Journal of Advanced Research 44 (2023) 53–70

Contents lists available at ScienceDirect

Journal of Advanced Research

journal homepage: www.elsevier.com/locate/jare

Review

Polysaccharide-based biopolymer hydrogels for heavy metal detection and adsorption

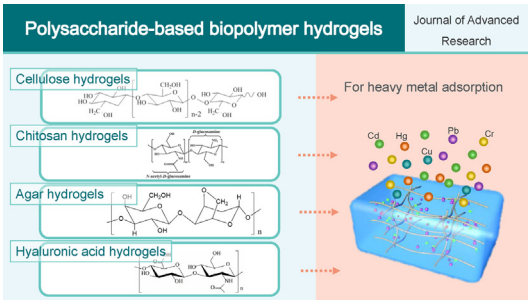
Chenxi Zhao [a,b,1], Guangyang Liu [a,*,1], Qiyue Tan [a,b], Mingkun Gao [a], Ge Chen [a], Xiaodong Huang [a], Xiaomin Xu [a], Lingyun Li [a], Jing Wang [c], Yaowei Zhang [b,*], Donghui Xu [a,*]

[a] Institute of Vegetables and Flowers, Chinese Academy of Agricultural Sciences, Key Laboratory of Vegetables Quality and Safety Control, Ministry of Agriculture of China, Beijing 100081, People's Republic of China
[b] College of Horticulture, Northeast Agricultural University, Harbin 150030, People's Republic of China
[c] Institute of Quality Standard and Testing Technology for Agro Products, Chinese Academy of Agricultural Sciences, Key Laboratory of Agrifood Safety and Quality, Ministry of Agriculture of China, Beijing 100081, People's Republic of China

HIGHLIGHTS

- Synthesis and classification of polysaccharide-based biopolymer hydrogels.
- Recent advances in the use of polysaccharide-based hydrogels for heavy metal adsorption and detection were discussed.
- The adsorption mechanism of polysaccharide-based hydrogels on heavy metal ions was analyzed.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 27 January 2022
Revised 14 March 2022
Accepted 9 April 2022
Available online 16 April 2022

Keywords:
Biopolymers
Hydrogels
Heavy metal ion
Adsorption

ABSTRACT

Background: With rapid development in agriculture and industry, water polluted with heavy metallic ions has come to be a serious problem. Adsorption-based methods are simple, efficient, and broadly used to eliminate heavy metals. Conventional adsorption materials have the problems of secondary environmental contamination. Hydrogels are considered effective adsorbents, and those prepared from biopolymers are biocompatible, biodegradable, non-toxic, safe to handle, and increasingly used to adsorb heavy metal ions.

Aim of review: The natural origin and easy degradability of biopolymer hydrogels make them potential for development in environmental remediation. Its water absorption capacity enables it to efficiently adsorb various pollutants in the aqueous environment, and its internal pore channels increase the specific surface area for adsorption, which can provide abundant active binding sites for heavy metal ions through chemical modification.

Key scientific concept of review: As the most representative of biopolymer hydrogels, polysaccharide-based hydrogels are diverse, physically and chemically stable, and can undergo complex chemical modifications to enhance their performance, thus exhibiting superior ability to remove contaminants. This review summarizes the preparation methods of hydrogels, followed by a discussion of the main categories and applications of polysaccharide-based biopolymer hydrogels.

Peer review under responsibility of Cairo University.

* Corresponding authors.
E-mail addresses: liuguangyang@caas.cn (G. Liu), zhyw1271@126.com (Y. Zhang), xudonghui@caas.cn (D. Xu).
[1] Co-authors with equal contributions.

https://doi.org/10.1016/j.jare.2022.04.005
2090-1232/

Introduction

Rapid economic development in recent decades has resulted in a number of issues, including environmental degradation and water pollution. Industrial wastes are discharged into the environment during the production of fertilizers, metals, batteries, and dyestuffs as well as during electroplating, resulting in heavy metal pollution of water bodies [1,2]. Heavy metal ions in wastewater enter the surroundings and ecological cycles in a variety of forms, together with inorganic metal ions, hydrated metal ions, hydroxyl complexes, carbonate complexes, and complexes mixed with natural matter, and are absorbed and enriched by aquatic plants, animals, and microorganisms (Fig. 1a). They may also interact with more than a few inorganic colloids, organic colloids, and organic–inorganic complexes in water or sediment and sooner or later agglomerate to settle at the backside of the water body. Heavy metal ions, including cadmium, copper, and nickel, accumulate in aquatic organisms, and owing to their high toxicity, excessive permeability, and non-degradability, set off physiological and developmental disorders, eventually posing serious threats to human fitness and ecosystems. The accumulation of heavy metal ions in human organs can lead to illnesses such as cancer, hypertension, and kidney failure. The outcomes of some of these heavy metal ions on the human physique are listed in Table 1. Therefore, effective elimination of heavy metal ions is beneficial to the environment and human health [3].

Methods commonly used to deal with wastewater contain chemical and biological processes, adsorption, membrane separation, chemical precipitation and ion exchange [4,5]. The majority such strategies are costly, inefficient, and inclined to second-hand contamination. Chemical precipitation, which coagulates and flocculates contaminants such as heavy metal ions into coarse precipitates for removal, can be a relatively simple process, but requires the use of excess material and produces toxic solid waste [6,7]. In contrast, adsorption-based methods are efficient, cost-effective, and effortless to implement [8]. Moreover, adsorbents are touchy to poisonous pollution and do not produce secondary detrimental substances. Adsorption-based methods are extensively used in water treatment and are regarded one of the most cost-efficient techniques to remove heavy metal ions [9]. Adsorption is classified as chemical and physical adsorption; in each category, adsorbents with desirable affinity for heavy metal ions are used to eliminate these ions from water. The mechanisms of action with heavy metal ions consist of ion exchange, electrostatic interaction, metallic complexation, and π-π conjugation. Adsorbents are categorized and chosen in accordance to the affinity of their active sites for the heavy metal ion, thus attaining superb treatment.

Table 1
Harm to the human body from different heavy metal ions.

Heavy metal ion	Harm
Pb^{2+}	Causes reproductive system damage, brain tissue damage, neurological toxicity
Cu^{2+}	Cause anemia, liver damage, and intestinal damage
Cr^{6+}	Carcinogenicity, causing mutations and genetic defects
Hg^{2+}	Cause abdominal pain, diarrhea, muscle tremors, and mental disorders
Cd^{2+}	Cause liver/kidney damage and joint pain
Ni^{2+}	Cause skin damage, acute gastroenteritis, and heart muscle damage

Traditional adsorbents, which includes activated carbon, zeolite, artificial resin, mesoporous zirconium phosphate, alumina, silica gel, diatomaceous earth, and algae, have restricted functions owing to their low adsorption effectivity and bad regeneration performance. Advanced adsorbent materials for treating water containing heavy metal ions should be simple and efficient, have high adsorption rates, be reusable and easily degradable with little harm to the environment [10]. As rising adsorbents, hydrogels have special physicochemical residences and notable ability to remove a wide range of contaminants [11]; specifically, they are tender polymeric substances comprising three-dimensional networks of physical or chemical crosslinks, which imparts flexibility, elasticity, permeability, and the capacity to absorb massive quantities of water (hundreds of instances their dry weight) [12]. Hydrogels can be segmented into synthetic polymer hydrogels and biopolymer hydrogels according to their raw materials. Biopolymer hydrogels, additionally recognized as natural polymer hydrogels, are constructed from biopolymers; they are biocompatible, degradable, non-toxic, and protected to handle, as a consequence assembly the necessities of sustainability. Importantly, they have promising applications in the treating of water which contains heavy metal ions. Polysaccharide-based hydrogels, an important subset of biopolymer hydrogels, include cellulose hydrogels, chitosan hydrogels, agar hydrogels, and hyaluronic acid (HA) hydrogels. As shown in Fig. 1b, which shows the growth trend of published articles about hydrogels as well as polysaccharide-based hydrogels from 2016 to 2021, polysaccharide-based hydro-

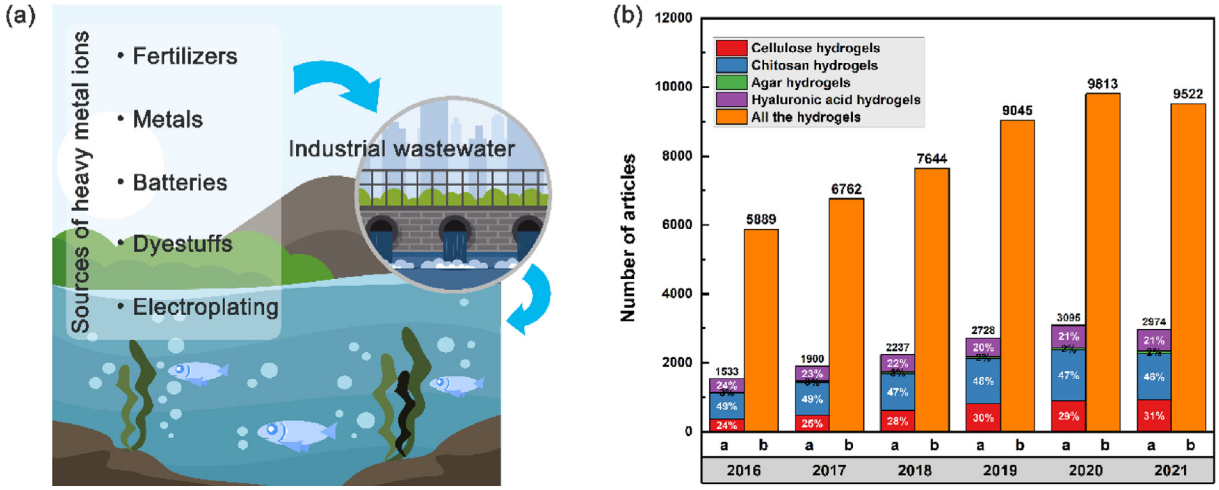


Fig. 1. (a) The sources of heavy metal ions and their harmful effects on the water environment. (b) Trends in the number of articles published on polysaccharide-based hydrogels (a) and all types of hydrogels (b) from 2016 to 2021 (Web of Science).

gels as a major category of hydrogels accounted for about 30% of the total number of hydrogel articles published, and among the articles about polysaccharide-based hydrogels, the number of chitosan hydrogels was the largest. Composites of polysaccharide-based hydrogels are characterised by chemical and physical stability, clean surfaces, polymer community flexibility, reusability, and multifunctionality [13]. Therefore, they exhibit excellent adsorption and removal of diverse kinds of pollutants, and their utility in heavy metal ion removal is developing rapidly.

This review focuses on the rapid development of biopolymer hydrogels in recent years. The preparation methods of hydrogels and the main classifications of polysaccharide-based biopolymer hydrogels are summarized. The applications of these hydrogels in heavy metal adsorption and their adsorption mechanisms are discussed. Finally, the latest research on polysaccharide-based biopolymer hydrogels and their unique prospects in heavy metal adsorption are covered.

Synthesis of hydrogels based on crosslinking methods

Methods used to prepare hydrogels can be categorized into crosslinking and initiation methods. The former can be further divided into physical and chemical crosslinking preparations, while the latter can be divided into chemical initiation, plasma initiation, and radiation initiation.

Physical crosslinking

Physically crosslinked hydrogels are normally organized with the aid of crosslinking through polymer chain entanglement, hydrogen bonding, ionic bonding, hydrophobic interaction, and non-permanent forces, such as electrostatic gravitational force [14]. The hydrogels prepared using this approach are dissolved or melted at high temperatures, and the ensuing gel state disappears when the prerequisites change; therefore, they are also referred to as reversible hydrogels. Physical crosslinks are easy to prepare and crosslinking agents can be avoided, so the organized hydrogels gain from higher biocompatibility, low or even non-toxicity, and convenient degradability, making them ‘green’ and non-polluting. For example, crosslinking with different ions via inter-ionic interactions can be used to form alginate hydrogels, while crosslinking via hydrogen bonding between polymer chain segments is used to structure agarose gels.

Nanocellulose hydrogels prepared using physical methods have special functional groups, usually amino (—NH_2) and carboxyl (—COOH), which enables the formation of hydrogels with high porosity and water absorption. Maiti et al. prepared a multicomponent chitosan-based hydrogel using a physical crosslinking method and found that the carbonyl group (C═O) of the introduced guar oxide gum was involved in the crosslinking process (Fig. 2a) [15]. Polydopamine has exact biocompatibility and biodegradability, and its functional groups, like amine, imine, and catechol, can be used as binding sites. Hydrogels prepared by the way of physically crosslinking polydopamine into the nanocellulose network not only have improved strength but also respond to near-infrared radiation and pH changes [16].

Fluorescent polymeric hydrogels (FPHs), a new research interest in luminescent materials, which have tunable luminescence properties on top of a hydrogel structure formed by crosslinking a hydrophilic polymer network [17]. Since FPHs are present as special water-swollen quasi-solids, unlike conventional materials present in a single form as solid or liquid, they have many hopeful properties in both solid and solution conditions; therefore, they are promising in a myriad of applications. Individual quantum dot pairs are unable to specifically identify the target and can selectively detect various substances when combined with hydrogels [18]. Functionalized superabsorbent nanohydrogels prepared by fluorescent semiconductor quantum dots immobilized in polysaccharides from gum tragacanth (GT) can detect glucose [19]. There are fewer studies on quantum dots embedded in natural polymer hydrogels, which deserve more exploration. Carbon dots, also known as carbon quantum dots (CDs), have grown quickly in recent years as new carbon-based fluorescent nanomaterials for heavy metal ions detection [20], biosensors, drug administration, and biological imaging due to their biocompatibility, low toxicity, and fluorescence. On the other hand, CDs are chemically inert and super-soluble in water with sizes smaller than 10 nm, which are easy to combine for functionalization [21,22]. Hybrid hydrogel membranes primarily based on CDs can both optically detect and remove heavy metal ions. As a fluorescent probe, CDs have been able to be chemically modified to obtain a specific structure and then crosslinked with other compounds to form a hydrogel. Carbon nanodots (CNDs) are nanomaterials with powerful optical properties that have been extensively studied in the medical field and ion detection, with the advantages of low toxicity and water solubility [23]. The high-strength fluorescent hydrogels prepared by physically crosslinking CNDs with poly (vinyl alcohol) have noticeably increased tensile and compressive properties and desirable self-healing behavior and could be used for rapid heavy metal ion detection [24].

Chemical crosslinking

Chemical crosslinking is the formation of chemical covalent bonds in three-dimensional stable hydrogels, and it includes copolymerization crosslinking, graft polymerization crosslinking, interpenetrating network crosslinking, radiation polymerization crosslinking, and enzymatic polymerization crosslinking [25]. Because these hydrogels do not disintegrate or melt when heated, they are also known as perpetual hydrogels. Copolymerization crosslinking is the direct crosslinking and polymerization of one or more low molecular weight water-soluble comonomers in the existence of a crosslinking agent by chemical or radiation initiation. Graft polymerization crosslinking mostly results in a hydrogel grafted to a carrier with a particular strength, which might improve the original gel’s performance and mechanical strength, hence widening its application range. Interpenetrating network crosslinking involves the utilization of two or more independently crosslinked polymers or natural polymers to create an interpenetrating network structure by crosslinking and interpenetration.

