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IL versus DES: Impact on chitin pretreatment to afford high quality and highly functionalizable chitosan

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PURPOSE OF THE ABSTRACT

Chitosan, a biopolysaccharide composed of glucosamine units linked together by ?-1,4 bonding, is usually produced by deacetylation of chitin, which is mainly extracted from crustacean shells, insect cuticles or other microorganisms such as bacteria, fungus and mycetes. Both, chitin and chitosan, are biocompatible, biodegradable and non-toxic. In addition to being soluble in acidic media, chitosan also presents versatile biological activity and has gained considerable interests for biomedical applications.[1] Even if those properties are well known and promising in various scientific fields, some drawbacks stand against its development: (i) the extraction and purification of chitin is costly and environmentally burdening due to the huge amount of waste water produced during both processes [2] (ii) chemical treatments used to obtain chitosan from chitin adversely affect the physical and chemical properties of these biopolymers [3] and (iii) the use of chitosan in its original form is a limitation for many applications (i. e. poor solubility at physiological pH, low mechanical strength) and modifications are needed. Due to its generally high crystallinity index, chemical deacetylation of chitin through concentrated alkali treatment has a low success rate to obtain a highly deacetylated chitosan in only one cycle of reaction. Therefore, the reaction must be repeated several times, significantly increasing the cost and the polluting nature of this process as well as entailing a molecular weight heterogeneity.
In a recent work, we have demonstrated that chitin extracted from Bombyx eri (BE) insect larvae can be a very good alternative for the chitin production, as this insect's cuticle contains less minerals and possesses a lower degree of crystallinity than the commercial shrimp source. We also demonstrated that an ionic liquid (IL) pretreatment on insect chitin at different purity degrees enhanced its digestibility by chitinase, leading to high yields of mono and chito- oligomers compared to shrimp shells.[4] In addition, 1-ethyl-3-methylimidazolium

[C2mim][OAc] was not only able to solubilize chitin by disrupting the hydrogen bonding between the fibers making chitin less crystalline, but it could also eliminate residual proteins contained in the raw chitin biomasses while maintaining a high molecular weight.[5]

Given that controversy still exists on IL toxicity and its degradability, deep eutectic solvents (DES) have attracted the attention of the scientific community as an alternative to ionic liquids. DES are composed of at least one hydrogen donor and one hydrogen acceptor at different ratio. DES share similar properties with ILs (low melting point, low vapor pressure, non-inflammable and good dissolving abilities). They are usually claimed as less toxic than ILs because they can be composed of non-toxic natural compounds (NADES) and can be produced at a cheapest price compared to ILs.[6] Recently, DES based on choline chloride have been studied in the extraction of chitin even if their acidity generally leads to the production of chitin with low molecular weights.[7]

Therefore, we herein compare the impact of both DES/IL-pretreatments on the efficiency of the chemical deacetylation of chitin carried out over two insect sources (Bombyx eri, BE and Hermetia illucens, HI) and shrimp shells (S). The results showed that chitosans obtained from IL-pretreated chitins from BE larva, present lower acetylation degrees (13-17%) than DES-pretreated samples (18-27%). A selective N-acylation reaction with oleic acid has also been performed on the purest and most deacetylated chitosans leading to high substitution degrees (up to 27%). The overall approach validates the proper chitin source and processing methodology to achieve high quality and highly functionalizable chitosan.[8]

FIGURES

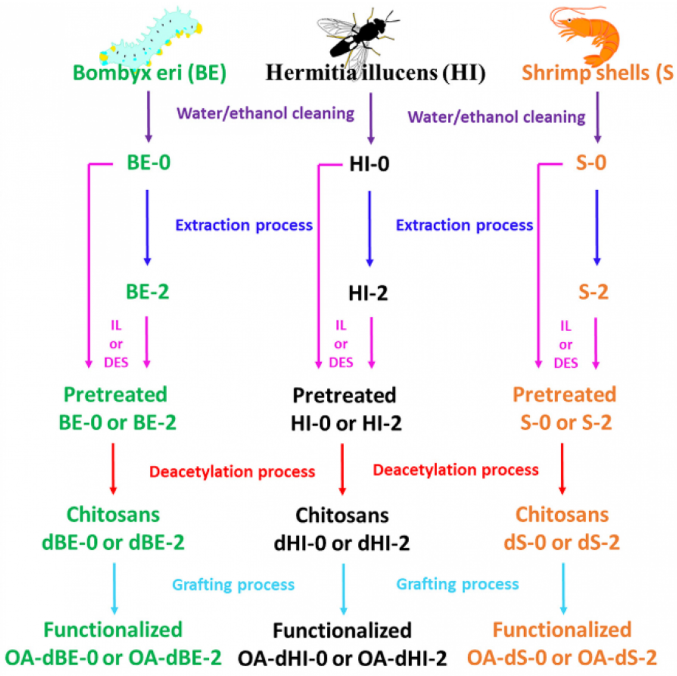

FIGURE 1

Figure 1.

From raw chitin biomasses to functionalized chitosans.

FIGURE 2

KEYWORDS

Chitin | Chitosan | Deep eutectic solvent | Ionic Liquid

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