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Recent Advances in Chitosan-based Nanocomposite Membrane Materials for Water Treatment

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ABSTRACT

In recent years, research on chitosan (CS)-based nanocomposite membranes has made significant progress in the field of water treatment. This innovative membrane material incorporates a variety of excellent biological properties, including the biocompatibility and adsorption properties of the natural polymer chitosan (CS) and the introduction of nanotechnology. Furthermore, it enables the composite material to have excellent functional characteristics, such as higher water flux and selectivity. Furthermore, the enhancement of the structural and intrinsic properties of membrane materials will facilitate the attainment of further advancements in a multitude of performance characteristics, including stability, durability, and adsorption selectivity. Consequently, this field has become a promising area of research in water treatment technology, attracting extensive research and attention. However, the publication of a large number of related research reports in recent years, accompanied by numerous and complex performance optimization schemes and research ideas, has resulted in a paucity of articles that summarize these performance optimization strategies and research paths. Consequently, there are few meaningful references for subsequent research. In light of the aforementioned considerations, this paper will provide a comprehensive review of the most recent research advances in the field of water treatment, with a particular focus on the latest research strategies and frameworks for optimizing the performance of related materials. Furthermore, this paper will illustrate the innovative and beneficial applications of such materials from various vantage points, including their sources and preparation processes. It is anticipated that this paper will serve as a valuable source of inspiration for further research in this field.

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1. Introduction

1.1. Background and Significance of Water Treatment

Freshwater resources on Earth constitute only a mere fraction of the total water (only about 2.5 percent), and 87 per cent of this is glacial and snow and ice water, which is inaccessible to humans [1]. The phenomenon of global warming has led to an increase in the occurrence of extreme weather events, which has in turn exacerbated the global water scarcity crisis [2]. Over the past decades, freshwater scarcity has emerged as a significant global concern, driven by rapid population growth and industrialization expansion. This has led to more than 2 billion people residing in water-scarce countries, as evidenced by data from [3]. It is therefore of paramount importance to enhance the efficacy of existing water utilization, as well as to devise additional water access strategies, in order to cope with the mounting water scarcity. Furthermore, the problem is predicted to worsen in the coming years due to a number of factors, including climate change and environmental pollution. The traditional methods of water use, such as groundwater extraction and rainwater harvesting, are no longer sufficient to meet the growing demand. In particular, in arid and semi-arid regions and island countries, water treatment technology has begun to emerge as an effective solution and is being widely used [4]. As technology continues to advance and costs decrease, water treatment has become an important means of increasing the supply of freshwater.

The application of water treatment technology is not only capable of resolving the issue of global freshwater scarcity, but also of enhancing the security of water supply, promoting the socio-economic development of coastal areas, improving the living conditions of the population, promoting technological innovation and industrial upgrading of related industries, and safeguarding national security. Furthermore, water treatment technology plays a pivotal role in addressing challenges such as the threat to water security posed by global climate change [5] and the problems caused by sea level rise.

The available evidence indicates that the global capacity for water treatment is increasing at a consistent rate every year and the total global capacity for water treatment is estimated to be now close to 100 million m^3/day [6]. Nevertheless, it is notable that nearly 70% of freshwater desalination is currently employed for agricultural irrigation purposes, with approximately 21% being utilized for industrial manufacturing and only 9% being used for drinking water [7]. Currently, traditional water treatment methods, such as distillation and electrodialysis, are characterized by high energy consumption, complex operation and application limitations, which limit the application of traditional water treatment technologies to meet the growing demand for water. Consequently, there is a pressing necessity for the development of novel water treatment technologies that can be deployed on a large scale, are energy-efficient and environmentally benign, and exhibit enhanced treatment efficacies. Currently, several countries have initiated research and development of water treatment technologies. While some progress has been made, these countries still face various challenges. Furthermore, China is also engaged in this field. The desalination of seawater has emerged as a significant concern for countries around the globe.

1.2. Overview of Current Water Treatment Technologies

The current water treatment technologies have been developed to a considerable degree of maturity and diversification. Among these, the more mature water treatment technologies that can be applied on a large scale are mainly thermal and membrane methods [8]. The former process involves the conversion of brine into vapor and subsequent condensation of the vapor into purified fresh water. Among the most popular thermal water treatment technologies are multi-stage flash evaporation (MSF), multi-effect distillation (MED), electrodialysis (ED), and thermal vapor compression (TVC) [8]. The latter employs pressurization to facilitate the passage of brine through a semi-permeable membrane, thereby enabling the selective separation of salt from water. The most common membrane-based water treatment technologies, such as reverse osmosis (RO) and nanofiltration (NF), are representative of this approach. Each of these technologies has its own advantages in different application scenarios. The specific choice of which water treatment technology is the most economically viable must take into account a number of factors, such as local seawater quality, energy costs, usage and demand. However, regardless of whether the technology in question is thermal or membrane-based, both types of technology require a significant input of energy. Nevertheless, upon consideration of several factors, membrane water treatment technology is still regarded as the most prevalent technology in the market today, due to its low operational cost and relatively low energy demand [9]. In particular, RO membranes are much less energy consuming (SEC < 3.1kWh/m^3) compared to other technologies [10, 11]. Since the development of the first asymmetric reverse osmosis (RO) membranes in 1960, the commercial value of membrane applications for large-scale water treatment as well as a variety of other industrial processes has been widely recognized around the world, driving the research and advancement of membrane materials (Fig. **1**). Thin film composite (TFC) membranes are the most well-known and widely used membrane type in water treatment. Research indicates that a significant amount of work has been conducted to fabricate high-performance TFC membranes suitable for use in reverse osmosis (RO) or nanofiltration (NF) technologies. It is evident that any form of membrane water treatment technology necessitates the utilization of core water treatment membrane materials that are capable of achieving high performance and stability in a multitude of aspects. Currently, the market is dominated by a number of traditional polymeric membrane materials, including polyamide (PA), polyimide (PI), polyether sulfone (PES), polyacrylonitrile (PAN), polyvinylidene fluoride (PVDF) and poly sulfone (PSF) [12].

The water treatment industry is currently experiencing a period of significant growth on a global scale. An increasing number of regions and countries are investing in research and development in the field of water treatment, and a growing number of water treatment projects are being constructed in order to meet the rising demand for this service. The report indicates that approximately 150 countries or regions worldwide have adopted water treatment technology. During the period between 2016 and 2019, the number of water treatment plants and the daily water production increased by 12.4% and 41.2%, respectively [13]. This evidence demonstrates the accelerated development of the technology. Globally, the Middle East is home to the largest water treatment capacity, with a 49.1% market share. North America and South America follow with 16.2% and 13.3% market shares, respectively. In total, approximately 90 million m^3 of water is desalinated on a daily basis [14].

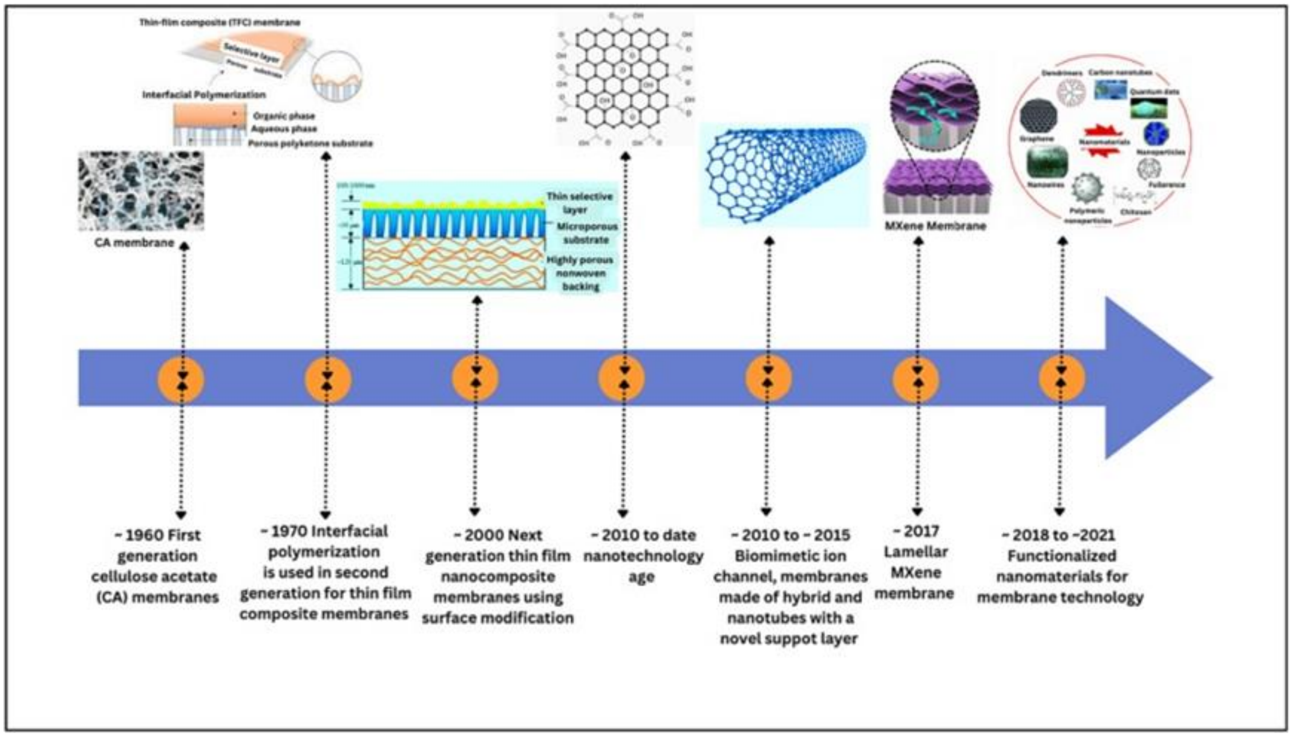

Figure 1: Trends and advances in membrane materials since 1960 [9].

1.3. The Potential of Nanomaterials and Chitosan in the Field of Water Treatment

Nanotechnology has a key role to play in solving the problem of water scarcity, and its great potential in water treatment has been demonstrated in research and has become one of the most important water treatment tools of the 21st century [15].

The successful discovery and fabrication of nano-channels has enabled the utilization of their cavities for the selective transport of small molecules at a sub-nanometer scale, a process facilitated by nanotechnology. The development of nanotechnology will facilitate the precise design of next-generation novel membrane materials at the molecular scale, which is expected to result in a paradigm shift in the water transport mechanism from the traditional solution diffusion to the molecular sieving effect. The rapid development of nanomaterials and nanotechnology has led to the emergence of a novel direction of research in water treatment technology as well as in the development of membrane materials. In addition to their small pore size, small diameter, resistance to corrosion and ageing characteristics, nanomaterials also possess good thermal, mechanical and electrical properties. Furthermore, their unique size exclusion phenomenon enables them to effectively separate water molecules, thereby increasing the value of their application in water filtration, particle separation and desalination [16]. Over the past two decades, the field of nanotechnology has witnessed a remarkable expansion, with a plethora of novel nanomaterials emerging in rapid succession. These materials have been subjected to a multitude of experimental and computational studies, which have corroborated their remarkable ability to facilitate rapid water transport and exhibit highly selective properties. The currently commonly used nanomaterials, which include traditional metal nanomaterials and metal oxide nanoparticles, nano-clays (montmorillonite and eclogite nanotubes), carbon nanotubes, graphene, and some others such as the emerging materials MOFs and POFs materials, have the ability to adsorb impurities, separate salts, and to a lesser extent, certain microorganisms [9]. Rambabu *et al.* employed date pulp waste (DPW) as a biological reducing agent and produced zinc oxide nanoparticles (DP-ZnO-NPs) using a green preparation technique. The authors then investigated the nanoparticles' effective dye degradation and antimicrobial properties in wastewater (Fig. **2**) [17].

