



Removal of organic pollutants and antibacterial properties of modified chitosan and their composites

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ABSTRACT

As a non-toxic and harmless natural polysaccharide, chitosan was widely used in water treatment, food processing, and drug transmission due to its rich hydroxyl and ammonia groups. However, the practical application of chitosan was limited due to its low mechanical strength and low solubility in acidic mediums. The chitosan composites modified by magnetization, cross-linking, grafting and other methods have stronger stability, better adsorption capacity and other excellent properties. The advances in the application of these chitosan composites during the removal of environmental organic pollutants are the main aim of this current review. The review showed that composites of chitosan are versatile adsorbents of a variety of dyes, pharmaceutical residues, humic acid, and its antibacterial properties can be discussed. Moreover, conclusions and future recommendations are provided to inspire for further researches.

Keywords: Modified chitosan; Adsorption; Organic pollutants; Antibacterial properties

1. Introduction

With the rapid development of the economy and the continuous improvement of industrialization, the living standards have been steadily improved, and the efficiency of industrial production has increased significantly. However, the pollution caused by human life and production is also increasing [1]. Organic pollution is one of the common types of pollution in water, and due to the wide variety and complex structure of organic matter, it is difficult to treat organic wastewater, which has become an important part of water environmental protection [2,3]. Human activities and industrial production generate a large amount of organic wastewater. Common organic pollutants in water mainly include synthetic organic substances, such as chemicals in industrial and agricultural wastewater, dyes in printing and dyeing wastewater, and natural organic substances, such as humus and proteins. These organic pollutants not only

cause adverse effects on the natural water environment, but also seriously endanger human health [4–6]. The main methods to remove organic pollutants in water are adsorption, coagulation, ultrafiltration and so on. Among them, the adsorption method is more widely used because of its simple operation and low-cost [7–9].

Chitosan is the only natural cationic polysaccharide that is readily biodegradable. The amino and hydroxyl groups in its molecules make it have good flocculation, film formation, adsorption, complexation and other properties [10]. The hydroxyl and amino groups on the molecular chain of chitosan are arranged regularly, so there are strong hydrogen bonds within and between molecules, resulting in that chitosan is not easy to dissolve under neutral or basic conditions and only dissolves under acidic conditions. Therefore, it is widely used in the field of water treatment to remove organic pollutants from wastewater, which is affected by solubility, easy loss, pH and nonporous performance.

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Unfortunately, natural polymers are often unable to remove pharmaceuticals from extremely complex wastewater [11]. Thus, to improve their effectiveness in removing pharmaceuticals from complicated wastewater, these polymers should be modified using chemical or physical techniques [12]. Chitosan can be modified to compensate for its limitations in application. These new composite materials have gained numerous positive aspects including increased stability, enhanced surface area, improved adsorption capacities, better recyclability, improved applicability under different reaction conditions.

This review article briefly described the common modification methods of chitosan. According to the related studies in the past 10 y, the applications of modified chitosan and its derivatives in organic wastewater treatment and its antibacterial properties were summarized. In particular, recent modification methods and treatment effects were listed in the table to facilitate comparison. Taking into account the rapid progress of relevant studies, some earlier studies may not be cited in the review or may simply be mentioned with their modification methods without statistical details.

2. Modification of chitosan

Chitosan is a polysaccharide produced after the N-deacetylation of chitin [13], as depicted in Fig. 1. In general, the removal of over 55% of the N-acetyl group can be called chitosan [14]. Chitosan is a natural high polymer, and unlike the properties of most polymers, it has excellent biocompatibility, biodegradability, adsorption properties, etc. [15]. The polycationic nature of chitosan enables it to interact with different types of molecules. In addition to free highly reactive functional groups, its cationic nature and hydrophilicity ensure that it can be used as an adsorbent with high binding capacity for various metal ions, dyes and macromolecules [16]. However, its low porosity, low specific surface area, low solubility and high crystallinity are the main disadvantages of its application [17]. Therefore, changing the physical and chemical properties of chitosan to make its derivatives have more suitable properties is the main way to expand the application scope of chitosan [18].

The modification methods of chitosan can be divided into physical and chemical methods. The physical methods mainly change the physical form of chitosan, chitosan can be transformed into powder, film, gel, microsphere and so on through modification. After the modification of morphological change, the defects of chitosan itself, such as low mechanical strength, weak acid stability, low porosity and low specific surface area, can be overcome, so that a large number of functional groups on the chitosan surface can function better in the adsorption process. The chemical methods mainly use chitosan as the functional monomer, and replace and reorganize the functional groups such as amino and hydroxyl and other functional groups on its carbon chain to improve the removal efficiency of chitosan and its derivatives for organic matter in water. The application of chitosan mainly has the disadvantages of low acid stability, weak mechanical strength, low thermal stability and low specific surface area. However, the main advantage of chitosan is the presence of modifiable positions in its chemical structure. There are three active functional groups in chitosan: amino at C2 position, secondary hydroxyl at C3 position and primary hydroxyl at C6 position. These three active groups give chitosan a lot of modification methods [19]. Modification methods such as cross-linking and grafting give chitosan new properties and produce compounds with new biological functions.

2.1. Cross-linked chitosan

The cross-linking modification of chitosan is generally through the reaction of the amino groups and hydroxyl groups on chitosan with the cross-linking agents, so that the molecular chain is cross-linked to obtain a three-dimensional network structure, thereby affecting the mechanical strength and solubility of chitosan [20]. Cross-linking modification plays an important role in enhancing the mechanical resistance of chitosan and reducing the solubility of chitosan molecules. Dialdehyde [21], sodium triphosphate [22], genipin [23] and epichlorohydrin [24] are often used as cross-linking agents in the cross-linking process of chitosan. It was shown that the adsorption capacity of chitosan is

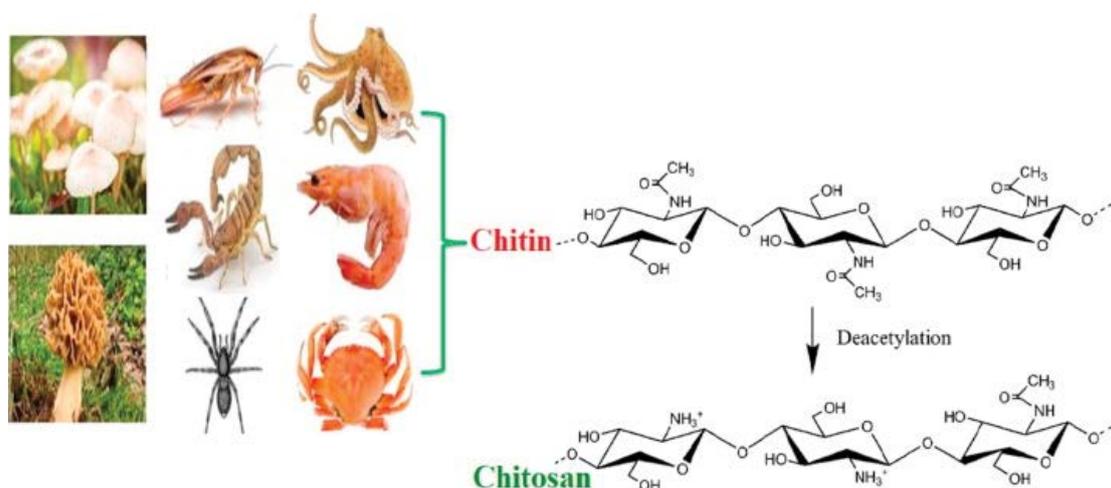


Fig. 1. Production of chitosan.

affected by the degree of cross-linking. In general, the higher the cross-linking degree, the higher the mechanical strength of chitosan, but the lower the adsorption capacity [25]. Therefore, an optimal condition needs to be found so that chitosan has good adsorption capacity, excellent mechanical strength and other properties at the same time.

2.2. Grafted chitosan

Grafting copolymerization is considered as a very promising modification method of chitosan. Although amino groups and hydroxyl groups on the chitosan molecular chain are limited and only absorb a few kinds of pollutants, chitosan can be combined with synthetic polymers with specific properties by grafting. Active groups on chitosan such as amino groups can produce free radicals under the action of evocating agent and graft with the monomer, making chitosan introduce new functional groups. Thus, the properties and applications of chitosan are increased to improving the effect of chitosan in water treatment.

Yazdani-Pedram et al. [26] found that grafting efficiency was closely related with the evocating agent, monomers, reaction time and temperature. Grafting can be carried out by free radicals, enzymes, etc. as initiators, and radiation induction is also a method to start grafting copolymerization [27], which is initiated without the addition of a catalyst, and can also control the extent of the reaction by adjusting the amount of irradiation. Pérez-Calixto et al. [28] compared grafting copolymerization after direct and indirect irradiation showing that the grafting rate of direct irradiation was greater than indirect irradiation. Chitosan/polymethacrylate composite were prepared by using azobisisobutyronitrile as the evocating agent, grafting methacrylic acid and α -methacrylic monomer to chitosan [29]. Chitosan/polymethacrylate composite could be used to adsorb Bromocresol Green from wastewater. After 3 cycles of tests, the adsorption rate of Bromocresol Green by chitosan/polymethacrylate composite still staying above 97%.

2.3. Magnetized chitosan

Magnetic chitosan is a new type of water treatment agent with efficient, environmentally friendly, economical and sustainable properties, which can solve many problems existing in water treatment, so people pay more and more attention to it. The magnetic modification of chitosan is mainly by wrapping the magnetic material with chitosan to form a polymer molecular chitosan microsphere with a magnetic core [30], or evenly distributing magnetic cores on the surface of chitosan microspheres (Fig. 2). At present, the methods for preparing magnetic chitosan microspheres mainly include embedding method, monomer polymerization method, in situ method and so on. Magnetic chitosan contains groups such as $-\text{OH}$, $-\text{NH}_2$, chitosan molecules wrap around the nanomagnetic particles. Therefore, the magnetic chitosan has the characteristics of large specific surface area, porosity, narrow particle size distribution, etc., as well as the advantage of easy recycling and reuse. The processing object of magnetic separation technology is magnetic waste water. Magnetic chitosan and its derivatives can adsorb various pollutants and then quickly remove pollutants in the

water through an external magnetic field. The application of magnetic chitosan microspheres has expanded the application of magnetic separation technology in water treatment.

