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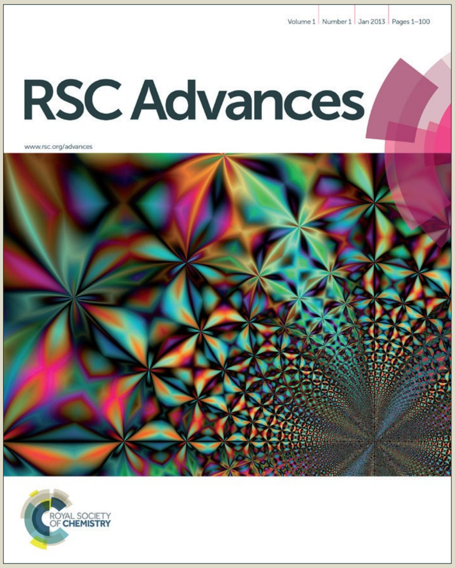

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Advances in cellulose-based superabsorbent hydrogels

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Abstract: This contribution provides a brief overview of recent progress in cellulose-based superabsorbent hydrogels fabrication approaches, materials and promising applications. At first, different synthesis methods were introduced, including physical crosslink as well as chemical crosslink ways. Second, some of the cellulose series original materials were introduced in this work. In addition, some applications and future research in cellulose-based superabsorbent hydrogels were also discussed in this review.

Keywords: cellulose-based superabsorbent hydrogels; absorbency ability; biodegradability; renewable.

1. Introduction

Since the appearance of a new concept "superabsorbent polymer" in 1950s, considerable interest has been attracted within the scientific community as well as the industrial world and rapid progress has been made in the past few decades because of the tremendous demand for superabsorbent materials in the sanitary industry. Superabsorbent hydrogels are hydrophilic networks with a high capacity of water uptake, which can absorb, swell and retain aqueous solutions up to hundreds of times their own weight (dry sample) [1][2][3]. Even though most of the superabsorbent hydrogels are produced from synthetic polymers (essentially acrylics) for their superior price-to-efficiency balance [4], the tendency of replacing the synthetics with “greener” alternatives is more overwhelming for the synthetic superabsorbent’s poor degradability and biocompatibility.

Cellulose, as one of the carbohydrate polymers, is the most abundant resource in nature, and is biocompatible, biodegradable, non-toxicity, low cost and renewable. Cellulose, which has abundant hydroxyl groups, can be used to prepare superabsorbent hydrogels easily with fascinating structures and properties.

Most recently, cellulose-based superabsorbent hydrogels have become ubiquitous and indispensable materials in many applications. Introducing cellulose series materials into the superabsorbent hydrogels can overcome the disadvantages of synthetic-based superabsorbent hydrogels to satisfy the utilization requirements and can endow the final products with excellent properties [5]. Thus, multifunctional superabsorbent materials could be achieved. Compared with the synthetic superabsorbent hydrogels, cellulose-based superabsorbent hydrogels have high absorbency, high strength, good salt-resistance, excellent biodegradable ability and biocompatibility, and other special functions that promise a wide range of applications in many fields.

Only limited reviews about cellulose-based superabsorbent hydrogels on its different category have appeared in the literature [6]. This review aims at highlighting the recent developments in cellulose-based superabsorbent hydrogels with emphasis on the preparation methods, original materials of cellulose and possible applications.

2.Preparation methods

Some preparation methods are used to get the target superabsorbent hydrogels. In general, they can be classified into two branches: chemical methods and physical methods. Chemical methods like aqueous solution polymerization, inverse-phase suspension polymerization, even microwave radiate method are as in the case. Meanwhile, physical cross-link techniques like freeze/thaw cycle technology, hydrogen bond crosslink etc. are also adapted in some cases [7]. And it is worth noting that some new techniques as interface contact technology [8], in situ photo-polymerization [9] etc. are emerging in recent years.

2.1 Chemical synthesis methods

Chemical synthesis methods are widely used to fabricate the cellulose-based superabsorbent hydrogels for the formation of covalently linkage, in essence. Typical chemical synthesis methods are stated as below.

2.1.1Aqueous solution polymerization

Among the homogeneous polymerizations, the solution polymerization is preferred due to better control of the heat of polymerization, lower cost and more convenient. Most of the cellulose-based superabsorbent hydrogels are produced in this way. Generally, the cellulose series macromolecular, monomer(s), initiator, and crosslinker(s) are freely soluble in water, or have good solubility in water. Once the initiator induced by the temperature or the radiation, the polymerization process start. After certain time, the product of this reaction can be dried out and pulverized for various applications.

