Chitosan: From Organic Pollutants to High- Value Polymeric Materials

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1 Introduction

Chitosan is a well-known biopolymer chemically obtained by partial deacetylation of the naturally occurring chitin ((1 → 4)-2-acetamido-2-deoxy-β-d-glucan) (Fig. 1).

After cellulose, chitin is the second most abundant natural polymer in the world. Despite the widespread occurrence of this polysaccharide, the main commercial natural sources of chitin have been crab and shrimp shells which are currently waste materials of the food processing industries.

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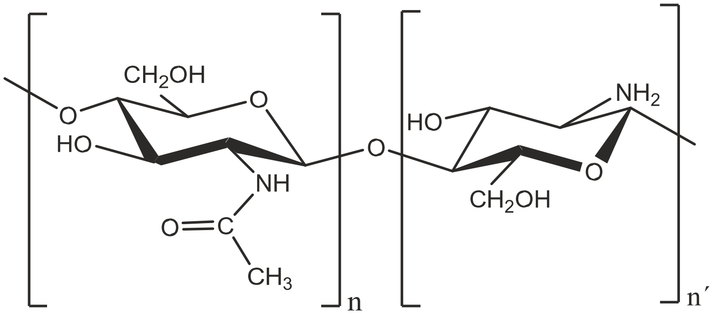

Fig. 1 Structure of partially acetylated chitosan

Because of chitosan polydispersity with respect to molecular weight, producers mainly refer to sample viscosity rather than molecular mass (Croisier and Jérôme 2013).

Besides, due to its poor water solubility, physical characterization of chitosan is not easy to perform. Different methods including pH-potentiometric titration, IR-spectroscopy, ^{1}H-NMR spectroscopy, UV-spectroscopy, colloidal titration, and enzymatic degradation are reported in the literature for the determination of chitosan deacetylation degree (Balázs and Sipos 2007), while its molecular mass is typically deduced from viscosimetry or determined by size exclusion chromatography (Croisier and Jérôme 2013).

Chitosan is the only positively charged, naturally occurring polysaccharide (Pavinatto et al. 2010). In fact, the amino groups of the D-glucosamine residues (Fig. 1) have a pKa value of 6.5 (Nilsen-Nygaard et al. 2015), meaning that the amino groups are predominantly positively charged at pH values below 6.5. At those pH values, chitosan becomes a polycation that can subsequently form ionic complexes with a wide variety of natural or synthetic anionic species such as lipids, proteins, and DNA (Croisier and Jérôme 2013; Madihally and Matthew 1999). Many of the chitosan biomedical or industrial applications are based on the ability of these polysaccharides to form this type of complexes.

For example, it binds negatively charged red blood cells thereby promoting clotting, and this hemostatic property has made it an important component in wound dressings. Similar to other cationic polymers, chitosan possesses antimicrobial properties. Although the mechanisms behind its antimicrobial nature are not completely understood, it is thought that because chitosan is cationic, it likely disrupts anions in bacterial cell walls leading to suppression of biosynthesis and disruption of mass transport across the cell walls (Levengood and Zhang 2014).

Feasibility studies of use of chitosan-based materials for water treatment are also undergoing (Rinaudo 2006). Besides, the complexing ability of chitosan is further exploited for beverages clarification.

On the other hand, glucosamine residues may be specifically reacted with aldehyde functions under mild conditions through reductive amination (Rinaudo 2006). Various functionalizations can be introduced along chitosan backbone by this technique to further extend chitosan field of applications (Croisier and Jérôme 2013).

Besides, the amino group, as well as the primary hydroxyl group, of the chitosan chains can be easily involved in substitution reactions. Grafting of monomers onto chitosan by nucleophilic displacement is described elsewhere.

As was discussed before, it is clear the versatility of chitosan as raw material to be modified in search for the physical and/or chemical properties required for numerous and diverse applications.

