RVq | Revista Virtual de Química

ISSN 1984-6835

Artigo

Recent Advances in Designing Hydrogels from Chitin and Chitin-Derivatives and their Impact on Environment and Agriculture: A Review

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Rev. Virtual Quim., **2017**, *9* (1), 370-386. Data de publicação na Web: 12 de dezembro de 2016

http://rvq.sbq.org.br

Recentes Avanços em Hidrogeis de Chitina e Derivados de Chitina e seu Impacto sobre Meio Ambiente e Agricultura: Uma Revisão

Resumo: Nosso objetivo é mostrar e discutir os dados mais relevantes sobre a abordagem de síntese e a caracterização de hidrogéis à base de quitina e derivados de quitina, como a quitosana, bem como suas aplicações em diversas tecnologias de materiais. A relevância atual e futura dos materiais à base de quitina, quitosana e derivados foi verificada pelo impressionante número de publicações científicas e tecnológicas (tanto papéis como patentes) que aparecem no dia-a-dia. Os hidrogéis, que apresentam propriedades semi-líquidas e semi-sólidas, tornaram-se uma grande promessa para aplicações onde o uso eficiente da água é essencial para melhorar as propriedades físico-químicas dos solos áridos. Eles também são eficazes no tratamento de águas contaminadas com corantes, chumbo cádmio, mercúrio, níquel e assim por diante, minimizando o impacto ambiental.

Palavras-chave: Hidrogel; polissacarídeo; polímero superabsorbente; condicionador de solo; recuperação de água.

Abstract

Our purpose is to show and discuss the most relevant data on the synthesis approach and the characterization of hydrogels based on chitin and chitin-derivatives, such as chitosan, as well as their applications in several materials technologies. The current and future relevance of materials based on chitin, chitosan and derivatives have been verified by the impressive number of scientific and technological publications (both papers and patents) that appears day-by-day. The hydrogels, which show half liquid-like and half solid-like properties, have become a great promise for applications where the efficient use of water is essential to improve the physical-chemical properties of the arid soils. They are also effective in treatment of waters contaminated with dyes, lead cadmium, mercury, nickel, and so on, minimizing the environmental impact.

Keywords: Hydrogel; Polysaccharide; Superabsorbent Polymer; Soil Conditioner; Water Recovery.

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DOI: **10.21577/1984-6835.20170021**

Volume 9, Número 1

Janeiro-Fevereiro 2017

Revista Virtual de Química
ISSN 1984-6835

Recent Advances in Designing Hydrogels from Chitin and Chitin-Derivatives and their Impact on Environment and Agriculture: A Review

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Recebido em 3 de novembro de 2016. Aceito para publicação em 12 de dezembro de 2016

1. Introduction

Nowadays, the scientist's efforts are addressed to hydrogels using cutting-edge techniques and reliable polymeric molecules to make them safer, non-toxic and environmentally friendly. In this sense, the polysaccharides have been recognized as an excellent macromolecular platform to synthesize hydrogels. On another note, this class of natural polymers has been pointed out as potential candidate to replace petroleum-based polymers.[1] Renewability, low cost, natural abundance, and biodegradability are some of the attractive characteristics showed by the polysaccharides. In addition, polysaccharides possess in their backbone a considerable number of functional groups, which can be chemically modified resulting in a wide variety of derivatives. Hence, the synthesis, characterization, and application of polysaccharide and polysaccharide-derivatives based hydrogels have been extensively reported in the literature.[2-5]

Chitin (Ct), the second most abundant polysaccharide in the earth after cellulose, has attracted considerable attention due to its very interesting properties; in special those related to its use in biological applications (e.g. non-toxicity, biodegradability, biocompatibility, cytocompatibility, antimicrobial and antioxidant activities, among others).[6-7] Ct is a linear polysaccharide consisting of varying amounts of β-(1→4)-linked2-amino-2-deoxy-β-D-glucopyranose (GlcN) and it is found predominantly in the shells of crustaceans, the cuticles of insects, and the cells walls of fungi[7]. Commercially, Ct has been extracted from crab and shrimp shells using acid treatment and its industrial uses include wastewater treatment (flocculation agent, removal of heavy metals, etc.), agricultural materials and as additive in textile, paper and food industries.[8,9] Moreover, Ct-derivatives raise the range of applicability of such versatile biopolymer. Chitosan (Cs), the chitin most known derivative, for instance, is obtained by Ct partial deacetylation under alkaline conditions and it has been used to prepare hydrogels, films, fibers and sponges, which are used in the biomedical domain.[10-13] Recently, elongated crystalline rod-like nanoparticles, known as 'nanowhiskers' have been extracted from Ct using acid hydrolysis.[14,15] Such nanoparticles have found use as reinforcement, crosslinking and antibacterial agent when incorporated within some polymeric matrices.[16-18]