These chemically crosslinked hydrogels are simple to prepare and have sturdy structures with suitable thermal and chemical stability. For example, acrylic acid and acrylamide can be selected as raw materials to form hydrogels in the existence of a crosslinking agent. Semi-interpenetrating network hydrogels can be prepared from chitosan by free radical grafting and crosslinking; a temperature-responsive hydrogel was prepared via the Michael addition reaction of the thioglycolic group (from polypropylene glycol-ethylene oxide) and the dopa-quinone structure (from chitosan) [26]. The hydrogels prepared by physical crosslinking method usually have the disadvantages of poor stability and easy dissolution, and the stability of hydrogels can be obviously enhanced by chemical crosslinking method. As shown in Fig. 2b, Hu et al. utilized sodium alginate (SA) and carboxymethyl cellulose (CMC) for the base materials, formed the inner core of polysaccharide by physical crosslinking, and then introduced a more stable synthetic polymer outer layer by chemical cross-linking, and successfully prepared a bilayer hydrogel with distinct internal and external structures, which improved the strength and stability of the hydrogel while eliminating the swelling of the inner core and the spreading of the inner content [27]. Zhao et al. prepared a mod-

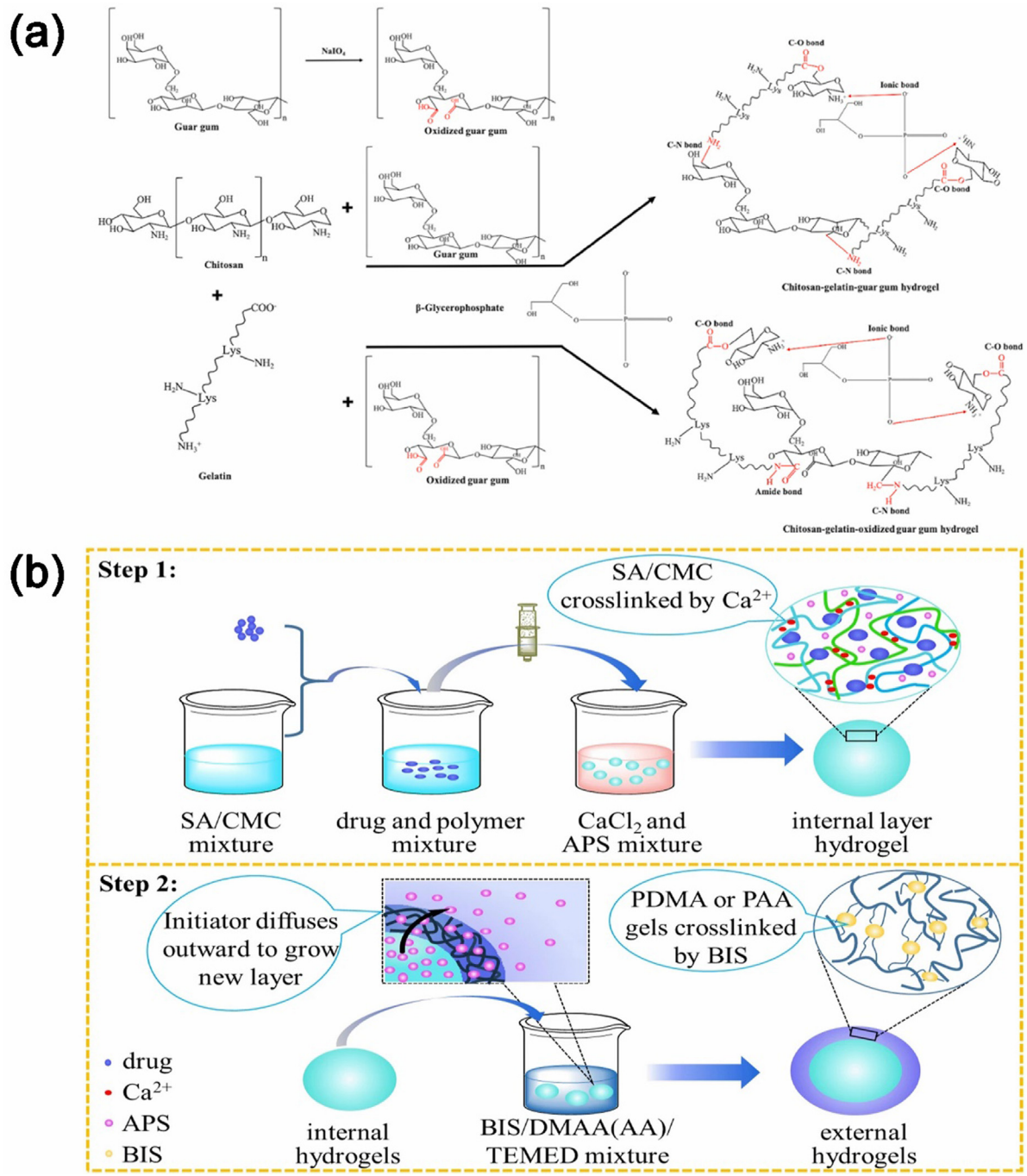


Fig. 2. (a) Schematic diagram of chitosan hydrogel prepared by physical crosslinking method [15]. (b) Schematic example of the process for preparing bilayer hydrogel by chemical crosslinking method [27].

ified cellulose hydrogel as a biosorbent by blending and crosslinking with acrylamide and acrylic acid, and the maximum adsorption capacities of the modified hydrogel reached 157.51, 393.28 and 289.97 mg/g for divalent copper ion (Cu^{2+}), divalent lead ion (Pb^{2+}) and divalent cadmium ion (Cd^{2+}), respectively [28].

Synthesis of hydrogels based on initiation methods

Chemical initiation

Chemical initiation requires the addition of initiators, like like potassium persulfate, ammonium persulfate and ammonium nitrate. The polymer chains are grafted and copolymerized with monomers to form three-dimensional mesh hydrogels. Due to the simplicity of operation and equipment, chemical initiation is the most common method for preparing hydrogels.

A cellulose hydrogel capable of conducting electricity was successfully synthesized by selecting ceric ammonium nitrate as initiator and accessing acrylamide and acrylonitrile copolymers on the cellulose chain, which has the advantages of ultra-stretchable, toughness, anti-freezing (Fig. 3a). As a result of the dipole–dipole and various hydrogen-bonding interactions in the three-dimensional crosslinked structure, this cellulose hydrogel exhibited top properties, which were high elasticity (90%), ultra-

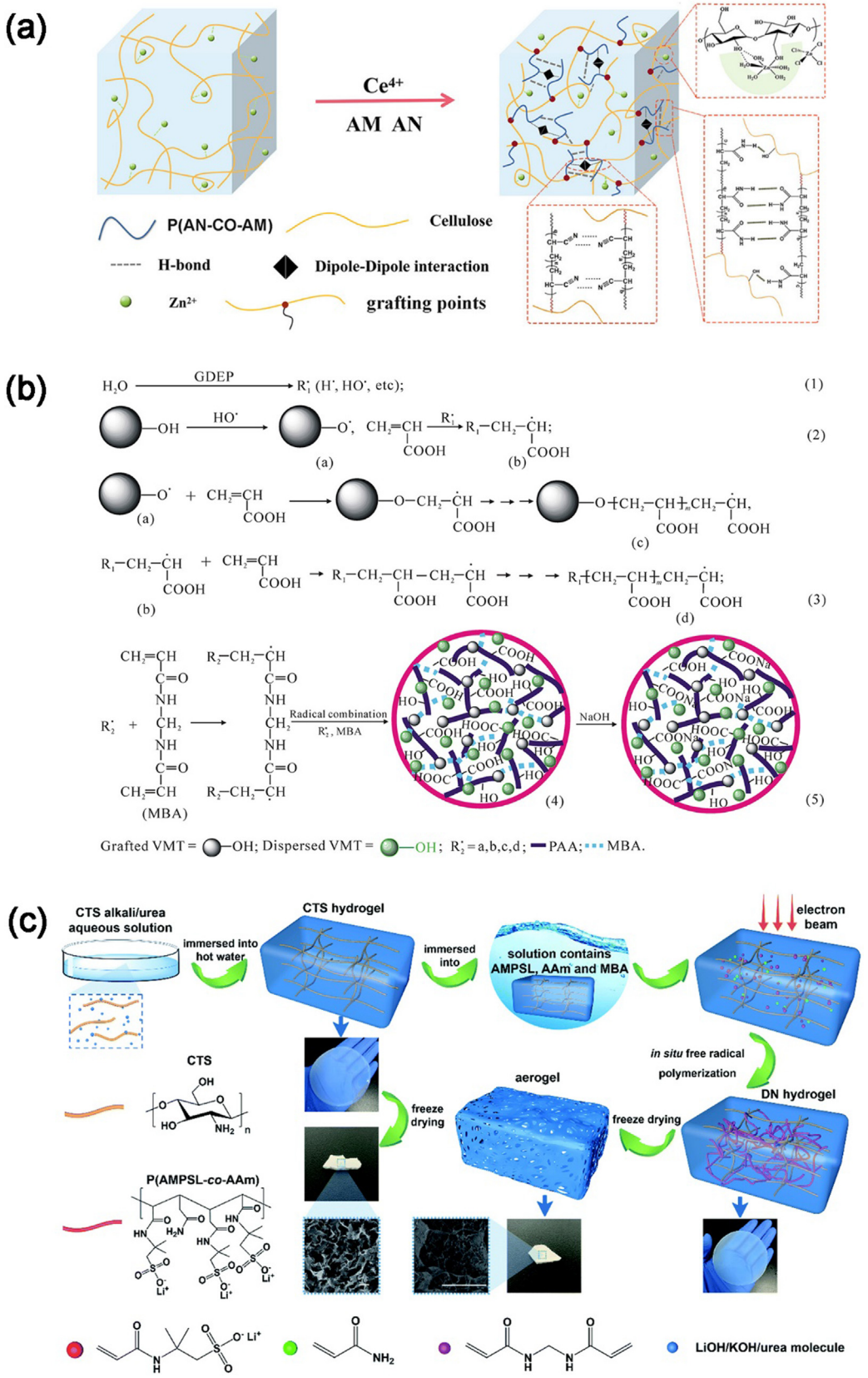


Fig. 3. (a) Process diagram for the preparation of cellulose hydrogels in the presence of chemical initiators [29]. (b) Preparation of hydrogels by Glow-discharge-electrolysis plasma [31]. (c) Process diagram of preparation of chitosan hydrogel by radiation-induced method [33].

stretchability (1730%), excellent toughness (1074.7 kJ/m^3), excellent tensile strength (160 kPa), and fatigue resistance properties [29].

Plasma initiation

Plasma from a glow discharge can be used to form significant amounts of free radicals, which then trigger the graft copolymerization of monomers to form hydrogels [30]. Plasma polymerization occurs without the addition of initiators, which has the advantages of mild conditions, controllability, and environmental friendliness. As an unconventional electrochemical process, glow-discharge-electrolysis plasma (GDEP) can induce some unusual chemical reactions, such as superficial modification and oxidative degradation. In addition, GDEP can be used for the synthesis of hydrogels. Fig. 3b illustrates a synthetic pathway for acrylic acid/vermiculite (AA/VMT) hydrogels [31]. The formation of numerous free radicals was achieved using GDEP, which led to a series of reactions, and the AA/VMT hydrogel synthesized by this method had an excellent thermal stability and remarkable adsorption effect on cationic dyes. GDEP is now often applied to the treatment of wastewater, and less research has been done on hydrogel synthesis, so how to prepare hydrogels with better performance by using GDEP deserves in-depth study.

Radiation initiation

Radiation initiation requires energy sources, such as high-energy electrons, microwave-, ultraviolet-, and γ-radiation, and is used to prepare hydrogels in the absence of initiators and crosslinking agents. The hydrogel prepared by radiation initiation has higher purity and is more environmentally friendly than other methods. However, it is only suitable for small-scale laboratory preparation as the cost is expensive. The photo-crosslinked hydrogel is covalently crosslinked underneath ultraviolet or visible light in the existence of photo-initiators, and visible light does not typically harm biological cells. Furthermore, photo-crosslinking for the duration of bioprinting facilitates the instantaneous synthesis of hydrogels with stable, well-defined architectures. Initiation using visible light can additionally keep away from the toxicity precipitated by using ultraviolet irradiation [32]. The network structure of the hydrogels synthesized by the radiation initiation method is greater homogeneous than those synthesized by conventional chemical initiation methods due to the fact that the radiation area of electron beam is wide and the penetrating power is certain, which makes the free radical polymerization in the hydrogels more uniform and faster initiation. Liu et al. used electron beam radiation to synthesize a new chitosan hydrogel, which has low cost due to cheap raw materials and convenient radiation process, and this double network structure hydrogel has high strength and is physically and chemically stable (Fig. 3c) [33]. Taşdelen et al. synthesized a new hydrogel composite for the removal of divalent manganese ion (Mn^{2+}) from aqueous solutions by gamma radiation with an adsorption capacity of 18.23 mg/g using chitosan, hyaluronic acid and itaconic acid as raw materials [34].

Classification of polysaccharide-based biopolymer hydrogels

Hydrogels are crosslinked polymers with a spatial network structure; they can be swollen in water and other biological fluids and retain a giant quantity of water without dissolution. Moreover, they can be classified into synthesized polymer hydrogels and naturally occurring polymer hydrogels according to their raw materials [35]. Raw materials for synthetic polymer hydrogels consist of acrylic acid, ethylene glycol, and vinyl alcohol. These monomers are notably derived from fossil resources. Synthetic polymer hydrogels have structures and properties that can be regulated, even though their degradation is slow. Compared with synthetic polymer hydrogels, biopolymer hydrogels have higher biodegradability and biocompatibility and consequently larger advantages for the treatment on heavy metal ions. Macromolecules from natural animals, plants, and microbes are usually known as natural polymers or biopolymers, which can be used as raw materials for biopolymer hydrogels. Macromolecules from plants include cellulose, lignin, starch, and protein, while macromolecules from animals encompass chitosan, casein, HA, chitin, protein, and dopamine. Macromolecules obtained from microorganisms are mainly polysaccharides. Polysaccharide-based hydrogels are broadly recognized as biomaterials owing to their remarkable biocompatibility, bioactivity, and biodegradability [36]; they are normally used as substances for drug delivery, wound dressing, and antibacterial devices [37].