2 Chitosan-Based Materials for Biomedical Application

Since long time ago, the scientific community has focused its attention on chitosan as a potential material for biomedical applications. This is because this polymer meets three essential properties that must have a material to be applied in the field of medicine: biocompatibility, biodegradability, and nontoxicity.

Since specific properties required for biomedical materials depend on the area of their application, the most common applications of chitosan-based material in the biomedical field are discussed separately.

2.1 Wound Dressing

Today, various forms of wound dressing materials based on chitin and chitosan derivatives are commercially available (e.g., HemCon® (HemCon Medical Technologies, Inc., Portland, OR), QuikClot® (Z-Medica Corporation, Wallingford, CT), and CELOX™ (SAM Medical, Tualatin, OR)) (Wedmore et al. 2006; Brown et al. 2009; Devlin et al. 2011). They have been developed mainly as external hemostatic agents in the control of hemorrhage and, at the same time, to achieve hemostasis when conventional methods fail.

Besides, there are studies which show that chitin-based dressings can accelerate repair of different tissues, facilitate contraction of wounds, and regulate secretion of the inflammatory mediators such as interleukin 8, prostaglandin E, interleukin 1 β, and others (Jayakumar et al. 2011).

2.2 Tissue Engineering

Although bones have the ability to regenerate when damaged, when bone defects are large enough or critical-sized, they cannot regenerate via normal physiological processes and require intervention in the form of bone grafts. The clinical standards for bone grafting are autograft, harvested from a secondary site in the patient, and allografts, harvested from cadavers and sterilized prior to use (Croisier and Jérôme 2013).

Bone tissue engineering, through the use of synthetic grafts to guide tissue regeneration, offers an alternative to autografts and allografts. A synthetic bone scaffold should be (1) osteoconductive to facilitate bone formation on its surface and (2) highly porous to allow for nutrient and waste transport, neovascularization/angiogenesis, and bone ingrowth. In addition a scaffold should have adequate mechanical strength, and it should degrade over time in concert with bone regeneration (Levengood and Zhang 2014).

Chitosan appears among the most promising biomaterials utilized for bone tissue engineering. The hydrophilic surface of the chitosan promotes cell adhesion and proliferation and evokes minimal foreign-body response. Besides, chitosan can be processed in multiple ways to produce a variety of three-dimensional scaffolds with different pore structures. In addition, hybrid materials with improve mechanical properties are also developed.

2.3 Drug Delivery

As was discussed above, the glucosamine primary amino groups are responsible for most of the biological properties of the chitosan, such as controlled drug release.

Several methods are described for controlling drug release, such as simple drug dissolution process, diffusion, erosion, membrane control, or osmotic systems. But, often, all these methods failed and ionic interactions are the only choice. A controlled release can be achieved for cationic drugs by using anionic polymeric excipients, for example, polyacrylates, sodium carboxymethyl cellulose, or alginate. In the case of anionic drugs, however, chitosan is the only choice (Bernkop-Schnürch and Dünnhaupt 2012).

Bhise et al. (2008), for instance, designed sustained release systems for the anionic drug naproxen using chitosan as drug carrier matrix. Using polyanionic drugs, the interactions between chitosan and the therapeutic agent are more pronounced, and stable complexes are formed from which the drug can be released over a prolonged time period. Sun et al. (2010), for example, designed enoxaparin/chitosan nanoparticulate delivery systems, providing very stable complexes that led to a significantly improved drug uptake.

Besides, chitosan can be homogenized with anionic polymeric excipients, such as polyacrylates, hyaluronic acid, alginate, or carrageenan, resulting in c omparatively stable complexes of high density. From such complex, drugs are slowly released through diffusion and erosion processes.

On the contrary, mucoadhesive properties of the chitosan were weak to be useful in the development of peptide and protein delivery systems (Jintapattanakit et al. 2009). However, because of the great versatility of the chitosan to be chemically transformed, it is feasible that a polymer with the mucoadhesion required for this application can be achieved.