3. Modified chitosan and its derivatives remove organic pollutants in water

3.1. Removal of dyes

Dyes are common water pollutants in industrial wastewater discharged from paper mills, textile mills, printing plants and dye manufacturing plants. Even low concentrations of dyes discharged into the water environment can prevent the penetration of light and oxygen, endangering the ecological environment in the water. Dyes are also toxic to humans and can damage human health through direct or indirect ways, such as causing skin allergies and even tumors. Therefore, it is very necessary for the removal of dyes in industrial wastewater. Chitosan has been extensively studied and used as dye removal materials [31].

Dyes can be divided into anionic dyes, cationic dyes and non-ionic dyes according to the charge difference. The principle of the removal of anionic dyes by chitosan is summarized by Chiou and Li [32]. The amino groups on chitosan are protonated in acidic medium, since the anionic dye is negatively charged and the surface of chitosan is positively charged, the contaminants are absorbed through electrostatic interaction. Chatterjee et al. [33] removed Methylene Blue from the aqueous solution by using sodium dodecyl sulfate gel to prepare chitosan beads. The results showed that the adsorption capacity of chitosan beads increased three times than chitosan. Because of its own cationic properties, chitosan is not suitable to remove the cationic dyes, so the researchers mostly solve this problem by modifying chitosan. Crini et al. [34] prepared grafted chitosan containing sulfonic groups and showed that the modified chitosan could remove cationic dyes well.

In recent years, Jawad et al. [35] tried to combine epichlorohydrin cross-linked chitosan with aluminosilicate mineral as a zwitterionic composite adsorbent. This zwitterionic composite adsorbent consisting of epichlorohydrin cross-linked chitosan/zeolite was able to remove dyes with different structure like anionic Reactive Red 120 and cationic Methylene Blue from the aqueous environment. The experimental results showed that the adsorption capacity of this compound adsorbent on Reactive Red 120 and Methylene Blue at 30°C is 284.2 and 156.1 mg/g. Marrakchi et al. [36]

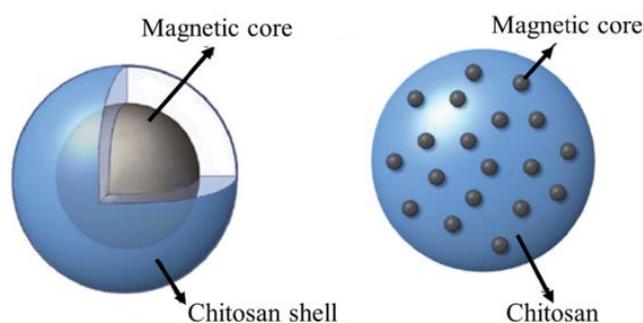


Fig. 2. Common magnetic chitosan structures.

prepared epichlorohydrin cross-linked chitosan/carbon-clay biohybrid adsorbent to adsorb cationic Methylene Blue and anionic azo Acid Blue 29. Methylene Blue and Acid Blue 29 were batch adsorbed with this hybrid adsorbent at an optimal weight ratio 40:60 of chitosan and carbon clay. The study confirmed the potential and effectiveness of their prepared biohybrid adsorbent for adsorbing these two dyes. The maximum adsorption capacity of this adsorbent for Methylene Blue and Acid Blue 29 is 95.31 and 167.35 mg/g at 50°C, respectively.

Basic dyes are a much more toxic type of dyes. They produce positively charged chromogenic groups upon ionization. Therefore, it is necessary to modify the chitosan with negatively charged groups, so that the modified chitosan can more easily react with basic dyes. Morais da Silva et al. [37] cross-linked chitosan with sodium tripolyphosphate to obtain chitosan microbeads that can be used to remove Basic Blue 7. The results showed that the maximum adsorption capacity of sodium tripolyphosphate cross-linked chitosan microbeads for Basic Blue 7 reached 1,174 mg/g at 25°C and pH 6.

Methylene Blue is a thiazide dye with a wide range of applications and can be used in dyeing, disinfection, medical treatment and other fields. However, Methylene Blue is mutagenic. After intravenous injection of Methylene Blue more than 500 mg/kg can cause nausea, dizziness, chest pain, etc. A high concentration of Methylene Blue can poison and kill animals. Jin et al. [38] prepared chitosan-derived three-dimensional porous carbon, a derivative of chitosan with large aperture channels. Three-dimensional porous carbon can efficiently remove Methylene Blue from water, and the adsorption capacity reaches a maximum value of 925.9 mg/g at 45°C.

There are many other studies on the removal of Methylene Blue by modified chitosan and its derivatives. Salama and Abou-Zeid [39] prepared ionic chitosan/silica nanocomposite to adsorb Methylene Blue, which can reach adsorption equilibrium within 60 min. The adsorption method conformed to the Langmuir adsorption model, and the maximum adsorption capacity in weak alkaline solution was 847.5 mg/g. Al-Wasidi et al. [40] prepared chitosan/Fe₃O₄/graphene oxide hydrogel and used it to remove Methylene Blue and Eriochrome Black T, with an optimal pH of 8 and 2, respectively. Under optimal conditions, the maximum adsorption capacity of the modified hydrogel for Methylene Blue and Chromium Black T was 261.78 and 289.85 mg/g. Yu et al. [41] prepared aminated magnetic chitosan microspheres by one-step method and then prepared magnetic grafted microspheres based on them, which were used to adsorb the anionic dye Reactive Brilliant Red and cationic dye Methylene Blue, respectively. The maximum adsorption capacity of aminated magnetic chitosan microspheres for Reactive Brilliant Red reached 637.41 mg/g at pH 2.0, and the maximum adsorption capacity of magnetic grafted chitosan microspheres for Methylene Blue reached 211.22 mg/g at pH 12.0. Mashkoor et al. [42] used magnetic Fe₃O₄ modified chitosan to adsorb Methylene Blue, which was proved to have good adsorption effect and can be efficiently recycled with a maximum adsorption capacity of 76.34 mg/g. Xu et al. [43] prepared poly(2-acrylamide-2-methylpropane sulfonic acid) grafted magnetic

chitosan microspheres by free radical polymerization to remove Methylene Blue. The results showed that the adsorption capacity improved with the increase of temperature and the maximum adsorption capacity reached 1,428 mg/g at 50°C, and the magnetic microspheres can be effectively recycled.

In addition to Methylene Blue, modified chitosan and its derivatives are also suitable for removing many common dyes. Li et al. [44] prepared a novel adsorbent by cross-linking epichlorohydrin to chitosan and studied the Congo Red solution as simulated dye wastewater. The research showed that under certain conditions, the adsorption capacity of chitosan adsorbent improved obviously with the increase of Congo Red concentration. Under the same conditions, the cross-linked chitosan adsorbent was better than chitosan, when the dose of modified chitosan was 30 mg, the adsorption time and temperature to reach the optimal adsorption rate were 120 min and 40°C, respectively. Lin et al. [45] prepared modified chitosan microspheres by emulsion cross-linking method. The maximum adsorption capacity of the chitosan microspheres for Congo Red and Acid Green 50 was 428.7 and 691.8 mg/g at 25°C, pH 3.0 respectively. The removal rate still remained at 92% after five cycles. Magnetic microspheres containing glutamine-modified chitosan were prepared by Tao et al. [46]. Compared with ordinary magnetic chitosan microspheres, they had more active adsorption sites. The removal rate of Acid Green 25 was improved, and the maximum adsorption capacity reached 698.95 mg/g. Sabarudin and Madjid [47] prepared cross-linked chitosan beads using tripolyphosphate and epichlorohydrin as cross-linking agents to adsorb Methyl Orange. It was found that low concentration of epichlorohydrin kept chitosan stable in acidic environment, meanwhile the concentration of tripolyphosphate and soaking time affected the aperture and morphology of chitosan beads. The adsorption efficiency of Methyl Orange was largely influenced by the porosity and rigidity of cross-linked chitosan beads. Therefore, sodium tripolyphosphate cross-linker effectively changed the adsorption efficiency of cross-linked chitosan beads for Methyl Orange. Under optimal conditions, the adsorption of Methyl Orange by cross-linked chitosan beads was 79.55 mg/g, and the adsorption rate constant was 1.29×10^{-3} /min. Li et al. [48] made a modified chitosan adsorbent from the 3-chlorine-2-hydroxypropyl trimethyl ammonium grafted chitosan with strong positive charge, which was used to adsorb Methyl Orange and Cr(VI) and the competitive adsorption of the two pollutants was optimal at pH 5. Khapre et al. [49] used formaldehyde as a cross-linker modified chitosan with aniline, and then cross-linked it through glutaraldehyde with alginic acid to synthesize chitosan-alginate composite containing aniline molecule. The composite was used to adsorb Methyl Orange, Brilliant Green and Patent Blue V with a maximum adsorption capacity of 198.09 mg/g (pH 6), 235.82 mg/g (pH 8) and 117.34 mg/g (pH 3), respectively. Liu et al. [50] prepared a chitosan/kaolin/Fe₃O₄ composite to remove Methyl Orange in water by using one-pot co-precipitation method. Due to the modification of chitosan, the adsorbent introduced the adsorption sites for anions, so that the removal rate of Methyl Orange reached more than 94%, and the maximum adsorption capacity reached 349.7 mg/g.