1.1. Basic concepts and distinguished properties of hydrogels

A particular class of macromolecular hydrogels is constituted of superabsorbent hydrogels (SHs), which are able to absorb and retain a large amount of water or aqueous liquids.[19,20] Studies have demonstrated that SHs show swelling ratio (i.e., the mass ratio of swollen gel to dry network) in the order of 1,000-2,000 folds. In light of this, SHs have been used in the countless applications, such as agriculture, hygienic and bio-related uses.[19,21] The most part of these unique materials is synthesized from the free-radical polymerization chemistry of hydrophilic monomers, resulting in networks composed of homo- or co-polymers, or from the grafting of such monomers onto the backbone of natural polymers. It is worth mentioning that the swelling capacity depends on the chemical nature of the ionisable groups along the polymer chains as well as it also depends on the crosslinkingdensity.[22] Generally, non-ionic or highly crosslinked hydrogels show lower swelling capacity when compared with ionic hydrogels or hydrogels of low cross-linking density. The charge density within the hydrogel matrix can be controlled by changing the pH and ionic strength.

According to pH, for example, functional groups along the polymer backbone can be ionized, which results in a substantial increase in the charge density inside the hydrogel network, causing electrostatic repulsion and consequently expansion of polymer chains.[23,24] As a consequence, the swelling capability is enhanced. In this context, the hydrogels which are able to dramatically change their volume and/or other properties in response to external stimuli, such as pH, ionic strength, temperature, solvent, electric or magnetic field, and others are designed as 'smart hydrogels'.[25,26] Overall, these stimuli-responsive hydrogels show a considerable scope of applications likely due to their rapid and significant response to the aforementioned stimuli, high swell and controllable mechanical properties. It must be mentioned that such responsiveness may be an intrinsic property, as that observed for the poly(*N*-isopropylacrylamide) hydrogels, a thermo-responsive material which undergoes hydrophilic/hydrophobic transition in response to temperature. Such characteristic also may be induced upon addition of metallic and/or magnetic nanoparticles, or antimicrobial agents tohydrogel.[27,28]

2. Chitin

The first reports on chitin isolation are attributed to the botanist Henry Braconnot in 1811 and to the chemist, Auguste Odier in 1823, both French researchers, in their works with mushrooms and insect cuticles, respectively.[29-30] However, at the time of their discoveries, the structure of that enigmatic substance insoluble in base or acid solutions was not fully comprehended. It took a century of researches when the Suisse chemist Albert Hofmann during his doctorate finally shed lights on the chitin structure. Chitin, the first natural carbohydrate polymer isolated, is composed of 2-acetamido-2-deoxy-D-glucose units connected by β-1,4glycosidic bonds (Figure 1).

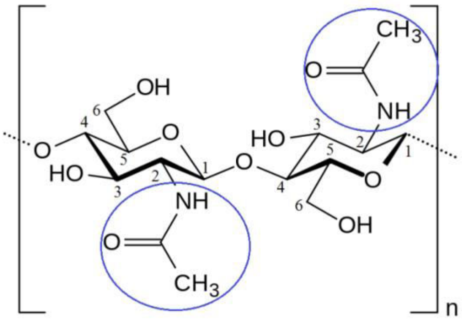

Figure 1. Repeating units of chitin: 2-acetamido-2-deoxy-D-glucose units connected by β-1,4glycosidic bonds

Chitin is commonly isolate with some degree of deacetylation (generally varying between 10 to 15 %) mainly due to the following aspects: (i) chitin is often physically or chemically bound to glycoproteins by the nitrogen atom at carbon 2; (ii) acids and bases are involved in the chitin extraction procedures and those chemicals can catalyze some hydrolysis of acetoamide groups.[9,31-33]