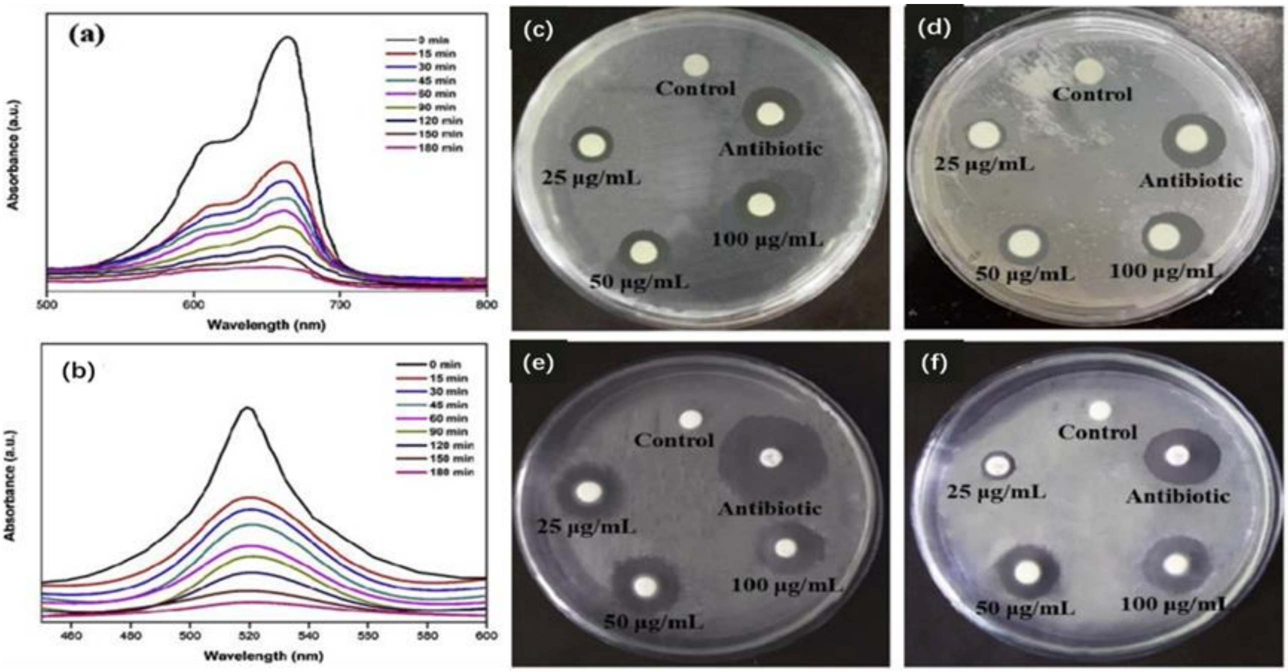

Figure 2: Photocatalytic dye degradation studies by DP-ZnO-NPs – (**a**) Absorption spectrum of MB dye samples; (**b**) Absorption spectrum of EY dye samples; Antibacterial activity of DP-ZnO-NPs – (**c**) *Streptococcus pyogenes*; (**d**) *Staphylococcus aureus*; (**e**) *Pseudomonas aeruginosa*, and (**f**) *Proteus mirabilis* [17].

In recent years, the doping of nanoparticles into membranes has emerged as a new research area of significant interest. Nanotechnology also plays a crucial role in improving the overall performance of membranes. The use of nanomaterials increases water permeability, mechanical strength, and effectively reduces membrane fouling [18]. The current cost of mass production of nanomaterials remains high, which significantly constrains their deployment in large-scale applications [19]. Additionally, their inherent hydrophobicity precludes their direct utilization in membranes, necessitating modification treatments. It has been demonstrated by existing studies that the growth and dispersion of nanomaterials in polymer solutions during membrane synthesis can significantly enhance their hydrophilicity and mass transfer properties. This provides new possibilities for combining polymers with nanomaterials to prepare novel membranes [19]. Nevertheless, there are certain obstacles to the successful incorporation of nanomaterials into membranes. For instance, the aggregation, high loss and poor stability of nanomaterials in membranes must be meticulously considered prior to preparation.

Biopolymers possess several advantageous properties, including high availability, biocompatibility and biodegradability. Consequently, they are frequently employed in a multitude of technological fields. Furthermore, they can be converted into various chemically or enzymatically modified derivatives for specific end uses, which represents an additional outstanding advantage [20, 21]. Among the plethora of biopolymers, chitosan stands out due to its exceptional antimicrobial properties, biocompatibility, biodegradability, and remarkable gelation properties [22]. Chitosan is the sole alkaline polysaccharide in nature produced by deacetylation of chitin. It is a significant biopolymer employed in pharmaceutical, chemical, and water treatment applications due to its favorable biocompatibility, bioactivity, non-toxicity, biodegradability, and hydrophilicity [23]. Chitin, also known as β-(1,4)-2-acetamido-2-deoxy-d-glucose, is a polysaccharide that is widely found in the shells of crustaceans, such as shrimps and insects, as well as in the cell walls of fungi and algae. Chitin, chitosan and cellulose share similar chemical structures and are polymers of six-carbon sugars with molecular weights exceeding one million. The origin and chemical structure of chitin and chitosan are illustrated in Fig. (**3**). The chain of the CS molecule exhibits a double helical structure with a helical pitch of 0.515 nm, comprising six sugar residues that form a helical plane [24]. The amino, hydroxyl and acetylamino groups on the chain are involved in the formation of intramolecular and intermolecular hydrogen bonding, which gives rise to a secondary structure. Furthermore, CS molecules possess a multitude of hydrogen bonds and are highly susceptible to the formation of crystalline regions, which results in the development of highly crystalline CS, thereby conferring excellent physical-mechanical properties, such as adsorption, film-forming, and fiber-forming [25].

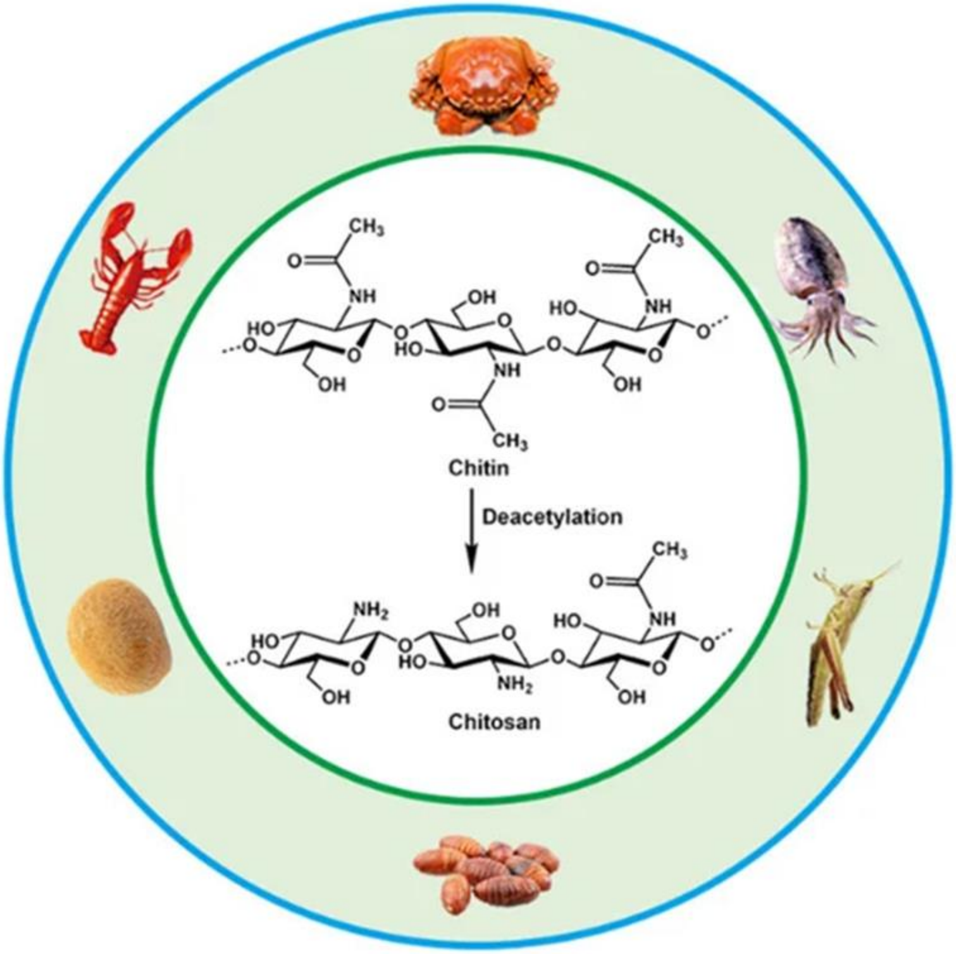

Figure 3: Origin and chemical structure of chitin and chitosan [23].

Chitosan is a polysaccharide that contains numerous active hydroxyl and amino groups, which can be readily modified through chemical means to enhance its physicochemical properties and biological activities. Furthermore, the hydroxyl and amino groups are hydrophilic, which enables the adsorption and diffusion of small molecules in CS-based membranes [26], rendering it an optimal functional material. Furthermore, chitosan is regarded as a promising material for water treatment membranes due to its facile modification, biocompatibility, non-toxicity, high permeability and selectivity, efficient flocculation and sedimentation, and excellent film-forming ability [27]. CS has been successfully applied to the preparation of membranes, including microfiltration (MF), ultrafiltration (UF), NF, forward osmosis (FO), and reverse osmosis (RO) membranes, by a variety of methods, including coating, cross-linking, blending, layer-by-layer self-assembly, and phase transformation [28].

1.4. Performance Advantages of Chitosan-based Nanocomposite Membranes

Biopolymer nanocomposites, which combine biopolymers with nanofillers, have emerged as a promising candidate for water treatment applications [29]. This paper is concerned with the combination of the biopolymer chitosan with nanomaterials. It is anticipated that the resulting chitosan-based nanocomposite membranes will integrate the benefits of the biopolymer chitosan with those of nanofillers, thereby enhancing the overall performance and water treatment efficiency of the composite membranes.

As previously stated, chitosan possesses a number of advantages in the field of water treatment, both in isolation and as part of a wider water treatment process. Nevertheless, the practical application of chitosan in the field of membrane technology is often constrained by a number of factors. For instance, the adsorption capacity of pure chitosan membranes for heavy metal ions and organic dyes remains relatively low, and selectivity is poor [30]. Furthermore, the amino groups ($-NH_2$) of pure chitosan membranes can be readily protonated into amine groups ($-NH_3^+$), which results in dissolution and loss of chitosan in acidic media, thereby hindering its regeneration. This further limits its applicability [31]. Chitosan is distinguished by its reticulated porous structure, large specific surface area, and abundance of reactive groups, including amino and hydroxyl groups. These characteristics enable the formation of stable chelates with filler materials in solution, creating new avenues for enhancing its performance and expanding its applications. Nanomaterials possess unique structures that enable them to form superior composite films with polymers. Furthermore, nanomaterials exhibit excellent dispersion in polymer matrices. This dispersion can be employed to reduce the hydrophobicity of carbon nanotubes, rendering them more readily utilized as membranes. This approach may also prove an effective solution to the challenges associated with uneven dispersion of nanomaterials. One of the most successful methods of dispersing nanomaterials in polymers is the sonication method, as it is relatively straightforward to filter the resulting dispersion to produce membranes. The modification of nanomaterials with polymeric materials, such as chitosan, resulted in a notable enhancement of the properties of the modified membranes. Furthermore, the interaction between CS and nanomaterials can also enhance the membrane properties. For instance, in GO/CS membranes, the carboxyl group in GO can be ionized, and the amino group in CS can be protonated, thereby enabling the formation of a strong electrostatic interaction between them. Furthermore, a robust hydrogen bonding network will be established between all the polar functional groups of CS and GO, which may contribute to the enhanced thermal, physical, and chemical stability of CS membranes [32]. In recent years, a variety of techniques have been employed to fabricate nanocomposites, including solution casting, *in situ* polymerization, and electrostatic spinning, which allows for the production of materials with well-controlled structures and properties [33].

1.5. Purpose of the Synthesis

The aim is to provide a synopsis of the current state of research on chitosan-based nanocomposite membrane materials in the field of water treatment. It covers a range of topics, including the preparation technology, performance optimization, and application progress of these materials. It aims to provide valuable insights and inspiration for researchers and practitioners in this field, with the ultimate goal of fostering further development and innovation in this area.

2. Preparation of Chitosan-based Nanocomposite Film

2.1. Preparation and Characterization of Nanomaterials

2.1.1. Preparation of Nanomaterials

Nanomaterials are typically categorized into three main types: organic, inorganic, and hybrid. Organic nanomaterials, exemplified by CNTs and graphene, are distinguished by their high selectivity, low contamination, light weight and flexibility, biocompatibility and low cost [34]. In contrast, inorganic nanomaterials, such as zero-valent metal nanoparticles and metal oxide nanoparticles, have a high surface area to volume ratio, high stability to high pressure and high temperature, better durability and high chemical resistance [35]. However, the production of inorganic nanomaterials is more costly than that of organic nanomaterials, and some of them may also be toxic [36]. Borrego *et al.* found that some inorganic nanomaterials, such as silver nanoparticles, with their high toxicity, can act as antimicrobials against viruses, bacteria, and fungi in water [37].

Nanofabrication technologies are divided into two main categories: top-down and bottom-up. The former is applied to microelectronics and the preparation of nanodevices, and the key technologies include photolithography, electron-beam etching, etc., which grinds, ablates, or etches the material from a larger size through traditional microfabrication methods until it produces nano-sized particles. The latter is widely used in the fabrication of nanoparticles, nanofilms, etc. Furthermore, the key technologies include chemical vapor deposition (CVD), self-assembly (MSA), and so forth, where complex structures are constructed from the molecular or atomic level through chemical reactions and self-assembly. The bottom-up approach is the most prevalent in commercial production, offering a cost-effective alternative to the top-down approach.