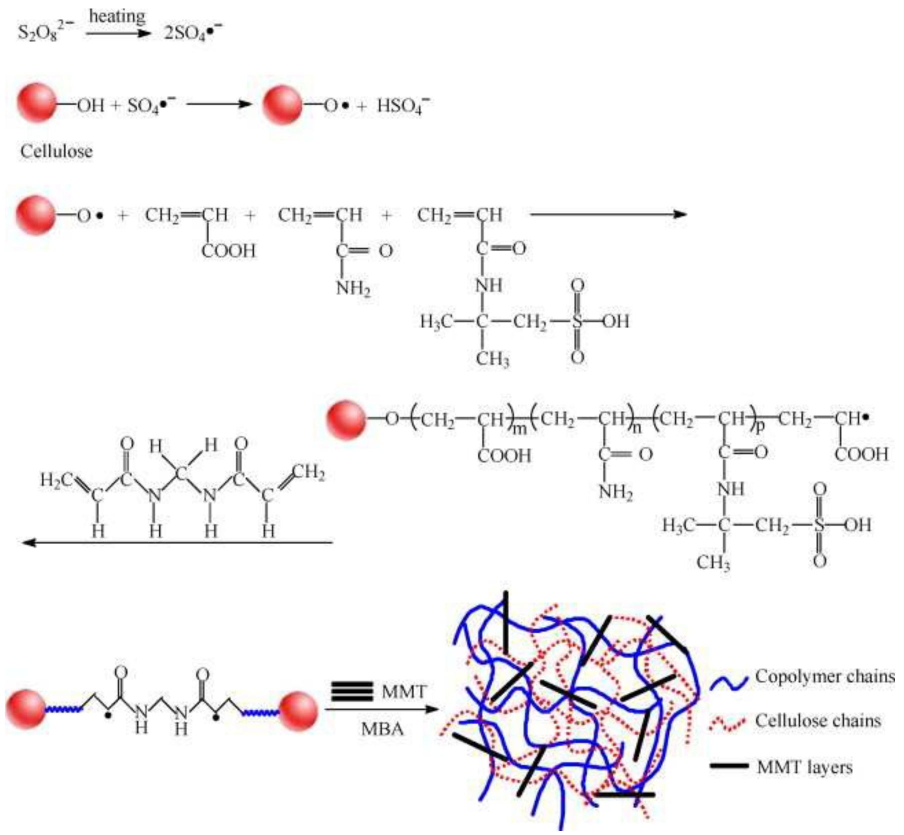

Figure 1 Proposed reaction mechanism for synthesis of cellulose-g-P(AA-co-AM-co-AMPS)/MMT superabsorbent hydrogels. Reprinted from Carbohydrate Polymers, 84(1), Bao Y, Ma J, Li N, Synthesis and swelling behaviors of sodium

carboxymethyl cellulose-g-poly (AA-co-AM-co-AMPS)/MMT superabsorbent hydrogel, 76-82. Copyright (2011), with permission from Elsevier.

The mechanism for solution polymerization synthesis cellulose-based superabsorbent hydrogels mainly attribute to the free-radical induced polymerization. The free radical polymerization is a process in which monomers are polymerized through the initiation of initiators. This kind of polymerization has been used so extensively because it has high polymerization rate and happens in an aqueous medium, which is safe and harmless. The cellulose macromolecular produce the free radical initiated by the initiator, then interact with the monomers forming the graft copolymer. The prominent induce approach is chemical induce， containing mono-induce system (for example, persulfate[10]), bi-induce system (like redox induce system[11][12][13]), and even ternary-induce system [14]. Besides, physical induce can also be adapted, such as Co-60 γ radiation-induced [15], Ce (IV) induced [16], microwave irradiation induce [17], radiation-induced plasma [18], etc.

Bao, et al. elaborated the reaction process [19] of cellulose-based inorganic/organic nanocomposite superabsorbent hydrogels by the solution polymerization. At first potassium persulfate was used to produce the initial free radicals under heating, and then these radicals captured the hydrogen from the hydroxyl groups on the cellulose substrate, generating the alkoxy radicals. The alkoxy radicals attacked the acrylic monomers in close vicinity of the reaction sites, leading to the chain initiation. Subsequently, these small molecules radicals became free radical donor to the neighbor molecules. Furthermore, in the presence of the cross-linker N, N-methylenebisacrylamide (NMBA) and filler powdery Na-MMT, the chain propagation developed quickly. Finally, the reaction ended by the coupling of the macromolecules. The formation mechanisms of cellulose-g-P (AA-co-AM-co-AMPS)/MMT superabsorbent hydrogel are shown in Fig. 1. Other works on the solution polymerization process are almost the same procedure with the nitrogen line purged before the reaction.

Except for polymerization in pure water aqueous reaction media, interaction in the mixture aqueous media assumed to be another routine to get cellulose-based superabsorbent hydrogels. Likewise, a cellulose-based superabsorbent hydrogel was fabricated by the interaction between cellulose and carboxymethyl cellulose sodium (CMC) in the alkaline/urea aqueous medium [20]. The process proceeded with nucleophilic attack of cross-linker epichlorohydrin between cellulose and CMC.

2.1.2 Inverse-phase suspension polymerization

Inverse-phase suspension polymerization is conducted in the dispersed and continuous phases. The dispersed phase is aqueous and the continuous phase is organic. The monomer is usually dissolved in the dispersed phase, and a surfactant is used to help the monomer and other aqueous reagents to be effectively dispersed throughout the continuous phase. Although particles with desirable sizes can be obtained by this technique, removal of the organic solvents, such as n-hexane and toluene, is a very challenging problem. This technique is appropriate for the polymerization of highly hydrophilic monomers, such as salts of acrylic and methacrylic acids, as well as acrylamide [21] etc.

When the superabsorbent hydrogels are used in controlled release or chromatography, they are needed in the form of particulates. To avoid the “gel blocking” caused by the irregular shaped pieces generated from grinding process, Liu et al. [22] produce hydroxypropyl methylcellulose (HPMC)-based porous gels in bead form by inverse-phase suspension polymerization, during which cyclohexane was used as the continuous phase, HPMC solution (10 wt%) was used as the dispersed phase.

For the industry, inverse-phase suspension polymerization is the second choice comparing with the solution polymerization in aqueous for its complexity and higher costs [23]. Searching among the recent five years literatures, the inverse-phase suspension polymerization tends to minimize.

2.1.3 Microwave irradiation polymerization

Microwave irradiation technology as an emerging polymerization skill, compared with the tradition approaches, display stronger penetrating ability, faster heating, cleaner and higher efficiency. The differences among the above polymerization approaches are listed in Table 1.