2.1. Methodologies to convert chitin-derivatives into hydrogel

Cs is the most important Ct derivative, being obtained mainly from alkaline hydrolysis. Cs has a better solubility than Ct and very much applicability because it contains amino moieties in its polysaccharide structure. On the other hand, *N,N,N*-trimethyl chitosan (TMC) is one of the most important Cs derivative. Several methodologies for TMC synthesis are described in the literature.[34-36] Cs reduction can be easily mediated by iodomethane in sodium iodide presence and strong alkaline condition, using *N*-methyl-2-pyrrolidone (NMP) as solvent.[37,38] Some authors reported the use of dimethylsulfate like reduction agent instead iodomethane, because it has higher stability and it can be used as solvent in the reaction for TMC production as well.[38-40] TMC free of O-methylation was synthesized from *N,N*-dimethyl chitosan (DMC) in presence of iodomethane and NMP.[38,41] In this case, DMC make be easily synthesized in formic acid/formaldehyde/water solution. Fully N-trimethylated TMC was formed from group protection strategies using iodomethane in NMP.[42] In this case, di-*tert*-butyl-dimethylsilyl (di-TBDMS) was used for protecting the hydroxyl sites on Cs moieties. TMC 100% N-quaternized and free of O-methylation presents better solubility in organic solvents than Cs, whereas the H-bond intensities among Cs chains decreased substantially.[42] Therefore, the larger number of reaction steps involved the synthesis of fully N-trimethylatedTMC can be considered one disadvantage of the protection strategy procedure.

Quaternization,[34,43] alkylation[34] hydrolysis,[34] acylation,[44] carboxylation,[45] sulfation,[46] sulfonation,[47] and thiolation,[48] are the most important methodologies used for several chemical modifications onto Ct/Cs backbones. Ct and Cs have in their chains, hydrophilic side groups, such hydroxyl and amino sites which are very reactive[34] and the vast majority of the Ct/Cs chemical modifications occur onto these sites.[34,45]

Reductive amination of Cs can be easily mediated by the reaction of Schiff bases with reducing agent, like sodium borohydride, sodium cyanoborohydride, among others.[49,50] The Schiff bases are obtained by condensation reaction with amino groups on Cs especially with aldehydes and ketones.[34] Several Cs derivatives were synthesized changing the starting aldehydes and ketones. For example, N-(cinnamyl) chitosan derivatives were prepared from Cs and aromatic cinamaldehydes, which contain different substituted groups on their aromatic rings (-R = -Cl, $-NO_2$, $-N(CH_3)_2$, $-O-CH_3$).[51] The reductions of imines (Schiff bases) with sodium borohydride allowed obtain Cs derivatives with a degree substitution ranging from 8-28 %.[51] Hydrophobic Cs derivatives also were prepared from reductive amination, using aldehydes of linear chains with greater carbonic contents and Cs hydrophobic derivatives with micellar capacities were formed.[52,53]

O-Alkylation of Ct was performed on C6-OH sites from reaction between p-benzoquinone (PBQ). This Ct derivative reacted with ethylenediamine to prepare an aminated Ct compound and, then, deacetylated to get an aminated Cs derivative.[54] Similarly, O-carboxymethyl chitin prepared from alkaline hydrolysis and carboxylation onto C6-OH position was mediated by monochloroacetic acid by nucleophilic substitution. Several acyl chlorides reacted with Ct to get acylated derivatives.[55]

N-[2-hydroxyl)-propyl-3-trimethyl ammonium] chitosan chloride was synthesized in ionic liquid from epoxide ring-opening on 2,3-epoxypropyltrimethyl ammonium chloride.[56] The substitution was performed onto amino groups, but could be mediated onto C6 position if the amino sites were protected by phthalic anhydride. The phthalic anhydride could be easily removed by reaction with hydrazine hydrated.[57] β-ciclodextrin (β-CD) was grafted on Ct molecules from tosylated β-CD and Ct. Tosylated β-CD reacted with ethylenediamine to get animated β-CD, and then it was grafted onto Ct by nucleophilic substitution.[58]

2-N-sulfated 6-O-carboxymethylchitosan and 2-N and 3,6-O sulphated chitosan were synthesized from trimethylamine sulphur trioxide/Na_2CO_3 and oleum ($H_2SO_4{\cdot}SO_3$) reagents. In these cases, the sulphatation was performed onto amino and hydroxyl groups.[59]

"Click" chemistry reaction is another approach used to produce Ct/Cs derivatives. In this case, two compounds react through a cycloaddition reaction. So, a chemoselective conjugation by alkyne-azide coupling occurs to get Ct/Cs derivatives obtained from "click" chemistry reactions.[60] In general, the reaction is catalysed by copper(I) or (II) and carried out in the presence of sodium ascorbate and water.