The preparation of nanomaterials is dependent on the specific application and desired properties. Consequently, different preparation methods result in nanomaterials with varying morphologies, sizes, and other physical properties and chemical compositions, which subsequently influence the final water treatment process [38]. employed a phase transition method to regulate the pore size and distribution within a polymer matrix through the application of temperature and pressure [38]. This method can be utilized to generate nanoporous membranes, composite membranes, and nanofibers. Carbon nanotubes, graphene and metal-organic framework (MOF) nanoparticles all have high water permeability and high desalination properties, rendering them more suitable for forming surface coatings on membrane surfaces by dip-coating, spin-coating, or electrostatic spinning [39, 40]. Liyanage *et al.* found that electrostatic spinning is a method that uses a high-voltage electric field to either pull a polymer solution or to melt through a small nozzle in order to produce fine fibers [41]. This method allows for the precise control of the diameter and alignment of the fibers, thus facilitating the production of a more uniform coating. Furthermore, solvothermal synthesis, hydrothermal synthesis, CVD and sol-gel are effective methods for the preparation of nanomaterials, as evidenced by the ability to prepare MOFs nanomaterials in large quantities using solvothermal synthesis.

However, from the perspective of being able to be applied commercially, the choice of a method that is cost-effective, scalable, versatile, and does not compromise the performance of the water treatment will be prioritized. At present, both sol-gel and chemical vapor deposition (CVD) methods appear to be viable options, both of which are commercially viable, scalable and highly cost-effective [38]. The sol-gel synthesis method allows for the simple preparation of a diverse range of metal oxide, ceramic and silica nanoparticles, which can be modified to suit the requirements of different environments [42]. CVD allows for the efficient deposition of stabilized metal, metal oxide and ceramic nanomaterials on the surface of aqueous membranes, resulting in the formation of highly purified, free-standing monolayers, multilayers, composites, or coatings with a specific particle size structure. This gives the membrane surface an excellent surface quality, as well as excellent dimensional stability of the membrane surface and greatly increasing the industrial scalability of the membrane [43]. Furthermore, the CVD method is considerably more straightforward to operate and allows for precise control of the thickness, composition and crystal structure of the deposited material, even at high temperatures. This greatly increases the commercial value of the process.

2.1.2. Characterization of Nanomaterials

The study of the properties of nanomaterials primarily focuses on the pore size, surface chemistry, mechanical strength, and biodegradability. Pore size and surface chemistry are key factors in determining the ability of nanomaterials to selectively remove salt ions during water treatment. This is a fundamental property of nanomaterials. The mechanical strength of nanomaterials affects the operational stability and durability of water treatment membranes. Finally, biodegradability represents a significant advantage for nanomaterials in reducing environmental pollution and promoting sustainable development [38]. The principal techniques employed include dynamic light scattering (DLS), zeta potential, scanning electron microscopy (SEM), transmission electron microscopy (TEM) and atomic force microscopy (AFM) [44].

2.2. Extraction and Modification of Chitosan

2.2.1. Extraction

Chitin is mainly extracted by two methods: chemical and biological. At present, the chemical extraction method has already achieved large-scale commercial application, but the large-scale application of the biological method needs to be considered according to a number of factors, such as the specific market situation and cost-effectiveness. The main source of chitin and chitosan is the shells of crustaceans, mainly crabs and shrimps. They are also found in the cell walls of certain fungi and insects. The chemical process consists of the following steps (e.g. Fig. **4**): deproteinization, demineralization and discoloration. Deproteinization is most commonly carried out using NaOH to break the chemical bonds between proteins and chitin, to partially deacetylate chitin and to reduce the molecular weight by hydrolysis. The next step is desalination, a process that removes minerals by breaking down calcium carbonate into calcium salts through treatment with hydrochloric acid [45]. Discoloration is an additional step to remove pigments such as β-carotene and astaxanthin from the extracted source to obtain a colorless product, and the process typically involves organic or inorganic solvents such as sodium hypochlorite, hydrogen peroxide and acetone [46]. While chemical methods are efficient, they can have some environmental impacts during the process.

Compared to chemical extraction methods, which use some chemical reagents and inevitably have some harmful effects on the environment and other disadvantages, biological methods choose to use enzymes and microorganisms to extract chitin, which is a more environmentally friendly process and does not change the structure of chitin, and has received more attention nowadays [47]. The extraction process involves both enzymatic deproteinization and fermentation using microorganisms [48].

Enzymatic deproteinization involves the use of proteases to remove proteins during the extraction process. The proteases commonly used are pepsin, trypsin, papain, alkaline enzyme, pancreatic enzyme [49] , the sources of which are mainly plant, animal and microbial. There are two types of microbial fermentation: lactic and non-lactic. In lactic acid fermentation, lactic acid strains are used to produce lactic acid by modifying glucose and then lowering the pH to prevent the growth of spoilage microorganisms [46]. The lactic acid is then reacted with calcium carbonate to form a calcium lactate precipitate, which is recovered and washed with water. While non-lactic fermentation uses some fungi and bacteria such as *Aspergillus* spp., *Bacillus* spp. and *Pseudomonas* spp., the different characteristics of the strains need to be considered to improve the efficiency of deproteinization and demineralization [50].

Chitosan is obtained by deacetylation of chitin using alkali or acid, and in scientific research chitin is often converted to chitosan by chemical or enzymatic methods [51]. As the glycosidic bonds of chitin are sensitive to acids, deacetylation is more commonly carried out with bases in chemical methods [52]. Deacetylation can be specifically divided into homogeneous and non-homogeneous methods according to the actual operation. The homogeneous method is used to obtain soluble chitosan, which is often prepared by dispersing chitin in concentrated NaOH at about 25°C for about 3 hours. Alkaline chitosan is then suspended in crushed ice at 0°C and the resulting product is deacetylated by up to 48-55%; the non-homogeneous method involves adding chitosan with hot concentrated NaOH for a few hours, resulting in insoluble chitosan which is tested for deacetylation by up to 85-99% [46]. Enzymatic deacetylation is principally a process of hydrolysis involving the

N-acetylamino bond in chitin, catalyzed by chitin deacetylase, which ultimately gives rise to the formation of chitosan. However, as naturally occurring chitin is crystalline and insoluble, enzymatic hydrolysis of this chitin is less effective. For this reason, crystalline chitin is subjected to certain pre-treatments such as grinding, heating and sonication [46].

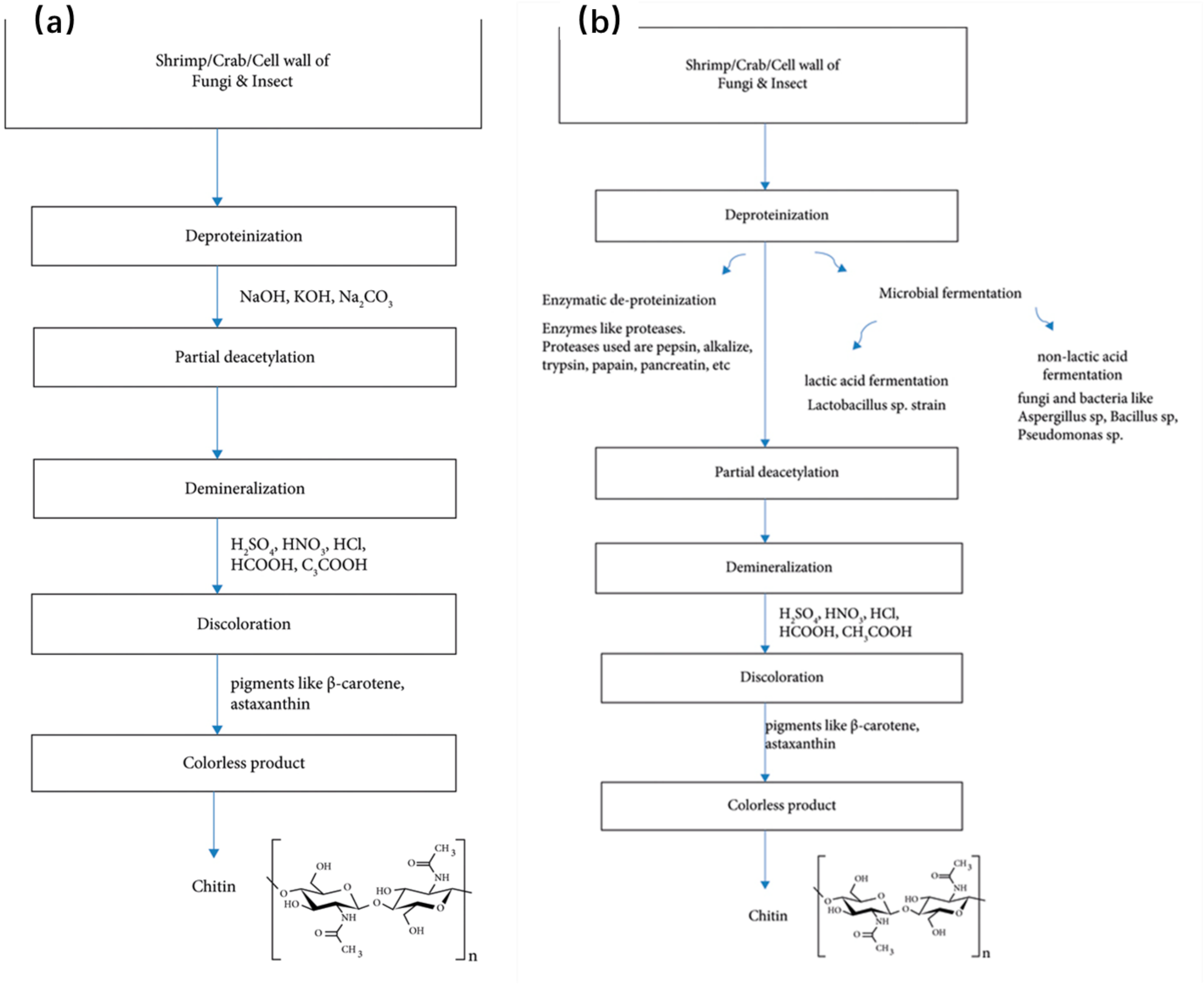

Figure 4: Schematic diagram of (a)chitin chemistry and (b)bio-extraction [46].

2.2.2. Modification

Although chitosan by itself has certain advantages in water treatment applications, it is still unable to meet the requirements in various application environments. For instance, chitosan exhibits low heat resistance, acid solubility, porosity, and mechanical strength, among other characteristics. In order to overcome these limitations, chitosan must be modified [53]. At present, physical, chemical and biological modification methods have been used to improve the selectivity, chemical stability, biological activity and other properties of chitosan by changing the nature and structure of chitosan and expecting to obtain more special effects. Such modifications are conducive to improving the overall application value of chitosan and broadening its application scope in various fields. Their advantages and disadvantages are listed in Table **1**, and some of the commonly used chemical modification methods are listed below.

Chitosan contains a large number of amino (-NH_2) and hydroxyl (-OH) groups, which can be easily chemically modified to improve its physical and chemical properties. If the regioselectivity of chitosan functional groups can be fully exploited in chemical modification, it can help in precise and well-controlled structural modification of chitosan, making it possible to synthesize chitosan derivatives with well-defined structures [54]. In addition, chemical modification of chitosan should not compromise its sustainability, but should also maintain its biodegradability, non-toxicity and antimicrobial properties [55].

Table 1: Advantages and disadvantages of chitosan modification methods.

Modified Methods	Advantages	Disadvantages
Physical methods	Ease of operation; create various application modes; affect physical properties (e.g. specific surface area and pore structure), etc.	Could not affect the chemical properties of chitosan (e.g. pH sensitivity)
Chemical modification	Introduce various functional groups; alter physicochemical properties; easy to scale up	Production of by-products; consumption of chemicals;
Biological modification	Mild reaction condition, high selectivity, low environmental pollution, and benign product safety	Low grafting/hydrolysis efficiency; long reaction time; high costs of enzymes preparations

The most commonly used methods for chemical modification of chitosan are N-substitution ($-NH_2$), O-substitution (-OH) and N, O-substitution, and it is often necessary to protect and deprotect the amino group during the modification process because the reactivity of the amino group ($-NH_2$) is higher than that of the hydroxyl group (-OH). It is noteworthy that chemical modification of chitosan is usually dominated by N-substitution because the $2-NH_2$ group has higher reactivity and is more likely to acquire new structures and bioactivities than the 3-OH and 6-OH groups. However, N-substitution inevitably interferes with the amino ($-NH_2$) activity, thus affecting its antimicrobial activity [56]. N-substitution can be divided into N-substitution with protector and N-substitution without protector. The synthesis of homo-N-quaternized chitosan derivatives by N-substitution with protective agents, including the protection of -OH groups by chemo-selective methods, is a topic of current interest [57], whereas N-substitution without protector involves the conversion of the amino group to quaternary ammonium salts by chemical reaction with quaternary phosphine or quaternary ammonium compounds to produce a range of derivatives with improved water solubility and biological properties, such as the preparation of N,N,N-trimethyl-chitosan chloride (TMC) [57]. N, O-substitution is commonly used to impart amphiphilic character to chitosan and also to improve the hydrophobicity and hydrophilicity of chitosan, which is mainly carried out in two ways (C6-hydroxyl oxidation and C2-amino substitution), converting the insoluble chitosan into the soluble one [54]. For example, Huo *et al*. developed thioglycolic acid modified N-octyl-O, N'-glycol chitosan with amphiphilic properties [58].