Muedas-Taípe et al. [51] prepared magnetic chitosan coated with tetraethyl orthosilicate and modified with ethylenediamine to adsorb Cibacron Brilliant Red 3B-A and Cibacron Brilliant Yellow 3G-P. This modified chitosan had a larger adsorption capacity compared to the unmodified magnetic chitosan, reaching a maximum adsorption capacity of 377.6 and 179.4 mg/g for the above two dyes, respectively. Jia et al. [52] synthesized magnetic chitosan nanoparticles by the one-pot hydroheat method and studied its adsorption capacity to the azo dye Amido Black 10B. The adsorption capacity of Amido Black 10B reached 124.8 mg/g at pH 2, and it had a simple preparation process and recovery rate. Chatterjee et al. [53] reacted alkali and sodium dodecyl sulfate with chitosan by alkaline gel method to obtain two kinds of chitosan derivatives, and then used polyethylene imine as grafting monomer to graft the two chitosan derivatives to obtain chitosan hydrogel particles, and the final products were used to adsorb Reactive Black 5, respectively. The results showed that the maximum adsorption capacity of two chitosan derivatives for Reactive Black 5 was 201.90 and 168.07 mg/g, and the maximum adsorption capacity of two chitosan hydrogel particles for Reactive Black 5 was 709.27 and 413.23 mg/g, which was significantly improved.

Some of the studies mentioned are listed in Table 1.

3.2. Removal of pharmaceutical and personal care products residues

With the continuous improvement of environmental protection policies and awareness, PPCPs (Pharmaceutical and Personal Care Products) as a new kind of pollutant have attracted increasing attention. There are many kinds of PPCPs, such as antibiotics, pesticides, veterinary drugs, painkillers, hair dyes, all belong to PPCPs. The unabsorbed parts of medicines enter municipal sewage through excreta, and most care products enter sewage directly by washing with water. Although PPCPs are of low concentration in sewage, they are capable of bioaccumulation and long-term harm, and their harm to the environment cannot be ignored.

Antibiotics are mainly used to treat various bacterial infections or pathogenic microbial infections, widely used in medical, agricultural, animal husbandry and other fields. For antibiotics are not fully absorbed by humans or animals resulting in a large number of antibiotics into the environment with excrement which can lead to increased drug resistance in sensitive bacteria and may even be some toxicity to other organisms, harm the ecological environment and human health [54]. Bai et al. [55] immersed nano-Fe₃O₄ into chitosan hydrogel by alkaline gel-pyrolysis process. During preparation, the pellets were first cross-linked with 5% glutaraldehyde and then pyrolysis in a reactor at 350°C with nitrogen. The study found that the prepared material was effective in removing doxycycline. Ahamad et al. [56] prepared Fe₃O₄@chitosan magnetic nanocomposites by using thiobarbituric acid and malondialdehyde. The analysis showed that the material had a very high surface area and porosity. The maximum adsorption capacity of tetracycline reached 215.31 mg/g under the optimal conditions of adsorbent dosage of 0.05 g and tetracycline concentration of 60 mg/L. Ma et al. [57] developed a new adsorbent of montmorillonite intercalated carboxymethyl chitosan (Mt-CMC)

(Fig. 3) to remove tetracycline. The experiments showed that the adsorption efficiency of Mt-CMC was mainly affected by pH and hardly affected by temperature. The maximum adsorption capacity reached 48.10 mg/g at pH 4. Nazraz et al. [58] synthesized a nanomaterial of MgO/chitosan/graphene oxide by hydrothermal method. Its high surface area of 294 m²/g gave it a higher adsorption capacity than the unmodified chitosan and graphene oxide. The maximum adsorption capacity for ciprofloxacin and norfloxacin was 1,111 and 1,000 mg/g, respectively, and the maximum equilibrium was at over 120 and 150 min. Pooresmaeil and Namazi [59] synthesized a magnetic cadmium-based MOFs and then modified it with chitosan to form Fe₃O₄@Cd@chitosan microspheres. The results show that under the conditions of pH 8.0 and adsorption time of 240 min, the material removed more than 75% of amoxicillin and the maximum adsorption capacity reached 103.09 mg/g. Some researchers carried out adsorption experiments on ciprofloxacin, amoxicillin and erythromycin using magnetic composite materials of activated carbon and chitosan. The maximum adsorption capacity of magnetic activated carbon/chitosan for ciprofloxacin, amoxicillin and erythromycin was 90.10, 526.31 and 178.57 mg/g, respectively [60].

MIL101 is a kind of metal-organic frameworks, with the advantages of large surface area and large aperture, which is widely used in adsorption researches. Vardhan Patel and Yadav [61] studied the removal of tetracycline by photocatalytic MIL101(Fe)/ZnO chitosan beads. This chitosan composite had a maximum adsorption capacity of tetracycline up to 31.12 mg/g. Chitosan beads could be renewable under solar light, and the removal rate was still more than 90% after five cycles. Danaloğlu et al. [62] used chitosan-grafted SiO₂/Fe₃O₄ nanoparticles to remove ciprofloxacin in water with a theoretical maximum adsorption capacity of 100.74 mg/g at 298 K. It was proved that increasing the temperature was not conducive to improving the adsorption efficiency. Yadav et al. [63] used Fe₃O₄ to transform MIL101(Fe) chitosan beads and tested the adsorption effect on doxycycline, tetracycline and ciprofloxacin. The optimal conditions were determined through experiments, and the composite had a maximum adsorption capacity for doxycycline, tetracycline, and ciprofloxacin of 33.20, 45.33 and 31.30 mg/g, respectively. The removal rate reached more than 99% with a good regeneration ability. Zhuo et al. [64] prepared MIL101(Cr)/sodium alginate and MIL101(Cr)/chitosan composite beads to remove benzoic acid, ibuprofen and ketoprofen. The aim is to compare with unmodified sodium alginate and chitosan beads. The adsorption capacity of MIL101(Cr)/CS beads was much higher than that of sodium alginate, chitosan and MIL101(Cr)/sodium alginate. The adsorption of the three PPCPs on MIL101(Cr)/chitosan reached the adsorption equilibrium after 180 min.

Phenolic compounds are widely used in industrial production and the production of PPCPs. Phenolic compounds are highly toxic substances, which can cause poisoning symptoms when ingested in a certain amount. High concentration of phenolic wastewater can cause the death of fish and crops. Fan et al. [65] reported the application of β-cyclodextrin grafted magnetic chitosan nanoparticles as adsorbent for the removal of hydroquinone in water. Modified chitosan had a high adsorption capacity to hydroquinone due

Table 1
Adsorption effects of modified chitosan and its derivatives on dyes in water

Adsorbent	Main modification mode	Dye	Q_{\max} (mg/g)	References
Chitosan-epichlorohydrin/zeolite	Cross-linking, blending	Reactive Red 120	284.2	Jawad et al. [35]
Chitosan-epichlorohydrin/zeolite	Cross-linking, blending	Methylene Blue	156.1	Jawad et al. [35]
Chitosan-epichlorohydrin/carbon–clay	Cross-linking, blending	Methylene Blue	95.31	Marrakchi et al. [36]
Chitosan-epichlorohydrin/carbon–clay	Cross-linking, blending	Acid Blue 29	167.35	Marrakchi et al. [36]
Chitosan-tripolyphosphate microbeads	Cross-linking	Basic Blue 7	1174	Morais da Silva et al. [37]
Chitosan-derived three-dimensional porous carbon	Pre-carbonization	Methylene Blue	925.9	Jin et al. [38]
Ionic chitosan/silica nanocomposite	Blending	Methylene Blue	847.5	Salama and Abou-Zeid [39]
Chitosan/Fe ₃ O ₄ /graphene oxide hydrogel	Cross-linking, blending	Methylene Blue	261.78	Al-Wasidi et al. [40]
Chitosan/Fe ₃ O ₄ /graphene oxide hydrogel	Cross-linking, blending	Eriochrome Black T	289.85	Al-Wasidi et al. [40]
Aminated magnetic chitosan microspheres	Amination	Methylene Blue	211.22	Yu et al. [41]
Aminated magnetic grafted chitosan microspheres	Amination, grafting	Reactive Brilliant Red	637.41	Yu et al. [41]
Polyacrylic acid grafting β -cyclodextrin/chitosan composite	Grafting, blending	Methylene Blue	76.34	Mashkooor et al. [42]
Poly(2-acrylamido-2-methylpropane sulfonic acid) grafted magnetic chitosan microspheres	Grafting, blending	Methylene Blue	1428	Xu et al. [43]
Diethylenetriamine and epichlorohydrin modified chitosan microspheres	Cross-linking	Congo Red	428.7	Lin et al. [45]
Diethylenetriamine and epichlorohydrin modified chitosan microspheres	Cross-linking	Acid Green 50	691.8	Lin et al. [45]
Glutamine modified chitosan magnetic composite microspheres	Grafting, blending	Acid Green 50	698.95	Tao et al. [46]
Tripolyphosphate and epichlorohydrin modified chitosan beads	Cross-linking	Methyl Orange	79.55	Sabarudin and Madjid [47]
Chitosan-alginate composite with aniline molecular	Cross-linking, blending	Methyl Orange	198.09	Khapre et al. [49]
Chitosan-alginate composite with aniline molecular	Cross-linking, blending	Brilliant Green	235.82	Khapre et al. [49]
Chitosan-alginate composite with aniline molecular	Cross-linking, blending	Patent Blue V	117.34	Khapre et al. [49]
Chitosan/kaolin/Fe ₃ O ₄ composite	Blending	Methyl Orange	349.7	Liu et al. [50]
Tetramethyl orthosilicate and ethylenediamine modified magnetized chitosan beads	Cross-linking, blending	Cibacron Brilliant Red 3B-A	377.6	Muedas-Taipe et al. [51]
Tetramethyl orthosilicate and ethylenediamine modified magnetized chitosan beads	Cross-linking, blending	Cibacron Brilliant Yellow 3G-P	179.4	Muedas-Taipe et al. [51]
Fe ₃ O ₄ /chitosan magnetic nanoparticles	Cross-linking, blending	Amido Black 10B	124.8	Jia et al. [52]
Polyethylenimine grafted chitosan/alkali hydrogel beads	Grafting, blending	Reactive Black 5	709.27	Chatterjee et al. [53]
Polyethylenimine grafted chitosan/sodium dodecyl sulfate hydrogel beads	Grafting, blending	Reactive Black 5	413.23	Chatterjee et al. [53]

to its unique large surface area and high surface reactivity. Heydaripour et al. [66] reported the removal of 4-chlorophenol and phenol using porous magnetic resin-grafted chitosan beads. With the increase of chitosan grafted by porous magnetic resin, the maximum removal capacity of phenol and 4-chlorophenol reached 188.6 and 99 mg/g, indicating that the highly efficient magnetic resin grafted chitosan was very effective for the removal of phenolic compounds in wastewater. Santos et al. [67] used $ZnFe_2O_4$ and chitosan to prepare magnetic particles to adsorb diclofenac, and the adsorbed magnetic particles were easily separated from

water under the action of magnetic field. The maximum adsorption amount was 188 mg/g at pH 4.0.