3. Uses of Chitin and Hydrogels from Chitosan and Chitosan Derivatives

3.1. As adsorbent for metallic ions from aqueous solution

Heavy metals tend to accumulate in living organisms due to their non-biodegradability, thus causing various diseases and disorders. As a consequence, the environmental pollution levels have increased to a great extent in the last years, leading to the development of suitable methods for removing these species from water and industrial wastewater.[61] Normally, aqueous solutions polluted by heavy metals may take long periods to recover and, sometimes, the recovery process is impracticable or impossible.[62] If inappropriately discharged as chemical residues in water, soil and air, they may be absorbed by plants and animals leading to intoxication of the food chain.[62] Owing to the considerable potential for metal contamination, a number of processes have been proposed for the remediation of water and industrial wastewater, including biological treatment, membrane separation, advanced oxidative processes, chemical precipitation, coagulation, ion exchange, electrochemistry process, adsorption and so forth.[63,64] Technologies using adsorption processes have proven to be more viable alternatives due to the following features: low cost of processing, low cost of instrumentation, ease of operation and no need for large facilities.[65] Adsorbents that may be used in the remediation of water and industrial wastewater include those from animal, organic and vegetable origins such as zeolites,[66] clays,[67] silicates,[68] by-products from shrimp-, crab-, krill- and silkworm-processing industries,[61,69] residues from agriculture such as rice rusk,[70] tree bark,[71] biomass,[72] lignin,[73] algae, leaves,[71] alginate[74] mosses,[75] polymer resins,[76] Ct,[77] amide,[78] Cs,[79] cyclodextrin[80]and hydrogels.[81]

From a technological viewpoint, polymer hydrogels are effectives for adsorption studies due to their chemical stability, selectivity and porous structure[4,82,83] Hydrogels of Ct or Ct-derivatives have been employed for the adsorption and removal of uranyl,[84] cadmium,[85] lead,[86] manganese,[87] mercury,[88] zinc ions and dye molecules[89] from aqueous solutions. Hydrogels of carboxymethylchitin and carboxymethylchitosan are effective in the removal of various metal cations from aqueous solutions.[90,91] Chitin-derivative hydrogels with magnetic properties may also be used as adsorbent material.[92,93] For instance, Cs-based magnetic hydrogels were used to remove textile dyes from industrial effluents[92] and adsorption of lead, cadmium and cupper from aqueous solutions.[94] Magnetic hydrogel based on polyacrylamide-grafted Cs was applied as an efficient adsorbent for the removal of copper, lead, and mercury ions from aqueous solutions in respective single, binary, and ternary metal mixtures.[88] It has been reported that the addition of different components in a hydrogel network improves their adsorption capacity[95] since such included compounds may function as dispersing agents to increase the interconnected porous structure of polymer hydrogels.[96,97] As an example, Cs functional hydrogel may be synthesized for the adsorption and removal of chromium ions from solutions with high efficiency.[95] Hydrogel based on poly(2-acrylamido-2-methylpropane sulfonic acid)/Cswas synthesized for adsorption and removal of cadmium and chromium from composed wastewater.[98] Different amounts of 2-acrylamido-2-methylpropane sulfonic acid influenced significantly the adsorption capacity of metals since the higher the amount of monomers used during the synthesis the higher the amount of active groups on the three-dimensional network for adsorption of metallic ions.[98]