On the other hand, there are many reports of *in situ* gelling formulation of chitosans. For instance, Gupta et al. (Gupta and Vyas 2010) developed an *in situ* gelling delivery system by the combination of polyacrylic acid and chitosan. The resulting formulation was in liquid state at pH 6.0 and underwent rapid transition into a viscous gel phase at physiological pH of 7.4 (Bernkop-Schnürch and Dünnhaupt 2012). The formulation was evaluated as an ophthalmic delivery system of an antiglaucoma drug, timolol maleate. The results demonstrated that developed formulation was therapeutically efficacious and showed a fickian (diffusion-controlled)-type release behavior over 24 h periods. The developed system is thus a viable alternative to conventional eye drops and can also prevent the rapid drainage as in case of liposomes.

3 Chitosan-Based Materials in Food Industries

One of the major challenges that food industry is facing nowadays is related to packaging; particularly, packaging of food with a short shelf life period. Traditionally, the materials selected to this function were plastics and their derivatives due to their effectiveness for food preservation. However, the use of plastics creates serious environmental problems (Aider 2010).

Unlike plastics, chitosan-based edible films can be consumed along with the foods which makes its use environmentally safe. They form transparent films with good mechanical properties (Hamed et al. 2016), act as barrier to gases, reduce moisture transfer, restrict oxygen uptake, control respiration rate, retard ethylene production, and prevent the loss of volatiles (Aider 2010). In addition to all the chitosan properties mentioned before, chitosan-based edible coatings are a source of dietary fiber, which allows them to be prebiotic stimulating beneficial bacteria in the gastrointestinal tract (Hamed et al. 2016). Also, they can carry additional functional ingredients (such as antioxidants and antimicrobial agents), enhancing safety and nutritional quality (Kerch 2015; Elsabee and Abdou 2013).

The impact of chitosan-based edible coatings on shelf life, microbiological quality, and biochemical processes during postharvest storage of fruits and vegetables has been described in a number of recent publications. Some examples that can be highlighted are tomato (Elsabee et al. 2008), Chinese water chestnut (Pen and Jiang 2003), carrot (Li and Barth 1998; Barry-Ryan et al. 2000), mango (Chien et al. 2007), strawberry (Hernandez-Munoz et al. 2008; Vu et al. 2011), blueberry (Duan et al. 2011), banana (Maqbool et al. 2010), lotus root (Xing et al. 2010), apple (Qi et al. 2011), and broccoli (Ansorena et al. 2011), among others. In addition, some other food products that were widely studied are ricotta cheese (Di Pierro et al. 2011), pink salmon (Sathivel et al. 2007), and silver carp (Fan et al. 2009).

For example, Vu et al. (2011) developed edible bioactive coating based on modified chitosan for increasing the shelf life of strawberries during storage. Figure 2 shows that uncoated strawberries are dehydrated and are largely contaminated by molds at day 10, whereas coated strawberries kept a good hydrated, red-colored appearance even at day 21.

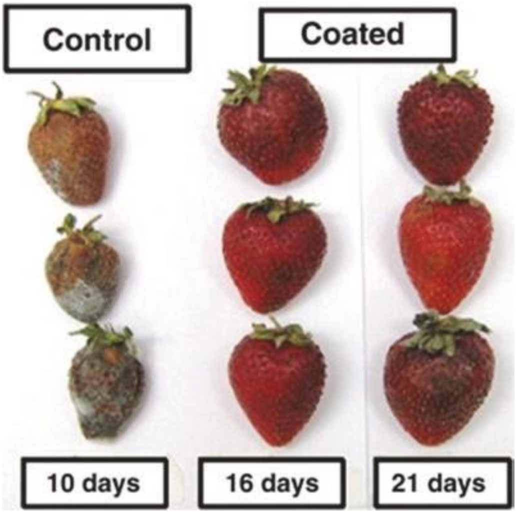

Fig. 2 Appearance of strawberries coated with modified chitosan-based formulation (Reprinted from Vu et al. 2011. Copyright (2011) with permission from Elsevier)

Another important aspect to be considered is the final cost of the product. Taking into account that the contribution of the packaging to the product total cost is highly significant, the cost of the raw material is one of the main factors to be analyzed. Besides the properties described above, from an economical point of view, chitosan also appears as an attractive raw material for food industries (Aider 2010).