As simple and without waste drainage, it is promising for the cleaner production of cellulose-based superabsorbent hydrogels. Giachi et al. [24] reported that the microwave-synthesized product possessed faster swelling and shrinking kinetics in comparison to the superabsorbent hydrogels prepared by conventional methods. Jelena et al. [25] investigated the influence of microwave synthesis on kinetics of polymerization and found that the polymerization rate increased significantly in comparison to the normal heating method. They deduced that this may be due to decreased activation energy and increased inherent energy of the crosslinker. Afterwards, M Pandey et al. [26] synthesized the bacterial cellulose (BC)/acrylamide (Am) hydrogels using the microwave irradiation method and the product show non-cytotoxic and hemocompatible. Besides, comparative study was made among freeze, microwave irradiation and combination of both methods [27]. Feng et al. [28] also prepared the cellulose-based superabsorbent hydrogels using flax shive under microwave irradiation. They chose potassium persulfate and N, N'-methylenebisarylamide (NMBA) as initiator and cross-linker, seperatively. Moreover, Wan et al. [29] grafted copolymer of methyl methacrylate on to the bamboo cellulose under microwave irradiation by using ceric ammonium nitrate as cross-linker. The effect of microwave power, microwave exposure time and initiator concentration on the graft copolymerization reactions were estimated and the optimum conditions of 160w microwave power, 9min exposure time were obtained for graft copolymerization. They found that the moisture absorption capacity of the graft copolymers decreased significantly with the increase in grafting percentage.

Table 1 Comparation among the three polymerization approaches.

Polymerization Type	Characterization
Aqueous solution polymerization	Easy-control, lower cost and stable; Mass shape products.
Inverse-phase suspension polymerization	Complex, higher costs and unstable; Particle products.
Microwave irradiation polymerization	Fast heat, high efficiency and clean. Mass shape products.

2.2 Physical synthesis methods

Unlike chemical synthesis methods, physical synthesis methods always refer to the molecular assembly crosslink by the hydrogen bond or the ionic bond between the polymers, or by the interaction between the polymers.

Cryogenic treatment was applied to obtain the cellulose-based superabsorbent hydrogels, which in contrast with the methodology undergoing at ambient temperature. The superabsorbent hydrogels of this process is so-called “cryogels”, which formed by the association of strong hydrogen bond. This strong hydrogen bond may be formed during one of the stages of the freeze/thaw circles: during freezing of the initial system, during storage of the samples in the frozen state, or during thawing of the frozen specimens. Guan et al. [30] prepared a novel cellulose-based superabsorbent hydrogels by repeating the freeze/thaw cycles, which induced physically crosslinked chains packing among these polymers. And then a phase separation caused the formation of compact structure after multiple freeze/thaw cycles, resulting in high mechanical strength and thermal stability. The highest compressive strength of 10.5 MPa was achieved by the 9 times of freeze/thaw cycles.

By combining UV irradiation and cryogenic treatment technology, researchers have prepared the cellulose-based superabsorbent hydrogels with high mechanical strength, pH sensitive swelling properties and good bio-adhesiveness. The incorporation of cellulose into the polymer network provided the possibility to use the cryogels as excipients for the Biopharmaceutics Classification System (BCS) Class 1 preparation of drug delivery, such as metronidazole [31]. From this research, we convince that the cellulose-based superabsorbent hydrogels will be a kind of promising drug delivery system in a near future

Electron beam irradiation technique was also applied to synthesis the cellulose-based superabsorbent hydrogels [32]. The resulting macroporous sponge-like structure cellulose-based superabsorbent hydrogels, which crosslinked by the strong hydrogen bond between the intermolecular, showed many promising features for an effective wound dressing, like the ability to absorb exudates, an optimal environment of water vapor transmission for wound healing, excellent biocompatibility and so on.

Except for irradiation physical crosslink, interaction between the polymers assumed to be another routine to get cellulose-based superabsorbent hydrogels. Likewise, a cellulose-based superabsorbent hydrogel was fabricated by the interaction between cellulose and carboxymethyl cellulose sodium in the alkaline/urea aqueous medium.

Besides, Zhang et al. reported a stable cellulose-based superabsorbent hydrogels based on the bamboo through dialysis the alkalization bamboo cellulose suspension against water followed by a short time of ultra-sonication [33]. The electrostatic repulsion between negatively charged -COO^-groups on the cellulose fibers generating during the oxidation process was assumed the driven force of the formation of the hydrogel. Compared with most methods for preparing cellulose hydrogels, which required complex and difficult dissolution processes usually with harmful solvents, the physical approach proposed here was quite environmentally friendly and effective.

2.3 Newly emerging approaches

Other than traditional superabsorbent hydrogels synthesis method, fast contact of solid-liquid interface technology is more facile and faster. The whole process is shown in Fig. 2. Researchers used 2% agarose solution as template gel-core, and obtained cellulose solution by adapted NaOH/urea solution system in low temperature After loading 10wt%

acetic acid on the template gel-core, the solid-liquid interface contact was performed by immersing the template gel-core into the cellulose solution to prepare the first cellulose layer. Furthermore, the multi-layered cellulose-based superabsorbent hydrogels were fabricated by repeating the soaking process [34]. Cellulose-based superabsorbent hydrogels can also be prepared from native celluloses (cotton cellulose) dissolved in lithium chloride and N-methyl-2-pyrrolidinone (LiCl/NMP) by esterification crosslinking with 1, 2, 3, 4-butanetetracarboxylic dianhydride (BTCA) [35]. Subsequently converse of un-reacted carboxyl groups to sodium carboxylates by addition of aqueous NaOH was performed to enhance the water affinity of the hydrogels. It was confirmed that the absorbency of cellulose-based superabsorbent hydrogels were enhanced as the average degree of polymerization (DP) of the starting cellulose increased. Using cotton cellulose with a high DP of about 2400 produced a superabsorbent hydrogels with an absorbency of 720 times its dry weight, which exceeded the absorbency of commercial crosslinked sodium polyacrylate superabsorbent hydrogels (SPA). The hydrogels exhibited good biodegradability, with a maximum degradation of 95% within 7 days.

Some physical methods are developed as well to make a contribution to the family of the cellulose-based superabsorbent hydrogels. Isobe et al. [36] prepared cellulose-based superabsorbent hydrogels from LiOH/urea solvent with alcoholic coagulation, and some adsorption measurements were conducted to the surface and structural properties of cellulose-based superabsorbent hydrogels from an alkali/urea solvent. Besides, highly aligned and covalently cross-linked hydrogel microfibers were obtained by the electrospinning technique, which provides a safely approach to fabricate nanoscaled to microscaled fibers [37]. The resulting cellulose-based superabsorbent hydrogel microfibers show great potential using in the active biological tissues, like replacement of the damage muscle tissue, etc.