Cellulose hydrogels

Cellulose is one of the most plentiful sources of natural macromolecules and has a vast array of applicability as a biodegradable hydrogel of biological origin [38]. As a typical linear polysaccharide, it comprises β-glucosidic bonds linking dehydrated *D-hexa*-cyclic glucose and is the foremost component of plants and naturally occurring fibers, as in cotton and linen (Fig. 4a). Cellulose and modified cellulose, e.g. by carboxymethylation and amination, are available as raw ingredients for cellulose hydrogels [39]. Natural cellulose is extraordinarily tough to dissolve in water owing to intermolecular hydrogen bonding, and its solubility in common solvents is also low. The key to preparing cellulose hydrogels lies in the technique used to dissolve cellulose, and new solvent systems, such as concentrated sulfuric acid/phosphoric acid, lithium chloride/dimethylacetamide, strong base/urea, ionic liquids, and *N*-methylmorpholine-*N*-oxide, which have been developed for cellulose. Fig. 4b illustrates the cellulose solubilization in cold phosphoric acid and reproduction in aqueous solvent, where phosphoric acid undergoes esterification reaction with the alcohol group of cellulose to formate cellulose-phosphate ester. Further addition of water causes a reverse (hydrolysis) response that can be used to regenerate cellulose [40]. Cellulose ethers can be dissolved in water and cross-linked to obtain cellulose hydrogels, which are readily available, inexpensive and environmentally friendly, for example, methyl cellulose, hydroxypropyl methyl cellulose, ethyl cellulose, hydroxyethyl cellulose (HEC) and CMC have been extensively used in the preparation process [38].

Intramolecular and intermolecular hydrogen bonds easily form in the case of the numerous hydroxyl groups in the cellulose molecule, which can be functionalized using a range of chemical modifications. The introduction of polymer polyethyleneimine (PEI), which consists of a massive quantity of imine groups, into CMC to prepare hydrogels can enhance the elimination of hexavalent chromium ion (Cr^{6+}) through protonated imine and extend the density of the cross-linked network of hydrogels, consequently effectively enhancing the mechanical properties of hydrogels (Fig. 4c) [4]. Hydrogels made from cellulose have large surface areas and high porosity, and their surface functional groups can adsorb both heavy metal ions in water via complexation and methyl blue in dyes via electrostatic interactions. Therefore, they can be utilized as adsorbents materials for water pollution. Fungi and bacteria existing in air, water, and soil can degrade cellulose and its derivatives and can additionally generate cellulose-specific enzymes. Therefore, cellulose-based hydrogels are environmentally friendly.

Highly absorbent cellulose-based hydrogels made from natural cellulose are also smart owing to their responsiveness to a variety

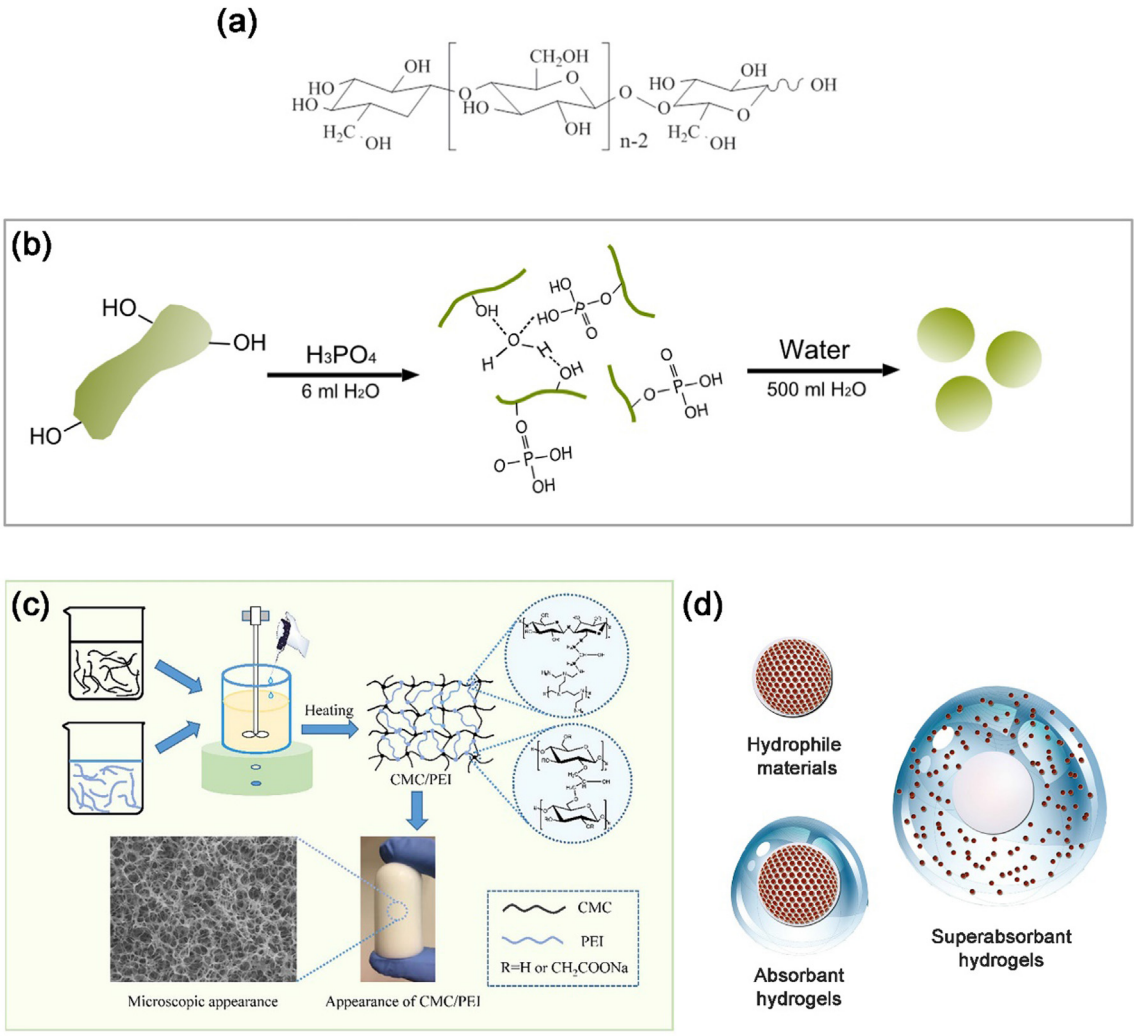


Fig. 4. (a) Chemical structure of cellulose. (b) Schematic illustration of the dissolution and regeneration of cellulose in different solvents [40]. (c) Schematic of the preparation of carboxymethyl cellulose/polyethyleneimine (CMC/PEI) [11]. (d) Schematic diagram of water exchange between superabsorbent hydrogel and external solvent [41].

of stimulations and therefore have obtained considerable attention (Fig. 4d) [41]. Cellulose-based hydrogels allow modification with the aid of grafting chelating groups onto their structure to adsorb particular heavy metal ions. In addition, acidolysis, enzymatic digestion, and oxidation of cellulose can yield nanocellulose with fibrous structures, and nanocellulose-based hydrogels prepared by using physical and chemical crosslinking are three-dimensional materials with pore constructions that promote super water absorption, water retention, and certain swelling properties.

Most industrially produced hydrogels are synthetically produced acrylate-based polymers that degrade sluggishly and are non-biodegradable, so they are deemed potential soil pollutants. Inexpensive and non-toxic materials derived entirely from renewable biological resources, such as modified lignocellulosic materials, have been developed and currently used in many functions due to their sustainability and biodegradability. Compared with acrylic-based hydrogels, those cellulose hydrogels are suitably flexible, more absorbent, and more easily degraded. CMC is an environmentally degradable polymer with many carboxyl groups that enable it to be hydrophilic and soluble in water, making it an ideal material for synthetic hydrogels with high absorption capacity and sensitivity to ions and pH. Taking CMC and HEC as raw materials and introducing acidic whey, Durpekova et al. synthesized a novel, degradable, and reproducible cellulose hydrogel with citric acid as the crosslinking agent, which has a good swelling potential to maintain soil quality and protect the aquatic environment [42].

Chitosan hydrogels

Chitosan, (1,4)-2-acetylamino-2-deoxy-*β*-*D*-glucan, is the only natural alkaline polysaccharide found in nature. It is the product of chitin deacetylation and its repeat unit involves *N*-acetyl-*D*-glucosamine and *D*-glucosamine connected by a *β*-(1–4) glycosidic bond (Fig. 5a) [43]. Chitosan is a naturally occurring macromolecule which is biodegradable in biological organisms, and its abundance is second only to cellulose. Chitosan is extensively found in marine shellfish mollusks, cells of lower algae bacteria, and arthropods (e.g., shrimps and crabs). Owing to their good biocompatibility and degradability, chitosan has been extensively applied for drug release, tissue engineered, and skin repair [26]. According to the different needs, chitosan could be utilized in powder or in other distinct forms (Fig. 5b) [44]. Chitosan is prosperous in active groups, has appropriate adsorption, chelation, and crosslinking effects, and it is effortlessly modified using special chemical techniques [45]. In latest years, chitosan has attracted tremendous interest as a raw material of biopolymer hydrogels due to its broad availability, desirable biocompatibility, high

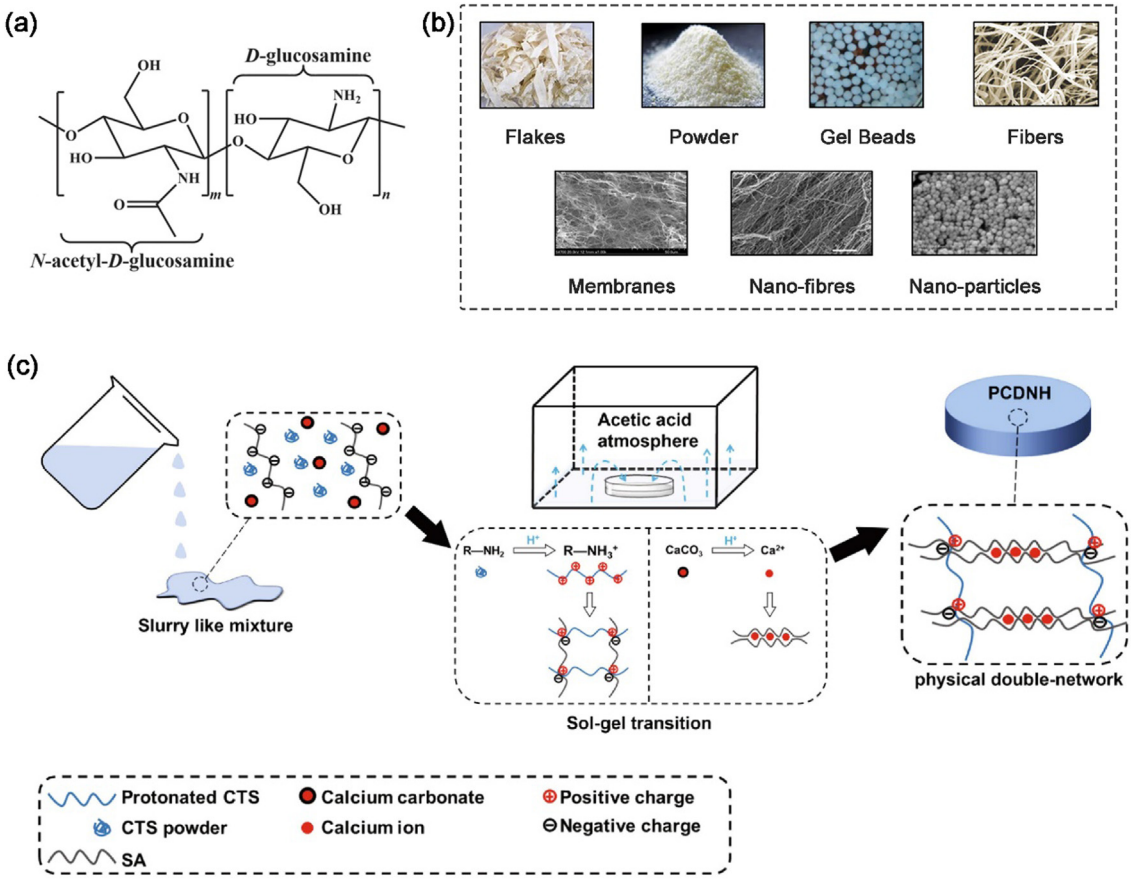


Fig. 5. (a) Chemical structure of chitosan. (b) Different forms of chitosan [44]. (c) Diagram of chitosan-based double network hydrogel preparation [46].

adsorption capability, biodegradability, and non-toxic degradation products. Because chitosan-based hydrogels and their derivatives have a massive range of active amino and hydroxyl groups that can dissociate cations, they can chelate with metallic ions and therefore play a crucial role in the process of removing heavy metal ions. Tang et al. prepared a novel chitosan-based double network hydrogel by physical crosslinking method (Fig. 5c) [46]. This hydrogel exhibits a porous structure, which gives it a larger specific surface area and more binding sites, and is able to adsorb metal ions such as Pb^{2+}, Cu^{2+} and Cd^{2+} with a maximum removal capacity of 176.50 mg/g, proving its excellent effect on the adsorption of heavy metal ions.

During the forming of chitosan-based hydrogels, intra- or intermolecular interaction of chitosan molecules have to be strong enough to form physical binding sites. In an alkaline environment, hydrogen bonding between chitosan molecule chains is promoted, leading to the formation of microcrystalline structures as physical binding sites. Highly soluble halide salts, such as calcium chloride, potassium chloride, and magnesium chloride, in the chitosan solution enhance the hydrophobic force between chitosan molecules due to the strong salting effect, and aggregation of molecular chains results in physical entanglement as physical binding sites. Alternatively, polyvalent anionic salts, such as sulfate and citrate, can be introduced to the chitosan solution to dehydrate the chitosan molecules, and *N*-glucosamine forms ligand bonds with the polyvalent anions, as a result forming an ionic crosslinked network with ionic ligand bonds as the physical binding sites.

The amino and hydroxyl groups contained in chitosan facilitate both physical and chemical crosslinking of chitosan, which has the benefits of low cost, useful resource renewability, biocompatibility, biodegradability, and multifunctionality [47]. Echazu et al. prepared pure chitosan physical gels by regenerating an aqueous acetate solution of chitosan in an excess alkaline coagulation bath. Recently, there has been an growing tendency to find out about the structure and overall performance of smart polymer hydrogels for specific applications [45]. Chitosan-based hydrogels have proper electro-sensitive response, and carboxymethyl chitosan hydrogels and chitosan/sodium carboxymethyl cellulose hydrogels have network structures that bend and contract with pH changes. Chitosan is only soluble in organic acid and inorganic acid solutions while is insoluble in water and alkaline solutions. Reactive groups that participate in hydrogen bonding have an effect on its water solubility but also provide the possibility of chemical modification. When hydrophilic groups, such as carboxymethyl chitosan, chitosan quaternary ammonium salt, chitosan hydrochloride, and guanidine chitosan, are added to the active groups of chitosan, chitosan derivatives with good water solubility can be obtained.