3.2. As adsorbent of dyes from wastewater resulting from industrial activities

Dyes used in textile industries are cytotoxic and cause nausea, lung and bladder cancer, congenital malformation, eczema, dermatitis, asthma, chronic bronchitis, tuberculosis and eye irritation.[99] Textile dyes as methylene blue and orange II which are widely employed in natural and synthetic fibers dying in the paper and cellulose industry[100] may cause cardiovascular problems. As anionic dyes interact with either cationic polymer groups or directly to fibers they have been widely employed in natural fiber dying including wool, cotton and silk.[86,101,102] In order to address these environmental issues, various natural and synthetic materials have been employed for remediation of water and industrial wastewater polluted with dyes by applying adsorption processes.[103] Other widely applied methods for remediation of water and industrial wastewater polluted with dyes include ion exchange,[104] coagulation and flocculation,[105] chemical precipitation,[106] electrochemical reaction,[107] electrodialysis,[108] reverse osmosis and membrane filtration.[109-112] Unlike the solid adsorbents, the polysaccharide-based hydrogels appear as excellent tool for the removal of aqueous solutes, including dyes and pigments,[103,113] Among various types of polysaccharide hydrogels, those ones based on chitin- and chitin-derivatives are promising adsorbents for the adsorption, removal and separation of anionic and cationic dyes from aqueous solutions.[94] Chitin and its derivatives may be converted into hydrogels and applied as excellent adsorbent materials for adsorption, removal and separation of different pollutant dyes from water and industrial wastewater.[114] However, the adsorption efficiency mainly depends on the type of applied hydrogel. Sometimes, the poor mechanical properties and low kinetics hinder hydrogel practical applications in adsorption of metallic ions and dyes.[115] Hybrid hydrogels may overcome these disadvantages because they are synthesized by combining the advantages of inorganic species with the hydrophilic three-dimensional polymer structure of a conventional hydrogel,[116] such as Cs/glutaraldehyde hydrogel,[117] hydrogel of poly(N-isopropylacrylamide) and poly(sodium acrylate),[118] Cs-g-poly(acrylic acid)/attapulgitehydrogel[119] and Cs-g-poly(acrylic acid)/attapulgite/sodium humate hydrogels. [96]

3.3. As soil conditioner in agriculture

Hydrogels based only on cross linked chitosan (Cs) are not superabsorbent due to the low solubility in water of Cs. So, to achieve desired superabsorbency characteristics, Cs have been chemically modified (or copolymerized)with highly hydrophilic moieties. For instance, Mahdavinia et al.,[120] prepared superabsorbent hydrogels by reacting Cs and polyacrylonitrile (PAN) under alkaline conditions (NaOH = 1 mol/L) at 90 ^{o}C. The pendant -C≡N groups of PAN react with –OH groups of Cs allowing obtain a 3D matrix. The material presented swelling degree up to 320 g/g and is dependent on pH. Huacai et al., grafted acrylic acid onto Cs at 60 ^{o}C under N_2 and at different powers of microwave irradiation.[121] Physic hydrogel obtained by mixing Cs (cationic) with anionic moieties presented super absorbency with potential for uses as soil conditioner. For instance, Sabadini et al., prepared superabsorbent hydrogels based on Acetyl gellan gum (HAGG) and Cs by crosslinking reaction throughout the ionic bond formation for soil conditioner.[122] This hydrogel absorbed more than 218 times with respect to its dry weight.

3.4. As nutrient carriers in agriculture

Nitrogen is present on vegetal (dry basis) in amounts ranging from 1 to 5 wt-%. Such an element is constituent of chemical structures as amino acids, nucleic acids, enzymes, chlorophyll, ADP, ATP and proteins. Despite being present in earth's atmosphere in ca. 78% (v/v), nitrogen is a limiting factor for vegetal production. The majority of living organisms cannot fix directly the nitrogen from its gaseous form, due to the breaking in capacity of triple covalent bonds (N≡N),characteristic of nitrogen molecule.[123] So, for food production based on nitrogen-based compounds such as ammonia (NH_3), ammonium (NH_4^+), nitrate (NO_3^-), nitrogen oxides (NO_x), nitric acid (HNO_3), urea, amines, proteins, nucleic acids, among others are added to soil.[124] The Food and Agriculture Organization (FAO) of the United Nations anticipated that the agricultural activity in the world will grow in ca. of 57% from 2000up to 2030.[125] Also, it is expected that developing countries will response for 72% of the whole agricultural production compared to 53% in 1961/63. In same direction, the total world production and consumption of fertilizers grew 4 to 5times from 1961 to 2002.[123]

The loss of nitrogen added to the soil, for helping the vegetal production, represents around 30% included the nitrate lixiviation, ammonia volatilization, emission of nitrogen-based gaseous compounds such as nitrous and nitric oxides, etc. Significant fraction of nitrogen is immobilized by microorganism present in through nitrification or denitrification processes causing low availability for plants and other microorganisms. This leads to increase of costs for agriculture production.[126] For instance, in USA, the annual cost due to loss of fertilizers through lixiviation or denitrification is 15.9 billions of dollars.[126,127] Also, the perceptual of contaminated water due to lixiviation of nitrogen excess used in agriculture changed from 2.2 (in 1960) to 38.6 (in 1980). There is an expectation that such percentage has been increased to more than 50% in 2000.[128]