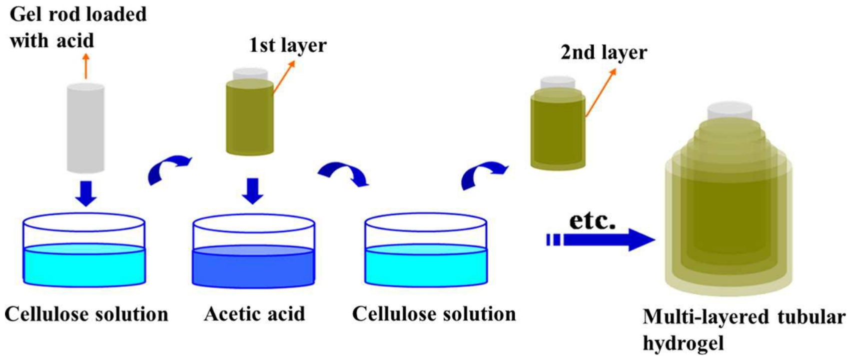

Figure 2 Physical synthesis methods of the fast solid−liquid interface contact technique. ([34]) Reprinted with permission from He M, Zhao Y, Duan J, et al. Fast Contact of solid–liquid interface created high strength multi-layered cellulose hydrogels with controllable size [J]. ACS Applied Materials & Interfaces, 2014, 6(3): 1872-1878.Copyright 2014 American Chemical Society

Except for the most common cross-linker NMBA, Senna et al. chose ethylenediamine tetra-acetic dianhydride (EDTAD) as cross-linker in the preparation of superabsorbent hydrogels from cellulose acetate with degree of substitution (DS) 2.5. The reaction process can be described as simultaneous crosslinking and grafting of EDTAD occurred by the formation of diester and monoester linkages [38].

3. Cellulose derived from different resources

According to the survey, the resources of the cellulose in the cellulose-based superabsorbent hydrogels are various, which include the native cellulose of the natural plants, cellulose derivatives, functional modified cellulose, bacterial cellulose. All of these resources used in the synthesis systems are expected to achieve with ideal superabsorbent hydrogels properties.

3.1 Native cellulose

Native cellulose own many advantages such as repetition usage, biodegradable, especially well salt-resistance and anti-/Mildew resistance compared with the starch [39]. Many plants in nature can provide the cellulose, such as wheat straw, cotton stalk flax and mulberry branches [40], which mainly act as the supporting materials in the plant cells in biological for its stiffness and water absorbency. Common native cellulose resources used in preparation cellulose-based superabsorbent hydrogels are showed in Fig. 3.

Liang et al. [41] adapted the wheat straw to finish the fabrication of superabsorbent hydrogels. To better use wheat straw and minimize its negative impact on environment, Liu et al. prepared a semi-interpenetrating polymer networks (semi-IPNs) cellulose-based superabsorbent hydrogels which composed of wheat straw cellulose-g-poly (potassium acrylate) (WSC-g-PKA) network and linear polyvinyl alcohol (PVA) by polymerization in the presence of a redox initiating system[14]. The results showed that the semi-IPNs cellulose-based superabsorbent hydrogels prepared under optimized synthesis condition gave the best water absorption of 266.82 g/g in distilled water and 34.32 g/g in 0.9 wt% NaCl solution.

Currently, cotton stalks are mostly burned on the ground since they are harboring diseases that could affect future cotton crops. However, cotton stalks are abundant, cheap, biodegradable and annually renewable, and some attempts have been made to study on the potentials of utilizing cotton stalks. For example, the modified maleylated cotton stalk was used to prepare the superabsorbent hydrogels by Sawut et al. [42]. The modified cotton stalk cellulose has the better hydrophilicity and is easier to graft monomer than cellulose. The maximum water absorbency of the obtained cellulose-based superabsorbent was 1125 g/g in distilled water and 126 g/g in 0.9 wt% aqueous NaCl solution. Compared to the cellulose from other sources, the flax cellulose has longer molecular chain which means that it has more active groups on single molecular chain and has better hydrophilicity, and is easier to modify. Wu et al. [43] successfully prepared a new, low-cost, and eco-friendly cellulose-based superabsorbent hydrogels from flax yarn waste. Their results showed that under the optimized conditions, the water absorbencies of the obtained superabsorbent hydrogels were 875 g/g distilled water, 490 g/g natural rainwater, and 90 g/g 0.9 wt% aqueous NaCl solution.

Nguyen et al. made the cost effective and scalable recipe for fabricating biodegradable cellulose aerogels from waste paper available. The product is highly absorbent, absorbing 18–20 times its weight in liquid. Coating the aerogel with methyltrimethoxysilane improves its hydrophobicity without affecting its absorbency [44]. Mechanically, the aerogel is flexible yet strong making a wide range of applications possible. Besides the above, cotton and viscose waste textiles [45] were also included into the native cellulose family to synthesis the cellulose-based superabsorbent hydrogels.

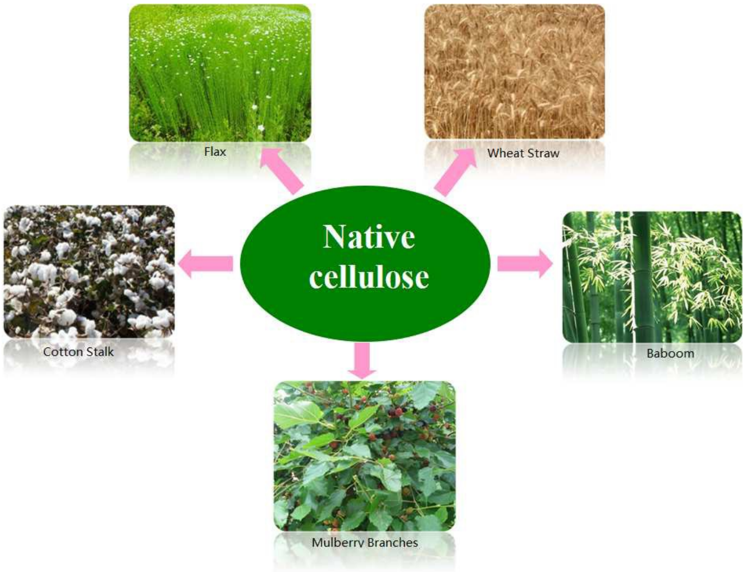

Figure 3 Common native cellulose resources used in preparation cellulose-based superabsorbent hydrogels.