Agar hydrogels

Extracted primarily from *Gracilariaceae* and *Gelidiaceae*, Agar is a seaweed polysaccharide that undergoes gelation and is a complicated combination of polysaccharides consisting of two main components, agarose and agar pectin, as shown in Fig. 6a. The shape of agar molecules is influenced by temperature. When the solution is gradually cooled from higher temperatures, the two-dimensional linear agar molecules form a three-dimensional structure under the action of hydrogen bonds and the molecular form changes to a double helix shape. When the temperature is further reduced,

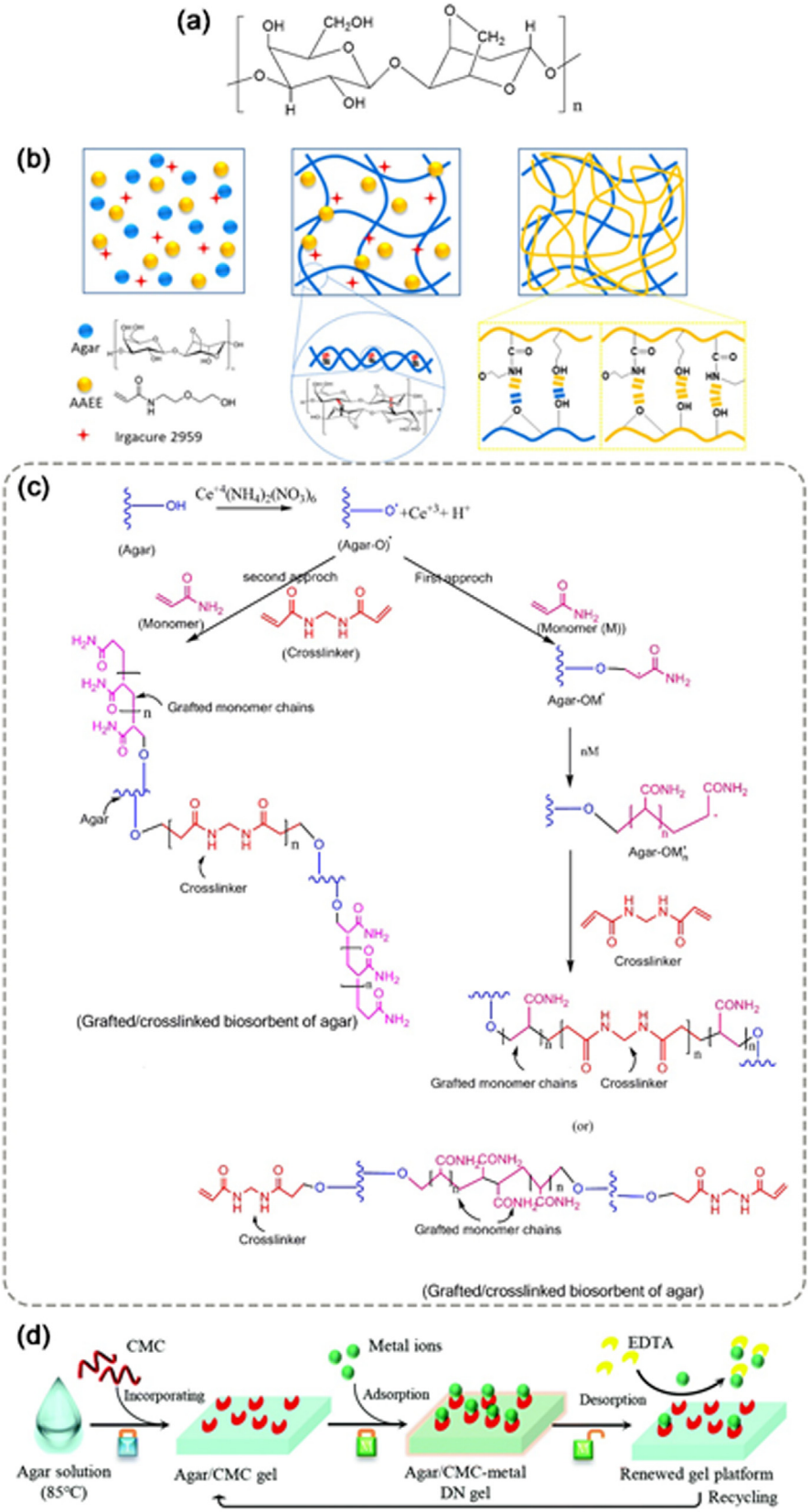


Fig. 6. (a) Chemical structure of agar. (b) Synthesis of agar/pAAEE double-network hydrogels [36]. (c) Schematic diagram of the agar-based biosorbents preparation [50]. (d) Schematic diagram of the preparation of agar-based double-network hydrogels [51].

the aggregation of the double-helical agar molecules leads to the transformation of the agar solution into a harder gel state. Depending on the transparency and strength of the formed hydrogel, the use of agar varies, with stronger agar hydrogels being more widespread [48].

A durable composite network hydrogel based on agar was prepared by Zhang et al. The agar helical bundles form a three-dimensional agar network under the action of hydrogen bonding, while pAAEE (N-poly(acryloylaminoethoxyethanol)) is introduced later (Fig. 6b) [49]. The pAAEE network gives the hydrogel higher mechanical properties due to further chain entanglement. In addition, there is a dynamic/cooperative physical interaction between the agar network and the pAAEE network as well as within their respective networks, and this interaction also exists between the whole and the surface, which ultimately manifests itself in the strong reversible surface adhesion of this agar hydrogel and improves its durability.

Among the modification techniques of agar, grafting and crosslinking are two commonly used methods. The biosorbents prepared from agar has fantastic hydrophilicity and high swelling rate, and has functional groups that can be used to complex with metal ions, which could be applied to adsorb heavy metal ions in water bodies (Fig. 6c) [50]. Yan et al. synthesized an agar-based double-network hydrogel based on metal coordination chemistry with an excellent chelating ability matrix, leading to a sequence of metal-liganded double-network gels via spontaneously complexing metal ions, which include most of the ions such as Cu^{2+} and trivalent chromium ion (Cr^{3+}) (Fig. 6d) [51].

Hyaluronic acid hydrogels

HA has significant biological functions and is a natural polyanion and glycosaminoglycan, most abundant in bacteria and connective tissues of higher animals [52]. It is composed of alternating β-1,4-glucuronide and β-1,3-acetylamino glucosamine bonded repeat units (Fig. 7a). Moreover, it is tasteless, odorless, non-toxic, hydrophilic, and moisture-absorbing, and it has good fluidity, lubricity, high viscoelasticity, and pseudo-plasticity, accordingly promoting its use in eye and orthopedic surgical procedure to prevent post-operative adhesion [53,54]. It is also used as a carrier for topical ophthalmic and dermal drugs, and it is broadly used in cosmetics [55]. The dissolved HA hydrogels are colorless, transparent gel-like solids; they are yellowish hard solids after air-drying at room temperature and white sponge-like gels after lyophilization. The volume of the dried gel is significantly smaller than that of the originally prepared hydrogel due to shrinkage of the gel by dehydration.

HA has tremendous biological and physicochemical properties, such as biocompatibility, biodegradability, water retention, and lubricity, which can be used to prepare biopolymer hydrogels. Gao et al. successfully prepared *N*-hydroxy sulfosuccinimide activated hyaluronic acid (HA-sNHS) with tunable physical properties from activated hyaluronic acid as the base material and without the addition of crosslinkers or initiators [56]. The results proven that HA hydrogels had desirable biodegradability and cytocompatibility (Fig. 7b). The water content of hydrogels can be expanded with the adding of HA. Biopolymer hydrogels prepared by using solvent evaporation with HA, hydrolyzed collagen, and chitosan as raw materials have remarkable properties. With the addition of HA, the hydrogel surface is smoother and swelling is greater, while the porosity is unchanged [57].

HA has hydrogen bonds between monosaccharides, and hydrophobic hydrogen atoms form hydrophobic zones in the axial direction, which locks water firmly inside—an amount up to 1000 times its weight. The interaction between the hydrogen bonds and the hydrophobic zones in the molecule results in a net-like structure with gel-like elasticity and liquid-like viscosity. The existence of a large amount of reactive groups, like primary hydroxyl, secondary hydroxyl, carboxyl, and acetylamino groups, on the HA molecular chains facilitates chemical modification explore a variety of derivative materials having enhanced properties. A thiol-Michael addition reaction can occur among methacrylate groups and thiol groups. Taking advantage of this mechanism, Coogan et al. fabricated micro-porous HA hydrogels with hyaluronic acid methacrylate (HAMA) and dithiothreitol (DTT) (Fig. 7c) [58], and the degradation of micro-porous HA hydrogels was enhanced in contract with nonporous HA hydrogels.

Gum tragacanth hydrogels

GT is a natural polysaccharide composed mainly of *D*-galactose, *D*-galacturonic acid and rhamnose, with primary and secondary hydroxyl and carboxylic acid groups present in the molecule, and the precise microstructure of GT has not been widely achieved

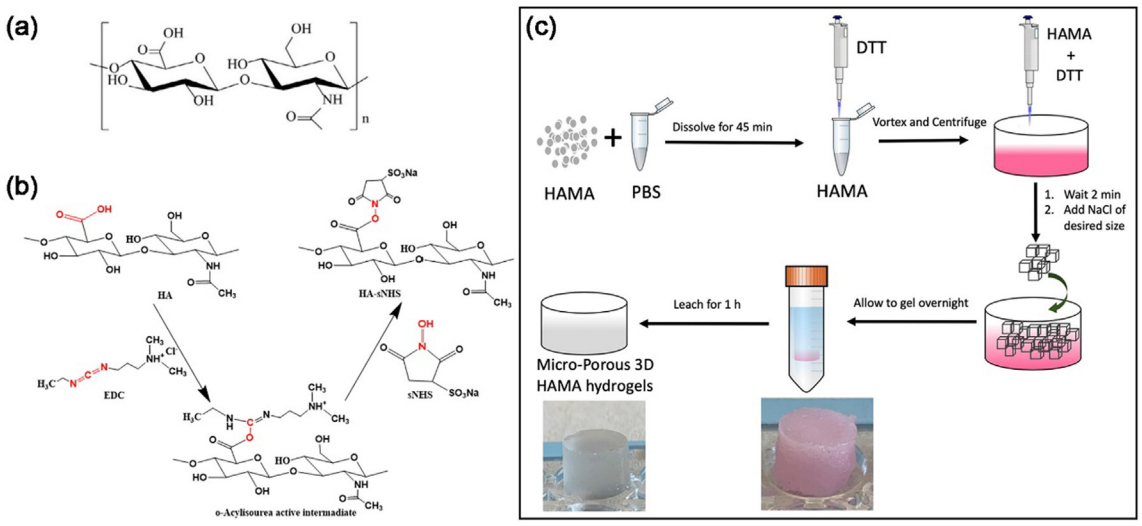


Fig. 7. (a) Chemical structure of hyaluronic acid. (b) Synthetic scheme of hydroxy sulfosuccinimide activated hyaluronic acid (HA-sNHS) [56]. (c) Synthesis process of hyaluronic acid hydrogel [58].

due to its structural diversity and complexity [59]. GT is stable over a wide pH range, and the various groups present in the structure provide the required sites for grafting different monomers with functional chelating groups, making it easy to functionalize, for example, polysaccharide hydrogels can be prepared by functionalizing GT polysaccharides with sulfonic acid groups in the presence of potassium persulfate as initiator [60]. GT is biocompatible and functionalized GT hydrogels can be used to develop promising biosorbents for water treatment by removing ions from water through ion exchange mechanisms and electrostatic interactions [61,62]. Masoumi et al. grafted polyacrylonitrile onto GT followed by amidoxime oxidation to prepare a nanosized hydrogel with amido-oxime functional groups, and this polysaccharide nanosized hydrogel was able to remove metal ions from aqueous solutions with maximum adsorption capacities of 100.0, 76.92, 71.42 and 66.67 mg/g for divalent cobalt ion (Co^{2+}), divalent zinc ion (Zn^{2+}), Cr^{3+} and Cd^{2+}, respectively [63].

Mechanisms of adsorption and detection

Internal structure and characteristics

Hydrogels are analogous to ion exchange resins in that they remove contaminants from aqueous solutions by electrostatic attraction. Due to the existence of functional groups like amino, carboxyl, and hydroxyl groups in the molecular structure of hydrogels, their adsorption capacity is enhanced; therefore, they are super-efficient adsorbents for the removal of contaminants [64]. Moreover, their unique three-dimensional structures promote good swelling, mechanical properties, and reusability, which are conducive to the removal and recycling of heavy metal ions. Through modifying the functional groups, the structure and properties of the hydrogel could be purposefully altered [65].

The hydrogel skeleton contains a variety of hydrophilic groups that can complex with and immobilize metal ions. Moreover, the three-dimensional network structure of the hydrogel can ensure that the metal ions are uniformly dispersed to prevent the aggregation and oxidation of metal ions [66]. The bound water in hydrogels provides support to maintain a certain shape; it also provides nano-transport channels for the free diffusion of small water-soluble molecules and can participate in hydrogen bonding, thus serving as additional active sites for interactions between the hydrogel and molecules in solution, which is suitable for adsorbing heavy metal ions in the aqueous environment. The polymers that make up hydrogels have diverse polar functional groups, including oxhydryl (—OH) and —NH_2, as well as amide group (—$CONH_2$), and sulfonyl group (—SO_3H). There are physical or chemical interactions between the polymer chains, such as hydrogen bonding, covalent bonding, van der Waals forces, etc. This allows the hydrogel to maintain a more stable structure with a higher water content. This property makes the hydrogel to bind to heavy metal ions by chelation and electrostatic attraction for effective removal [11].

The strength of a hydrogel's adhesion affects its effectiveness in removing contaminants. Factors affecting this property include the spatial environment to which the hydrogel is exposed and the interactions between its internal components, such as the polymer content. In air, hydrogels are more likely to adhere to hydrophilic surfaces, but less likely to interact with hydrophobic surfaces. Fig. 8a demonstrates the adhesion mechanism of hydrogels in different spatial environments [35]. When the hydrogel is in contact with a hydrophilic surface in air, a water meniscus is formed at the edge of the touching surface because of the wetting caused by the water flowing out of the hydrogel, and the hydrogel adheres well to the hydrophilic surface due to the intermolecular interaction with the contact area and capillary adhesion. In contrast, when the hydrogel is submerged in an aqueous environment, the hydrogel surface is in full contact with water, and adhesion is formed mainly by the interaction between the surface and the internal polymer.