In addition, cross-linking modification is also an important approach; cross-linkers have different forms of bifunctionality, such as straight, branched and cyclic chains, which can generally be achieved either chemically (use of cross-linking agents; cross-linking corresponds to the creation of covalent bonds between linear chains) or physically (creation of non-covalent bonds between polymer chains by thermal curing, electron beam or ultraviolet irradiation processes) [59]. Chitosan itself is a linear molecule and cross-linking reactions can create new chemical bonds between the chains of chitosan molecules and produce a strong three-dimensional network that can improve the solubility, structural or thermal stability and mechanical properties of chitosan [54]. The compatibility between the cross-linker and chitosan must be considered prior to cross-linking modification in order to produce appropriate interactions. In general, if the molecular weight of the chitosan is low (usually less than 1 × 104 g/mol) then its molecular structure can be crosslinked and only after crosslinking can suitable mechanical, structural and thermal properties be achieved [54]. In addition, crosslinking agents need to be used at specific temperatures (between 40 and 150°C), and some crosslinking agents themselves have multifunctional or dual reactivity, self-crosslinking and high crosslinking density yields, which need to be taken into account before use [54].

In summary, many derivatives can be obtained by N-substitution, O-substitution and N, O-substitution reactions, which improve the properties of chitosan such as water solubility, biocompatibility, biodegradability and antimicrobial activity. In addition, the cross-linking reaction of chitosan significantly improves the physicochemical properties of chitosan, such as its mechanical and thermal properties, but there are still some shortcomings. In future research, several modification methods can be combined to overcome the shortcomings of a single modification method of chitosan and improve the overall performance of chitosan.

2.3. Preparation of Chitosan-based Nanocomposite Films

The successful preparation of chitosan-based nanocomposites requires careful selection of monomers, fillers and other composites, as well as the application of different synthesis techniques. This highlights the importance of the design and synthesis process in the production [60]. Depending on the structure and properties of the nanocomposite film, different techniques such as solution casting, *in situ* polymerization, melt blending and electrostatic spinning can be used [61]. Specific preparation methods also need to be selected and optimized in detail depending on the properties of the desired materials and applications.

Solution casting: chitosan is dissolved, then the nanofillers are dispersed in a polymer solution, and finally the mixture is cast onto a mildew or substrate and dried to produce a solid nanocomposite film material (Fig. **5a**) [62], with the advantage that the dispersion of nanofillers and the overall composition of the nanocomposite material can be easily controlled in a specific way. In addition, the mixture of chitosan and nanomaterials is uniformly sprayed onto the substrate using spraying techniques, and uniform and better performing composite membranes can also be obtained by, for example, drying or evaporation.

In situ polymerization: This method uses a chemical reaction in which chitosan is first synthesized or partially polymerized in the presence of nanofillers, as shown in (Fig. **5b**). The nanofiller is the nucleation site for the polymerization reaction and the chitosan surrounds the nanomaterials to eventually form a nanocomposite structure [63]. The advantage of this method is that there is a good interfacial bond between the nanofiller and the polymer matrix, which can effectively solve the problems of poor mechanical strength, low stability and poor dispersion of the composite film.

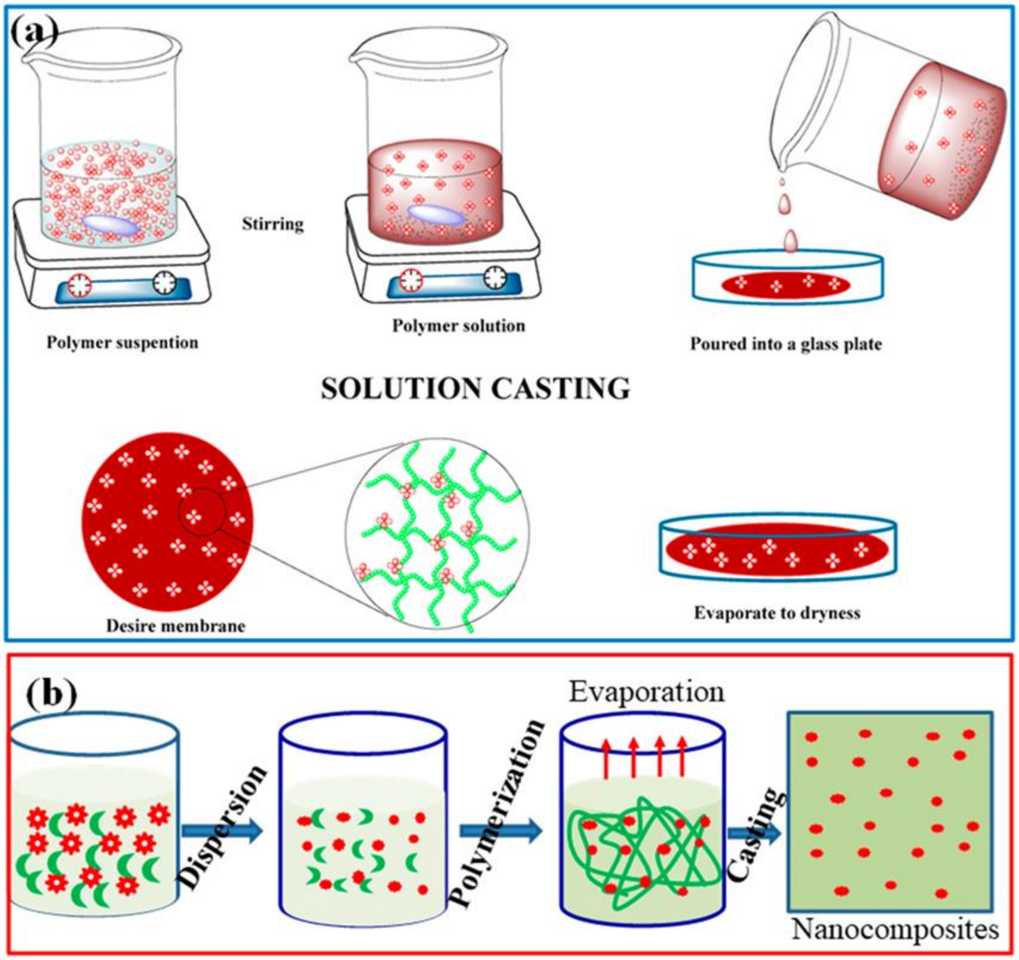

Figure 5: Schematic diagram of polymer nanocomposites synthesis process (**a**) Solution casting [62]. (**b**) *In situ* polymerization [63].

Melt blending: This method is relatively simple and scalable for large-scale production of biopolymer nanocomposites. The biopolymer chitosan is first melted and nanofillers are added, then mixed and cured to obtain homogeneous nanocomposites (Fig. **6a**) [64].

Electrostatic spinning: Electrostatic spinning is often used to produce nanofiber-based nanocomposites, with the advantage of being able to precisely control the diameter and distribution of the nanofibers to tailor the properties for different applications. The process involves electrostatic spinning of a polymer solution containing nanofillers to form ultrafine fibers, then forming the nanofibers into high surface regional macropore structures, and finally forming the spun fibers into different water treatment membranes. The process is divided into mono electrostatic spinning and coaxial electrostatic spinning (Fig. **6b**) [65].

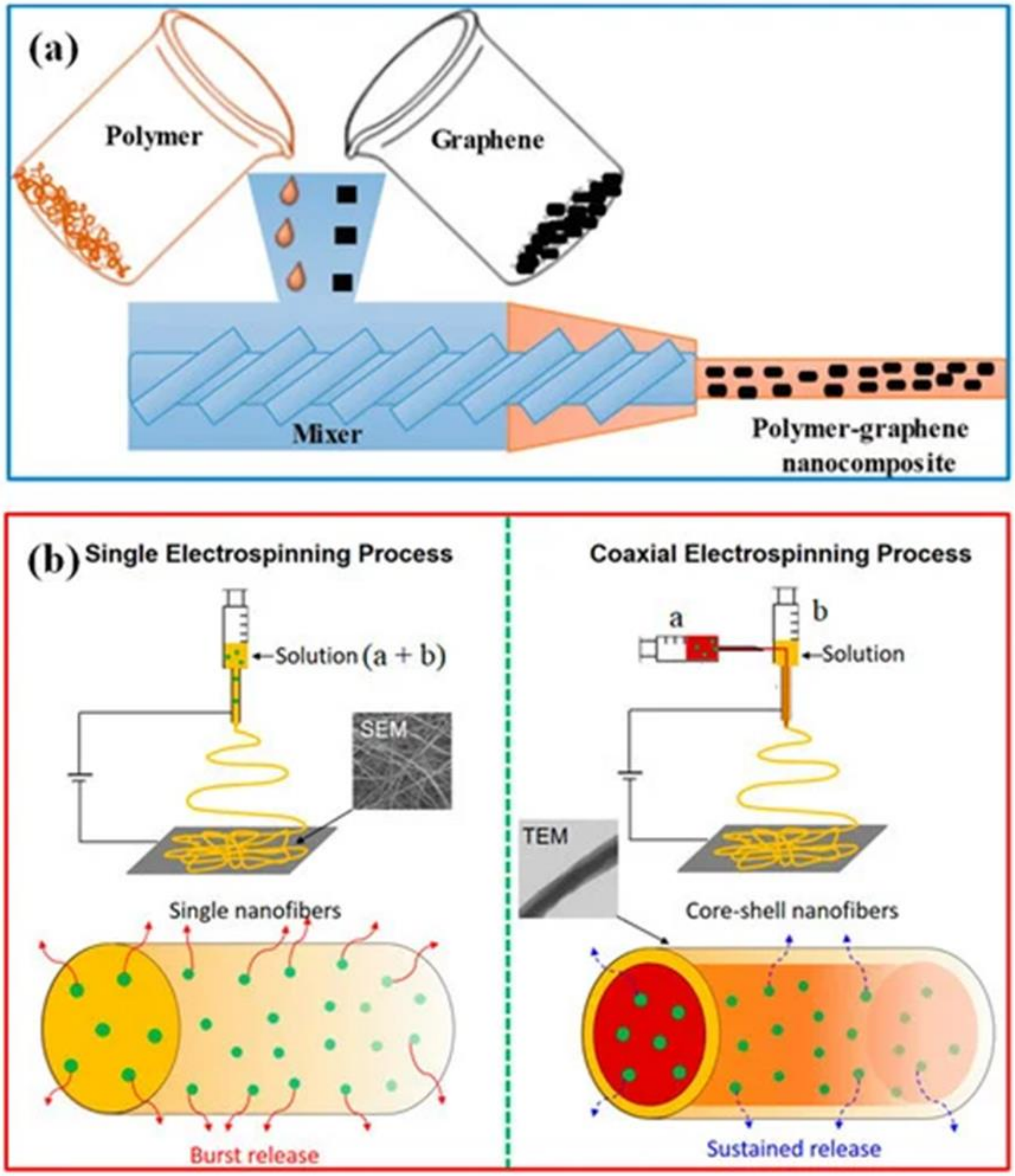

Figure 6: (**a**) Schematic diagram of melt blending [64]. (**b**) Monostatic and coaxial electrostatic spinning processes [65].

Furthermore, freeze casting (ice templating) and drying methods represent flexible processes for the fabrication of porous materials, which are frequently employed in the preparation of scaffold materials in tissue engineering [66]. In recent years these techniques have attracted considerable attention [67, 68].

The process of preparing chitosan-based nanocomposite membranes involves dispersing nanofillers in the chitosan matrix to produce a homogeneous dispersion of nanomaterials and chitosan, which is one of the keys to determining membrane properties. Chemical and mechanical methods are effective techniques for improving the dispersion of nanoparticles. Chemical methods such as the use of surfactants are effective in improving the interaction between the organic phase of the chitosan matrix and the inorganic phase of the nanoparticles. The esterification process entails the hydrolysis of vinyl-trimethoxy-silane within an alcoholic solution, and represents an efficacious methodology for the silanization of nanodiamonds [69]. Mechanical methods such as dispersion of nanoparticles on a polymer matrix by stirring. Ultrasonic or high frequency ultrasonic dispersion is also commonly used and provides a more homogeneous dispersion compared to stirring methods. In addition, mechanical or chemical methods complemented by atomic layer deposition and plasma techniques can be effective in solving nanoparticle aggregation problems [70]. It is important to note that achieving a homogeneous dispersion is crucial, as inhomogeneous dispersion results in poor compatibility, while poor compatibility between the polymer matrix and nanofillers leads to defective membranes, which adversely affect the mechanical properties of the entire polymer nanocomposite [71].

3. Optimization of the Performance of Chitosan-based Nanocomposite Membranes

3.1. Improvement of Water Flux and Desalination Rate

The water flux of chitosan membrane is relatively low, and the porosity of natural chitosan membrane is 73.0%, which limits the application of the membrane in high water flux and large-scale desalination process. Modification of chitosan by doping with nanomaterials can enhance its performance and increase the surface porosity to improve the water flux and desalination efficiency.