4 Chitosan-Based Materials for Water Treatment

Water is an indispensable element for the viability and development of every civilization. This unquestionable fact challenges to take actions aimed at minimizing the deterioration that this vital resource has suffered in recent decades, due to the industrial, domestic, and agricultural wastes generated by human activities. These activities generate wastewater which contains both inorganic and organic pollutants. Some of the common pollutants are phenols, dyes, detergents, insecticides, pesticides, and heavy metals (Bhatnagar and Sillanpää 2009).

A number of methods such as coagulation, membrane process, adsorption, dialysis, photocatalytic degradation, ion-exchange resins, and biological methods have generally been used for the removal of toxic pollutants from water and wastewater (Bhatnagar and Sillanpää 2009). Although the type of the process to be employed may depend on nature of pollutant, adsorption process is one of the most popular. The increasing demand for new and economic processes for water treatment has led many research groups to investigate the possibility of using waste biomaterials for metal uptake (Bailey et al. 1999; Guibal 2004).

In this context, there are many reports of the potential of chitin and chitosan as adsorbent for dyes or metal removal from contaminated water. Beside, some international companies purchase industrial grade chitosan for wastewater treatment (Kyzas and Bikiaris 2015).

Some of the advances in this field are summarized below.

4.1 *Critical Analysis of Feasibility of Use of Chitosan-Based Materials for Metal Removal*

Chromium is one of the major trace heavy metal pollutants in the environment (Volesky 2001). It is well known that while Cr (III) is an essential nutrient required for sugar and fat metabolism, Cr (VI) is an extremely carcinogenic agent (Costa 1997). Therefore, it is essential to accurately define the individual quantity of Cr (VI) (Rossi et al. 2017).

Taking into account that in acidic aqueous medium, at low concentration, Cr (VI) exists as anion ($HCrO_{4^-}$), while at the same conditions Cr (III) exists as a positive ion, the use of an anion exchanger as solid sorbent is a good alternative for chromium speciation.

Considering that the pKa value of chitosan is 6.50, at pH below 5, more than 90% of the amino groups are in their protonated form ($-NH_3^+$) (Rojas et al. 2005), and chitosan derivatives have been proposed as an anionic exchanger. There are many articles published regarding the use of chitosan-based materials as adsorbents for chromium (VI) removal (Bhatt et al. 2015; Qin et al. 2003; Malarvizhi et al. 2010; Lee et al. 2005; Li et al. 2009; Whitacre 2014; Sharma et al. 2017; Rojas et al. 2005).

On the other hand, the contamination of natural waters by arsenic as arsenites As (III) and arsenates As (V) is also a serious problem in several countries. In addition to arsenic contamination from industry (Chatterjee et al. 1993), the high concentrations of arsenic found in groundwater and surface waters have raised concerns in many parts of the world, including Bangladesh (Nickson et al. 1998), Taiwan (Liao et al. 2005), India (Mazumder et al. 2010), Chile, Vietnam (Mazumder et al. 2010), the United States (Welch et al. 2000), and Argentina (Sabbatini et al. 2010).

Since arsenic in aqueous systems is in anionic form, like the Cr (VI), the use of protonated chitosan derivatives for the removal of arsenic from water was also a strategy evaluated by several research groups (Kwok et al. 2014; Boddu et al. 2008; Rahim and Mas Haris 2015).

However, taking into account the acidic lability of the glycosidic bonds, the stability of the chitosan and their derivatives at the pH values required for the amino groups remain mainly protonated is doubtful. This limitation makes unlikely the success of the industrial implementation of chitosan derivatives for the removal of metallic anions.

