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Review

Industrial applications of crustacean by-products (chitin, chitosan, and chitooligosaccharides): A review

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ABSTRACT

Background: Food processing produces large quantities of by-products. Disposal of waste can lead to environmental and human health problems, yet often they can be turned into high value, useful products. For example, crustacean shell wastes from shrimp, crab, lobster, and krill contain large amounts of chitin, a polysaccharide that may be extracted after deproteinisation and demineralization of the exoskeletons.

Scope and approach: This review summarizes the current state of knowledge of these crustacean shellfish wastes and the various ways to use chitin. This biopolymer and its derivatives, such as chitosan, have many biological activities (e.g., anti-cancer, antioxidant, and immune-enhancing) and can be used in various applications (e.g., medical, cosmetic, food, and textile).

Key findings and conclusions: Due to the huge waste produced each year by the shellfish processing industry and the absence of waste management which represent an environmental hazard, the extraction of chitin from crustaceans' shells may be a solution to minimize the waste and to produce valuable compound which possess biological properties with application in many fields. As a food waste, it is important to also be aware of the non-food uses of these wastes.

1. Introduction

Modern food production generates a large quantity of by-products most of which are still underutilized. Yet, these food wastes may often contain several usable substances of high value including some that may have important health benefits. Generation of waste during the processing of food is unavoidable and disposal can be one of the major problems for those industries and for society. Especially if not done properly it can have negative impacts on the environment (i.e., pollution), create risks to human health, and a loss of income to the waste generator. For example, the seafood processing industry produces a large quantity of by-products and discards (heads, tails, skins, scales, viscera, backbones, and shells). These residual materials may be an excellent source of proteins, lipids, pigments, and small molecules. In addition the shell materials may be a source of chitinous materials.

There has been an interest with respect to better use of chitin, which is the second most available polysaccharide after cellulose. It is a fairly ubiquitous compound produced by many organisms: fungi and algae cell walls, insects' exoskeletons, mollusks (endoskeleton of cephalopods) and crustaceans' shells. Annually, it has been estimated that on the order of 10^{10}–10^{11} tons are produced by living organisms (Revathi, Saravanan, & Shanmugam, 2012). However, commercially chitin is mainly recovered from marine sources, i.e., the crustaceans processing industries. In fact more than 10,000 tons could be available every year from shellfish waste (Merzendorfer, 2011), which would provide sufficient raw material if the appropriate commercial procedures for value-added processes were developed.

Chitin is obtained from crustaceans' exoskeletons after demineralization and deproteinisation treatments. However, one of the limitations in the use of this biopolymer on a large-scale is its water insolubility. Therefore, water-soluble derivatives have been produced. Chitosan is the most important of these. It is obtained after

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Abbreviations: BHA, Butylated hydroxyanisole; BHT, Butylated hydroxytoluene; CN, Chitin nanofibrils; COS, Chitooligosaccharide; COX-2, Cytooxygenase-2; IL-6, Interleukine 6; LPS, Lipopolysaccharide; PGE2, Prostaglandin E2; ROS, Reactive oxygen species; TBARS, Thiobarbituric acid reactive substances; TBHQ, Tertiary butylhydroquinone; TNF-α, Tumor necrosis factor-α.

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deacetylation of chitin and it is the only natural cationic polysaccharide known (Du et al., 2014). Chitin and its derivatives are renewable, biocompatible, biodegradable, and non-toxic compounds that have many biological properties such as: anti-cancer (Salah et al., 2013), antioxidant (Yen, Yang, & Mau, 2008), antimicrobial (Goy, de Britto, & Assis, 2009) and anti-coagulant (Vongchan, Sajomsang, Kasinrerk, Subyen, & Kongtawelert, 2003) properties. In addition, they are used as biomaterials in a wide range of applications: for biomedical purposes such as for artificial skin, bones, and cartilage regeneration (Dash, Chiellini, Ottenbrite, & Chiellini, 2011; Parvez et al., 2012), for food preservation such as for edible films (Muzzarelli & Muzzarelli, 2005), and for pharmaceutical purposes such as for drug delivery (Riva et al., 2011).