Introduction of different substances affects the hydrogel properties

Composite hydrogels have superior properties compared to single polysaccharide-based hydrogels, and the introduction of different compounds into the hydrogel can lead to additional physical and chemical properties [67]. Fig. 8b demonstrates the interaction mechanism between the hydrogel and heavy metal ions. The addition of cationic polymers to hydrogels can significantly remove oxygen anions such as chromate, expanding the ability to adsorb contaminants that can be used in water treatment. The content ratios of the constituents of composite hydrogels also affect their performance. Nanocomposite hydrogels based on protofibrillated nanocellulose containing cellulose nanofibrillated (CNF) have an increased number of intramolecular carboxyl groups as CNF increases, thus improving the hydrogel swelling capacity and producing greater thermal stability and chemical and mechanical stability, changes in these properties will affect their reuse times [68]. The addition of vinyl monomers to hydrogels gives them pH-sensitive properties and the ability to remove heavy metal ions from water, e.g., the use of glycidyl methacrylate (GMA) modified hemicellulose can produce vinyl macromonomers on the basis of which composite hydrogels are prepared that exhibit efficient uptake of Cr^{6+}, Cu^{2+}, and pentavalent arsenic ion (As^{5+}) [69]. SA from seaweed is a degradable biopolymer that exists in the anionic form above pH 3.4–3.7, and the presence of carboxyl groups in its molecular chain gives it good metal ion adsorption ability [70,71], and the tensile properties of the composite polysaccharide-based hydrogels incorporating SA are also significantly improved, maintaining biocompatibility and swelling ability while improving the deficiency point that most hydrogels are very brittle [72]. Graphene oxide (GO) is a solid material containing hydrophilic oxidized polar groups that can exchange ions with metal ions or positively charged organic molecules, and binding to hydrogels can improve the adsorption performance of adsorbents [73]. The chemical stability, swelling properties and adsorption performance of the GT/GO composite hydrogels prepared under the condition of cerium ammonium nitrate as initiator were improved, and the adsorption amounts of Pb^{2+}, Cd^{2+} and monovalent silver ion (Ag^{+}) reached 142.50, 112.50 and 132.12 mg/g, respectively [74]. Ferroferric oxide (Fe_3O_4) nanoparticles have high specific surface area and mechanical strength, which can improve the thermal and chemical stability of the hydrogel after embedding, in addition, the adsorption properties of the hydrogel are enhanced due to the improved electrostatic interactions [75]. More importantly, the composite hydrogel embedded with nanoparticles has the advantage of easy collection, recovery and no pollution under magnetic field due to the unique magnetic properties of Fe_3O_4 [76]. Sahraei et al. prepared a novel magnetic polysaccharide-based hydrogel microspheres from GT, polyvinyl alcohol (PVA) and GO doped with Fe_3O_4 nanoparticles. The laminar structure, high specific surface area and the presence of a large number of hydrophilic polar groups within the molecule of GO improved the swelling, mechanical strength and adsorption capacity of the hydrogel microspheres, and the addition of Fe_3O_4 promoted the separation of the beads from the solution and further improved the adsorption capacity of the hydrogel microspheres under electrostatic interaction, and the adsorption of Pb^{2+} and Cu^{2+} reached 81.78 and 69.67 mg/g, respectively, which still exhibited high activity after three recycling cycles [59].

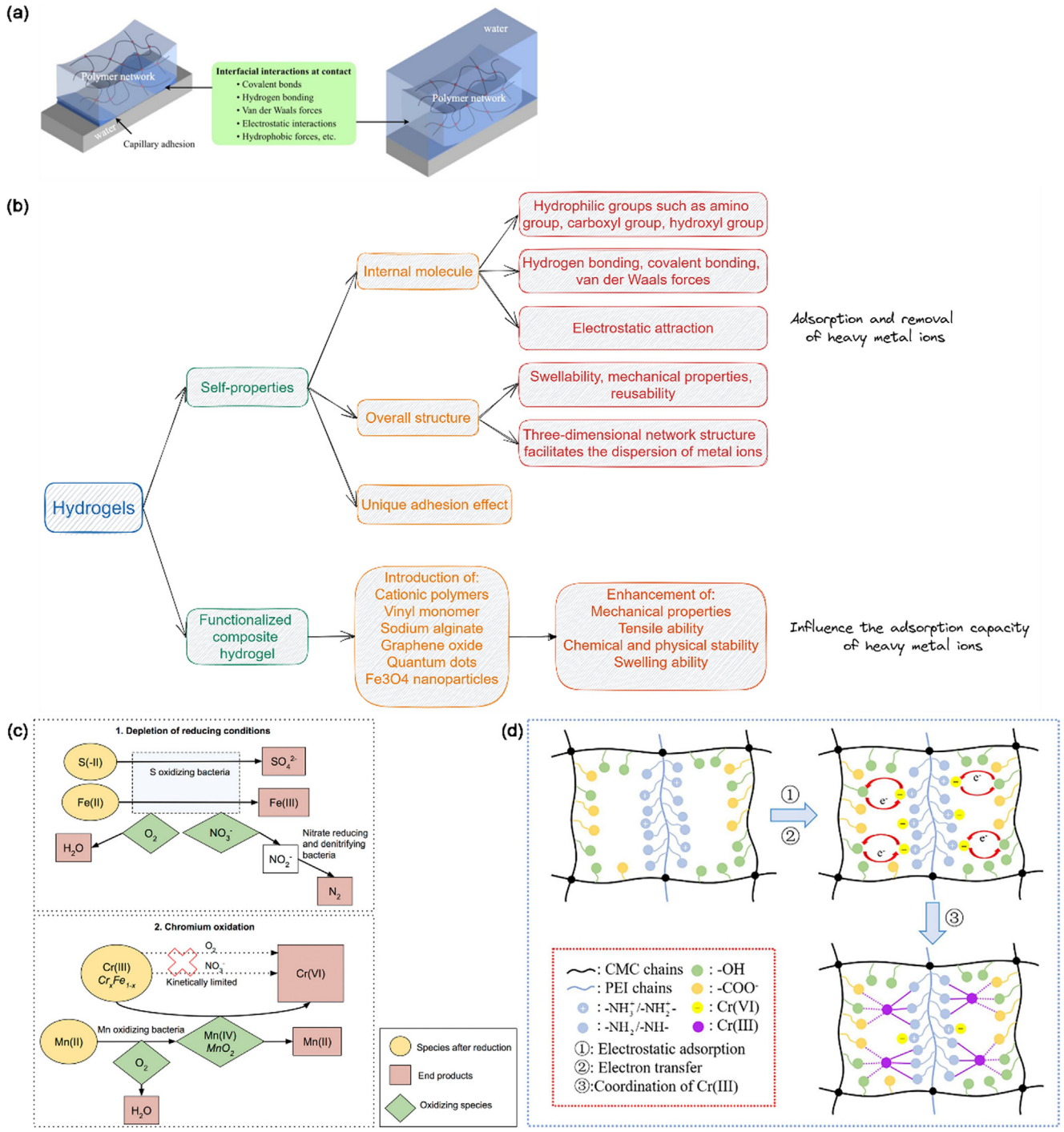


Fig. 8. (a) Interaction of hydrogels with contact surfaces in different spatial environments [35]. (b) Interaction mechanism diagram between hydrogel and heavy metal ions. (c) Transformation pathways of different valence states of chromium ions [78]. (d) Chromium removal mechanism of CMC/PEI internal [11].

Applications of polysaccharide-based biopolymer hydrogels

Industrial development and human activities have brought a lot of pollution to the environment, among which water pollution caused by heavy metal ions is one of the most serious problems [77]. Heavy metal ions are often produced during industrial production, and some of them are very toxic and can cause serious harm to aquatic ecosystems when they enter by industrial wastewater [78]. For example, in the production of stainless steel can cause chromium pollution, including Cr^{3+} and Cr^{6+}, the former is almost inactive and less hazardous, however, the latter is toxic and easily soluble, harmful to the environment, but also lead to cancer and other diseases threatening people's health (Fig. 8c). To date, various techniques, consisting of reduction, adsorption photocatalysis, and membrane separation, have been investigated to get rid of hexavalent chromium from wastewater [78]. As an excellent adsorbent material, novel hydrogels with high selectivity for pollutants in water have been developed and used to eliminate heavy metal ions [79]. For example, carboxymethyl cellulose/polyethyleneimine hydrogel was synthesized using a facile one-step way; its protonated imine groups first adsorbed hexavalent chromium through electrostatic interactions and its oxidizing hydroxyl

groups subsequently reduced Cr^{6+} to Cr^{3+} (Fig. 8d). Moreover, trivalent chromium generated in situ was immobilized thru coordination with nitrogen and oxygen and removed via precipitation [11].

Polysaccharides are natural, biodegradable and relatively low cost polymers that can adsorb heavy metals from contaminated aquatic environments [80]. Polysaccharide-based hydrogels are derived from biopolymers such as cellulose and chitosan and are highly efficient adsorbents [81,82]. The different types of polysaccharide-based hydrogels and their preparation for the adsorption or detection of heavy metal ions are given in Table 2.

Lead damages the human central nervous system and is toxic to kidney and brain function. Pb^{2+} in wastewater in general comes from the battery industry, electronic manufacturing, mining, smelting, painting, and fertilizers [83]. Using modified biopolymer materials, Pb^{2+} can be removed from aqueous solutions by reactive functional groups on their surfaces [84]. Wang et al. prepared a chitosan-2D montmorillonite hydrogel with high specific surface area and porous structure for the adsorption of Pb^{2+} in water, and the adsorption capacity reached 76.74 mg/g [85].

Copper is also a common heavy metal contaminant, and it is often used in the manufacture of paper and pigments. Excessive accumulation of copper in the human body can cause immunotoxicity and anemia, as well as damage to the kidneys and liver. The composite hydrogel obtained from chitosan-based preparation can adsorb Cu^{2+} from sewage, and its reusability without significant loss of initial properties was demonstrated with three adsorption–desorption cycles; notably, the environmental impact of this adsorbent is minimal [86].

Hydrogels containing magnetite have been synthesized to adsorb Cu^{2+}. The greatest benefit of polysaccharide-based hydrogels containing magnetite is that the adsorption can be activated by applying an external magnetic field [87]. Thus, adsorption and recovery of both hydrogel and adsorbate can be achieved without using chemicals such as hydrogen chloride (HCl) or nitric acid (HNO_3). Paulino et al. used chitosan-based hydrogels containing magnetite to remove Pb^{2+}, Cd^{2+}, and Cu^{2+} ions from water, and both the magnetic hydrogel and adsorbed metal ions were readily recovered by the application of an external homogenous magnetic field [87]. Chitosan-iron(III) hydrogel, synthesized by chelating chitosan and ferric salt, is cost-effective and environmentally friendly, and it can remove dyes rapidly and successfully in alkaline conditions [88].

Mercury binds to proteins containing sulfhydryl and selenium groups and enters the cell matrix, thereby impairing its normal function. Exposure to high doses of mercury can cause severe damage to the brain, central nervous system, kidneys and other related organs, leading to multi-organ failure [89,90]. Lone et al. prepared a composite hydrogel using gelatin and chitosan cross-linked, which was able to selectively adsorb divalent mercury ion (Hg^{2+}) in water with a removal rate of 98% [91].

Cadmium and nickel, commonly used in batteries, coatings and metalworking industries, are toxic contaminants that can accumulate in the human body in organs such as the liver and kidneys and even cause cancer [92–95]. Kundu et al. prepared a novel composite hydrogel based on CMC, microcrystalline cellulose and xylan in alkaline medium for the adsorption of Cd^{2+} and divalent nickel ions (Ni^{2+}) from aqueous solutions using glycol diglycidyl ether as a cross-linking agent, with maximum adsorption capacities of 61.44 and 55.85 mg/g, respectively [96].

Table 2
Adsorption and detection of heavy metal ions by different polysaccharide-based hydrogels.

Adsorbent	Preparation method	Adsorbed or detected heavy metal ions	Adsorption capacity (mg/g)	References
magnetic sodium alginate/carboxymethyl cellulose	co-precipitation and subsequent freezing–thawing	Mn^{2+}, Pb^{2+}, and Cu^{2+}	71.83、89.49 and 105.93	[98]
fluorescent lignin-based hydrogel with cellulose nanofibers and carbon dots	chemically initiated free radical polymerization	Cr^{6+}	599.9	[99]
hydrogel based on methacrylated carboxymethyl cellulose and lignosulfonate	microwave-assisted hydrothermal carbonization	Cu^{2+}	145	[100]
cellulose nanofiber and sodium alginate	Physical crosslinking	Pb^{2+}	318.47	[101]
carbon dots/cellulose hydrogel	hydrothermal reaction	Hg^{2+}	–	[102]
Carboxymethylcellulose/hydroxyethyl cellulose hydrogel films	citric acid as a non-toxic crosslinking agent	Cd^{2+}	126.58	[103]
carboxymethyl cellulose-graft-poly(acrylic acid) hydrogel	*N,N*'-methylenebisacrylamide as a crosslinking-agent	Ni^{2+}	366.11	[104]
chitosan/orange peel hydrogel	Ceric ammonium nitrate as initiator, *N,N*'-methylenebisacrylamide as crosslinker	Cr^{6+} and Cu^{2+}	178.34 and 181.88	[105]
carboxylated chitosan/carboxylated nanocellulose hydrogel beads	physical crosslinking	Pb^{2+}	334.92	[106]
Spherical-shaped graphene oxide-embedded chitosan/gelatin hydrogel	glutaraldehyde as crosslinker	Pb^{2+}, Cd^{2+}, Hg^{2+}, and Cr^{3+}	–	[107]
thiophene–chitosan hydrogel	Schiff base condensation strategy	Hg^{2+}	20.53	[108]
calcium alginate/carboxymethylated chitosan/Na-bentonite	4-phenylsemicarbazide as a modifier	Ni^{2+}	159	[109]
polyvinyl alcohol/chitosan/ polydopamine-functionalized graphene oxide hydrogels	instantaneous gelation method	Cu^{2+}, Pb^{2+} and Cd^{2+}	210.94, 236.20 and 214.98	[110]
chitosan/hyaluronic acid /itaconic acid hydrogel	gamma radiation	Mn^{2+}	18.23	[34]
diethylaminoethyl dextran hydrogel	Epichlorohydrin as crosslinker	Zn^{2+}, Mn^{2+}, Pb^{2+} and Cd^{2+}	509.83, 132.60, 34.29 and 2.51	[111]
sodium alginate/polyethyleneimine composite hydrogel	chemical crosslinking	Cu^{2+} and Pb^{2+}	322.6 and 344.8	[112]
gum tragacanth-cl-*N,N*-dimethylacrylamide hydrogel	*N,N*'-methylenebisacrylamide (NMBA) and potassium persulfate (KPS) as cross-linker and initiator	Hg^{2+} and Cr^{6+}	666.6 and 473.9	[113]
chitosan/gelatin fluorescent hydrogel	maleic acid as a cross-linking agent	Cr^{6+}	–	[114]
DNA–chitosan hydrogel	electrostatic cross-linking	Hg^{2+}, Pb^{2+}, Cd^{2+}, and Cu^{2+}	–	[115]
chitosan/calcium alginate/bentonite composite hydrogel	physical crosslinking	Pb^{2+}, Cu^{2+} and Cd^{2+}	434.89, 115.30 and 102.38	[116]

Degreasing cotton is a product obtained from cotton through a series of chemical treatments, which has the characteristics of non-pollution, soft and thin fiber, and easy delamination. As degreasing cotton is widely used in the medical industry, it produces a large amount of waste degreasing cotton, which is easy to cause waste of resources. Degreasing cotton is mainly composed of cellulose, hemicellulose and lignin and is rich in polysaccharides. Fan et al. prepared a novel chitosan/ethylenediaminetetraacetic acid biochar acrylic-based hydrogel using waste degreasing cotton to realize the reuse of degreasing cotton. The hydrogel was able to adsorb heavy metal ions efficiently, and the adsorption capacities of Pb^{2+} and Cu^{2+} reached 1105.78 and 678.04 mg/g, respectively, moreover, the adsorption capacity and recovery of heavy metal ions of the adsorbent remained at a high level after five cycles [97].