3.1.1. Improvement of Water Flux

The water flux of chitosan-based nanocomposite membranes can be improved in two ways, one is to use the pore effect of nanoparticles to increase the number of channels, pore size distribution and pore rate of the membrane, for example, we can use nanotechnology such as nano-etching and nano-templating to precisely control the size and distribution of pore sizes of nanocomposite membranes as well as to increase the porosity, so as to enlarge the permeable area of the membrane and improve the water flux. The second is to improve the hydrophilicity of the membrane, the artificial introduction of hydrophilic groups can well improve the water flux of the membrane, for example, the introduction of hydroxyl, carboxyl, etc. through chemical modification can increase the hydrophilicity of the membrane surface, thus reducing the resistance of water molecules to pass through the membrane and improve the water flux. In addition, some hydrophilic nanomaterials can also be selected for blending, for example, when titanium dioxide and such hydrophilic nanoparticles are selected as fillers, the hydrophilicity of the composite membrane is obviously enhanced and the resistance of water molecules passing through the membrane can also be reduced. Yousefi *et al*. reported the modification of TiO2 nanoparticles with polydopamine (PDA) and the preparation of polycarbonate (PC) nanocomposite membranes via non-solvent induced phase separation (NIPS) process for the disposal of oily wastewater (OW). Tests showed that the addition of TiO2 nanoparticles resulted in an increase in the hydrophilicity and porosity of the pure PC membranes and the formation of large pores on the surface and in the cross section of the composite membranes (e.g. Fig. **7**) [72]. Kebria *et al*. developed ZIF-8/chitosan modified PVDF membranes and found that the modified membranes had high the liquid entry pressure of water (L E Pw), water flux and separation capacity, which has high potential for application in membrane distillation process. The analytical results are shown in Fig. (**8**), which confirms the presence and good dispersion of ZIF-8 in ultrathin layers [73]. In addition, the tests showed that the modified membrane has higher water flux (~350%) and NaCl rejection.

3.1.2. Improving the Desalination Performance

To further improve the desalination performance of the composite membrane, it can be achieved by the three directions of enhancing the electrostatic repulsion between the cationic groups of chitosan and the salt anions, the sieving effect of nanoparticles, and the spatial site blocking effect formed by the uniform distribution of nanoparticles.

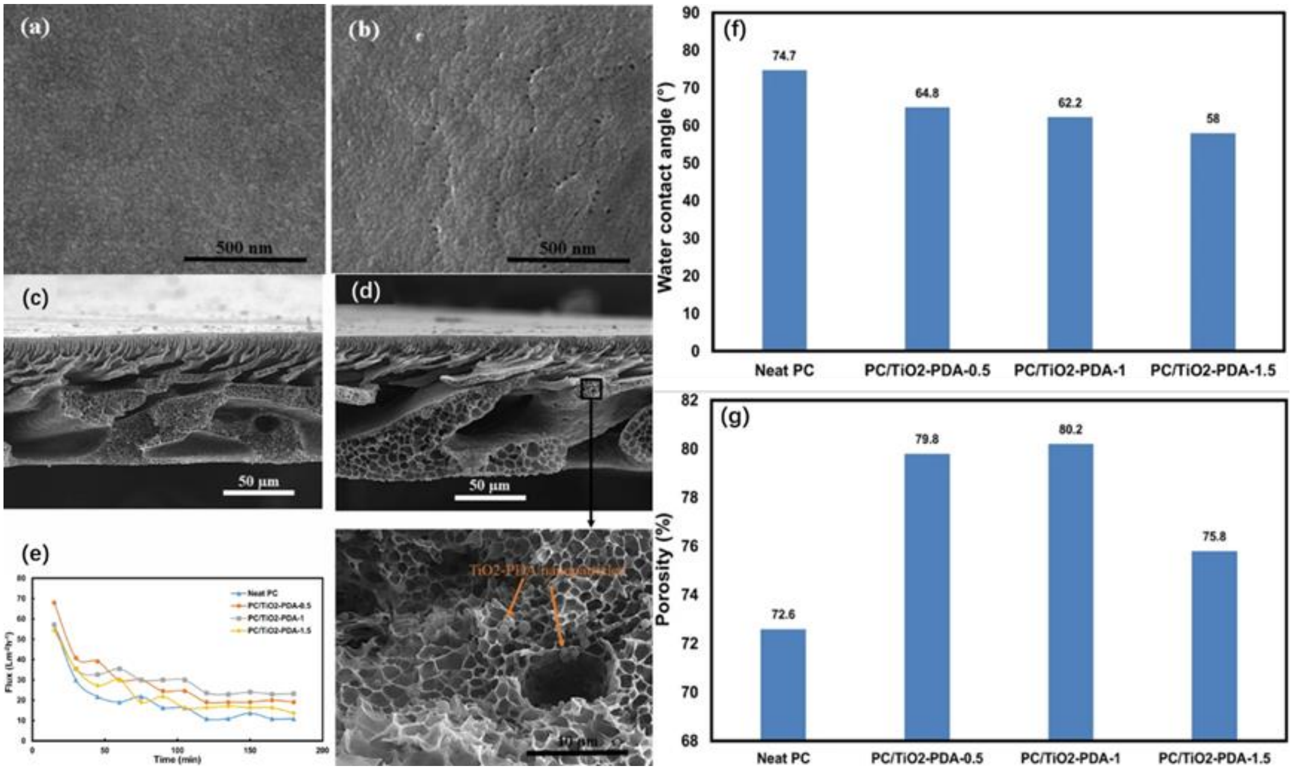

Figure 7: (**a**) Surface FE-SEM images of pure PC and (**b**) composite membranes; (**c**) cross-sectional FE-SEM images of pure PC and (**d**) composite membranes; (**e**) OW treatment vs. time for different membranes; (**f**) water contact angle and (**g**) porosity test for pure PC and composite membranes [72].

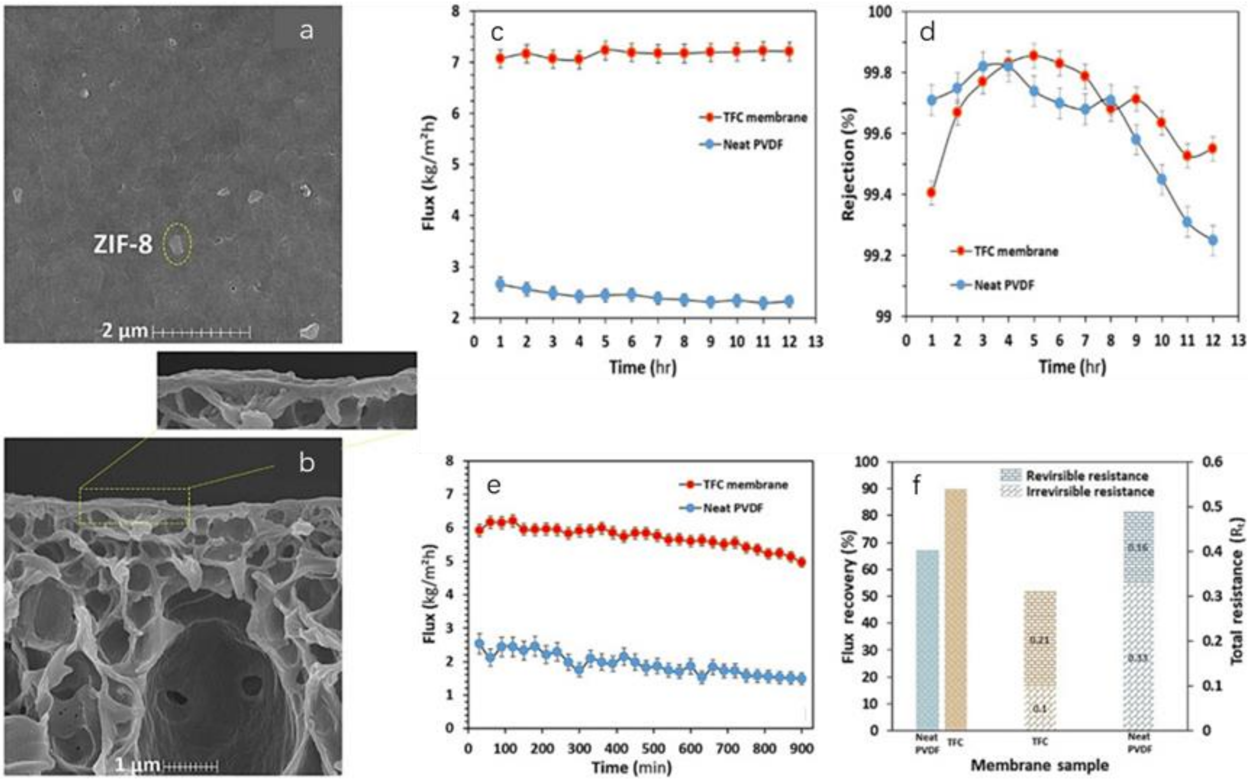

Figure 8: (**a**) Surface FE-SEM image and (**b**) cross-sectional FE-SEM image of the modified membranes; water flux (**c**) and desalination rate (**d**) of the membranes during the AGMD test versus operating time; results of the seawater fouling test (**e**) and anti-fouling performance of the membranes (**f**) [73].

By optimizing the sieving effect of nanomaterials, the salt and impurities in seawater can be effectively trapped and removed, thus achieving the purpose of improving the desalination rate. In general, the desalination process can be further optimized by optimizing the size, shape and surface properties of nanomaterials to better adapt to the sieve pore structure and improve the sieving efficiency, and also by introducing some advanced sieving techniques such as electric field assisted sieving.

The spatial barrier effect, also known as the steric effect, refers mainly to the spatial obstruction caused by the proximity of certain small molecules in a molecule. The uniform distribution of nanomaterials and the formation of an effective spatial barrier form a physical barrier that prevents the passage of salt and contaminant molecules in seawater, improving the desalination rate. This can generally be achieved by optimizing nanomaterial preparation and dispersion techniques, as well as adjusting their surface structure and properties. Liu *et al*. reported a simple etching method to form nanopores, which altered the two-dimensional nanochannel structure in the GO, creating holes that increased the water flux of the film. Meanwhile, the etching process also reduces the number of oxygen-containing functional groups on the GO layer and improves the desalination rate; and the dip-coating method was used to modify polyelectrolytes on the HGO surface to improve the electrostatic repulsion and enhance the hydrophilicity and charge potential of the film surface, which improved the water flux and desalination rate of the composite film, and provided a new solution to improve the sieving performance and water transport performance of GO membranes for water treatment [74].

It is worth noting that the improvement of water flux and desalination are often a pair of contradictory performance indicators, the increase of water flux often leads to the decrease of desalination performance, and vice versa, the improvement of desalination often sacrifices the magnitude of water flux. In practical application, according to the specific use of the situation to balance the two characteristics to achieve the best overall effect.

3.2. Improving Salt, Antimicrobial and Pollution Resistance

3.2.1. Improving Salt Resistance

In order to improve the salt resistance of the membrane, a feasible method is to increase the structural stability and salt resistance of the membrane by strengthening the cross-linking between chitosan and nanoparticles. This process requires appropriate adjustment of the type and amount of cross-linking agent. In addition, the use of chemical branching and physical coating techniques to modify the membrane surface with salt-resistant functional groups and coatings to form a protective layer is also considered an effective means of enhancement. The salt resistance of nanocomposite membranes is highly dependent on the incorporation of nanomaterials, so the selection of suitable nanofillers is the simplest strategy. To improve the stability of the membrane in high salt environments, these nanomaterials must be selected to ensure that they have excellent salt resistance, chemical stability and the required mechanical strength. For example, nanoparticles can be filled into the interstices of the membrane material to form an effective physical barrier to block the passage of salt, and can also react chemically with chitosan to form chemical bonds.

3.2.2. Enhancement of Antimicrobial Activity

The simplest and most direct enhancement method in chitosan is to introduce nanoparticles with antimicrobial activity, such as silver nanoparticles or zinc oxide nanoparticles, to construct a composite membrane with excellent antimicrobial activity. These nanoparticles have broad-spectrum antimicrobial properties and are able to disrupt the cell walls or cell membranes of bacteria, effectively inhibiting the proliferation of bacteria on the membrane surface. At the same time, enhancing the antimicrobial properties of membranes can also effectively reduce biological contamination of membrane materials. For example, Fahrina *et al*. developed a hydrophilic antimicrobial membrane additive based on PEG-AgNPs using a simple sol-gel method and added it to PES to investigate its performance in resisting biofouling; it was found that the additive significantly increased the water flux through the membrane and also showed optimal resistance to biofouling as well as a low tendency to irreversible biofouling (Fig. **9**) [75]. In addition, the antimicrobial properties of chitosan itself were further enhanced by modulating the molecular weight and degree of deacetylation of chitosan. Alternatively, the antimicrobial effect of the composite film can be synergistically enhanced by compounding chitosan with other antimicrobial agents, such as physically or chemically mixing chitosan with antimicrobial agents. The direct introduction of new antimicrobial functional groups or coatings onto the surface of the membrane through surface modification and functionalization can also significantly enhance the antimicrobial performance of the membrane, for example by regulating the surface charge, hydrophilicity and other properties of the membrane material so that it and the microbial cell membranes or cell walls in contact with each other disrupt their structure or function to achieve the antimicrobial purpose.