Data on the removal of pharmaceuticals in water by modified chitosan and its derivatives are summarized in Table 2.

3.3. Removal of the humic acid

Humic acid can combine with organic pollutants and metal ions to form toxic compounds, reduce degradability and cause pollution to water bodies. The protonated

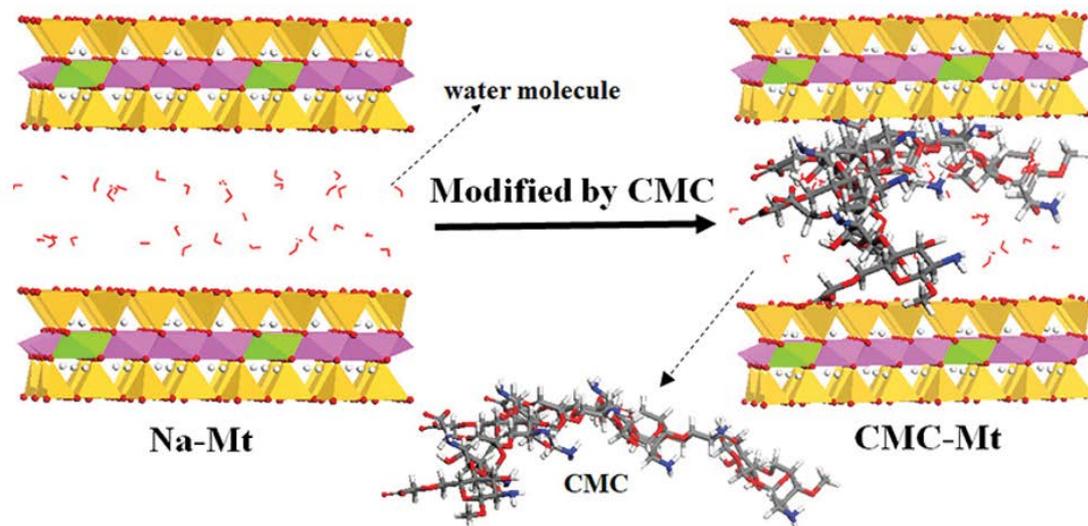


Fig. 3. Schematic diagram of Mt-CMC synthesis. Color legend for the atoms in the picture: Mg (purple), Al (green), Si (blue), C (gray), O (red), N (yellow), and H (white).

Table 2
Adsorption effect of modified chitosan and its derivatives on pharmaceuticals in water

Adsorbent	Main modification mode	Pharmaceuticals	Q_{max} (mg/g)	References
Fe_3O_4 @chitosan magnetic nanocomposites	Blending	Tetracycline	215.31	Ahamad et al. [56]
Montmorillonite intercalated carboxymethyl chitosan	Blending	Tetracycline	48.10	Ma et al. [57]
MgO/chitosan/graphene oxide nanosheets	Blending	Ciprofloxacin	1111	Nazraz et al. [58]
MgO/chitosan/graphene oxide nanosheets	Blending	Norfloxacin	1000	Nazraz et al. [58]
Fe_3O_4 @Cd@chitosan microspheres	Blending	Amoxicillin	103.09	Pooresmaeil and Namazi [59]
Magnetic activated carbon/chitosan	Blending	Ciprofloxacin	90.10	Danaloğlu et al. [60]
Magnetic activated carbon/chitosan	Blending	Amoxicillin	526.31	Danaloğlu et al. [60]
Magnetic activated carbon/chitosan	Blending	Erythromycin	178.57	Danaloğlu et al. [60]
Photocatalytic MIL101(Fe)/ZnO chitosan beads	Blending	Tetracycline	31.12	Vardhan Patel and Yadav [61]
Chitosan grafting SiO_2/Fe_3O_4 nanoparticles	Grafting, blending	Ciprofloxacin	100.74	Danaloğlu et al. [62]
Fe_3O_4 /MIL101(Fe) chitosan beads	Blending	Doxycycline	33.20	Yadav et al. [63]
Fe_3O_4 /MIL101(Fe) chitosan beads	Blending	Tetracycline	45.33	Yadav et al. [63]
Fe_3O_4 /MIL101(Fe) chitosan beads	Blending	Ciprofloxacin	31.30	Yadav et al. [63]
Porous magnetic resin grafting chitosan beads	Grafting, blending	4-Chlorophenol	99	Heydaripour et al. [66]
Porous magnetic resin grafting chitosan beads	Grafting, blending	Phenol	188.6	Heydaripour et al. [66]
$ZnFe_2O_4$ /chitosan magnetic particles	Blending	Diclofenac	188	Santos et al. [67]

amino groups on the surface of amino adsorbent can form a complex with the dissociated carboxyl groups and phenol hydroxyl groups by humic acid, which can efficiently adsorb humic acid in water. Therefore, chitosan adsorbent has a good effect on removing humic acid in water.

You et al. [68] prepared polyacrylamide grafted magnetic chitosan by in situ coprecipitation method and studied the effect of this material on removing humic acid in water. Polyacrylamide grafted magnetic chitosan had the best adsorption of humic acid in water with a removal rate higher than 80% and the theoretical adsorption capacity reached 120.77 mg/g at pH 7.0. Dong et al. [69] prepared epichlorohydrin cross-linked magnetic chitosan nanoparticles by in situ coprecipitation. They found that the equilibrium adsorption capacity of humic acid was only 7.4 mg/L at solution pH was 10, but significantly increased to 29.3 mg/L when the pH decreased to 4. Low ionic strength made stronger interaction between humic acid and magnetic chitosan nanoparticles. They prepared the magnetic chitosan nanoparticles with a surface area of 108.32 m²/g, and the maximum adsorption capacity of humic acid was 32.6 mg/g at 25°C [70]. Liu and Zhou [71] first proposed using polyacrylamide/chitosan semi-interpenetrating network hydrogel to remove humic acid. It proved again that the adsorption capacity increased effectively at low ionic strength and increased with the temperature. Then the maximum adsorption capacity reached 166.3 mg/g at 25°C. Wang et al. [72] prepared a magnetic nanocomposite, Fe₃O₄@chitosan@phenylalanine, and studied its adsorption effect of humic acid in water. The results showed that the amidogen and phenyl of phenylalanine strengthened the interaction between Fe₃O₄@chitosan@phenylalanine and humic acid. Its maximum adsorption capacity reached 33.5 mg/g, and it showed good adsorption performance after 8 regeneration cycles. A sulphuric acid cross-linked chitosan/PEC film was synthesized and applied to adsorb humic acid from water by Siswanta et al. [73]. The results showed that the film was suitable for pH 2 to 12 with a maximum adsorption capacity of 50.0 mg/g. Maghsoodloo et al. [74] prepared a new adsorbent by modifying granular activated carbon with chitosan. Within a certain range, the adsorption effect of the material on humic acid increases with the decrease of pH. The maximum adsorption capacity reached 71.4 mg/g at pH 4. Dehghani et al. [75] synthesized further processed bentonite/chitosan composite and studied the influence of pH, time, adsorbent dosage and other factors on the adsorption effect. Experiments showed that

the maximum adsorption capacity of humic acid achieved 91.36 mg/g at pH 4 and 25°C. Modified bentonite/chitosan material had good removal effect and low preparation cost, which was a very promising material in the field of humic acid adsorption.

Some of the data are sorted into Table 3.

3.4. Removal of the proteins

Proteins are the basic organic matter that constitute cells and the biological macromolecules composed of amino acids. Both excrement and human production activities will discharge a large amount of protein into water bodies, thus causing pollution to water. Chitosan, cellulose adsorbent and other polysaccharide composite have good adsorbability and hydrophilicity. They can maintain the macromolecular structure of proteins and avoid their denaturation during the adsorption process. Therefore, they are widely used for protein removal.

Cheng et al. [76] removed proteins in water by three methods: lime flocculation, transglutaminase polymerization and chitosan flocculation, respectively. Compared with the first two methods, chitosan flocculation is more effective in removing proteins. Chitosan flocculation removed 61.21% of the protein within 60 min at a chitosan concentration of 0.8 g/L and pH 5.5. Cellulose/chitosan composite sponge was prepared by Liu et al. [77]. Composite sponge was not only environmentally friendly, but also had excellent adsorption effect because of a 62.95% porosity. Due to the advantages of the porous structure and groups of chitosan, the adsorption capacity of the cellulose/chitosan composite sponge reached 200.56 mg/g for bovine serum albumin at pH 5.5. Ai et al. [78] reasonably solved the fragile structure of graphene and poor hydrophilic of chitosan by combining graphene with chitosan, and prepared graphene/chitosan composite microspheres with high mechanical strength and large adsorption capacity through grafting modification. The maximum adsorption capacity of bovine serum albumin and hemoglobin was 76.01 mg/g (pH 5.8) and 189.21 mg/g (pH 6.8), respectively. Mahdavinia and Etemadi [79] synthesized novel magnetic beads by modifying magnetic Fe₃O₄ nanoparticles with κ-carrageenan/carboxymethyl chitosan biopolymers. This magnetic chitosan composite showed a good adsorption effect on bovine serum albumin and the maximum adsorption of bovine serum albumin reached 73.3 mg/g. Kim et al. [80] prepared a kind of cross-linked chitosan by using dialdehyde cellulose and chitosan.