Conclusion and future trends

With rapid progress in industries and technologies and concomitant rise in living standards, water pollution has emerged as a serious problem. Wastewater containing various pollutants is discharged into rivers to enter the ecosystem cycle, causing irreversible damage to the environment. In addition to water pollution caused by textile dyes and pharmaceutical industries, for example, heavy metal ions from industrial processes are also a major source of water pollution. Various heavy metal ions, such as Pb^{2+} and Co^{2+}, accumulate in living organisms and cannot be excreted through metabolism, eventually causing serious harm to human health through the food chain cycle. Most of the heavy metal ions are toxic, and apart from direct damage to organs, they can cause mutations and are carcinogenic. Therefore, the elimination of such pollution from wastewater and the surroundings is of great significance, especially for potable water, and deserves immediate attention.

Hydrogel is a polymeric substance with high water absorption capacity, the form of which is between solid and liquid, and its internal structure is a three-dimensional network with tough characteristics. Hydrogel is hydrophilic and insoluble in water, so it can exchange water between its internal and external water phases that come into contact with it, and the solute molecules contained in external water can thus enter the hydrogel. As a result, it can be used for treatment of wastewater containing heavy metal ions.

Polysaccharide-based biopolymer hydrogels have a remarkable ability to remove metal ions owing to their diverse functional groups, such as amino, carboxyl, hydroxyl, and epoxy groups. The efficiency of hydrogels in removing metal ions is mainly attributed to these functional groups and their surface chemistry. In addition to their superior adsorption capacity, biopolymer hydrogels are flexible and can be reused after the adsorbed pollutants are removed, which renders them both environmentally friendly and economically efficient. Therefore, biopolymer hydrogels have attracted research attention and have good prospects in the area of heavy metal adsorption. Biopolymer hydrogels are non-toxic and stable in a variety of acidic and alkaline environments and therefore have become the preferred material for heavy metal removal.

Polysaccharide-based biopolymer hydrogels prepared using a single natural raw material are often unstable; therefore, composites are often used in practical applications. In the preparation of polysaccharide hydrogels, the structure of natural polysaccharide molecules will be damaged, which will affect the performance of the hydrogels. In order to expand the performance and usage of polysaccharide-based hydrogels, chemical modification of single polysaccharide hydrogels is often carried out to introduce functionalized groups, and the final composite hydrogels obtained are greatly enhanced in mechanical strength and adsorption properties, in addition to making up for some defects. The composite polysaccharide-based hydrogel, as an efficient adsorbent, can adsorb heavy metal ions rapidly and in large quantities, and is easily recoverable and reusable. By combining with other components, hydrogels with unused efficacy can be obtained, and polysaccharide-based hydrogels with more stability, specificity and adsorption capacity have been developed for wider applications in water treatment.

Biomaterial-based hydrogels have superb physical properties, chemical properties, degradability, low toxicity, and easy availability, making them a promising material for decontamination. This paper provides an overview of latest advancements in polysaccharide-based hydrogels with favorable adsorbability and selectivity for the treatment of wastewater contaminated with heavy metal ions.

Compliance with Ethics Requirements

This article does not contain any studies with human or animal subjects.

CRediT authorship contribution statement

Chenxi Zhao: Conceptualization, Writing – original draft, Writing – review & editing. **Guangyang Liu:** Investigation, Writing – review & editing. **Qiyue Tan:** Visualization. **Mingkun Gao:** Visualization. **Ge Chen:** Resources. **Xiaodong Huang:** Supervision. **Xiaomin Xu:** Supervision. **Lingyun Li:** . **Jing Wang:** Project administration. **Yaowei Zhang:** Supervision, Project administration. **Donghui Xu:** Funding acquisition.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgements

This work was supported by the National Key R&D Program of China (2020YFD1000300), the National Natural Science Foundation of China (31701695 and 31872947), the Agricultural Science and Technology Innovation Program of CAAS (CAAS-ZDRW202011 and CAAS-XTCX2019025), the Special Fund for the Industrial System Construction of Modern Agriculture of China (CARS-23-E03), and the Risk Assessment on Vegetable Products (GJFP20210201).

References

[1] Patel YN, Patel MP. Adsorption of azo dyes from water by new poly (3-acrylamidopropyl)-trimethylammonium chloride-co-N, N-dimethylacrylamide superabsorbent hydrogel—Equilibrium and kinetic studies, Journal of Environmental. Chem Eng 2013;1(4):1368–74.

[2] Roa K, Oyarce E, Boulett A, ALSamman M, Oyarzún D, Pizarro GDC, et al. Lignocellulose-based materials and their application in the removal of dyes from water: A review. Sustainable MaterTechnol 2021;29:e00320. doi: https://doi.org/10.1016/j.susmat.2021.e00320.

[3] Qiu J, Fan P, Feng Y, Liu F, Ling C, Li A. Comparison of the adsorption behaviors for methylene blue on two renewable gels with different physical state. Environ Pollut 2019;254:113117. doi: https://doi.org/10.1016/j.envpol.2019.113117.

[4] Liu Y, Hu L, Tan B, Li J, Gao X, He Y, et al. Adsorption behavior of heavy metal ions from aqueous solution onto composite dextran-chitosan macromolecule resin adsorbent. Int J Biol Macromol 2019;141:738–46. doi: https://doi.org/10.1016/j.ijbiomac.2019.09.044.

[5] Fu F, Wang Q. Removal of heavy metal ions from wastewaters: a review. J Environ Manage 2011;92(3):407–18. doi: https://doi.org/10.1016/j.jenvman.2010.11.011.

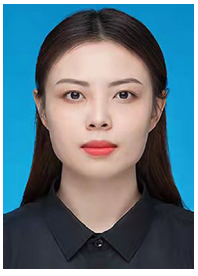
[6] Akpor O. Remediation of heavy metals in drinking water and wastewater treatment systems: Processes and applications. Int J Phys Sci 2010;5:1807–17.
[7] Feng D, Aldrich C, Tan H. Treatment of acid mine water by use of heavy metal precipitation and ion exchange. Miner Eng 2000;13:623–42.
[8] Li M, Huang W, Tang B, Fang Q, Ling X, Lv A. Characterizations and n-Hexane Vapor Adsorption of a Series of MOF/Alginates. Ind Eng Chem Res 2020;59 (42):18835–43. doi: https://doi.org/10.1021/acs.iecr.9b06744.
[9] Wu Q, He H, Zhou H, Xue F, Zhu H, Zhou S, et al. Multiple active sites cellulose-based adsorbent for the removal of low-level Cu(II), Pb(II) and Cr(VI) via multiple cooperative mechanisms. Carbohydr Polym 2020;233:115860. doi: https://doi.org/10.1016/j.carbpol.2020.115860.
[10] Santander P, Butter B, Oyarce E, Yáñez M, Xiao L-P, Sánchez J. Lignin-based adsorbent materials for metal ion removal from wastewater: A review. Ind Crops Prod 2021;167:113510. doi: https://doi.org/10.1016/j.indcrop.2021.113510.
[11] Song L, Liu F, Zhu C, Li A. Facile one-step fabrication of carboxymethyl cellulose based hydrogel for highly efficient removal of Cr(VI) under mild acidic condition. Chem Eng J 2019;369:641–51. doi: https://doi.org/10.1016/j.cej.2019.03.126.
[12] Calcagnile P, Sibillano T, Giannini C, Sannino A, Demitri C. Biodegradable poly (lactic acid)/cellulose-based superabsorbent hydrogel composite material as water and fertilizer reservoir in agricultural applications. J Appl Polym Sci 2019;136(21):47546. doi: https://doi.org/10.1002/app.v136.2110.1002/app.47546.
[13] Wang H, Wu J, Qiu J, Zhang K, Shao J, Yan L. In situ formation of a renewable cellulose hydrogel electrolyte for high-performance flexible all-solid-state asymmetric supercapacitors. Sustainable Energy Fuels 2019;3(11):3109–15.
[14] Kozicki M, Kołodziejczyk M, Szynkowska M, Pawlaczyk A, Leśniewska E, Matusiak A, et al. Hydrogels made from chitosan and silver nitrate. Carbohydr Polym 2016;140:74–87. doi: https://doi.org/10.1016/j.carbpol.2015.12.017.
[15] Maiti S, Khillar PS, Mishra D, Nambiraj NA, Jaiswal AK. Physical and self–crosslinking mechanism and characterization of chitosan-gelatin-oxidized guar gum hydrogel. Polym Test 2021;97:107155. doi: https://doi.org/10.1016/j.polymertesting.2021.107155.
[16] Liu Y, Sui Y, Liu C, Liu C, Wu M, Li B, et al. A physically crosslinked polydopamine/nanocellulose hydrogel as potential versatile vehicles for drug delivery and wound healing. Carbohydr Polym 2018;188:27–36. doi: https://doi.org/10.1016/j.carbpol.2018.01.093.
[17] Wei S, Li Z, Lu W, Liu H, Zhang J, Chen T, et al. Multicolor Fluorescent Polymeric Hydrogels. Angew Chem Int Ed Engl 2021;60(16):8608–24. doi: https://doi.org/10.1002/anie.202007506.
[18] Qasemi S, Ghaemy M. Highly sensitive and strongly fluorescent gum tragacanth based superabsorbent hydrogel as a new biosensor for glucose optical detection. J Mater Chem C 2020;8(12):4148–56.
[19] Qasemi S, Ghaemy M. Novel superabsorbent biosensor nanohydrogel based on gum tragacanth polysaccharide for optical detection of glucose. Int J Biol Macromol 2020;151:901–8. doi: https://doi.org/10.1016/j.ijbiomac.2020.02.231.
[20] Zhang D, Tian X, Li H, Zhao Y, Chen L. Novel fluorescent hydrogel for the adsorption and detection of Fe (III). Colloids Surf, A 2021;608:125563. doi: https://doi.org/10.1016/j.colsurfa.2020.125563.
[21] Rahmani Z, Ghaemy M. One-step hydrothermal-assisted synthesis of highly fluorescent N-doped carbon dots from gum tragacanth: Luminescent stability and sensitive probe for Au3+ ions. Opt Mater 2019;97:109356. doi: https://doi.org/10.1016/j.optmat.2019.109356.
[22] Rahmani Z, Ghaemy M, Olad A. Preparation of nanogels based on kappa-carrageenan/chitosan and N-doped carbon dots: study of drug delivery behavior. Polym Bull 2021;78(5):2709–26. doi: https://doi.org/10.1007/s00289-020-03236-x.
[23] Naik V, Zantye P, Gunjal D, Gore A, Anbhule P, Kowshik M, et al. Nitrogen-Doped Carbon Dots via Hydrothermal Synthesis: Naked Eye Fluorescent Sensor for Dopamine and Used for Multicolor Cell Imaging. ACS Appl Bio Mater 2019;2(5):2069–77. doi: https://doi.org/10.1021/acsabm.9b0010110.1021/acsabm.9b00101.s001.
[24] Shao J, Yu Q, Wang S, Hu Y, Guo Z, Kang K, et al. Poly(vinyl alcohol)–Carbon Nanodots Fluorescent Hydrogel with Superior Mechanical Properties and Sensitive to Detection of Iron(III) Ions. Macromol Mater Eng 2019;304 (11):1900326. doi: https://doi.org/10.1002/mame.201900326.
[25] Behera S, Mahanwar PA. Superabsorbent polymers in agriculture and other applications: a review. Polymer-Plastics Technol Mater 2020;59(4):341–56. doi: https://doi.org/10.1080/25740881.2019.1647239.
[26] Ryu JH, Lee Y, Kong WH, Kim TG, Park TG, Lee H. Catechol-functionalized chitosan/pluronic hydrogels for tissue adhesives and hemostatic materials. Biomacromolecules 2011;12(7):2653–9. doi: https://doi.org/10.1021/bm200464x.
[27] Hu Y, Hu S, Zhang S, Dong S, Hu J, Kang L, et al. A double-layer hydrogel based on alginate-carboxymethyl cellulose and synthetic polymer as sustained drug delivery system. Sci Rep 2021;11(1). doi: https://doi.org/10.1038/s41598-021-88503-1.
[28] Zhao B, Jiang H, Lin Z, Xu S, Xie J, Zhang A. Preparation of acrylamide/acrylic acid cellulose hydrogels for the adsorption of heavy metal ions. Carbohydr Polym 2019;224:115022. doi: https://doi.org/10.1016/j.carbpol.2019.115022.
[29] Chen D, Zhao X, Wei X, Zhang J, Wang D, Lu H, Jia P. Ultrastretchable, Tough, Antifreezing, and Conductive Cellulose Hydrogel for Wearable Strain Sensor. ACS Appl Mater Interfaces 2020;12:53247–56. doi: https://doi.org/10.1021/acsami.0c14935.
[30] Yu J, Lu Q, Zheng J, Li Y. Chitosan/attapulgite/poly(acrylic acid) hydrogel prepared by glow-discharge electrolysis plasma as a reusable adsorbent for selective removal of Pb2+ ions. Iran Polym J 2019;28(10):881–93. doi: https://doi.org/10.1007/s13726-019-00751-1.
[31] Lu Q, Zheng J, Yu J, Yang S, Ma D, Yang W, et al. Synthesis and Adsorption Properties for Cationic Dyes of Acrylic Acid/Vermiculite Hydrogel Initiated by Glow-Discharge-Electrolysis Plasma. Adv Polym Tech 2018;37(4):996–1007. doi: https://doi.org/10.1002/adv.21748.
[32] Shin JY, Yeo YH, Jeong JE, Park SA, Park WH. Dual-crosslinked methylcellulose hydrogels for 3D bioprinting applications. Carbohydr Polym 2020;238:116192. doi: https://doi.org/10.1016/j.carbpol.2020.116192.
[33] Liu Z, Ma R, Du W, Yang G, Chen T. Radiation-initiated high strength chitosan/lithium sulfonate double network hydrogel/aerogel with porosity and stability for efficient CO2 capture. RSC Adv 2021;11(33):20486–97.
[34] Taşdelen B, Çifçi Dİ, Meriç S. Preparation and characterization of chitosan/hyaluronic acid/itaconic acid hydrogel composite to remove manganese in aqueous solution. Desalin Water Treat 2021;209:204–11. doi: https://doi.org/10.5004/dwt.2021.26640.
[35] Zhang W, Wang R, Sun Z, Zhu X, Zhao Q, Zhang T, et al. Catechol-functionalized hydrogels: biomimetic design, adhesion mechanism, and biomedical applications. Chem Soc Rev 2020;49(2):433–64.
[36] Sabbagh N, Akbari A, Arsalani N, Eftekhari-Sis B, Hamishekar H. Halloysite-based hybrid bionanocomposite hydrogels as potential drug delivery systems. Appl Clay Sci 2017;148:48–55. doi: https://doi.org/10.1016/j.clay.2017.08.009.
[37] Huang B, Liu M, Zhou C. Chitosan composite hydrogels reinforced with natural clay nanotubes. Carbohydr Polym 2017;175:689–98. doi: https://doi.org/10.1016/j.carbpol.2017.08.039.
[38] Sannino A, Demitri C, Madaghiele M. Biodegradable Cellulose-based Hydrogels: Design and Applications. Materials 2009;2:353–73. doi: https://doi.org/10.3390/ma2020353.
[39] Rop K, Mbui D, Njomo N, Karuku GN, Michira I, Ajayi RF. Biodegradable water hyacinth cellulose-graft-poly(ammonium acrylate-co-acrylic acid) polymer hydrogel for potential agricultural application. Heliyon 2019;5(3):e01416. doi: https://doi.org/10.1016/j.heliyon.2019.e01416.
[40] Kassem I, Kassab Z, Khouloud M, Sehaqui H, Bouhfid R, Jacquemin J, et al. Phosphoric acid-mediated green preparation of regenerated cellulose spheres and their use for all-cellulose cross-linked superabsorbent hydrogels. Int J Biol Macromol 2020;162:136–49. doi: https://doi.org/10.1016/j.ijbiomac.2020.06.136.
[41] Ghorbani S, Eyni H, Bazaz SR, Nazari H, Asl LS, Zaferani H, Kiani V, Mehrizi AA, Soleimani M. Hydrogels Based on Cellulose and its Derivatives: Applications, Synthesis, and Characteristics. Polym. Sci., Series A 2019;60:707–22. doi: https://doi.org/10.1134/s0965545x18060044.
[42] Durpekova S, Filatova K, Cisar J, Ronzova A, Kutalkova E, Sedlarik V. A Novel Hydrogel Based on Renewable Materials for Agricultural Application. Int. J. Polym. Sci. 2020;2020:1–13. doi: https://doi.org/10.1155/2020/8363418.
[43] Ferreira MOG, Leite LLR, de Lima IS, Barreto HM, Nunes LCC, Ribeiro AB, et al. da Silva Filho, Chitosan Hydrogel in combination with Nerolidol for healing wounds. Carbohydr Polym 2016;152:409–18. doi: https://doi.org/10.1016/j.carbpol.2016.07.037.
[44] Pal P, Pal A, Nakashima K, Yadav BK. Applications of chitosan in environmental remediation: A review. Chemosphere 2021;266:128934. doi: https://doi.org/10.1016/j.chemosphere.2020.128934.
[45] Alvarez Echazu MI, Olivetti CE, Anesini C, Perez CJ, Alvarez GS, Desimone MF. Development and evaluation of thymol-chitosan hydrogels with antimicrobial-antioxidant activity for oral local delivery. Mate. Sci Eng C Mater Biol Appl 2017;81:588–96. doi: https://doi.org/10.1016/j.msec.2017.08.059.
[46] Tang S, Yang J, Lin L, Peng K, Chen Y, Jin S, et al. Construction of physically crosslinked chitosan/sodium alginate/calcium ion double-network hydrogel and its application to heavy metal ions removal. Chem Eng J 2020;393:124728. doi: https://doi.org/10.1016/j.cej.2020.124728.
[47] Liu H, Li W, Wen W, Luo B, Liu M, Ding S, et al. Mechanical properties and osteogenic activity of poly(l-lactide) fibrous membrane synergistically enhanced by chitosan nanofibers and polydopamine layer. Mater Sci Eng C Mater Biol Appl 2017;81:280–90. doi: https://doi.org/10.1016/j.msec.2017.08.010.
[48] Zhang C, An D, Xiao Q, Weng H, Zhang Y, Yang Q, et al. Preparation, characterization, and modification mechanism of agar treated with hydrogen peroxide at different temperatures. Food Hydrocolloids 2020;101:105527. doi: https://doi.org/10.1016/j.foodhyd.2019.105527.
[49] Zhang Y, Ren B, Xie S, Cai Y, Wang T, Feng Z, et al. Multiple Physical Cross-Linker Strategy To Achieve Mechanically Tough and Reversible Properties of Double-Network Hydrogels in Bulk and on Surfaces. ACS Appl Polym Mater 2019;1(4):701–13. doi: https://doi.org/10.1021/acsapm.8b0023210.1021/acsapm.8b00232.s001.
[50] Rani GU, Konreddy AK, Mishra S. Novel hybrid biosorbents of agar: Swelling behaviour, heavy metal ions and dye removal efficacies. Int J Biol Macromol 2018;117:902–10. doi: https://doi.org/10.1016/j.ijbiomac.2018.05.163.
[51] Yan K, Xu F, Wang C, Li Y, Chen Y, Li X, et al. A multifunctional metal-biopolymer coordinated double network hydrogel combined with multi-stimulus responsiveness, self-healing, shape memory and antibacterial properties. Biomater Sci 2020;8(11):3193–201.