3.2.3. Improving the Fouling Resistance

Improving the fouling resistance of the membrane often involves improving the hydrophobicity of the membrane to reduce the adsorption and accumulation of contaminants on the membrane surface. However, increasing the hydrophobicity will lead to a decrease in membrane water flux and desalination performance, how to balance the relationship between the two sides, researchers need to carefully consider the actual environmental conditions, choose the appropriate membrane preparation process. For this reason, some anti-pollution agents, such as surfactants or antimicrobial agents, are artificially added to the membrane preparation process to improve the membrane's resistance to pollution and inhibit the adhesion and accumulation of pollutants, while minimizing the impact on the membrane's water flux and salt resistance.

Li *et al*. successfully developed a ZnO/PHMB membrane with excellent antimicrobial and fouling resistance, which demonstrated 95.23% bactericidal rate in static antimicrobial test and 95.75% bactericidal rate in dynamic filtration antimicrobial test (e.g. Fig. **10**) [76]. It is important to note that whether it is the antimicrobial, salt or fouling resistance of the composite membrane that is being improved, its effect on other membrane properties (e.g. water flux and desalination) must be considered. When using chemical reagents (e.g. antimicrobials) to enhance membrane performance, attention must also be paid to the biosafety and environmental friendliness of such reagents to ensure that membranes are sustainable and environmentally friendly in practice.

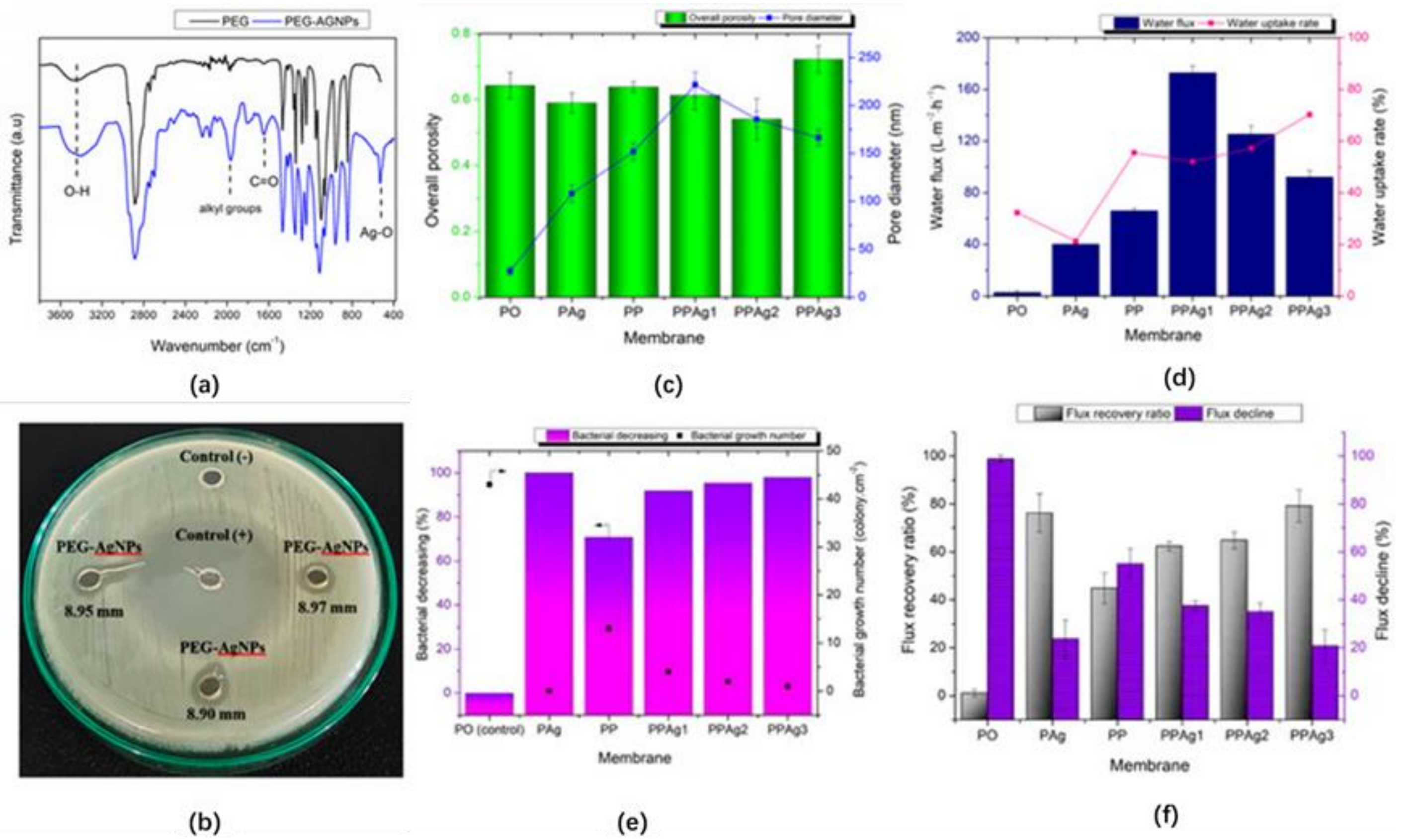

Figure 9: (**a**) FTIR spectra; (**b**) anti-bacterial performance of the PEG-AgNPs; (**c**) Membrane porosity and pore diameter; (**d**) water uptake rate and clean water flux; (**e**) Anti-bacterial determination of the membrane surface; (**f**) anti-biofouling performance of membranes, in terms of flux recovery and flux decline [75].

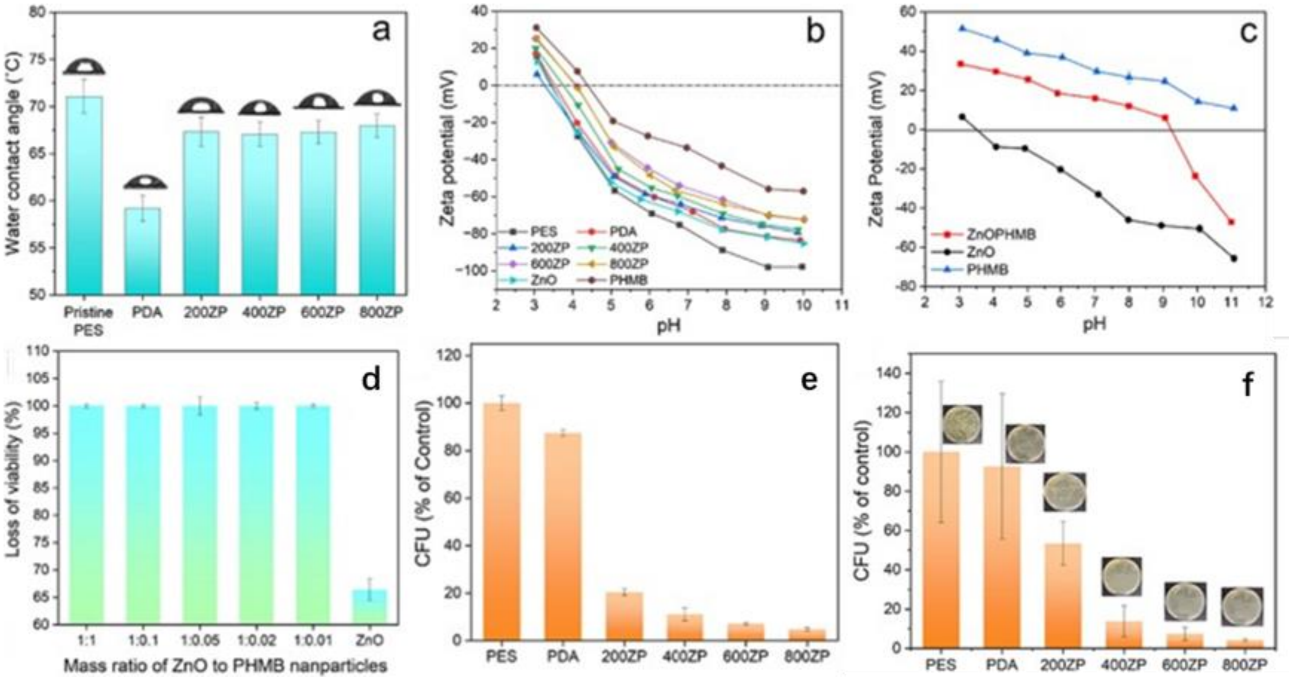

Figure 10: (**a**) Water contact angle of the membrane, zeta potential of (**b**) the membrane, and (**c**) the nanomaterials, (**d**) bactericidal properties of crude ZnO nanoparticles and synthesized ZnO/PHMB nanocomposites, (**e**) static antimicrobial properties of the membrane and (**f**) antimicrobial properties of membranes during dynamic *E. coli* synthetic wastewater filtration [76].

3.3. Enhancement of Mechanical Strength and Stability

The mechanical and stability properties of natural chitosan are relatively poor. For instance, at temperatures between 220 and 320 degrees Celsius, chitosan experiences a 50 per cent reduction in its weight. The properties of chitosan composites can be significantly enhanced by the incorporation of two or more materials [66].

To enhance the mechanical strength and stability of the composite membrane, some nano-enhancers (such as nanocellulose, graphene, etc.) with high strength and stability can be considered for addition to the chitosan matrix. These nano-enhancers can form interactions with chitosan, thus effectively enhancing the mechanical properties of the membrane, including tensile strength. Zeng *et al*. employed nanocellulose (NCC) to augment the mechanical properties and thermal stability of CS/PVP/β-CD, thereby enhancing its adsorption performance under acidic conditions (Fig. **11**) [77]. Yang *et al*. synthesized CS/GO nanocomposites by self-assembly, resulting in a significant increase in tensile strength and Young's modulus of the composites, by approximately 122% and 64%, respectively [78]. The elongation at the point of rupture was also significantly enhanced by the addition of only 1 wt% GO, in comparison to that of pure chitosan (Fig. **12**) [78].

In order to enhance mechanical strength and stability, it is possible to refine the cross-linking structure of the membrane. Selecting an appropriate cross-linking agent and method while controlling the density of cross-linking has been demonstrated to significantly enhance the internal network structure of the membrane. This ultimately achieves the desired outcome. For instance, bifunctional glutaraldehyde and epichlorohydrin represent the most commonly utilized cross-linking agents [79]. These agents react with hydroxyl or amino groups on linear macromolecular chains of chitosan, forming a three-dimensional network structure. This network structure serves to stabilize chitosan both chemically and mechanically [80]. In addition, the utilization of multilayer structural designs, the introduction of additional support or reinforcement layers within the composite membrane, enables the simultaneous enhancement of strength and stability, thus preserving the membrane's inherent separation performance. Liu *et al*. developed a novel cross-linking strategy based on the Schiff base reaction to prepare NGO/ONFC/CS foams with distinctive functional groups. This approach enhanced the adsorption and recyclable properties of the material. Furthermore, the material demonstrated excellent selective adsorption for anionic dyes

[81]. In the context of membrane preparation, the implementation of meticulous membrane preparation conditions ensures the uniformity and stability of the resulting composite membrane. Appropriate heat treatment and post-treatment of the resulting membrane can enhance its mechanical strength, stability and durability. Heat treatment can increase the degree of cross-linking and crystallinity within the membrane, while post-treatment can be used to modify the membrane's surface.