Table 3
Adsorption effect of modified chitosan and its derivatives on humic acid in water

Adsorbent	Main modification mode	Q_{max} (mg/g)	References
Polyacrylamide grafted magnetic chitosan	Grafting, blending	120.77	You et al. [68]
Magnetic chitosan nanoparticles	Cross-linking, blending	32.6	Dong et al. [70]
Polyacrylamide/chitosan semi-interpenetrating network hydrogel	Blending	166.3	Liu and Zhou [71]
Fe ₃ O ₄ @chitosan@phenylalanine	Blending	33.5	Wang et al. [72]
Sulphuric acid Cross-linked chitosan/PEC film	Cross-linking, blending	50.0	Siswanta et al. [73]
Granular activated carbon/chitosan	Blending	71.4	Maghsoodloo et al. [74]
Bentonite/chitosan composite	Blending	91.36	Dehghani et al. [75]

The dialdehyde cellulose cross-linked chitosan showed excellent adsorption effect on the bovine serum albumin at pH 5.5. The adsorption capacity of bovine serum albumin was improved with the increase of bovine serum albumin concentration. The maximum adsorption of bovine serum albumin reached 1300 mg/g. A novel Fe₃O₄/graphene oxide/chitosan composite was developed to adsorb proteins by Ye et al. [81]. Protein cytochrome C was used as the model target to evaluate the adsorption performance of it. And the maximum adsorption capacity was 13.3 mg/g. The magnetic carboxymethyl chitosan nanoparticles were developed by Wang et al. [82] as an effective adsorbent for bovine serum albumin. The results showed that the Langmuir equation leads to the lowest value of the error function, and the maximum adsorption capacity was 163.45 mg/g.

Some of the studies mentioned are listed in Table 4.

The main raw materials for the preparation of chitosan could be derived from discarded shrimp shells and crab shells to realize waste utilization, which also conformed to the rules of 3R (reducing, reusing and recycling). In addition, due to the rapid development of relevant studies and the continuous emergence of new processes, the cost price of modified chitosan and its composites showed a downward trend year by year. In particular, most of the modified chitosan and its complex can be directly recycled in the

application of protein removal, which is a green and pollution-free material.

3.5. Antimicrobial activities

Chitosan not only has good biocompatibility and low toxicity, but also has unique biological properties, such as antibacterial effect [83] and antitumor [84] effect. The broad-spectrum bacterial resistance of chitosan has been widely recognized, as shown in Table 5 [85], but the antimicrobial mechanism is relatively complex and may be influenced by multiple factors. Generally believed that chitosan has three main antibacterial mechanisms: (1) Using its positively charged $-NH_3^+$ reacts with anionic phosphate groups on the bacterial cell wall to destroy the surface charge, so that intracellular substances seep out due to changes in permeability. (2) Chitosan extracts metal ions by chelation, disrupting the bacterial cell wall [86]. (3) Chitosan damages the DNA of microorganisms, thereby inhibiting the synthesis of mRNA and protein [87]. Chitosan molecules induce hydrolyase enzymes be able to destroy the cell wall of microorganisms and inhibit DNA transcription, as depicted in Fig. 4.

Deacetylation, mass concentration and molecular structure are generally believed to be related to the antimicrobial effect of chitosan [88].

Table 4
Adsorption effect of modified chitosan and its derivatives on proteins in water

Adsorbent	Main modification mode	Proteins	Q _{max} (mg/g)	References
Cellulose/chitosan composite sponge	Blending	Bovine serum albumin	200.56	Liu et al. [77]
Graphene/chitosan composite microspheres	Blending	Bovine serum albumin	76.01	Ai et al. [78]
Graphene/chitosan composite microspheres	Blending	Hemoglobin	189.21	Ai et al. [78]
Magnetic κ-carrageenan/carboxymethyl chitosan biopolymers	Blending	Bovine serum albumin	73.3	Mahdavinia and Etemadi [79]
Dialdehyde cellulose cross-linked chitosan	Cross-linking	Bovine serum albumin	1300	Kim et al. [80]
Fe ₃ O ₄ /graphene oxide/chitosan composite	Blending	Protein cytochrome C	13.3	Ye et al. [81]
Magnetic carboxymethyl chitosan nanoparticles	Blending	Bovine serum albumin	163.45	Wang et al. [82]

Table 5
Antimicrobial activities of chitosan

Bacteria	MIC (μg/mL)	Fungi	MIC (μg/mL)
<i>Agrobacterium tumefaciens</i>	100	<i>Botrytis cinerea</i>	10
<i>Bacillus cereus</i>	1,000	<i>Drechslera sorokiniana</i>	10
<i>Corynebacterium michiganense</i>	10	<i>Fusarium oxysporum</i>	100
<i>Erwinia</i> ssp.	500	<i>Micronectriella nivialis</i>	10
<i>Erwinia carotovora</i> ssp.	200	<i>Pyricularia oryzae</i>	5,000
<i>Escherichia coli</i>	20	<i>Rhizoctonia solani</i>	1,000
<i>Klebsiella pneumoniae</i>	700	<i>Trichophyton equinum</i>	2,500
<i>Micrococcus luteus</i>	20		
<i>Pseudomonas fluorescens</i>	500		
<i>Staphylococcus aureus</i>	20		
<i>Xanthomonas campestris</i>	500		

MIC, minimum growth inhibitory concentration.

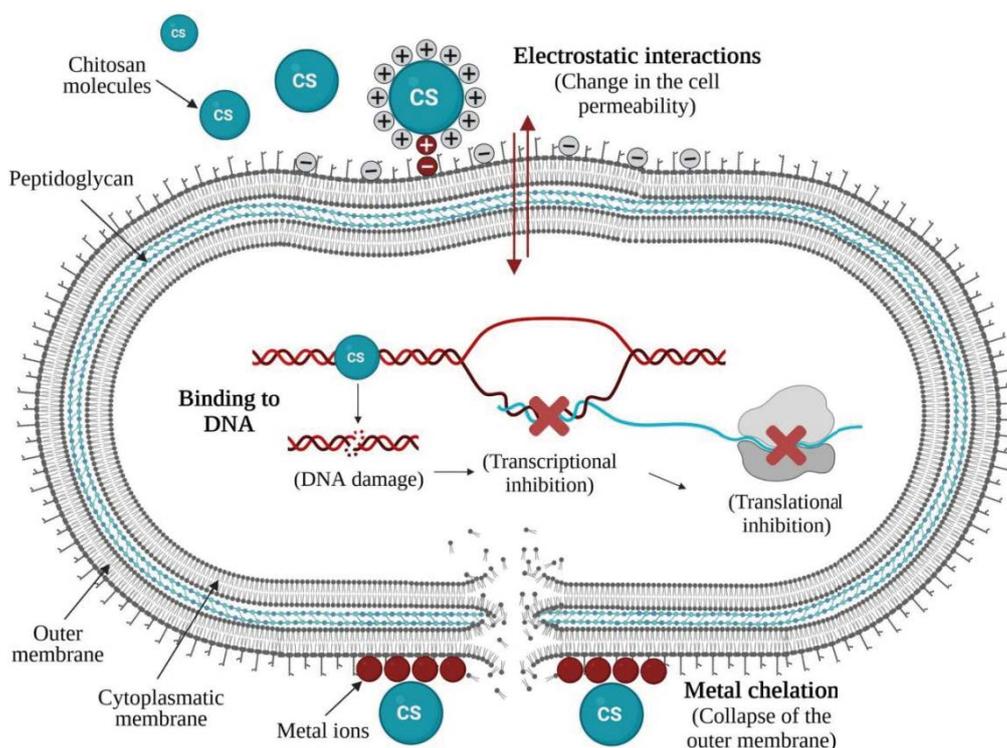


Fig. 4. Antibacterial mechanisms of chitosan.

The disadvantages of chitosan make it limited in practical applications, so scholars prepared a variety of chitosan derivatives and studied their antimicrobial activity. Studies showed that carboxymethyl chitosan, benzenesulfonic chitosan, chitosan quaternary ammonium salt, hydroxypropyl chitosan and other derivatives had strong antibacterial activity. Sun et al [89] successfully prepared sulfonated chitosan by adding 1,3-propanesultone to the amino groups of chitosan under acidic conditions and used it to test for antimicrobial activity. Experiments showed that the minimum inhibitory concentrations (MIC) of water-soluble chitosan against *Escherichia coli* and *Staphylococcus aureus* were 500 and 4,000 $\mu\text{g}/\text{mL}$, respectively, while sulfonated chitosan could reach 130 and 2,000 $\mu\text{g}/\text{mL}$. The antibacterial properties of sulfated chitosan are much stronger. Diao et al. [90] grafted quercetin and chitosan at a molar ratio of 0.02:1, which not only enhanced the oxidation resistance, but also improved the water solubility of chitosan. Because the amino groups of chitosan were involved in grafting with quercetin, the antibacterial resistance of the modified chitosan had decreased, but it still had strong antibacterial activity against Gram-stained positive bacteria. The MIC for *Bacillus subtilis*, *Micrococcus luteus* and *Staphylococcus aureus* was 64, 128 and 512 $\mu\text{g}/\text{mL}$, respectively.

Carboxymethyl chitosan is a well-water-soluble chitosan derivative whose N-substituted derivatives can be detected antimicrobial activity. Mohamed et al. [91] synthesized a series of quaternized N-substituted carboxymethyl chitosan and studied these derivatives against three kinds of bacteria: *Streptococcus pneumoniae*, *Bacillus subtilis*, *Escherichia coli* and three kinds of fungus: *Aspergillus fumigatus*, *Geotrichum candidum*, *Candida albicans*. The results showed that most

of these derivatives showed good antimicrobial properties, with MIC of 6.25–300.75 $\mu\text{g}/\text{mL}$ for bacteria and 3.25–125 $\mu\text{g}/\text{mL}$ for fungus. Wang and Jiang [92] prepared p-hydroxybenzoic acid-grafted chitosan by free radical-regulated grafting approach. Compared with chitosan, the composite had significantly enhanced antimicrobial properties against a wide variety of gram negative and positive bacteria. Meanwhile, it exhibited a much higher biological activity.

