (Pure Chitin - fully acetylated: 6.685)
- Level of Acetylation (DA): 89.98%+/-2.17
- Level of Deproteinization: 89.21%+/-1.26.

B-Chitosan

- Relation C/N: 5.231+/-0.07 (Pure Chitosan- fully deacetylated: 5.143)
- Level of Deacetylation (DDA): 93.27%+/-0.57- Ultrapure level.

Spectroscopy of Infrared transformed of Fourier (EITF) (RTA Technic; Fully attenuated reflectance)

Analysis of wave numbers in range of 400 and 4000 cm-1, where the typical bands that identify the characteristics of the functional groups of both compounds are highlighted (Amides I and II hydroxyl group) -with numerical values of wave numbers (v:cm-1) and of Transfer (%T) obtained- confirming its proper nature (Figure 1) In the same way the spectrum of the initial raw material is itself included (endoskeleton of the *Loligo* spp) to value the difference in its own molecular composition and in the extracts obtained: B-Chitin and B-Chitosan.

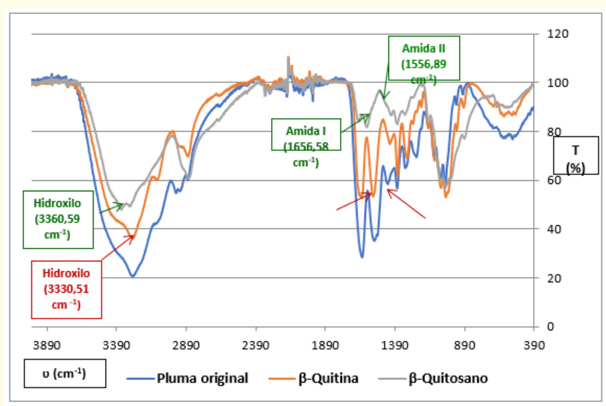

Figure 1: Comparative spectrums (EITF) of the original cuttlebone of the Loligo spp and extracts from the B-Chitin and B-Chitosan obtained from the cuttlebone pointing their most characteristic bands.

B- Chitin

- Hydroxyl Group Band: Located in the position: v=3330.51 cm-1, - with a Transfer value (%T) equal to 41.37%T
- Amide I Band: v = 1650.79 cm-1,%T = 54.51
- Amide II Band: v =156.30 cm-1,%T = 54.99
- B-Chitosan
- Hydroxyl Group Band: v = 3360.59 cm-1; 41.37%T
- Amide I Band: v = 1656.58cm-1(84.84%T)
- Amide II Band: v = 1556.89 cm-1,%T = 88.25.

The amide bands are of the most importance because they correlate the level of the acetylation in the chitin (DA) and deacetylation (DDA) in the chitosan, frequently taken as witness bands, while the hydroxyl group band is usually used as reference band (Brugnerotto., *et al.* 2001). We must highlight that in the case of the B-chitin, a sole band is given for the Amide I – unlike the a-chitin where there are two (Berghoff, 2011) Likewise, the Amide II band is of crucial importance in the characterization of the Chitosan, because it points the qualitative and quantitative presence of amino groups, resulting of the deacetylation process suffered by the chitin in its transformation to this final product.

Benefits and uses of the chitosan

The industrial process of marine origin food generates globally a huge volume of sub-products. The continuous demand of food on the part of an incessantly increasing population, the overexploitation of several natural resources and the global climate change only worsen this difficult situation.

The sub-products are rich in bioactive molecules that may be used in an efficient manner, finding usages in the food industry, cosmetic and medical/ pharmaceutic. With a responsible utilization, concepts of industrial ecology, such as “industrial symbiosis” from a circular economy perspective, would be assumed, where the “waste” is used as raw material to obtain bioactive compounds and its transformation in new and profitable products with different usages. The sub-products of marine origin, rich in nitrogen and phosphorus, have been used in the formulation of food for animals, ground fertilizers or means of planting to grow microorganisms. From the great diversity of potential biomolecules which can be obtained from the sub-products of marine origin, the most interesting are proteins like the collagen and the jellies, and the enzymes as proteases and lipases, also fatty acids, specially the Omega-3 group and polysaccharides.