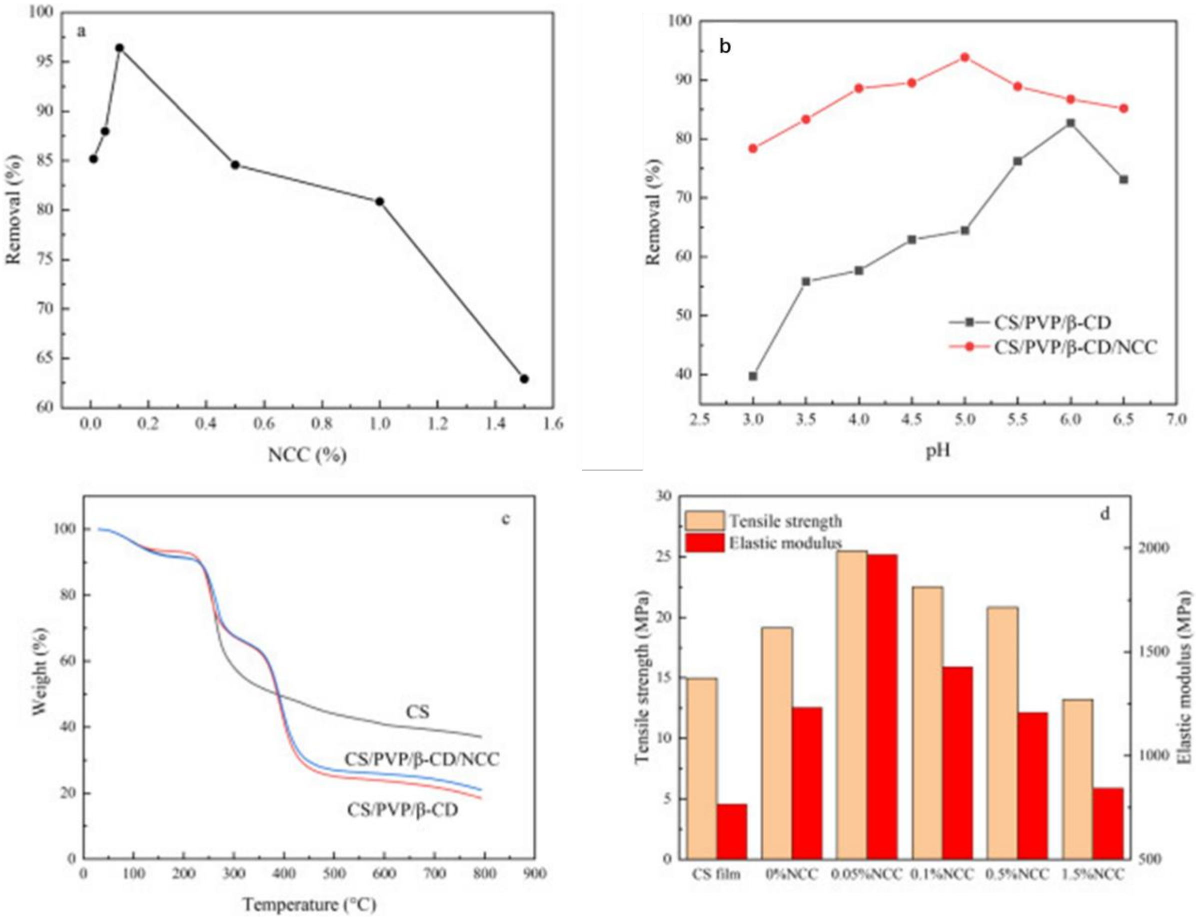

Figure 11: Effects of (**a**) content of NCC, (**b**) Ph; (**c**) TGA curves of CS, CS/PVP/β-CD, and CS/PVP/β-CD/NCC; (**d**) tensile strength and elastic modulus of the film with varying NCC contents [77].

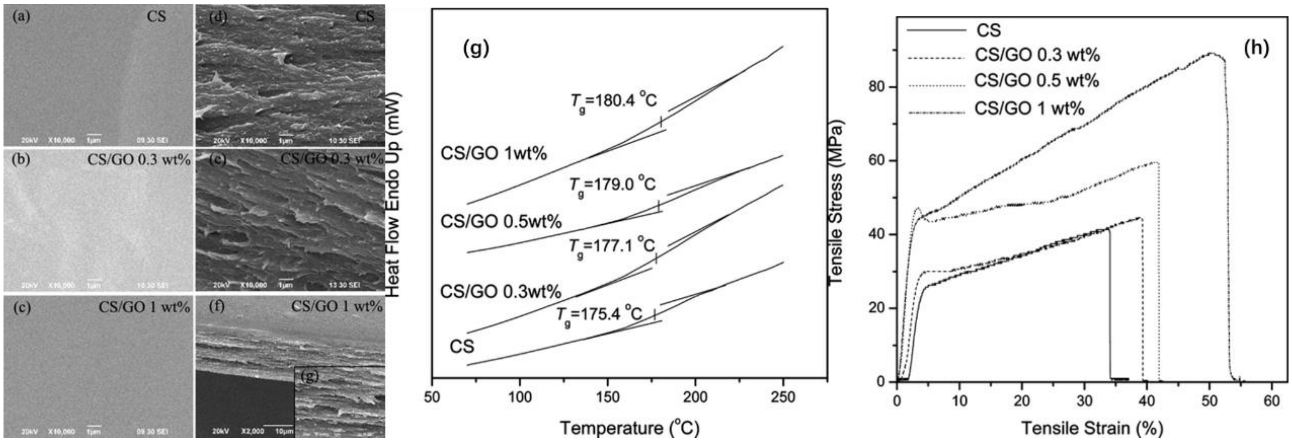

Figure 12: SEM film-surface images (**a**−**c**) and fracture-surface images (**d**−**g**) of CS and CS/GO nanocomposites; (**g**) DSC traces of CS and CS/GO nanocomposites; (**h**) Stress−strain behaviors for the films of CS/GO nanocomposites with different GO loadings [78].

4. Application Prospects and Challenges of Chitosan-based Nanocomposite Membranes

4.1. The status of Applications and a Case Study of Practical Use in the Field of Water Treatment are Presented

Membrane filtration technologies are classified according to pore size into reverse and forward osmosis (RO/FO), nanofiltration (NF), ultrafiltration (UF) and microfiltration (MF) [61]. While RO has the potential to provide the highest levels of water purity, NF membranes are now being used as a new technology for water treatment [82]. Because NF have a very small pore size (about 1 nm), this helps to remove larger molecules from smaller ones, and also helps to effectively remove protozoa, viruses and bacteria [82, 83].

In addition, the pursuit of water high recovery and the minimization of saline water volume represent common goals, although the specific treatment requirements may vary considerably depending upon the water source and end use in question. The current application of chitosan-based nanocomposite membranes in the field of water treatment is primarily focused on two areas: firstly, as a support layer or functional layer of reverse osmosis membranes to enhance permeability and selectivity of the membrane; and secondly, as the primary material of nanofiltration or ultrafiltration membranes to remove impurities, such as organic colloids, inorganic particles, and microorganisms, from seawater.

Chitosan-based nanocomposite membranes exhibit excellent permeability and selectivity when used as a support or functional layer of reverse osmosis membranes. The selective doping of different nanomaterials enables the pore size and distribution of the membrane to be effectively controlled, thereby improving its water flux, retention rate and other performances. This allows for the precise separation of different substances. Similarly, the incorporation of nanomaterials can also facilitate the formation of additional water transport pathways and adsorption sites, which can enhance the permeability and selectivity of the membrane. Notably, chitosan membranes are inherently susceptible to physical defects such as water insolubility and brittleness in the dry state; these limitations restrict their suitability for use in reverse osmosis membranes.

Chitosan-based nanocomposite membranes are also a promising material with significant advantages in the composition of nanofiltration or ultrafiltration membrane materials. The utilization of ultrafiltration technology enables this novel membrane material to effectively remove impurities, including suspended solids, colloids and microorganisms, from seawater, thereby meeting the requisite standards for water quality in water treatment projects. The utilization of nanofiltration technology enables chitosan-based nanocomposite membranes to be employed in a broader range of applications, particularly in the fields of water treatment and resource recovery. This membrane material exhibits a Donnan effect with anions in water, which enables more precise and effective separation. Nevertheless, the efficiency of nanofiltration technology, which is a pressure-driven separation technology, is contingent upon the performance of the membrane material.

4.2. Challenges and Problems

Although chitosan-based nanocomposites have the potential to be effective in water treatment applications, there are certain limitations that must be taken into account.

One of the principal challenges is to devise methods for improving scalability and cost-effectiveness in large-scale production. The preparation and production costs of chitosan-based nanocomposites remain significant challenges that must be addressed. The key to the widespread adoption of these new membrane materials is the ability to reduce production costs while maintaining cost-effectiveness and ensuring performance. Although chitosan-based nanocomposites can be regenerated and reusable, the efficiency of the regeneration process is still low. Therefore, it is necessary to consider how to improve the stability and reusability of nanocomposites.

Another significant challenge is the efficient dispersion of nanofillers within the chitosan matrix, as well as the reduction of agglomeration phenomena observed in nanomaterials. Furthermore, A study by Abou Kana *et al*.

demonstrated that the dose and size of nanoparticles significantly influence the removal efficiency of toxic elements, including copper, chromium, manganese, zinc and lead, from wastewater. This is a crucial factor that cannot be overlooked [84].the current promotion of sustainable development necessitates that researchers consider the synthesis, regeneration, and disposal of nanocomposites. The regeneration strategies currently employed can be categorized into three main groups: chemical, thermal and biological. Among these, chemical methods are most suitable for chitosan-based nanocomposites due to the properties and structure of chitosan, and the chemical regeneration methods are simple and low-cost [85]. During the regeneration process, organic solvents such as ethanol, methanol and acetone are typically used for dissolution and desorption [86].While the high selectivity of composite membranes may be advantageous, it may also restrict their suitability to specific types of seawater environments. Consequently, in order for membrane materials to be commercially viable, they must be developed with greater versatility.

Another significant challenge is to achieve a balance between selectivity and versatility. The expectation that such water treatment membrane materials will be able to desalinate seawater while harvesting useful and rare resources, such as rare metals, will necessitate that research and development staff consider the choice of functionality with greater care. Concurrently, the expansion of the range of available materials is of paramount importance in order to meet the challenges of water treatment in a multitude of environments.

Although composites are considered environmentally friendly, there is a paucity of studies that assess the toxicity of nanocomposites introduced into the environment. Consequently, more effective research methods need to be designed in this area. Furthermore, there is a lack of consensus regarding the most appropriate risk assessment methodologies for certain toxic exposures to nanomaterials. Additionally, there is ongoing debate surrounding the long-term viability of nanomaterials in water purification systems [87]. Although various scientific studies have been conducted regarding the risk assessment of nanomaterials for designing membrane-based water treatment systems, there is still a lack of sufficient understanding of the health issues of nanomaterials [88]. The case of carbon nanotube materials (CNTs) serves to illustrate the potential toxicity of nanomaterials. Animal studies have confirmed that CNTs can cause fibrosis, genetic damage, lung cancer, fetal malformations or fetal loss, growth retardation, inflammation, and even death [89]. Pristine carbon nanotubes are known for their great toxicity to living organisms, and thus more research is still needed to minimize or eliminate toxicity associated with nanomaterials. As reported by Ihsanullah, functionalized carbon nanotubes exhibit reduced toxicity compared to pristine carbon nanotubes. This may be attributed to the absence of metal catalysts in functionalized carbon nanotubes. The use of functionalized carbon nanotubes in place of pristine carbon nanotubes can effectively minimize the toxicity of carbon nanotubes in a given system [90]. Zhang *et al*. subsequently presented a straightforward elimination method that can entirely degrade carbon nanotubes into carbon oxides and carbonate ions through direct treatment with sodium hypochlorite solution [91].

Furthermore, it is essential to consider the compatibility of this novel membrane material with existing water treatment processes and infrastructure. It is anticipated that the majority of water treatment facilities and systems in developed countries will remain unchanged for an extended period. Consequently, it is necessary to determine how the technology can be implemented in the near term with minimal alterations to existing facilities [92]. Finally, it is important to consider the operational and maintenance requirements of this membrane material. Consequently, it is imperative for researchers to design more durable membrane materials that are straightforward to maintain and replace, as well as to establish corresponding operational and maintenance systems to safeguard the desalination process. Despite the aforementioned limitations, there are opportunities for innovation through research and development, which may lead to the development of more advanced nanocomposites and enhanced synthesis methods [93].

4.3. Future Development Direction and Potential Application Areas

In the field of environmental protection, Worldwide, 40,000 pigments are manufactured in different industries, and 15% of these are discharged directly into water. Therefore, pollutants such as heavy metals, dyes and pharmaceuticals in wastewater must be removed from the environment as soon as possible [94, 95]. Adsorption is an advanced method for removing pollutants from wastewater and has received widespread attention because it requires minimal energy, is versatile in design and operation, and does not produce environmentally harmful by-products [96]. The use of chitosan as a biosorbent for wastewater treatment is an effective strategy [97]. The combination of nanomaterials and chitosan can significantly enhance the adsorption and separation efficiency, and be employed in wastewater treatment to adsorb heavy metals, dyes, and organic pollutants, thereby reducing pollution. The report indicates that adsorbents comprising chitosan and nanomaterial composites have been employed in the remediation of chromium (VI), arsenic (III), arsenic (V), cadmium (II), lead (II), nickel (II), copper (II) and a plethora of other environmental applications. Furthermore, the adsorbents have attracted significant interest in the field of dye processing [98]. Wei *et al*. prepared a composite material, UiO-66/CB, with strong adsorption properties against A s(III) was prepared by using the gelation freeze casting method. This method not only dispersed the UiO-66 homogeneously in the network pores of CB, but also effectively activated the UiO-66 nanoparticles, thus increasing the utilization efficiency of active sites. The method permitted the uniform dispersion of UiO-66 in the network pores of CB, which retained its high activity, while also effectively activating the UiO-66 nanoparticles, thereby enhancing the utilization efficiency of the active sites. Following testing, the maximum adsorption capacity of the material for A s(III) was found to be at least 47.9 mg/g at pH = 7, which was significantly higher than that of the original UiO-66 (7.9 mg/g). This discovery offers a novel approach to the preparation of high-performance and simple bio-composite adsorbents of MOFs, which can be utilized for the treatment of heavy metal wastewater (Fig. **13**) [99]. One of the major problems today is the contamination of waterways and environments by dye effluents, a situation that requires more attention and research to be effectively removed. Methyl orange (MO), one of the dye effluents, is of particular interest. Ediati and colleagues have reported a method using CS/UiO-66 composites as MO adsorbents [100]. The impregnation method was employed to combine UiO-66 with Cs, which both avoided the destruction of the crystal structure of UiO-66 due to the ice template method and demonstrated the effect of the different mass numbers of Cs and UiO-66 on the adsorption performance. Furthermore, the experimental results demonstrated that the highest adsorption capacity value of 370 was achieved. The Cs (5)/UiO-66 adsorbent exhibited a maximum adsorption capacity of 370 mg/g when the amount of Cs added was 0.025 g (Fig. **14**) [100]. In addition, chitosan-based composites in combination with nanomaterials or natural antimicrobials have been found to be very useful in extending shelf-life and maintaining post-harvest product quality for use in the food industry, as well as being used as food additives for functions such as thickening, emulsification, freshness retention and preservation [101]. Additionally, they are themselves environmentally friendly, biodegradable, and reusable materials. In the medical field, chitosan nanocomposites are anticipated to become a pivotal raw material for the fabrication of hemostatic dressings and biological tissue repair materials due to their distinctive biocompatibility and anti-inflammatory and antibacterial properties. Chitosan composite membranes have been developed to stimulate cell migration and proliferation, bone tissue engineering scaffold materials for the attachment of matrix and the promotion of cell proliferation, and chitosan nanofibrous membranes for use as antimicrobial wound dressings to facilitate wound healing [102, 103]. In conclusion, chitosan-based nanocomposites, a novel material with a wide range of applications and significant commercial potential, can play a pivotal role in various fields, including medical, food, environmental protection, and industrial agricultural production.