On the basis of a chitosan quaternary ammonium salt with good water-soluble, Cui et al. [93] prepared its derivative: N-2-hydroxypropyltrimethyl ammonium chloride chitosan-potassium 2-((5-bromo-2-hydroxybenzylidene)amino) acetate), which showed good inhibitory effect on both bacteria and fungi. The inhibition rate of this derivative against *Escherichia coli* and *Staphylococcus aureus* could reach 100% at the concentration of 0.1 mg/mL. Moreover, it also reached the 100% inhibition on *Fusarium oxysporum* f. sp. cubense and *Botrytis cinerea* at the concentration of 0.5 mg/mL. Min et al. [94] prepared quaternary ammonium chitosan by introducing N-(3-chloro-2-hydroxypropyl) trimethyl ammonium chloride into chitosan, and then grafted nisin on the quaternary ammonium chitosan. Experiments showed that nisin grafted quaternary ammonium chitosan had a significant inhibitory effect on gram positive bacteria and gram negative bacteria. In addition, it also had excellent antioxidant properties.

4. Conclusions and recommendations

Due to their excellent adsorption properties, chitosan-based adsorbents have been widely studied for the removal of organic pollutants in water [95]. In this review,

the removal of organic pollutants in water and antibacterial activities of chitosan and their composites were reviewed. The modification of chitosan is necessary for its practical application. There are various modification methods of chitosan. The most common modifications in this review involved combining chitosan with magnetic nanoparticles, graphene oxide, biochar, metals and other minerals. Suitable modification materials and methods should be selected according to the characteristics of pollutants to improve the application efficiency and range of chitosan. The future development of chitosan can focus on the following points: (1) Develop more kinds of chitosan-based adsorbents by cross-linking, grafting, magnetization modification, compounding, etc. to improve the adsorption efficiency of pollutants. (2) Explore more economical and convenient preparation and modification methods of chitosan, reduce the material cost, and improve the reuse rate of materials. (3) Although the cross-linking of chitosan can improve the stability, it will affect the adsorption capacity. So it is particularly important to find the balance with the best benefit. (4) Develop chitosan composites that can be applied to complex wastewater containing multiple pollutants instead of a single pollutant, expand the scope of practical applications. Chitosan is rich in sources, non-toxic and harmless to the human body, in line with the concept of sustainable development, and shows great potential in many fields. Accelerating the exploration of chitosan application is of great significance to green development and environmental protection.

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References

- Y. Liu, L. Yang, W. Jiang, Qualitative and quantitative analysis of the relationship between water pollution and economic growth: a case study in Nansi Lake catchment, China, *Environ. Sci. Pollut. Res.*, 27 (2019) 4008–4020.
- A. Mishra, M. Kumari, Swati, R. Kumar, K. Iqbal, I.S. Thakur, Persistent organic pollutants in the environment: risk assessment, hazards, and mitigation strategies, *Bioresour. Technol. Rep.*, 19 (2022) 101143, doi: 10.1016/j.biteb.2022.101143.
- H. Lu, Q. Li, W. Feng, Application progress of O₃/UV advanced oxidation technology in the treatment of organic pollutants in water, *Sustainability-Basel*, 14 (2022) 1556, doi: 10.3390/su14031556.
- A. Popena, M. Włodarczyk-Makula, Hazard from sediments contaminated with persistent organic pollutants (pops), *Desal. Water Treat.*, 117 (2018) 318–328.
- H. Karimi-Maleh, A. Ayati, R. Davoodi, B. Tanhaei, F. Karimi, S. Malekmohammadi, Y. Orooji, L. Fu, M. Sillanpää, Recent advances in using of chitosan-based adsorbents for removal of pharmaceutical contaminants: a review, *J. Cleaner Prod.*, 291 (2021) 125880, doi: 10.1016/j.jclepro.2021.125880.
- S.I. Sinar Mashuri, M.L. Ibrahim, M.F. Kasim, M.S. Mastuli, U. Rashid, A.H. Abdullah, A. Islam, N.A. Mijan, Y.H. Tan, N. Mansir, N.H. Mohd Kaus, T.-Y. Yun Hin, Photocatalysis for organic wastewater treatment: from the basis to current challenges for society, *Catalysts*, 10 (2020) 1260, doi: 10.3390/catal10111260.
- K. Li, M. Zhou, L. Liang, L. Jiang, W. Wang, Ultrahigh-surface-area activated carbon aerogels derived from glucose for high-performance organic pollutants adsorption, *J. Colloid Interface Sci.*, 546 (2019) 333–343.
- B. Qiu, Q. Shao, J. Shi, C. Yang, H. Chu, Application of biochar for the adsorption of organic pollutants from wastewater: modification strategies, mechanisms and challenges, *Sep. Purif. Technol.*, 300 (2022) 121925, doi: 10.1016/j.seppur.2022.121925.
- Y.-h. Li, F.-m. Chang, B. Huang, Y.-p. Song, H.-y. Zhao, K.-j. Wang, Activated carbon preparation from pyrolysis char of sewage sludge and its adsorption performance for organic compounds in sewage, *Fuel*, 266 (2020) 117053, doi: 10.1016/j.fuel.2020.117053.
- S. Liu, B. Huang, L. Chai, Y. Liu, G. Zeng, X. Wang, W. Zeng, M. Shang, J. Deng, Z. Zhou, Enhancement of As(V) adsorption from aqueous solution by a magnetic chitosan/biochar composite, *RSC Adv.*, 7 (2017) 10891–10900.
- V.K. Thakur, A.S. Singha, M.K. Thakur, Surface modification of natural polymers to impart low water absorbency, *Int. J. Polym. Anal. Charact.*, 17 (2012) 133–143.
- S.A. Ishak, M.F. Murshed, H. Md Akil, N. Ismail, S.Z. Md Rasib, A.A.S. Al-Gheethi, The application of modified natural polymers in toxicant dye compounds wastewater: a review, *Water*, 12 (2020) 2032, doi: 10.3390/w12072032.
- B. Tanhaei, A. Ayati, E. Iakovleva, M. Sillanpää, Efficient carbon interlayered magnetic chitosan adsorbent for anionic dye removal: synthesis, characterization and adsorption study, *Int. J. Biol. Macromol.*, 164 (2020) 3621–3631.
- H. Jiang, J. Liang, J.T. Grant, W. Su, T.J. Bunning, T.M. Cooper, W.W. Adams, Characterization of chitosan and rare-earth-metal-ion doped chitosan films, *Macromol. Chem. Phys.*, 198 (1997) 1561–1578.
- T. Boominathan, A. Sivaramakrishna, Recent advances in the synthesis, properties, and applications of modified chitosan derivatives: challenges and opportunities, *Top. Curr. Chem.*, 379 (2021) 19, doi: 10.1007/s41061-021-00331-z.
- A. Ayati, B. Tanhaei, M. Sillanpää, Lead(II)-ion removal by ethylenediaminetetraacetic acid ligand functionalized magnetic chitosan–aluminum oxide–iron oxide nanoadsorbents and microadsorbents: equilibrium, kinetics, and thermodynamics, *J. Appl. Polym. Sci.*, 134 (2017) 44360, doi: 10.1002/app.44360.
- W. Qiu, M. Vakili, G. Cagnetta, J. Huang, G. Yu, Effect of high energy ball milling on organic pollutant adsorption properties of chitosan, *Int. J. Biol. Macromol.*, 148 (2020) 543–549.
- S.A. Qamar, M. Ashiq, M. Jahangeer, A. Riasat, M. Bilal, Chitosan-based hybrid materials as adsorbents for textile dyes—a review, *Case Stud. Chem. Environ. Eng.*, 2 (2020) 100021, doi: 10.1016/j.cscee.2020.100021.
- N.A. Negm, H.H.H. Hefni, A.A.A. Abd-Elal, E.A. Badr, M.T.H. Abou Kana, Advancement on modification of chitosan biopolymer and its potential applications, *Int. J. Biol. Macromol.*, 152 (2020) 681–702.
- S. Abraham, D. Rajamanick, B. Srinivasan, Preparation, characterization and cross-linking of chitosan by microwave assisted synthesis, *Sci. Int.*, 6 (2018) 18–30.
- K.C. Gupta, F.H. Jabrail, Glutaraldehyde and glyoxal cross-linked chitosan microspheres for controlled delivery of centchroman, *Carbohydr. Res.*, 341 (2006) 744–756.
- C. Mao, S.A. Imtiaz, Y. Zhang, Competitive adsorption of Ag(I) and Cu(II) by tripolyphosphate cross-linked chitosan beads, *J. Appl. Polym. Sci.*, 132 (2015) 42717, doi: 10.1002/app.42717.
- M. Fernandes, I.C. Gonçalves, S. Nardecchia, I.F. Amaral, M.A. Barbosa, M.C. Martins, Modulation of stability and mucoadhesive properties of chitosan microspheres for therapeutic gastric application, *Int. J. Pharm.*, 454 (2013) 116–124.
- C. Li, J. Cui, F. Wang, W. Peng, Y. He, Adsorption removal of Congo Red by epichlorohydrin-modified cross-linked chitosan adsorbent, *Desal. Water Treat.*, 57 (2015) 14060–14066.
- T.Y.A. Essel, A. Koomson, M.-P. Seniagya, G.P. Cobbold, S.K. Kwofie, B.O. Asimeng, P.K. Arthur, G. Awandare, E.K. Tiburu, Chitosan composites synthesized using acetic acid and tetraethylorthosilicate respond differently to Methylene Blue adsorption, *Polymers*, 10 (2018) 466, doi: 10.3390/polym10050466.
- M. Yazdani-Pedram, J. Retuert, R. Quijada, Hydrogels based on modified chitosan, 1. Synthesis and swelling behavior of