[52] Huang S, Chen H-J, Deng Y-P, You X-H, Fang Q-H, Lin M. Preparation of novel stable microbicidal hydrogel films as potential wound dressing. Polym Degrad Stab 2020;181:109349. doi: https://doi.org/10.1016/j.polymdegradstab.2020.109349.
[53] Wiercińska J, Winiecki J, Wronczewska A, Lebioda A, Pławski K, Rhone P, et al. The use of hyaluronic acid hydrogel as a tumour bed marker in breast-conserving therapy. Radiother Oncol 2020;152:8–13. doi: https://doi.org/10.1016/j.radonc.2020.07.041.
[54] Lee EJ, Kang E, Kang S-W, Huh KM. Thermo-irreversible glycol chitosan/hyaluronic acid blend hydrogel for injectable tissue engineering. Carbohydr Polym 2020;244:116432. doi: https://doi.org/10.1016/j.carbpol.2020.116432.
[55] Sharifzadeh G, Wahit MU, Soheilmoghaddam M, Whye WT, Pasbakhsh P. Kappa-carrageenan/halloysite nanocomposite hydrogels as potential drug delivery systems. J Taiwan Inst Chem Eng 2016;67:426–34. doi: https://doi.org/10.1016/j.jtice.2016.07.027.
[56] Gao Y, Liu Q, Kong W, Wang J, He L, Guo L, et al. Activated hyaluronic acid/collagen composite hydrogel with tunable physical properties and improved biological properties. Int J Biol Macromol 2020;164:2186–96. doi: https://doi.org/10.1016/j.ijbiomac.2020.07.319.
[57] Chuysinuan P, Thanyacharoen T, Thongchai K, Techasakul S, Ummartyotin S. Preparation of chitosan/hydrolyzed collagen/hyaluronic acid based hydrogel composite with caffeic acid addition. Int J Biol Macromol 2020;162:1937–43. doi: https://doi.org/10.1016/j.ijbiomac.2020.08.139.
[58] Coogan KR, Stone PT, Sempertegui ND, Rao SS. Fabrication of micro-porous hyaluronic acid hydrogels through salt leaching. Eur Polym J 2020;135:109870. doi: https://doi.org/10.1016/j.eurpolymj.2020.109870.
[59] Sahraei R, Sekhavat Pour Z, Ghaemy M. Novel magnetic bio-sorbent hydrogel beads based on modified gum tragacanth/graphene oxide: Removal of heavy metals and dyes from water. J Cleaner Prod 2017;142:2973–84. doi: https://doi.org/10.1016/j.jclepro.2016.10.170.
[60] Mohammadian M, Sahraei R, Ghaemy M. Synthesis and fabrication of antibacterial hydrogel beads based on modified-gum tragacanth/poly(vinyl alcohol)/Ag0 highly efficient sorbent for hard water softening. Chemosphere 2019;225:259–69. doi: https://doi.org/10.1016/j.chemosphere.2019.03.040.
[61] Shojaipour M, Ghaemy M. Highly efficient and antibacterial ion exchanger based on graphene oxide for removal of chromate and nitrate from water: synthesis, characterization and application. New J Chem 2021;45(1):268–81.
[62] Shojaipour M, Ghaemy M, Amininasab SM. Removal of NO3(-) ions from water using bioadsorbent based on gum tragacanth carbohydrate biopolymer. Carbohydr Polym 2020;227:115367. doi: https://doi.org/10.1016/j.carbpol.2019.115367.
[63] Masoumi A, Ghaemy M. Removal of metal ions from water using nanohydrogel tragacanth gum-g-polyamidoxime: Isotherm and kinetic study. Carbohydr Polym 2014;108:206–15. doi: https://doi.org/10.1016/j.carbpol.2014.02.083.
[64] Li J, Jia X, Yin L. Hydrogel: Diversity of Structures and Applications in Food Science. Food Rev Int 2021;37(3):313–72. doi: https://doi.org/10.1080/87559129.2020.1858313.
[65] Elsawy MA, Smith AM, Hodson N, Squires A, Miller AF, Saiani A. Modification of beta-Sheet Forming Peptide Hydrophobic Face: Effect on Self-Assembly and Gelation. Langmuir 2016;32:4917–23. doi: https://doi.org/10.1021/acs.langmuir.5b03841.
[66] Godiya CB, Martins Ruotolo LA, Cai W. Functional biobased hydrogels for the removal of aqueous hazardous pollutants: current status, challenges, and future perspectives. J Mater Chem A 2020;8(41):21585–612.
[67] ALSamman MT, Sánchez J. Recent advances on hydrogels based on chitosan and alginate for the adsorption of dyes and metal ions from water. Arabian J Chem 2021;14(12):103455. doi: https://doi.org/10.1016/j.arabjc.2021.103455.
[68] Roa K, Tapiero Y, Thotiyl MO, Sánchez J. Hydrogels Based on Poly([2-(acryloxy)ethyl] Trimethylammonium Chloride) and Nanocellulose Applied to Remove Methyl Orange Dye from Water. Polymers (Basel) 2021;13(14):2265. doi: https://doi.org/10.3390/polym13142265.
[69] Sanchez J, Dax D, Tapiero Y, Xu C, Willfor S. Bio-Based Hydrogels With Ion Exchange Properties Applied to Remove Cu(II), Cr(VI), and As(V) Ions From Water. Front Bioeng Biotechnol 2021;9:656472. doi: https://doi.org/10.3389/fbioe.2021.656472.
[70] Oyarce E, Santander P, Butter B, Pizarro GDC, Sánchez J. Use of sodium alginate biopolymer as an extracting agent of methylene blue in the polymer-enhanced ultrafiltration technique. J Appl Polym Sci 2021;138(34):50844. doi: https://doi.org/10.1002/app.v138.3410.1002/app.50844.
[71] Butter B, Santander P, Pizarro GDC, Oyarzun DP, Tasca F, Sanchez J. Electrochemical reduction of Cr(VI) in the presence of sodium alginate and its application in water purification. J Environ Sci (China) 2021;101:304–12. doi: https://doi.org/10.1016/j.jes.2020.08.033.
[72] Zhu C, Yang R, Hua X, Chen H, Xu J, Wu R, et al. Highly stretchable HA/SA hydrogels for tissue engineering. J Biomater Sci Polym Ed 2018;29(5):543–61. doi: https://doi.org/10.1080/09205063.2018.1426425.
[73] Sahraei R, Hemmati K, Ghaemy M. Adsorptive removal of toxic metals and cationic dyes by magnetic adsorbent based on functionalized graphene oxide from water. RSC Adv 2016;6(76):72487–99.
[74] Sahraei R, Ghaemy M. Synthesis of modified gum tragacanth/graphene oxide composite hydrogel for heavy metal ions removal and preparation of silver nanocomposite for antibacterial activity. Carbohydr Polym 2017;157:823–33. doi: https://doi.org/10.1016/j.carbpol.2016.10.059.
[75] Sahraei R, Shahalizade T, Ghaemy M, Mahdavi H. Fabrication of cellulose acetate/Fe3O4@GO-APTS-poly(AMPS-co-MA) mixed matrix membrane and its evaluation on anionic dyes removal. Cellulose 2018;25(6):3519–32. doi: https://doi.org/10.1007/s10570-018-1800-9.
[76] Masoumi A, Ghaemy M, Bakht AN. Removal of Metal Ions from Water Using Poly(MMA-co-MA)/Modified-Fe3O4 Magnetic Nanocomposite: Isotherm and Kinetic Study. Ind Eng Chem Res 2014;53(19):8188–97. doi: https://doi.org/10.1021/ie5000906.
[77] Zhang M, Song L, Jiang H, Li S, Shao Y, Yang J, et al. Biomass based hydrogel as an adsorbent for the fast removal of heavy metal ions from aqueous solutions. J Mater Chem A 2017;5(7):3434–46.
[78] Varadharajan C, Beller HR, Bill M, Brodie EL, Conrad ME, Han R, et al. Reoxidation of Chromium(III) Products Formed under Different Biogeochemical Regimes. Environ Sci Technol 2017;51(9):4918–27. doi: https://doi.org/10.1021/acs.est.6b06044.
[79] Kaur K, Jindal R. Comparative study on the behaviour of Chitosan-Gelatin based Hydrogel and nanocomposite ion exchanger synthesized under microwave conditions towards photocatalytic removal of cationic dyes. Carbohydr Polym 2019;207:398–410. doi: https://doi.org/10.1016/j.carbpol.2018.12.002.
[80] Musarurwa H, Tavengwa NT. Application of carboxymethyl polysaccharides as bio-sorbents for the sequestration of heavy metals in aquatic environments. Carbohydr Polym 2020;237:116142. doi: https://doi.org/10.1016/j.carbpol.2020.116142.
[81] Omer AM, Dey R, Eltaweil AS, Abd El-Monaem EM, Ziora ZM. Insights into recent advances of chitosan-based adsorbents for sustainable removal of heavy metals and anions. Arabian J Chem 2022;15(2):103543. doi: https://doi.org/10.1016/j.arabjc.2021.103543.
[82] Russo T, Fucile P, Giacometti R, Sannino F. Sustainable Removal of Contaminants by Biopolymers: A Novel Approach for Wastewater Treatment. Current State and Future Perspectives. Processes 2021;9. doi: https://doi.org/10.3390/pr9040719.
[83] Wang N, Xu X, Li H, Zhai J, Yuan L, Zhang K, et al. Preparation and Application of a Xanthate-Modified Thiourea Chitosan Sponge for the Removal of Pb(II) from Aqueous Solutions. Ind Eng Chem Res 2016;55(17):4960–8. doi: https://doi.org/10.1021/acs.iecr.6b00694.
[84] Masoumi A, Hemmati K, Ghaemy M. Low-cost nanoparticles sorbent from modified rice husk and a copolymer for efficient removal of Pb(II) and crystal violet from water. Chemosphere 2016;146:253–62. doi: https://doi.org/10.1016/j.chemosphere.2015.12.017.
[85] Wang W, Zhao Y, Yi H, Chen T, Kang S, Zhang T, et al. Pb(II) removal from water using porous hydrogel of chitosan-2D montmorillonite. Int J Biol Macromol 2019;128:85–93. doi: https://doi.org/10.1016/j.ijbiomac.2019.01.098.
[86] Milosavljević NB, Ristić MĐ, Perić-Grujić AA, Filipović JM, Štrbac SB, Rakočević ZL, et al. Removal of Cu2+ ions using hydrogels of chitosan, itaconic and methacrylic acid: FTIR, SEM/EDX, AFM, kinetic and equilibrium study. Colloids Surf, A 2011;388(1-3):59–69. doi: https://doi.org/10.1016/j.colsurfa.2011.08.011.
[87] Paulino AT, Belfiore LA, Kubota LT, Muniz EC, Almeida VC, Tambourgi EB. Effect of magnetite on the adsorption behavior of Pb(II), Cd(II), and Cu(II) in chitosan-based hydrogels. Desalination 2011;275(1-3):187–96. doi: https://doi.org/10.1016/j.desal.2011.02.056.
[88] Shen C, Shen Y, Wen Y, Wang H, Liu W. Fast and highly efficient removal of dyes under alkaline conditions using magnetic chitosan-Fe(III) hydrogel. Water Res 2011;45(16):5200–10. doi: https://doi.org/10.1016/j.watres.2011.07.018.
[89] Sarkar K, Ansari Z, Sen K. Detoxification of Hg(II) from aqueous and enzyme media: Pristine vs. tailored calcium alginate hydrogels. Int J Biol Macromol 2016;91:165–73. doi: https://doi.org/10.1016/j.ijbiomac.2016.05.049.
[90] Zhuang YT, Zhang X, Wang DH, Yu YL, Wang JH. Three-dimensional molybdenum disulfide/graphene hydrogel with tunable heterointerfaces for high selective Hg(II) scavenging. J Colloid Interface Sci 2018;514:715–22. doi: https://doi.org/10.1016/j.jcis.2017.12.082.
[91] Lone S, Yoon DH, Lee H, Cheong IW. Gelatin–chitosan hydrogel particles for efficient removal of Hg(ii) from wastewater. Environ Sci Water Res Technol 2019;5:83–90. doi: https://doi.org/10.1039/c8ew00678d.
[92] Martinková E, Chrastný V, Francová M, Šípková A, Čuřík J, Myška O, et al. Cadmium isotope fractionation of materials derived from various industrial processes. J Hazard Mater 2016;302:114–9. doi: https://doi.org/10.1016/j.jhazmat.2015.09.039.
[93] Gobrecht J, McDyre C, Comotto J, Reynolds M. Induction of cytotoxic and genotoxic damage following exposure of V79 cells to cadmium chloride, Mutation Research/Genetic Toxicology and Environmental. Mutagenesis 2017;816–817:12–7. doi: https://doi.org/10.1016/j.mrgentox.2017.03.001.
[94] Karbarz M, Khalil AM, Wolowicz K, Kaniewska K, Romanski J, Stojek Z. Efficient removal of cadmium and lead ions from water by hydrogels modified with cystine, Journal of Environmental. Chem Eng 2018;6(4):3962–70.
[95] Jia Q, Li D, Gao X, Yan J, Ma Q, Meng F. Hydrazinolyzed cellulose-g-polymethyl acrylate as adsorbent for efficient removal of Cu(II) and Ni(II) ions from aqueous solution. J Chem Technol Biotechnol 2016;91(5):1378–86. doi: https://doi.org/10.1002/jctb.4734.
[96] Kundu D, Mondal SK, Banerjee T. Development of β-Cyclodextrin-Cellulose/Hemicellulose-Based Hydrogels for the Removal of Cd(II) and Ni(II):