The waste produced each year by the shellfish processing industries represent a practical challenge. With approximately 75% of the total weight of crustaceans (shrimp, crabs, prawns, lobster, and krill) ending up as by-products (Kuddus & Ahmad, 2013) and the current lack of acceptable waste management options there is a potentially large environmental hazard concern. Usually, seafood wastes are thrown away at sea, burned, landfilled, or simply left out to spoil (Xu et al., 2013). Therefore, the extraction of chitin from crustaceans' shells and its use as is or after further processing may be a way to minimize the waste and to produce valuable compounds with remarkable biological properties and crucial application in various fields.

This paper reviews the efforts to add value to crustacean shell wastes by producing high value substances, mainly chitin and its derivatives, which are starting to become used commercially.

2. Crustaceans processing shell wastes as a source of valuable products

The amounts of chitin from shell wastes vary with species (Table 1) and seasons, but, in general, the exoskeletons contain about 30–40% proteins, 30–50% minerals (mainly calcium carbonate), and 20–30% chitin along with others compounds such as pigments (e.g., astaxanthin) and lipids (Vani & Stanley, 2013; Hayes, 2011).

3. Chitin

After cellulose, chitin $(C_8H_{13}O_5N)_n$ is the second most abundant biopolymer on earth (Synowiecki & Al-Khateeb, 2003; Xu et al., 2013). Cellulose and chitin are polysaccharides with structural similarity; chitin has an acetamide group ($NH{-}CO{-}CH_3$) at C-2 in place of the hydroxyl group in cellulose (Thirunavukkarasu, Dhinamala, & Moses Inbaraj, 2011). Chitin can be obtained from various sources (Table 2), it is mainly found in the exoskeletons of arthropods (insects, crustaceans, and arachnids) and mollusks (beaks and endoskeleton of cephalopods). However, various microorganisms also produce chitin including the cell walls of fungi and yeasts, and the spines of diatoms (Sharp, 2013; Merzendorfer & Zimoch, 2003; Jothi & Nachiyar, 2012). The crustacean shells such as those from crabs and shrimps are the most important chitin source for commercial use due to the availability of wastes from the seafood processing industry (Kaur & Dhillon, 2013). Chitin gives living organisms a strong structure.

The first discovery of chitin was made in 1811 by Professor Henri Braconnot. The polysaccharide was isolated from mushrooms and was named fungine. Later, in 1823, Odier found the same substance in the exoskeleton of insects and named it chitin. This term comes from the Greek words "chiton" which means tunic or envelope (Souza, Almeida, Colwell, & Rivera, 2011; Ferraro et al., 2010). In 1859, Roughet discovered that chitin could be transformed into a water soluble form after chemical manipulation. After that in 1870, this modified chitin was named chitosan. Despite, the early discovery of chitin, the amount and quality of recent research has expanded the information available (Cheba, 2011).

Table 1
Examples of chitin content from different sources.

Organisms	Chitin content (%)	References
Crustaceans		
Nephro (lobster)	69.8[a]	Synowiecki & Al-Khateeb, 2003
Euphausia superb (krill)	24[a]	Arbia et al., 2013
Homarus (lobster)	60–75[a]	
Crangon crangon (Shrimp)	17.8[a]	
Lepas (goose barnacle)	58.3[a]	
Chionoecetes opilio (Crab)	26.6[a]	
Insects		
Blatella (cockroach)	18.4[a]	Kaur & Dhillon, 2013
Coleoptera (ladybird)	27–35[a]	
Diptera	54.8[a]	
Pieris (butterfly)	64.0[a]	
Bombyx (silk worm)	44.2[a]	
Galleria (wax worm)	33.7[a]	
Fungi		
Aspergillus niger	42.0[b]	Synowiecki & Al-Khateeb, 2003
Penicillium notatum	18.5[b]	
Penicillium chrysogenum	19.5–42[b]	
Saccharomyces gutulata	2.3[b]	
Mucor rouxii	9.4[b]	
Siboglinidae	33[c]	Crini, Guibal, Morcellet, Torri, & Badot, 2009
Cnidaria	3–30[d]	Crini et al., 2009
Brachiopod	4–29[a]	Crini et al., 2009
Mollusks	6–40[e]	Crini et al., 2009
Squid, cuttlefish, octopus		

[a] chitin % compared to the dry mass of exoskeletons.
[b] chitn % relative to the dry mass of mycelium.
[c] chitin % is given compared to the dry mass of tube worm.
[d] chitin % is given compared to the dry mass of membranes and egg capsules.
[e] chitin % is based on the dry mass of cuttlebone, pen and beaks.