To our knowledge, a new kind of native cellulose origin was bacterial cellulose [46]. Bacterial cellulose (BC) has similar chemical structure, crystallinity and mechanical strength with the plant cellulose, while absorption capacity of BC is greater than those of plant cellulose [47], which has led to the utilization of BC in the absorbing hydrogel field. For example, Halake et al. [9] exactly use the cellulose produced by the bacterial to reach their goal.

3.2 Cellulose derivatives

Quantities cellulose derivatives such as carboxymethyl cellulose (CMC), hydroxypropyl methyl-cellulose, methyl cellulose and hydroxyethyl cellulose have been exploited to prepare cellulose-based superabsorbent hydrogels [48].

Among all the superabsorbent hydrogels prepared with cellulose derivatives, the superabsorbent hydrogels involved carboxymethyl cellulose owns the highest equilibrium water absorbency and swelling rate in distilled water and saline solution. Yang et al. prepared the injectable polysaccharide superabsorbent hydrogels [49] to make it possible used in the drug delivery vehicles or tissue engineering matrices with the help of carboxymethyl cellulose. Meanwhile, Eyholzer et al. [50] fabricated the bio-composite superabsorbent hydrogels for replacement of the native human nucleus pulposus (NP) in intervertebral disks in the presence of the carboxymethylated, nanofibrillated cellulose powder. Cellulose microfibers, nanowhiskers, or nanofibers have been successfully used as reinforcing fillers in a series of synthetic and natural superabsorbent hydrogels. The main reason for this reinforcement of cellulose nanofibers is due to its high aspect ratio of around 20-50, low density of 1.56 g/cm^3, high elastic modulus estimated at 145 GPa, and strength, reported to be 7500 MPa [51]. Aouada et al. [52] reported a simple, fast, and low cost strategy for the synthesis of micro and nanocomposites superabsorbent hydrogels by adding cellulose nanofibers as reinforcing agents, obtained by acid hydrolysis. It was found that the incorporation of cellulose nanofibers affected the crystallinity of superabsorbent hydrogels, thus contributing to improvement in mechanical and hydrophilic properties of superabsorbent hydrogels. It was also observed that cellulose nanoparticles improved the mechanical properties of superabsorbent hydrogels without negatively impacting their thermal and hydrophilic properties.

Evermore, Hong et al. extracted the cellulose nanofibrils from sustainable natural sources. And they proved that the hydrogel moduli may be tuned by appropriate choice of divalent or trivalent cations (Ca^{2+}, Zn^{2+}, Cu^{2+}, Al^{3+}, and Fe^{3+}) [53]. In addition, to provide valuable knowledge for designing high performance nanocomposite superabsorbent hydrogels with cellulose as a raw material, Yang et al. used two sources of cellulose nanocrystals (CNCs) with different aspect ratios to model the reinforcement process. It could be achieved that the values of aspect ratios and nonpermanent interactions between the fillers and matrix dominate the reinforcement [54].

Table 2 Summary of the mainly used cellulose derivatives and its corresponding superabsorbent hydrogels

cellulose derivatives	corresponding superabsorbent hydrogels preparation methods	applications	reference
carboxymethyl cellulose	solution polymerization, in situ polymerization	biomedical, agriculture,	19, 20, 48, 49, 57, 62, 82, 85
methyl cellulose	solution polymerization, in situ polymerization	release fertilizer,	48, 64, 82
hydroxyethyl cellulose	solution polymerization, cryogenic treatment	smart materials	31, 48
hydroxypropyl methyl cellulose	solution polymerization, inverse-phase suspension polymerization	controlled release	22, 48
cellulose acetate	chemical cross-linkage	drug carrier system	55,74

Cellulose acetate (CA), as a well-known derivative of cellulose, is produced either by heterogeneous or homogeneous acetylation of cellulose. Senna et al. described a detailed synthesis process of cellulose-based superabsorbent hydrogels using cellulose acetate [55] as material.

Except for the common etherification product of cellulose, hydrazide or aldehyde functionalized [56] product of cellulose were also reported recently in contributing construct the cellulose-based superabsorbent hydrogels. For instance, quaternized cellulose [57] was cross-linked with carboxymethyl cellulose in NaOH aqueous solution in the presence of epichlorohydrin (ECH).

4. Application fields

A number of superabsorbent hydrogel products with cellulose-based have been either available commercially or in the process of development. In addition, many patents about cellulose-based superabsorbent hydrogels have been granted for various possible applications. Most of these used for agricultural and horticulture, personal health care field, water treatments, biomedical fields and the stimuli-response smart behavior applications. Additionally, many promising applications as protective barriers for volatile organic compounds spilled in the environment and as absorbents for waste oil [58] had also been explored.

4.1 Agriculture and horticulture

As we all know, arid is still a threat for many countries as far, especially in Africa, South America and west of Asia. To improve the soil conditions in these areas, Li et al. applied the superabsorbent hydrogels as a kind of soil additives, they examined the changes of water content, soil microbial activity, biomass and the crop yield between the original soil and the modified soil. It turns out that the addition of the superabsorbent hydrogels into the soil not only leave no detectable adverse effects, but also bring benefits to the soil physical properties and the crop yield [59]. The research conducted by Demitri et al. [60] might have a revolutionary impact on the optimization of water resources management in agriculture. The proposed cellulose-based superabsorbent hydrogels allowed an efficient storage and sustained release of water to the soil and the plant roots, showing potential as water reservoir in agriculture.