Synthesis, Kinetics, and Adsorption Aspects. J Chem Eng Data 2019;64 (6):2601–17. doi: https://doi.org/10.1021/acs.jced.9b00088.
[97] Fan X, Wang X, Cai Y, Xie H, Han S, Hao C. Functionalized cotton charcoal/chitosan biomass-based hydrogel for capturing Pb(2+), Cu(2+) and MB. J Hazard Mater 2022;423:127191. doi: https://doi.org/10.1016/j.jhazmat.2021.127191.
[98] Wu S, Guo J, Wang Y, Huang C, Hu Y. Facile preparation of magnetic sodium alginate/carboxymethyl cellulose composite hydrogel for removal of heavy metal ions from aqueous solution. J Mater Sci 2021;56(23):13096–107. doi: https://doi.org/10.1007/s10853-021-06044-4.
[99] Yuan H, Peng J, Ren T, Luo Q, Luo Y, Zhang N, et al. Novel fluorescent lignin-based hydrogel with cellulose nanofibers and carbon dots for highly efficient adsorption and detection of Cr(VI). Sci Total Environ 2021;760:143395. doi: https://doi.org/10.1016/j.scitotenv.2020.143395.
[100] Melilli G, Yao J, Chiappone A, Sangermano M, Hakkarainen M. Photocurable "all-lignocellulose" derived hydrogel nanocomposites for adsorption of cationic contaminants. Sustainable Mater Technol 2021;27:e00243. doi: https://doi.org/10.1016/j.susmat.2020.e00243.
[101] Zhao H, Ouyang X-K, Yang L-Y. Adsorption of lead ions from aqueous solutions by porous cellulose nanofiber–sodium alginate hydrogel beads. J Mol Liq 2021;324:115122. doi: https://doi.org/10.1016/j.molliq.2020.115122.
[102] Huang H, Ge H, Ren Z, Huang Z, Xu M, Wang X. Controllable Synthesis of Biocompatible Fluorescent Carbon Dots From Cellulose Hydrogel for the Specific Detection of Hg(2). Front Bioeng Biotechnol 2021;9:617097. doi: https://doi.org/10.3389/fbioe.2021.617097.
[103] Ayouch I, Kassem I, Kassab Z, Barrak I, Barhoun A, Jacquemin J, et al. Crosslinked carboxymethyl cellulose-hydroxyethyl cellulose hydrogel films for adsorption of cadmium and methylene blue from aqueous solutions. Surf Interfaces 2021;24:101124. doi: https://doi.org/10.1016/j.surfin.2021.101124.
[104] Huang H, Ge H, Ren Z, Huang Z, Xu M, Wang X. Controllable Synthesis of Biocompatible Fluorescent Carbon Dots From Cellulose Hydrogel for the Specific Detection of Hg2+. Front Bioeng Biotechnol 2021;9. doi: https://doi.org/10.3389/fbioe.2021.617097.
[105] Pavithra S, Thandapani G, Sugashini S, Sudha PN, Alkhamis HH, Alrefaei AF, et al. Batch adsorption studies on surface tailored chitosan/orange peel hydrogel composite for the removal of Cr(VI) and Cu(II) ions from synthetic wastewater. Chemosphere 2021;271:129415. doi: https://doi.org/10.1016/j.chemosphere.2020.129415.
[106] Xu X, Ouyang X-K, Yang L-Y. Adsorption of Pb(II) from aqueous solutions using crosslinked carboxylated chitosan/carboxylated nanocellulose hydrogel beads. J Mol Liq 2021;322:114523. doi: https://doi.org/10.1016/j.molliq.2020.114523.
[107] Perumal S, Atchudan R, Yoon DH, Joo J, Cheong IW. Graphene oxide-embedded chitosan/gelatin hydrogel particles for the adsorptions of multiple heavy metal ions. J Mater Sci 2020;55(22):9354–63. doi: https://doi.org/10.1007/s10853-020-04651-1.
[108] Maity S, Naskar N, Jana B, Lahiri S, Ganguly J. Fabrication of thiophene-chitosan hydrogel-trap for efficient immobilization of mercury (II) from aqueous environs. Carbohydr Polym 2021;251:116999. doi: https://doi.org/10.1016/j.carbpol.2020.116999.
[109] Shehzad H, Ahmed E, Din MI, Farooqi ZH, Arshad M, Sharif A, et al. Facile Synthesis of Novel Carboxymethyl-Chitosan/Sodium Alginate Grafted with Amino-Carbamate Moiety/Bentonite Clay Composite for Effective Biosorption of Ni (II) from Aqueous Solution. Z Phys Chem 2021;235(5):583–607. doi: https://doi.org/10.1515/zpch-2019-1555.
[110] Li T, Liu X, Li L, Wang Y, Ma P, Chen M, et al. Polydopamine-functionalized graphene oxide compounded with polyvinyl alcohol/chitosan hydrogels on the recyclable adsorption of cu(II), Pb(II) and cd(II) from aqueous solution. J Polym Res 2019;26(12). doi: https://doi.org/10.1007/s10965-019-1971-6.
[111] Demirbilek C, Dinç CÖ. Synthesis of diethylaminoethyl dextran hydrogel and its heavy metal ion adsorption characteristics. Carbohydr Polym 2012;90 (2):1159–67. doi: https://doi.org/10.1016/j.carbpol.2012.06.068.
[112] Godiya CB, Liang M, Sayed SM, Li D, Lu X. Novel alginate/polyethyleneimine hydrogel adsorbent for cascaded removal and utilization of Cu(2+) and Pb(2+) ions. J Environ Manage 2019;232:829–41. doi: https://doi.org/10.1016/j.jenvman.2018.11.131.
[113] Sharma B, Thakur S, Trache D, Yazdani Nezhad H, Thakur VK. Microwave-Assisted Rapid Synthesis of Reduced Graphene Oxide-Based Gum Tragacanth Hydrogel Nanocomposite for Heavy Metal Ions Adsorption. Nanomaterials (Basel) 2020;10(8):1616. doi: https://doi.org/10.3390/nano10081616.
[114] Sethi S, Medha, Singh G, Sharma R, Kaith BS, Sharma N, et al. Fluorescent hydrogel of chitosan and gelatin cross-linked with maleic acid for optical detection of heavy metals. J Appl Polym Sci 2022;139(15):51941. doi: https://doi.org/10.1002/app.v139.1510.1002/app.51941.
[115] Chan K, Morikawa K, Shibata N, Zinchenko A. Adsorptive Removal of Heavy Metal Ions, Organic Dyes, and Pharmaceuticals by DNA-Chitosan Hydrogels. Gels 2021;7(3):112. doi: https://doi.org/10.3390/gels7030112.
[116] Lin Z, Yang Y, Liang Z, Zeng L, Zhang A. Preparation of Chitosan/Calcium Alginate/Bentonite Composite Hydrogel and Its Heavy Metal Ions Adsorption Properties. Polymers (Basel) 2021;13(11):1891. doi: https://doi.org/10.3390/polym13111891.

Chenxi Zhao is a M.S. candidate at Northeastern Agricultural University and is co-trained by the Institute of Vegetable and Flower Research (IVF CAAS), Chinese Academy of Agricultural Sciences. She has curiosity for research in scientific field, and her research interests are material science synthesis and quality and safety of agricultural products.

Guangyang Liu received his Doctor degree major in Chemical Engineering and Technology from School of Chemistry and Chemical Engineering, Harbin Institute of Technology in 2016. He is an assistant researcher of the Institute of Vegetables and flowers, Chinese Academy of Agricultural Sciences (IVF CAAS). His research focused on agricultural nanotechnology R&D and applications.



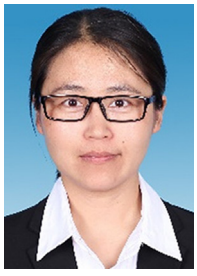
Qiyue Tan is a M.S. candidate at Northeastern Agricultural University and is co-trained by the Institute of Vegetable and Flower Research (IVF CAAS), Chinese Academy of Agricultural Sciences.

Mingkun Gao received his master's degree from the Chinese Academy of Agricultural Sciences in 2022. He is now pursuing a PhD degree under the tutelage of academician Jihong Yu at the school of Chemical, Jilin University. His research is focused on synthesis mechanism and structural regulation of porous materials.

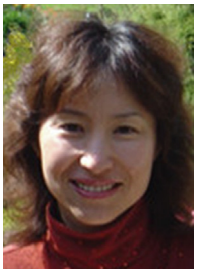
Ge Chen received her M.S. degree major in food science in 2017, and received her Doctor degree major in Quality of Agro-products and Food Safety from institutue of quality standard & testing technology for agroproducts, Chinese Academy of Agriculutural Sciences in 2020. She is an assistant researcher of the Institute of Vegetables and flowers, Chinese Academy of Agricultural Sciences (IVF CAAS). Her research focused on quality safety of agricultural product.

Xiaodong Huang is an associate professor of the Institute of Vegetables and flowers, Chinese Academy of Agricultural Sciences (IVF CAAS). His current research is mainly focused on pesticides residue and environmental analysis. He majored in Pesticide Science and holds Ph.D. degree from College of Science, China Agricultural University (CAU).

Xiaomin Xu received her Doctor degree from School of Chemistry and Chemical Engineering, Hunan University in 2014. She is an assistant researcher of the Institute of Vegetables and flowers, Chinese Academy of Agricultural Sciences (IVF CAAS). Her research focused on quality safety of agricultural product.



Lingyun Li received her M.S. degree from State Key Laboratory of Elemento-organic Chemistry, Nankai University in 2009. She is an assistant researcher of the Institute of Vegetables and flowers, Chinese Academy of Agricultural Sciences (IVF CAAS).



Jing Wang received B.S. degree from Heilongjiang University in 1985. she was working in the Northeast Agriculture University between 1985 and 1996.After obtained her PhD, she was appointed to be an associate professor, professor of the Northeast Agriculture University and of Harbin Institute of Technology from 1996 to 2005. She is currently a professor and director of residues research department of the Institute of Quality Standards & Testing Technology for Agroproducts, CAAS. She has engaged in studies of food safety and testing technology/screening novel products with bioactivities.

Yaowei Zhang received his M.S. degree from the School of Horticulture, Northeastern Agricultural University in 2002 and his Ph.D. degree in vegetable science from Northeastern Agricultural University in 2016. Currently, he is a researcher in the College of Horticulture, Northeastern Agricultural University. His research focuses on genetic improvement of cabbage germplasm resources and new variety selection.

Donghui Xu received his M.S. degree from School of Horticulture, Northeast Agricultural University in 2004 and received his Doctor degree major in Molecular breeding from the Institute of Vegetables and flowers, Chinese Academy of Agricultural Sciences in 2007. He is researcher of the Institute of Vegetables and flowers, Chinese Academy of Agricultural Sciences. His research focused on quality safety of agricultural product.