The Chitosan has many usages and they are increasing with the ongoing survey as well as its commercial value, which has exponentially raised last years. Depending on its deacetylation level (DDA), purity and molecular weight, the chitosan will have usages in treatments with water and soil - technic level; 50 - 70% DDA- as well as food industry, cosmetics – pure chitosan; 70 - 90% DDA- and medical/pharmaceutical – chitosan ultrapure; > 90% DDA. This polymer has attracted more interest in the biomedical sector, especially in the creation of tridimensional structures of scaffolding that permit the growing and the cellular differentiation with therapeutic purposes in material engineering. The chitosan has also demonstrated to be an excellent transport system of liberation directed and controlled by the nutrients, drugs and other bioactive compounds, also an excellent substitute of plastics in biofilm forms. Among other usages there are the following:

- **Fat absorbent**: It removes the fat and cholesterol from the digestive system, it extracts it from the stomach, and it excretes it in the duodenum; it has usages as salutary nutritional additive. Food that contain chitosan reduce the obesity, cholesterol levels and the incidence in the colon cancer.
- **Ointment to heal wounds**
- **Bandage for wounds**: Used for burns, superficial wounds and skin grafts.
- **Surgical sutures**: To stay in the tissue the sufficient time in order to allow the healing and then it slowly dissolves itself; it is not necessary to be eliminated. Unlike other suture materials which are absorbed by the body, these do not cause allergic reactions.
- **Ophthalmology**: Both contact lens and intraocular lenses used in the cataract’s surgery must have a significative characteristic permeability to the gases. The chitin and chitosan may the lens be more permeable to the oxygen than other materials. This is useful for the injured eyes, because they help to heal wounds. Also, the chitin does not adhere to the ocular wounds; this makes that the removal of the lens from the eyes is more secure.
- **Dental**: Given that the chitin can regenerate the connective tissue that covers the teeth near the gums, it has the possibility to treat periodontal diseases such as gingivitis and periodontitis

- **Orthopedics**: The chitin has demonstrated to have many possibilities in Orthopedics as agent to help the bones be healed. The filaments and rods of the chitin also have the capability of use as artificial temporal ligaments for the knees and other orthopedic usages that require a less rigid fixation.
- **Glucosamine**: The chitin is also used in the producing of glucosamine, that gives basic components for the body to produce and repair the cartilage. There also exists a great capability for the chitosan as an alternative to the collagen in the wrinkle's treatment, acne, scars and other damages in the soft part of the skin.
- **Food Ingredients**: They allow the food processors to recycle proteins from the processing wastes of food for animals; they have nutritional benefits and control the release of nutritional additives in ruminant animals
- **Agriculture:** The chitin and chitosan have three potential uses in the agriculture; such as seed treatment, nematocidal and nutritional ingredient. The enzymes have the capability of being adjuvant insecticide. They work attacking the chitin that exists in the exoskeleton of the insects.
- **Hair Care**: The chitosan and the hair are complementary because they have opposite electrical charges: positive and negative chitosan for the hair. A transparent solution that contains chitosan forms a transparent and elastic film on the hair, which increases its softness and mechanical resistance. The material may also form a sort of gel when it is melted with mixtures of alcohol and water. Chitin powder may be used directly in the shampoo.
- **Oral care**: Both chitin and chitosan may be used in toothpaste, mouthwash and chewing gums. They refresh the breath and avoid the creation of dental plaque and caries. The salts of the chitosan aggregated to the toothpaste mask the disagreeable taste of the oxide of silicon and their binder powder in order to maintain their granulate formulas. Both the chitin and the chitosan absorb yeast, a fungus that is adhered to the teeth and turns them into candidate to clean false teeth.

Conclusion

The objective of this survey is to place on value fishing products, previously considered as non-valid and unexploited, in order to give them a second life being more efficient, sustainable and environmentally friendly; that is the purpose followed by Pereira Group in all the stages we develop, both extraction, processing, commercialization and distribution of our products.