Pesticides, the most cost-effective means of pest and weed control in agriculture, are also recognized as a source of potential adverse environmental impact. Superabsorbent hydrogels based on the cellulose series used as carriers for pesticides is of special interest in terms of both economic and sustainable development. Encapsulating the herbicides into the cellulose-based superabsorbent hydrogels could be used to slow the release rate of these herbicides [61].

To minimize the hazard influence of the herbicide-acetochlor, for example, potential toxicity to non-target organisms in the farmland, Li et al. developed the controlled-release formulations of acetochlor, which provides an improvement in safety to the user and non-target organisms and a reduction of the herbicide application rates and leaching in soils. By using CMC gel and different types of clay, the controlled-release formulations of herbicide acetochlor were prepared. The performance of inorganic clays in dried gel formulations on slowing the release of acetochlor is related to their sorption capacities while the organic clay did not lead to the slowest release. In addition, according to the parameters of an empirical equation used to fit herbicide-release data, the release of acetochlor from clay/CMC gel formulations is controlled by diffusion mechanism [62].

Laftah et al. [63] evaluated the effect of polymer hydrogels composite (PHGC) based on cotton microfiber on the sandy soil holding capacity, urea leaching loss rate (ULLR), and okra plant growth. Their results showed that cotton microfiber has a prominent effect on the swelling rate, re-swelling capacity, and biodegradability of PHGC. Okra plant growth and ULLR were positively affected by PHGC and the best leaching loss rate of 33.3 % was observed for the lowest urea loaded sample. Even more, Bortolin et al [64] has proved that PAAm/methyl cellulose/montmorillonite superabsorbent hydrogels imparted the synergistic effects for the slow release of fertilizers. All their results revealed that the cellulose-based hydrogels effectively slow the loss of nitrogen via volatilization of ammonia.

4.2 Personal health care

Superabsorbent hydrogels are widely used in hygienic field like disposable diapers and female napkins for their ability to absorb and retain large amount of secreted fluids, such as, urine, blood etc. It was reported that the first generation commercial superabsorbent hydrogels was produced in Japan in 1978 as a component of female napkins. Then it was rapidly extended its market all over the world for the ability to retain the secreted liquids under pressure. In a word, superabsorbent hydrogels have caused a huge revolution in the personal health care industry [4]. At present, superabsorbent hydrogels that contained in sanitary napkin are also primarily polymerized by acrylic acid (AA) or acrylamide (AM), which are costly, poorly degradable and environmentally unfriendly. Liu et al. provided novel tactics by incorporation of flax yarn waste into superabsorbent hydrogels for sanitary napkin applications [65]. Their results showed that the product exhibit excellent biodegradability, superabsorbent and retention ability of artificial blood solution compared to those of the currently marketed sanitary napkin products.

Although more convenient, suitable, and comfortable disposable health care products [66] [67] [68] have extensively been applied in modern time, biodegradable health care products haven't either been industrialized or been commercially available. In view of the foregoing, the key technique of converting the cellulose-based superabsorbent hydrogels into the core layer of health care products needs to be broken through.

4.3 Water treatments

Rapid industry developments leads a series of problems to the environment, for example, water contamination. A number of technologies have been developed for water treatments, mainly including adsorption, chemical oxidation, pressurized membrane based separation and so on. While owing to the increased energy consumption and the latent second pollution caused by traditional materials, researchers have shifted their attention to the cellulose-based superabsorbent hydrogels.

To deal with the polluted streams by heavy metals like Pb^{2+}, Zhou et al. prepared a novel magnetic hydrogel beads, which blended chitosan with amine-functionalized magnetite nanoparticles, carboxylated cellulose nanofibrils(CCNFs), and poly(vinyl alcohol) by an instantaneous gelation method. This new magnetic hydrogel beads can absorb Pb^{2+} in sewage quickly and effectively with a high value of 171.0mg/g, which can be attributed to the numerous carboxylate groups on the CCNFs and the abundant hydroxyl and amino groups on the chitosan [69]. Tripathy et al. have investigated the five metal ion sorption (i.e. Cu^{2+}, Ni^{2+}, Zn^{2+}, Pb^{2+} and Hg^{2+}) behavior of cellulose-based superabsorbent hydrogels. Results showed that the values of the five percent ion uptake were 13.8, 11.5, 9.8, 9.0 and 8.7 at the maximum values, separately [12]. Their results also showed that the sorption percent values increase directly as the graft ratio increases, indicating that the sorption sites increase [13]. Besides, cyanoethyl cellulose-based superabsorbent hydrogels were obtained to apply for the adsorption of copper (II) ions from aqueous solution. The authors reckoned that metal-ion removal depends on the protonation and deprotonation properties of its acidic and basic groups, namely pH value [70].

Apart from the pollution from the metal ion, frequent oil spills and increasingly oil pollution from industrial wastewater have already been another resource of the water contamination. In order to reach energy-efficient and cost-effective separation of water from oil, Rohrbach et al. created a nanocellulose-based filter by a dipping and drying process of coating the filter with a layer of nanofibrillated cellulose superabsorbent hydrogel. The filter's efficiency can reach 99.1% [71]. The water oil separation process is shown in Fig. 4.