- poly(acrylic acid) grafted chitosan, *Macromol. Chem. Phys.*, 201 (2000) 923–930.
- [27] H. Mittal, S.S. Ray, B.S. Kaith, J.K. Bhatia, Sukriti, J. Sharma, S.M. Alhassan, Recent progress in the structural modification of chitosan for applications in diversified biomedical fields, *Eur. Polym. J.*, 109 (2018) 402–434.
- [28] M.P. Pérez-Calixto, A. Ortega, L. Garcia-Uriostegui, G. Burillo, Synthesis and characterization of N-vinylcaprolactam/N,N-dimethylacrylamide grafted onto chitosan networks by gamma radiation, *Radiat. Phys. Chem.*, 119 (2016) 228–235.
- [29] D. Liu, J. Yuan, J. Li, G. Zhang, Preparation of chitosan poly(methacrylate) composites for adsorption of Bromocresol Green, *ACS Omega*, 4 (2019) 12680–12686.
- [30] V.R. Shaumbwa, D. Liu, B. Archer, J. Li, F. Su, Preparation and application of magnetic chitosan in environmental remediation and other fields: a review, *J. Appl. Polym. Sci.*, 138 (2021) 51241, doi: 10.1002/app.51241.
- [31] G. Crini, G. Torri, E. Lichtfouse, G.Z. Kyzas, L.D. Wilson, N. Morin-Crini, Dye removal by biosorption using cross-linked chitosan-based hydrogels, *Environ. Chem. Lett.*, 17 (2019) 1645–1666.
- [32] M.S. Chiou, H.Y. Li, Adsorption behavior of reactive dye in aqueous solution on chemical cross-linked chitosan beads, *Chemosphere*, 50 (2003) 1095–1105.
- [33] S. Chatterjee, T. Chatterjee, S.R. Lim, S.H. Woo, Adsorption of a cationic dye, Methylene Blue, on to chitosan hydrogel beads generated by anionic surfactant gelation, *Environ. Technol.*, 32 (2011) 1503–1514.
- [34] G. Crini, F. Gimbert, C. Robert, B. Martel, O. Adam, N. Morin-Crini, F. De Giorgi, P.-M. Badot, The removal of Basic Blue 3 from aqueous solutions by chitosan-based adsorbent: batch studies, *J. Hazard. Mater.*, 153 (2008) 96–106.
- [35] A.H. Jawad, A.S. Abdulhameed, A. Reghioia, Z.M. Yaseen, Zwitterion composite chitosan-epichlorohydrin/zeolite for adsorption of Methylene Blue and Reactive Red 120 dyes, *Int. J. Biol. Macromol.*, 163 (2020) 756–765.
- [36] F. Marrakchi, B.H. Hameed, E.H. Hummadi, Mesoporous biohybrid epichlorohydrin cross-linked chitosan/carbon-clay adsorbent for effective cationic and anionic dyes adsorption, *Int. J. Biol. Macromol.*, 163 (2020) 1079–1086.
- [37] P.M. Morais da Silva, N.G. Camparotto, K.T. Grego Lira, C.S. Franco Picone, P. Prediger, Adsorptive removal of basic dye onto sustainable chitosan beads: equilibrium, kinetics, stability, continuous-mode adsorption and mechanism, *Sustainable Chem. Pharm.*, 18 (2020) 100318, doi: 10.1016/j.scp.2020.100318.
- [38] Q. Jin, Y. Li, D. Yang, J. Cui, Chitosan-derived three-dimensional porous carbon for fast removal of Methylene Blue from wastewater, *RSC Adv.*, 8 (2018) 1255–1264.
- [39] A. Salama, R.E. Abou-Zeid, Ionic chitosan/silica nanocomposite as efficient adsorbent for organic dyes, *Int. J. Biol. Macromol.*, 188 (2021) 404–410.
- [40] A.S. Al-Wasidi, Y.G. Abouelreash, S. AlReshaidan, A.M. Naglah, Application of novel modified chitosan hydrogel composite for the efficient removal of Eriochrome Black T and Methylene Blue dyes from aqueous media, *J. Inorg. Organomet. Polym. Mater.*, 32 (2022) 1142–1158.
- [41] S. Yu, J. Cui, H. Jiang, C. Zhong, J. Meng, Facile fabrication of functional chitosan microspheres and study on their effective cationic/anionic dyes removal from aqueous solution, *Int. J. Biol. Macromol.*, 134 (2019) 830–837.
- [42] F. Mashkoor, A. Nasar, C. Jeong, Magnetized chitosan nanocomposite as an effective adsorbent for the removal of Methylene Blue and malachite green dyes, *Biomass Convers. Biorefin.*, (2022), doi: 10.1007/s13399-021-02282-3.
- [43] B. Xu, H. Zheng, Y. Wang, Y. An, K. Luo, C. Zhao, W. Xiang, Poly(2-acrylamido-2-methylpropane sulfonic acid) grafted magnetic chitosan microspheres: preparation, characterization and dye adsorption, *Int. J. Biol. Macromol.*, 112 (2018) 648–655.
- [44] C. Li, J. Cui, F. Wang, W. Peng, Y. He, Adsorption removal of Congo Red by epichlorohydrin-modified cross-linked chitosan adsorbent, *Desal. Water Treat.*, 57 (2015) 14060–14066.
- [45] Y. Lin, H. Wang, J. Gong, J. Yang, S. Hu, L. Mei, J. Huang, Preparation of modified chitosan microspheres and their anionic dye adsorption behaviors, *J. Chem. Eng. Chin. Univ.*, 31 (2017) 470–477 (In Chinese).
- [46] X. Tao, K. Li, H. Yan, H. Yang, A. Li, Simultaneous removal of acid green 25 and mercury ions from aqueous solutions using glutamine modified chitosan magnetic composite microspheres, *Environ. Pollut.*, 209 (2016) 21–29.
- [47] A. Sabarudin, A.D. Madjid, Preparation and kinetic studies of cross-linked chitosan beads using dual cross-linkers of tripolyphosphate and epichlorohydrin for adsorption of Methyl Orange, *Sci. World J.*, 2021 (2021) 1–11.
- [48] K. Li, P. Li, J. Cai, S. Xiao, H. Yang, A. Li, Efficient adsorption of both Methyl Orange and chromium from their aqueous mixtures using a quaternary ammonium salt modified chitosan magnetic composite adsorbent, *Chemosphere*, 154 (2016) 310–318.
- [49] M.A. Khapre, S. Pandey, R.M. Jugade, Glutaraldehyde-cross-linked chitosan-alginate composite for organic dyes removal from aqueous solutions, *Int. J. Biol. Macromol.*, 190 (2021) 862–875.
- [50] D.-M. Liu, C. Dong, J. Zhong, S. Ren, Y. Chen, T. Qiu, Facile preparation of chitosan modified magnetic kaolin by one-pot coprecipitation method for efficient removal of Methyl Orange, *Carbohydr. Polym.*, 245 (2020) 116572, doi: 10.1016/j.carbpol.2020.116572.
- [51] G. Muedas-Taípe, I.M. Maza Mejía, F.A. Santillan, C.J. Velásquez, Y.J.O. Asencios, Removal of azo dyes in aqueous solutions using magnetized and chemically modified chitosan beads, *Mater. Chem. Phys.*, 256 (2020) 123595, doi: 10.1016/j.matchemphys.2020.123595.
- [52] W.X. Jia, D.T. Lu, S.M. Shuang, J. Yang, C. Dong, Facile synthesis of chitosan modified Fe₃O₄ magnetic nanoparticles for azo dye Amido Black 10B adsorption, *J. Nano Res.*, 49 (2017) 149–162.
- [53] S. Chatterjee, T. Chatterjee, S.H. Woo, Influence of the polyethyleneimine grafting on the adsorption capacity of chitosan beads for Reactive Black 5 from aqueous solutions, *Chem. Eng. J.*, 166 (2011) 168–175.
- [54] E.M. Abd El-Monaem, A.S. Eltaweil, H.M. Elshishini, M. Hosny, M.M. Abou Alsoaud, N.F. Attia, G.M. El-Subruiti, A.M. Omer, Sustainable adsorptive removal of antibiotic residues by chitosan composites: an insight into current developments and future recommendations, *Arabian J. Chem.*, 15 (2022) 103743, doi: 10.1016/j.arabjc.2022.103743.
- [55] B. Bai, X. Xu, C. Li, J. Xing, H. Wang, Y. Suo, Magnetic Fe₃O₄@chitosan carbon microbeads: removal of doxycycline from aqueous solutions through a fixed bed via sequential adsorption and heterogeneous Fenton-like regeneration, *J. Nanomater.*, 2018 (2018) 1–14.
- [56] T. Ahamad, M. Naushad, T. Al-Shahrani, N. Al-Hokbany, S.M. Alshehri, Preparation of chitosan based magnetic nanocomposite for tetracycline adsorption: kinetic and thermodynamic studies, *Int. J. Biol. Macromol.*, 147 (2020) 258–267.
- [57] J. Ma, Y. Lei, M. Khan, F. Wang, Y. Chu, W. Lei, M. Xia, S. Zhu, Adsorption properties, kinetics & thermodynamics of tetracycline on carboxymethyl-chitosan reformed montmorillonite, *Int. J. Biol. Macromol.*, 124 (2019) 557–567.
- [58] M. Nazraz, Y. Yamini, H. Asiabi, Chitosan-based sorbent for efficient removal and extraction of ciprofloxacin and norfloxacin from aqueous solutions, *Microchim. Acta*, 186 (2019) 459, doi: 10.1007/s00604-019-3563-x.
- [59] M. Pooresmaeil, H. Namazi, Chitosan coated Fe₃O₄@Cd-MOF microspheres as an effective adsorbent for the removal of the amoxicillin from aqueous solution, *Int. J. Biol. Macromol.*, 191 (2021) 108–117.
- [60] S.T. Danaloğlu, Ş.S. Bayazit, Ö. Kerkez Kuyumcu, M.A. Salam, Efficient removal of antibiotics by a novel magnetic adsorbent: magnetic activated carbon/chitosan (MACC) nanocomposite, *J. Mol. Liq.*, 240 (2017) 589–596.
- [61] R. Vardhan Patel, A. Yadav, Photocatalytic MIL101(Fe)/ZnO chitosan composites for adsorptive removal of tetracycline