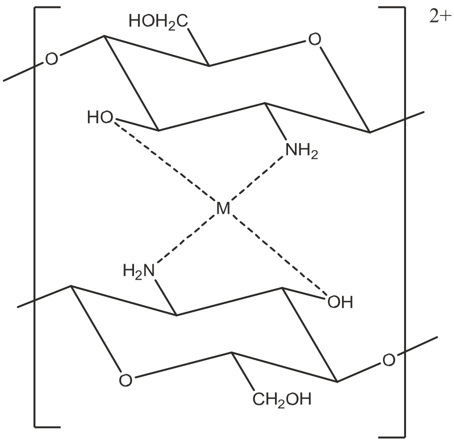

Fig. 3 Chitosan–metal ion complex

In the case of cations, such as lead, mercury, copper, cobalt, and cadmium, among others, the main mechanism involved in the metal retention is chelation rather than ion exchanger (Varma et al. 2004).

This could be attributed to the major role of the amino groups of chitosan chain, which served as coordination site for metal binding. In addition, the formation of a chitosan–metal ion complex may involve some hydroxyl groups (Fig. 3) (Gerente et al. 2007).

In acidic conditions, the amino groups of chitosan are protonated after reacting with H^+ ions as follows:

$$RNH\ H_2 + {}^{+}\ RNH_3^{+} \tag{1}$$

$$M^{2+} + nRNH_2\ M\ RNH\text{-}[\quad {}_2]^{2}{}_{n}{}^{+} \tag{2}$$

where M and RNH_2 represent metal and the amino group of chitosan, respectively, while *n* is the number of the unprotonated chitosan bound to the metal. Combination of Eqs. 1 and 2 gives the overall reaction as follows (Barakat 2011):

$$M^{2+} + nRNH_3^{+}\ M\ RNH\text{-}[\quad {}_2]^{2}{}_{n}{}^{+} + nH^{+} \tag{3}$$

Equation 3 shows that an increase in pH enhances the formation of metal–chitosan complexes. Low pH favors the protonation of the amino sites diminishing the metal-chelating ability of chitosan, and this suggests that at a neutral pH, more metal ions will be adsorbed, depending on their concentrations. On the other hand, with further increase in the solution pH, the formation of metal hydroxide decreases the concentration of free metal cations which leads to the reduction in their removal. The optimum pH for the maximum removal depends on the nature of the cation but is always above 5.0 (Anitha et al. 2015).

Higher values of pH imply less degradation of the polysaccharide, which makes, from this point of view, the implementation of this material much more likely for wastewater treatments. In this context, the capacity of chitosan and their derivate for removing cations is well established (Bassi et al. 2000; Liu et al. 2016; Esmaeili and Khoshnevisan 2016; Zhang et al. 2016; Igberase and Osifo 2015).

Since the economic feasibility of the usage of the absorbent on industrial scale is related to its reusability, many studies looking for the number of cycles of regeneration were carried out.

Unfortunately, the acidic media usually used in this process lead to a fast degradation of the polysaccharide. In this condition, after five cycles of adsorption–desorption, a significant degradation was observed (Liu et al. 2016; Igberase and Osifo 2015).

Ethylenediaminetetraacetic acid (EDTA) could be a good alternative to remove metallic cations from the adsorbent without using an acidic medium. There are reports of high-efficiency metal recovery using this chelate agent, but further studies should be carried out (Chui et al. 1996; Igberase and Osifo 2015).

4.2 Chitosan-Based Materials as Adsorbent for Dye Removal

The main industrial wastewater sources are textile, paper, printing, leather, food, and plastic industries. Among them, one of the most worrying pollutants on wastewater is dyes because it not only can aesthetically cause issues but also it is harmful to biological organisms and ecology.