Due to the elevated economic cost and also to the environmental risks related to excessive uses of nitrogen-based fertilizers/nutrients in soil, there is a continue and growing interest for amelioration of soil nutrients retention, i.e., process that lead to lowering the loss of nitrogen. Researchers aimed at develop new technologies for increase the efficiency of nutrient release to the plants. Granulated fertilizers based on zinc phosphate, ammonia and urea encapsulated by carboxymethyl chitosan and N-maleyl chitosan hydrogels have been developed.[129] The Cs derivative-based hydrogel promoted an increase in humidity retention and a better pH-control of soil. The encapsulation of fertilizer onto hydrogel was made through direct aspersion. This is a simple technique and can be scaled up to industrial process.[129,130] Wu and Liu (2008) performed aspersion of hydrogel to encapsulate NPK fertilizer granules using a rotating reactor.[131] Spherical nanoparticles of Cs and polymethacrylic acid were prepared by Corradini et al. [132]aiming the loading and further release of NPK fertilizers as potential use in agriculture. The average size was close to 70 nm (in dry state). In swollen state the average diameter of particles as well as the zeta potential changed with the concentration of phosphorous (P), nitrogen (N) and potassium (K) loaded from urea, calcium phosphate and potassium chloride, respectively, in liquid media dispersing the colloidal particles.[132]

The dicyandiamide (DCD) may reduce by 76% the lixiviation of nitrate in soil[133] and also reduces the emission of N_2O by 70%.[134] The DCD possesses half-live estimated ca. 110 days at 5 °C and 20 days at 25 °C;[135] so it can be quickly degraded in soil.[136] Minet et al. (2013) used glyoxal-crosslinked Cs for controlled released of dicyandiamide (DCD).

The DCD combined to linear Cs (not crosslinked) was easily available: 84% of whole DCD released in water after 9 h of immersion; and from 74% to 98% after 7 days as dispersed in soil. The DCD encapsulated on hydrogel, made of Cs crosslinked by glyoxal, released the DCD slowly: 19% under 9 h as immersed in water; and only 33% after 7 days in soil even under high rainfall conditions.[130] Higher content of glyoxal leads to a more crosslinked matrix promoting a delay in the release of DCD in water and in soil, as well.

It can be highlighted that Cs and Cs derivatives-based hydrogels can be used in agriculture for controlling the release of nutrients for the plants. The physical and chemical structures of hydrogel control the release rate in soil.[137] By this methodology, the plant nutrition is increased and the environment protection, as well, and the whole economy is improved due to the enhanced efficiency of nutrient/fertilizer used on agriculture production.[138] The use of hydrogels in agriculture further reduces the leaching of minerals and nitrogen compounds to water.[139] Thereby, reducing the environmental liabilities of agricultural production can be the greatest contribution of hydrogels for world food production.

4. Future Trends and Perspectives

Important challenges or trends in this field to be addressed:

a) to scale up new materials based on Cs or Cs-derivatives allowing higher production at low cost for large scale application, e.g. in agriculture (as soil conditioner/carrier nutrients) or in environmental control (as adsorbent for metallic or colorants from industrial effluents).

b) no essays were performed with plant cultures for evaluate the expected effect of hydrogel on the synergistic process such as the fast growing and vegetal productivity. So, farm-soil studies are welcome to consolidate the promising results.

5. Conclusions

This review deals the synthesis, the characterization, the properties and the application of hydrogels based on Cs and Cs-derivatives to different technological fields (environmental, and agriculture). According to chemical and physical structures of Cs and Cs-derivatives based hydrogels, they can be used as absorbent (dyes, metallic ions, etc.) in environment preservation or mitigating effects of wastewater; in agriculture (as water retention for soil conditioning and nutrient/fertilizer carriers). Despite the existing wide range in properties-application, some challenges need to be overcome. More comprehensive studies will expand the understanding of structure-properties-applications relationship. The perspective for uses of Cs and Cs-derivatives (as hydrogels or not) is growing in near future.

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