- antibiotics from the aqueous stream, *J. Mol. Struct.*, 1252 (2022) 132128, doi: 10.1016/j.molstruc.2021.132128.
- [62] S.T. Danahoglu, Ö. Kerkez Kuyumcu, M. Abdel Salam, Ş.S. Bayazit, Chitosan grafted $\text{SiO}_2\text{-Fe}_3\text{O}_4$ nanoparticles for removal of antibiotics from water, *Environ. Sci. Pollut. Res.*, 25 (2018) 36661–36670.
- [63] P. Yadav, A. Yadav, P.K. Labhassetwar, Sustainable adsorptive removal of antibiotics from aqueous streams using Fe_3O_4 -functionalized MIL101(Fe) chitosan composite beads, *Environ. Sci. Pollut. Res.*, 29 (2022) 37204–37217.
- [64] N. Zhuo, Y. Lan, W. Yang, Z. Yang, X. Li, X. Zhou, Y. Liu, J. Shen, X. Zhang, Adsorption of three selected pharmaceuticals and personal care products (PPCPs) onto MIL-101(Cr)/natural polymer composite beads, *Sep. Purif. Technol.*, 177 (2017) 272–280.
- [65] L. Fan, M. Li, Z. Lv, M. Sun, C. Luo, F. Lu, H. Qiu, Fabrication of magnetic chitosan nanoparticles grafted with β -cyclodextrin as effective adsorbents toward hydroquinol, *Colloids Surf., B*, 95 (2012) 42–49.
- [66] J. Heydaripour, M. Gazi, A.A. Oladipo, H.O. Gulcan, Porous magnetic resin-G-chitosan beads for adsorptive removal of phenolic compounds, *Int. J. Biol. Macromol.*, 123 (2019) 1125–1131.
- [67] J.M.N. dos Santos, C.R. Pereira, E.L. Foletto, G.L. Dotto, Alternative synthesis for ZnFe_2O_4 /chitosan magnetic particles to remove diclofenac from water by adsorption, *Int. J. Biol. Macromol.*, 131 (2019) 301–308.
- [68] W. You, H. Liu, J. Cao, Y. Shen, W. Chen, Removal of humic acid from water by magnetic chitosan-grafted polyacrylamide, *Environ. Sci.*, 39 (2018) 5532–5540 (in Chinese).
- [69] C. Dong, W. Chen, C. Liu, Y. Liu, H. Liu, Synthesis of magnetic chitosan nanoparticle and its adsorption property for humic acid from aqueous solution, *Colloids Surf., A*, 446 (2014) 179–189.
- [70] C. Dong, W. Chen, C. Liu, Preparation of novel magnetic chitosan nanoparticle and its application for removal of humic acid from aqueous solution, *Appl. Surf. Sci.*, 292 (2014) 1067–1076.
- [71] Z. Liu, S. Zhou, Removal of humic acid from aqueous solution using polyacrylamide/chitosan semi-IPN hydrogel, *Water Sci. Technol.*, 2017 (2018) 16–26.
- [72] S. Wang, E. Li, Y. Li, J. Li, Z. Du, F. Cheng, Enhanced removal of dissolved humic acid from water using eco-friendly phenylalanine-modified-chitosan Fe_3O_4 magnetic nanoparticles, *ChemistrySelect*, 5 (2020) 4285–4291.
- [73] D. Siswanta, F. Farida, D. Zunaim, N.H. Aprilita, Adsorption of HA (humic acid) using sulfuric acid-cross-linked chitosan/pectin polyelectrolyte complex film, *J. Phys. Conf. Ser.*, 1156 (2019) 012003.
- [74] S. Maghsoodloo, B. Noroozi, A.K. Haghi, G.A. Sorial, Consequence of chitosan treating on the adsorption of humic acid by granular activated carbon, *J. Hazard. Mater.*, 191 (2011) 380–387.
- [75] M.H. Dehghani, A. Zarei, A. Mesdaghinia, R. Nabizadeh, M. Alimohammadi, M. Afsharnia, G. McKay, Production and application of a treated bentonite–chitosan composite for the efficient removal of humic acid from aqueous solution, *Chem. Eng. Res. Des.*, 140 (2018) 102–115.
- [76] J. Cheng, S. Xie, S. Wang, Y. Xue, L. Jiang, L. Liu, Optimization of protein removal from soybean whey wastewater using chitosan ultrafiltration, *J. Food Process Eng.*, 40 (2016) e12370, doi: 10.1111/jfpe.12370.
- [77] C. Liu, J. Yu, J. You, Z. Wang, M. Zhang, L. Shi, X. Zhuang, Cellulose/chitosan composite sponge for efficient protein adsorption, *Ind. Eng. Chem. Res.*, 60 (2021) 9159–9166.
- [78] H. Ai, W. Wang, K. Du, Preparation of graphene/chitosan composite microspheres (G/CS microspheres) and its protein adsorption evaluation, *China Sci. Pap.*, 15 (2020) 1352–1358+1370 (in Chinese).
- [79] G.R. Mahdavinia, H. Etemadi, Surface modification of iron oxide nanoparticles with κ -carrageenan/carboxymethyl chitosan for effective adsorption of bovine serum albumin, *Arabian J. Chem.*, 12 (2019) 3692–3703.
- [80] U.-J. Kim, Y.R. Lee, T.H. Kang, J.W. Choi, S. Kimura, M. Wada, Protein adsorption of dialdehyde cellulose-cross-linked chitosan with high amino group contents, *Carbohydr. Polym.*, 163 (2017) 34–42.
- [81] N. Ye, Y. Xie, P. Shi, T. Gao, J. Ma, Synthesis of magnetite/graphene oxide/chitosan composite and its application for protein adsorption, *Mater. Sci. Eng., C*, 45 (2014) 8–14.
- [82] Z. Wang, T. Yue, Y. Yuan, R. Cai, C. Niu, C. Guo, Kinetics of adsorption of bovine serum albumin on magnetic carboxymethyl chitosan nanoparticles, *Int. J. Biol. Macromol.*, 58 (2013) 57–65.
- [83] M. Yildirim-Aksoy, B.H. Beck, Antimicrobial activity of chitosan and a chitosan oligomer against bacterial pathogens of warmwater fish, *J. Appl. Microbiol.*, 122 (2017) 1570–1578.
- [84] F. Xie, R. Ding, W. He, Z. Liu, S. Fu, J. Wu, L. Yang, S. Lin, Q. Wen, In vivo antitumor effect of endostatin-loaded chitosan nanoparticles combined with paclitaxel on Lewis lung carcinoma, *Drug Delivery*, 24 (2017) 1410–1418.
- [85] X. Liu, Y. Guan, D. Yang, Z. Li, K. Yao, Antibacterial action of chitosan and carboxymethylated chitosan, *J. Appl. Polym. Sci.*, 79 (2001) 1324–1335.
- [86] X. Li, X. Feng, S. Yang, G. Fu, T. Wang, Z. Su, Chitosan kills *Escherichia coli* through damage to be of cell membrane mechanism, *Carbohydr. Polym.*, 79 (2010) 493–499.
- [87] M. Hosseinejad, S.M. Jafari, Evaluation of different factors affecting antimicrobial properties of chitosan, *Int. J. Biol. Macromol.*, 85 (2016) 467–475.
- [88] L. Liu, D. Wu, T. Wang, Research progress in antibacterial activity of chitosan and development of antibacterial textile, *J. Text. Res.*, 31 (2010) 145–150 (in Chinese).
- [89] Z. Sun, C. Shi, X. Wang, Q. Fang, J. Huang, Synthesis, characterization, and antimicrobial activities of sulfonated chitosan, *Carbohydr. Polym.*, 155 (2017) 321–328.
- [90] Y. Diao, X. Yu, C. Zhang, Y. Jing, Quercetin-grafted chitosan prepared by free radical grafting: characterization and evaluation of antioxidant and antibacterial properties, *J. Food Sci. Technol.*, 57 (2020) 2259–2268.
- [91] N.A. Mohamed, M.W. Sabaa, A.H. El-Ghandour, M.M. Abdel-Aziz, O.F. Abdel-Gawad, Quaternized n-substituted carboxymethyl chitosan derivatives as antimicrobial agents, *Int. J. Biol. Macromol.*, 60 (2013) 156–164.
- [92] J. Wang, Z. Jiang, Synthesis, characterisation, antioxidant and antibacterial properties of p-hydroxybenzoic acid-grafted chitosan conjugates, *Int. J. Food Sci. Technol.*, 57 (2021) 1283–1290.
- [93] J. Cui, X. Ji, Y. Mi, Q. Miao, F. Dong, W. Tan, Z. Guo, Antimicrobial and antioxidant activities of N-2-hydroxypropyltrimethyl ammonium chitosan derivatives bearing amino acid Schiff bases, *Mar. Drugs*, 20 (2022) 86, doi: 10.3390/md20020086.
- [94] L. Min, M. Liu, C. Zhu, L. Liu, Z. Rao, L. Fan, Synthesis and in vitro antimicrobial and antioxidant activities of quaternary ammonium chitosan modified with nisin, *J. Biomater. Sci., Polym. Ed.*, 28 (2017) 2034–2052.
- [95] J. Wang, S. Zhuang, Removal of various pollutants from water and wastewater by modified chitosan adsorbents, *Crit. Rev. Env. Sci. Technol.*, 47 (2017) 2331–2386.