The most obvious impact of dye discharge is the persisting nature of the color. Low concentration of dye in water is easily visible and can reduce photosynthetic activities in aquatic environments by preventing the penetration of light. In addition, dyes have direct and indirect toxic effects on humans as they are associated with cancer, jaundice, tumors, skin irritation, allergies, heart defects, and mutations (Vakili et al. 2014; Sakkayawong et al. 2005).

Given their synthetic origin and complex aromatic structures, dyes are non-biodegradable substances that remain stable under different conditions. Due to their inert properties and the normally low concentration of dye molecules, their removal from wastewater is a complex challenge. Moreover, the high cost to remove trace amounts of impurities causes the conventional methods of removing dyes become unfavorable to be applied at a large scale (Vakili et al. 2014).

Adsorption with activated carbon appears to be the best prospect of eliminating dyes. However, this adsorbent is expensive and difficult to regenerate after use (Sakkayawong et al. 2005). In search for alternatives to activated carbon, adsorption techniques using chitosan composites have been developed to adsorb dyes as an alternative to conventional wastewater treatment processes (Vakili et al. 2014; Annadurai 2000; Cestari et al. 2008; Rosa et al. 2008; Crini 2006; Wong et al. 2004; Prado et al. 2004; Chatterjee et al. 2007; Gupta and Suhas 2009).

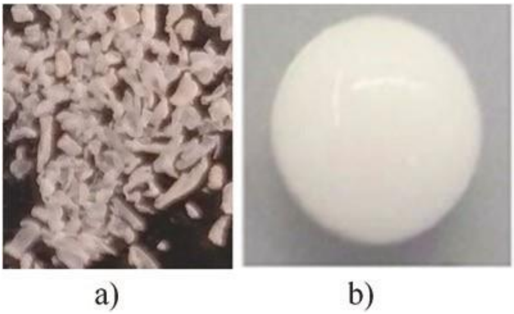

Fig. 4 Digital photos of (**a**) chitosan flakes. (**b**) Chitosan hydrogel bead (Reprinted from Luo et al. 2013. Copyright (2013) with permission from Elsevier)

Recently, hybrid materials based on chitosan have been developed and favorable synergistic effects were observed. For example, chitosan–zinc oxide nanoparticle composites exhibit remarkably improved mechanical properties, such as tensile strength (Mujeeb Rahman et al. 2016). Since its sorption capacity was not affected, this material has the potential to act as alternative industrial low-cost adsorbents (Abul et al. 2015).

On the other hand, Chang and Juang (2004) studied the chitosan/activated clay composites. They found that the adsorption capacity of the composite was comparable to chitosan bed, but the addition of activated clay enhances the capability of chitosan to agglomerate and round gel beads and improves the hardness of the beads. This is especially important for practical applications.

It is critical to keep in mind that chitosan can be molded in different shapes, such as flake, bead, fiber, or film, being flakes the easiest to obtain. Considering that dyes are removed by an adsorption process (a surface phenomenon), the efficacy of the treatment is related to the superficial area of the adsorbent. The adsorption capacity from bead-type chitosan (Fig. 4) is much greater than flake-type chitosan (Fig. 4) which is in agreement with the fact that the beads have a greater surface area than the flakes (Wan Ngah et al. 2002). Beads are prepared by casting an acidic chitosan solution into alkaline solution.

5 Conclusion

As can be seen from reading this chapter, chitosan has proved to be versatile for so many industrial applications and its versatility is the main value of this polymer.

However, the lability at acidic pH of chitosan is a limiting factor that affects mainly its industrial implementation for the removal of metallic anions from water.

In addition, the physical and mechanical properties may vary between two manufacturing batches due to the characteristic polydispersity of chitosan with respect to molecular weight and degree of acetylation. This variation could affect the industrial process and in some cases, when strict specifications are requested (e.g., drug delivery), increase the final cost of the product because a purification step prior to use is required.

Briefly, despite of the disadvantages mentioned before, due to its great versatility, its nontoxicity, its biodegradability, and the fact that it has a renewable resource, the industrial interest in chitosan and its application has been increasing remarkably in the last years.

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