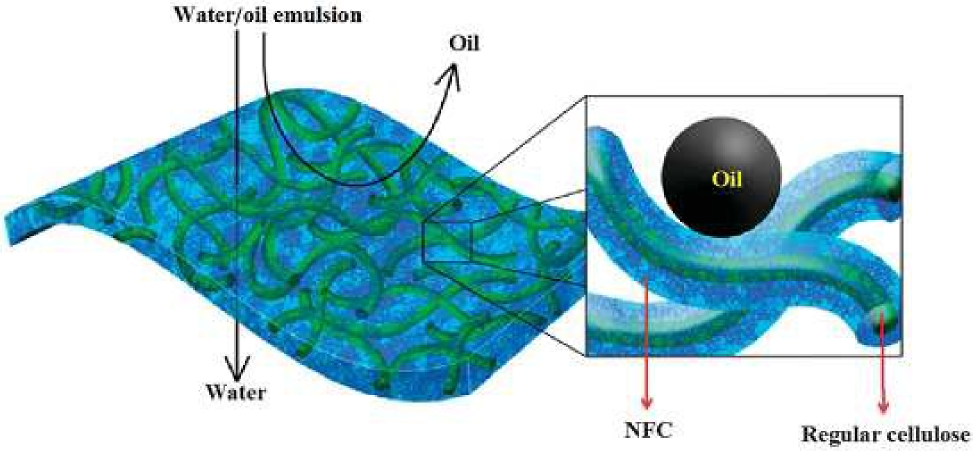

Figure 4 Schematic of water oil separation using a regular cellulose paper with a layer of coated cellulose-based superabsorbent hydrogel. Reproduced from Reference 71 with permission from The Royal Society of Chemistry.

Despite aforesaid researches, developing new strategies in water treatments using cellulose-based superabsorbent hydrogels are more overwhelming in the future.

4.4 Biomedical

Cellulose-based superabsorbent hydrogels are also widely used in biomedical field, for instance, drug delivery, tissue engineering, cell bioreactors, and micropatterning neural cell cultures. He et al. fabricated the onion-like and multi-layered tubular cellulose-based superabsorbent hydrogels for the first time. Cell toxicity experiment results indicated that the L929 cell can survive and proliferate in the larger interior space of the multi-layer cellulose-based superabsorbent hydrogels, showing great potential application in the biomedical field [34].

The injectable cellulose nanocrystals (CNC)-reinforced superabsorbent hydrogels prepared by Yang et al. [42] could maintain their original shape for more than 60 days when immersed in purified water or 10 mM PBS and exhibits the excellent storage modulus. Moreover, CHO−CNC-reinforced superabsorbent hydrogels is more elastic, more dimensionally stable, and facilitating higher nanoparticle loadings compared to hydrogels with unmodified CNCs, without sacrificing mechanical strength. The cytotoxicity test to NIH 3T3fibroblast cells showed that CNC-reinforced injectable hydrogels were of potential interest for various biomedical applications such as drug delivery vehicles or tissue engineering matrices.

As we all know, in the wound treatments field, wound dressings with good hydrophilicity and microorganism inhibition quality are rarely achieved simultaneously. To obtain the ideal materials for the wound dressings, researchers explored to use different treatment to modify the viscose fiber in its non-woven form. By using the alkali treatment or oxygen plasma treatment, the high hydrophilicity was achieved [72]. It turns out that the introduction of the silver chloride nanoparticles into the cellulose matrics markedly improved the antimicrobial activity, which can be ascribed to the broad spectrum antibacterial quality of the silver, and the hydrophilicity of the wound dressing was also improved in a degree in relation to the untreated viscose fiber. Comparing to the “alkaline treatment followed oxygen plasma treatment” two-step procedure, the one-step ammonium plasma treatment significantly improved hydrophilicity, but could not provide the desired antimicrobial activity on all of the used bacteria, as to S. Aureus, E.Coli, E. Faecalis and P. Aeruginosa, which means the one-step approach may have a limited antimicrobial activity in the clinical application. Anyway, the one-step ammonium plasma treatment for modifying the viscose fiber provided a new outlook to prove the potential of the feasibility and the developments toward the clinical application and the commercial production.

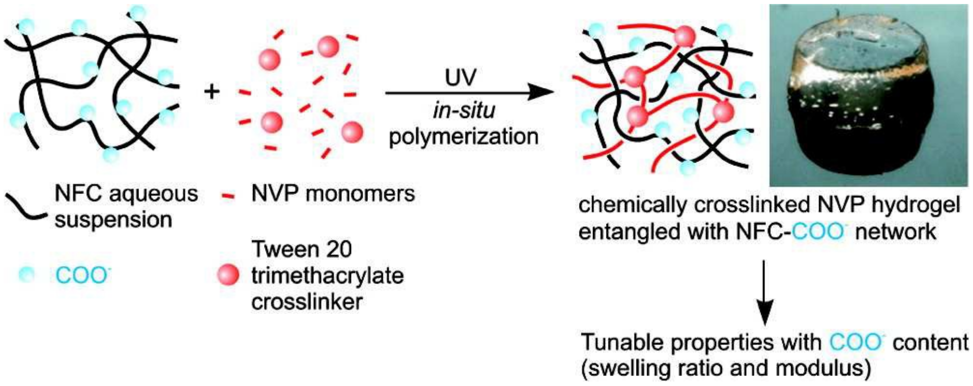

Figure 5 Biocomposite cellulose-based superabsorbent hydrogels promised for replacement of the human nucleus pulposus in intervertebral disks. ([50]) Reprinted with permission from Eyholzer C, Borges de Couraca A, Duc F, et al. Biocomposite hydrogels with carboxymethylated, nanofibrillated cellulose powder for replacement of the nucleus pulposus [J]. Biomacromolecules, 2011, 12(5): 1419-1427. Copyright 2011 American Chemical Society

Lin et al. have proved that cellulose-based superabsorbent hydrogels were used as drug carrier for in vitro release of doxorubicin and exhibited the behavior of prolonged drug release with special release kinetics [73]. To extend the application of the cellulose-based superabsorbent hydrogels, Eyholzer et al. prepared biocomposite superabsorbent hydrogels with carboxymethylated nanofibrillated cellulose (c-NFC) powder by UV polymerization of N-vinyl-2-pyrrolidone with Tween 20 trimethacrylate as a cross-linking agent for replacement of the native, human nucleus pulposus (NP) in intervertebral disks. Among the tested samples, the biocomposite superabsorbent hydrogels containing 0.4% v/v of c-NFC with a DS of 0.17 shows the closest behavior to native NP, which can be a breakthrough in treating the symptomatic intervertebral disk degeneration [50]. The entire process is shown in Fig. 5. Even more, the cellulose-based superabsorbent hydrogels have played a vital role in veterinary practice. Oliveira et al. adapted the cellulose acetate and 1, 2, 4, 5-benzenotetracarboxylic dianhydride to synthesis and assess the controlled release systems, which are usually designed to protect patients from unfavourable environments, provide them with more comfort, prevent side effects and improve efficiency through structural modifications of the drug carrier system [74]. Joshi et al. [75] have revealed that their cellulose-based superabsorbent hydrogels reversibility with temperature in physiological salt fluids such as simulated gastric and intestinal fluids have a better insight into the oral drug delivery systems [76]. Some studies on the anticancer drugs docetaxel, paclitaxel, and etoposide have already done by Jackson et al. [77].