The utilization of chitosan-based nanocomposites in water treatment is promising, although the current studies are still in an experimental phase. Before they can be commercialized and implemented on a large scale, further improvements and optimization are needed. In addition to research on membrane filters, the materials can also be used as sensors to detect different pollutants. It has been demonstrated that electrode surface modification materials can be successfully prepared, and that various biosensors can be developed based on the excellent film-forming ability and non-toxicity of CS/metal oxides [104, 105]. Furthermore, the incorporation of a third material, such as multi-walled carbon nanotubes or graphene, onto the CS/MONMs can be employed to modify the biosensors, thereby enhancing their ability to detect pollutants and increasing their sensitivity [106]. Zuo *et al*. reported a sensitive Pb (II) sensor based on Co_3O_4/reduced graphene oxide/chitosan (Co_3O_4/rGO/chitosan) nanocomposite modified glassy carbon electrode (GCE) [107] . The sensor simultaneously combines the advantageous electrical conductivity and elevated specific surface area of rGO, the robust adsorption of Pb (II) by Co3O4 nanomaterials, and the exemplary Pb (II) complex formation capacity of chitosan, with a detection limit of 0.35 nM.

However, the issue of the material's sustainability in practical applications has consistently been an evident limitation. In order to ensure the long-term stability and operation of membrane materials, it is also necessary for researchers to design and establish a corresponding, optimal operation and maintenance system. In addition, the ultimate objective of water treatment is not solely the removal of pollutants but also the enhancement of overall water quality [108]. This latter aspect is often overlooked, and thus requires researchers to focus on the assessment of post-treatment water chemistry [109]. The treated water was evaluated to necessitate significant improvements, including a reduction in turbidity, an enhanced pH balance, and a diminished concentration of heavy metals and organic compounds [110]. Techniques such as high-resolution mass spectrometry and advanced chromatography allow for a more thorough assessment of contaminant levels and the overall chemical composition of treated water [111]. In conclusion, the solution to the problem of water pollution is not merely a technological challenge; it is also a societal one, requiring a joint effort between researchers, industry and policymakers [112].

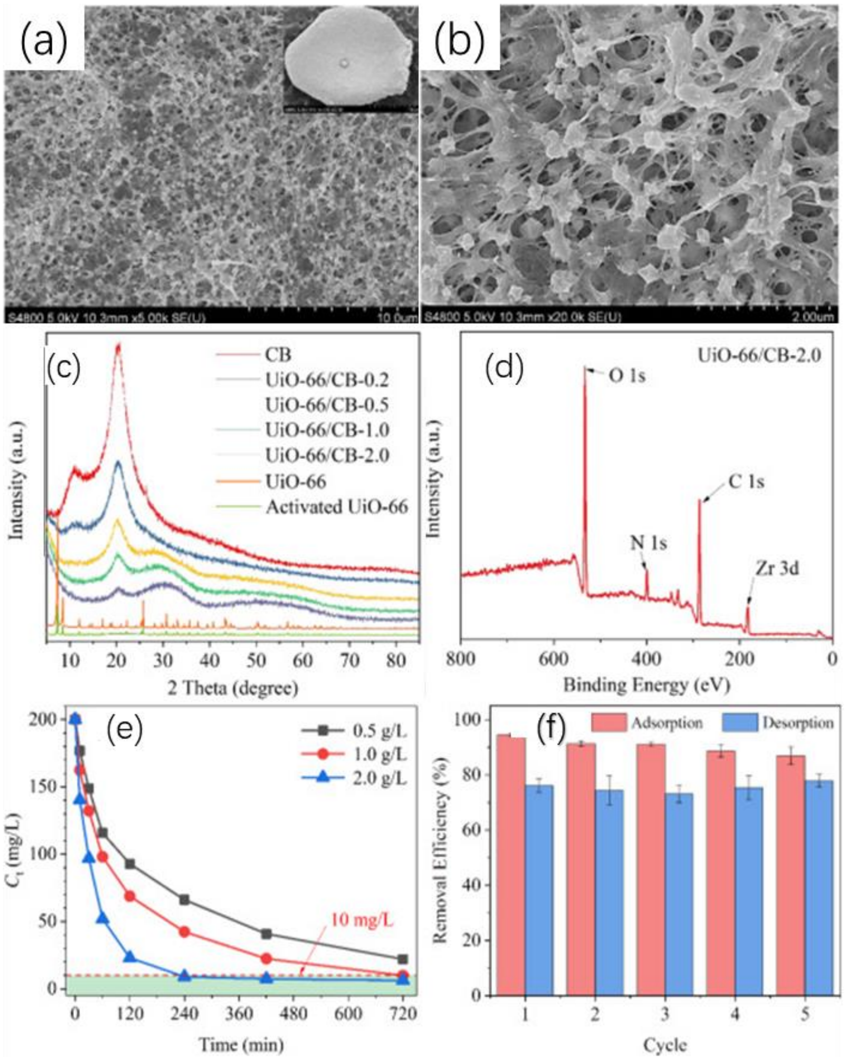

Figure 13: (**a**, **b**) SEM images of UiO-66/CB-2.0, (**c**) XRD patterns of UiO-66/CB, (**d**) XPS survey spectra of UiO-66/CB-2.0, (**e**) Performance of UiO-66/CB-2.0 in adsorption of As (III) from groundwater, (**f**) Performance of UiO-66/CB-2.0 for As (III) adsorption recovery [99].

5. Conclusion

5.1. Summary of Research on Chitosan-based Nanocomposite Membranes

The scarcity of fresh water resources will remain a pressing concern for the foreseeable future. Therefore, there is a pressing need to enhance existing water treatment technologies or to develop and prepare new water treatment technologies in order to ensure the provision of sufficient drinking water to meet the growing demand.

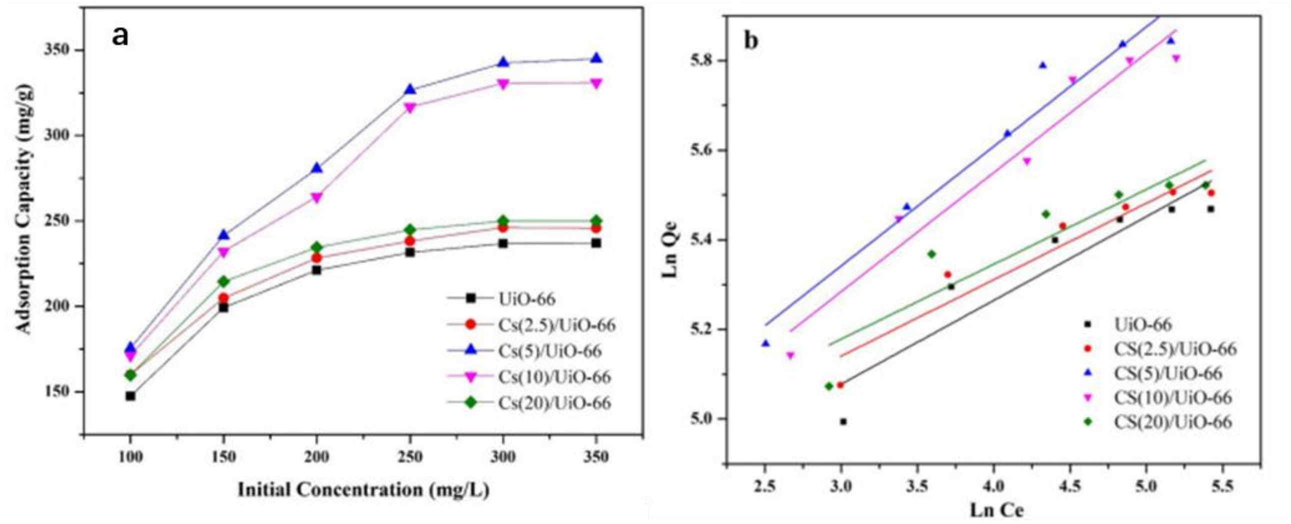

Figure 14: (**a**) Plot of concentration variation of MO adsorption, (**b**) Freundlich adsorption isotherm plot 1[100].

Chitosan-based nanocomposite membranes combine the natural advantages of the biopolymer chitosan with the features of nanotechnology, exhibiting excellent biocompatibility, bioactivity, as well as high permeability and selectivity. The application of chitosan-based nanocomposites in water treatment or aqueous treatment ensures the retention of particulate matter and the removal of pollutants from the water. The incorporation of nanofillers ensures both a high surface area and more efficient desalination treatment. Furthermore, the physical properties of chitosan-based nanocomposites, including stability, mechanical strength, and self-repairing ability, have been investigated and validated to some extent. This will result in reduced energy consumption and operational and maintenance costs, an extended service life, and an enhanced practicality of membrane materials. Nevertheless, there are still numerous constraints associated with the use of chitosan-based nanocomposite membranes for large-scale water treatment or water treatment in general, which will also impede the extensive deployment of these materials.

5.2. Proposed Areas for Future Research and Development

For several decades, nanotechnology has been a key area of research and development in the field of water treatment and water treatment with the goal of reducing the global freshwater crisis. Currently, numerous innovative technologies, including membrane filtration, ion exchange, distillation, and others, are attempting to utilize the new generation of nanomaterials, such as carbon nanotubes, graphene, zeolites, and others, in order to enhance existing technologies in terms of reduced energy consumption, more environmentally sustainable and cleaner technologies.

The potential of biopolymer nanocomposites across a range of research and application areas is considerable, and is attracting increasing investment from governments and businesses in many parts of the world. While there are numerous advantages of such materials for water treatment, there are also some disadvantages that must be considered. One such disadvantage is the potential risk associated with doping or depositing nanofillers onto polymer surfaces. Nanoparticles may be released and discharged into the environment, where they can accumulate over long periods of time. In order to make polymer nanocomposites an efficient and cost-effective water treatment technology, several aspects must be considered. These include the interaction between polymer nanocomposites and the substrate, the selection of nanomaterials and polymers, the optimization of the water treatment conditions, and the toxic effects on human health and the environment. At present, the utilization of polymer nanocomposites in water treatment is still in its infancy, and thus, a substantial amount of additional research is required to assess the efficacy of these disparate approaches and to develop cost-effective, selective, and recyclable biopolymer nanomaterials, as well as enhanced methodologies for their synthesis. These will be key areas of focus for future research. With further research, there is a strong expectation that this new membrane material will play an enhanced role in water treatment, providing an effective solution to the human freshwater shortage crisis.

This paper focuses on the nature of chitosan-based nanocomposites, their preparation and properties, availability, and the current status of their application in water treatment systems. Furthermore, this paper seeks to gain deeper insight into the potential of chitosan and nanomaterials for overcoming the bottleneck in membrane-based water and solute permeability in membrane-based water treatment systems by improving the performance efficiency of composite membrane materials for future applications. This will facilitate pioneering advances in the trade-off between permeability and selectivity. There is still much to be discovered about the optimal synthesis and preparation techniques of such novel membrane materials and their performance for commercial applications. Furthermore, the performance testing of membrane materials in real-world applications has not been accurately implemented to date. Consequently, it is anticipated that this work will provide novel insights into membrane-based water treatment and water treatment technologies. This will be achieved through the application of research strategies and tools on composite membrane materials and their application prospects, in terms of economic, environmental, and social aspects as well as feasibility for the development of novel water treatment membranes.

Conflict of Interest

The authors declare that there is no conflict of interest.

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