There has also been considerable interest in utilizing crosslinked-CMC as tablet disintegrants. The cellulose-based superabsorbent hydrogels in its powder form is mixed with other excipients and compressed to a tablet. Tablets containing cellulose-based superabsorbent hydrogels may soften at high humidity and may add instability concern to the moisture-sensitive drugs [78]. Rheometry test finished by Ngwuluka et al. have shown that their hybrid hydrogels product may be suitable polymeric material for achieving controlled zero-order drug delivery [79]. Furthermore, the cellulose-based superabsorbent hydrogels have also made a good contribution in non-immediate-release devices [80].

Appel et al. [81] investigated systematically the release mechanism/model of the physically cross-linked superabsorbent hydrogels by crosslink dynamics. It was determined that the cargo (containing the drugs) release processes from the cellulose-based superabsorbent hydrogels could be directly correlated with the dynamics of the physical interactions responsible for cross-linking and corresponding time-dependent mesh size.

Mechanically, cellulose-based superabsorbent hydrogels can be designed to have elastic and loss moduli similar to those of soft tissues, enabling their effective use in tissue engineering applications or as biological lubricants. Patenaude et al. [82] combined a series of synthetic oligomers and carbohydrate polymers, like methylcellulose, carboxymethyl cellulose, dextran, to create in situ gelling, hydrazone-cross-linked hydrogels using a double-barreled syringe. In this way, one property can (in many cases) be selectively modified while keeping other properties constant, providing a highly adaptable method of engineering injectable, rapidly gelling hydrogels for potential in vivo applications.

In the “smart” materials family, cellulose-based superabsorbent hydrogels tends to have wider applications in the field of biomedical. Herein, in this article, we focus on the pH-responsive, salt-responsive and thermal-responsive behavior of cellulose-based superabsorbent hydrogels. With the development of cellulose derivatives, mainly cellulose ether, some stimuli-responsive cellulose-based superabsorbent hydrogels have been developed from MC, HPC, HPMC, and CMC, by chemical or physical methods.

A kind of nanocomposites hydrogel was synthesized on the basis of poly (acrylamide-co-acrylate) and cellulose nanowhiskers by Spagnol et al. [83], which showed sensitive to the pH variation (2-12). Such on–off switching behavior as reversible swelling-deswelling has been reported

[84] and been seen as a good candidate for some of the technological applications. In the research of Wang et al., the hydrogels of CMC-g-poly (AA-co-AMPS) showed better reversible pH sensitivity in the pH 2.0 and 7.0 solutions, which makes the hydrogels available as a candidate for drug delivery systems [85].

Subsequently, Hebeish et al. [86] synthesized the smart cellulose-based superabsorbent hydrogels with sensitive response to the environment temperature stimuli. And researchers verify the potential promising for the application particularly in pharmaceutical field. Besides, Hu et al. [87] prepared cellulose-based superabsorbent hydrogels which exhibited smart swelling and shrinking behaviors in NaCl and $CaCl_2$ aqueous solution, showing salt-responsive adsorption behaviors in different media.

5. Outlook

This review seeks to describe the research progress of superabsorbent hydrogels based on cellulose from different angles over the past decades. Cellulose-based superabsorbent hydrogels have many favorable properties such as hydrophilicity, biodegradability, biocompatibility, transparency, low cost, and non-toxicity. Therefore, cellulose-based superabsorbent hydrogels have wide applications in agriculture and horticulture, personal health care, water treatments, biomedical and so on. However, some new fields need to be expanded, such as oil plugging agent, electro-chemistry and so on. We emphasized various methodologies, materials and achievements on these particular materials, and provided an overview of their applications as functional materials on a large scale. However, with the development of living standard, more demands are imposed. The mature conventional product could not meet the requirements.

Therefore, the future scientific researches on cellulose-based superabsorbent hydrogels need to be designed to meet the demands for different properties and exhibited many new performances, such as electronics, catalysis, and chemical and biomedical sensors, etc. From the point of view of industrial application, the superabsorbent hydrogels based on cellulose will surely result in new expansion fields with improved performance in terms of good mechanical strength, biocompatibility, biodegradation, non-toxicity, and anti-mildew performance. Therefore, the study on the preparation of the cellulose-based superabsorbent hydrogels is necessary to be developed. Moreover, cellulose is environmental friendly and low-cost material, which will form available substitute for petroleum-based materials in near future. Thus, we increasingly walk in a green area via replacing the synthetics with the bio-based materials, cellulose and its derivatives. Additionally, new materials and methods need to be found out and used in cellulose-based superabsorbent hydrogels in order to endow them with unique properties. Moreover, the preparation mechanism of cellulose-based superabsorbent hydrogels originated from an interdisciplinary angle needs to be further researched and the swelling kinetics of cellulose-based superabsorbent hydrogels in different media requires deeper investigation because more theoretical studies will lead to a better understanding and facilitate experimental trials ,and then to large-scale application.

With the continuous research of cellulose-based superabsorbent hydrogels, the properties of materials with cellulose will be excellent and the development prospect will be much brighter. It is hoped that this review will be helpful in this important field.

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