

Review

The Application of Chitosan-Based Adsorbents for the Removal of Hazardous Pollutants from Aqueous Solutions—A Review

Małgorzata A. Kaczorowska  and Daria Bożejewicz *

Faculty of Chemical Technology and Engineering, Bydgoszcz University of Science and Technology,
3 Seminaryjna Street, PL 85326 Bydgoszcz, Poland; malgorzata.kaczorowska@pbs.edu.pl

* Correspondence: daria.bozejewicz@pbs.edu.pl

Abstract: The development of simple, effective, economical, and environmentally friendly methods for removing hazardous substances of anthropogenic origin from aquatic systems is currently one of the greatest challenges, among others, due to the variety of pollutants and the transformations they may undergo in the environment. In recent years, there has been an increased interest in adsorption methods based on the use of natural polymers, including non-toxic chitosan (CS), which is characterized by good coating properties, biocompatibility, and biodegradability. This review concerns the latest developments (since 2019) in the application of novel chitosan-based materials for the removal of hazardous substances (e.g., metal and metalloid ions, synthetic dyes, pharmaceuticals) from aqueous solutions, with particular emphasis on their most important advantages and limitations, as well as their potential impact on sustainability.

Keywords: adsorption; chitosan adsorbents; water treatment; metal and metalloid ions; pharmaceuticals; synthetic dyes; sustainable development



Citation: Kaczorowska, M.A.; Bożejewicz, D. The Application of Chitosan-Based Adsorbents for the Removal of Hazardous Pollutants from Aqueous Solutions—A Review. *Sustainability* **2024**, *16*, 2615. <https://doi.org/10.3390/su16072615>

Academic Editors: Yawei Shi,
Jun Wang and Zonglin Pan

Received: 1 March 2024

Revised: 18 March 2024

Accepted: 20 March 2024

Published: 22 March 2024



Copyright: © 2024 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (<https://creativecommons.org/licenses/by/4.0/>).

1. Introduction

Economic and industrial development, urbanization, and climate change have contributed to the increased emission of different types of hazardous pollutants into the environment. Both well-known chemical compounds (e.g., toxic heavy metal ions) and new substances, so-called emerging contaminants (e.g., pharmaceuticals, whose properties and all their transformation paths have not always been well established), may pose a serious threat to the environment [1–3]. The increase in the amount and variety of anthropogenic-origin pollutants and the systematically expanding knowledge about their potential negative impact on living organisms and the natural environment have led to many studies on the possibility of modifying human activities (e.g., in a specific industry) in order to ensure the sustainable development of the ecological environment. For example, research is being carried out on the possibilities of industry transfer with regard to the environmental potential, on the optimization of construction processes using safer/healthier materials, or on proper and effective management in agriculture. However, due to the complexity of factors influencing the state of the environment, the research conducted is usually of a diverse nature and may also be related to ecological awareness, technology transfer, and “green” innovations [4–7]. Many studies conducted in recent years have also concerned water pollution and modifications to water treatment technologies. Water scarcity is a common resource problem around the world, and water is extremely susceptible to pollution; therefore, water pollution control and maintaining adequately clean waters are two of the key environmental challenges [8,9].

In addition to controlling water pollution, a very important problem is the elimination of hazardous substances from aquatic systems. Removal of various contaminants from polluted waters is usually carried out using a combination of different methods, the selection of which depends, among others, on the properties and amount of hazardous

substances present and also on what purpose the water will be used for after their removal. For example, in the case of water intended for drinking, acceptable concentration limits have been established for individual contaminants (e.g., metal and metalloid ions, pesticide residues, etc.), and the removal techniques used must be effective enough to eliminate these substances within the limits [10,11]. In general, methods that can be employed for removal processes due to their nature can be divided into chemical, biological, and physical. However, other classifications are also used; e.g., conventional methods, established processes, and emerging methods can be distinguished [10]. In the case of removing metal and metalloid ions, pharmaceuticals, or synthetic dyes from aqueous solutions, various techniques such as, among others, precipitation, coagulation, oxidation, membrane separation, ion exchange, evaporation, and adsorption were utilized ([3] and references therein). Because each method is characterized by certain advantages and limitations that affect the efficiency, sensitivity, and selectivity of the processes, other, more optimal solutions are systematically sought, and well-known methods are often modified to improve their performance [12]. At the same time, efforts are also made to ensure that the newly developed methods are environmentally friendly [13,14].

One of the methods that is usually characterized by high effectiveness, simple operation, high functionality, and relatively low costs is adsorption. Its important advantage in terms of environmental impact is the possibility of using numerous and diverse adsorbents, including eco-friendly bio-adsorbents [12]. Basically, two types of adsorption have been distinguished, i.e., physical adsorption (weakly specific, reversible, and with a small thermal effect) based on non-specific forces (e.g., van der Waals) and chemical adsorption, the so-called chemisorption (selective, often irreversible, and with a much greater thermal effect) based on adsorbate–adsorbent chemical reactions leading to the formation of ionic or covalent bonds [15]. Many of the developed adsorption methods can be used to remove various pollutants from water, wherein reversible adsorption-desorption properties are of particular interest because the use of appropriate adsorbents may also enable resource recovery (e.g., metal ions), which has a positive impact on sustainable development. Recovery is an extremely important operation in the case of metals used in key industrial sectors but not very widespread, such as, for example, highly scarce rhenium or precious metals (e.g., gold and platinum) [16,17]. Additionally, some of the modern adsorbents developed can have multi-functional applications; for example, they can serve as effective antibacterial materials and metal-selective sensing agents [18]. The group of well-known and frequently used adsorbents enabling efficient adsorption of various water pollutants includes, among others, activated carbon, zeolite, clay ore, and alumina. However, due to the growing interest in methods that bring additional environmental benefits, agricultural by-products, biological wastes, nanomaterials, and hydrogels are also increasingly utilized for this purpose [19,20]. Non-conventional, low-cost biosorbents originated from waste and by-products are usually characterized by low investment costs, simplicity of operation, and extraordinary efficiency, even with low concentration solutions. Moreover, their effectiveness can be relatively easily increased by physical or chemical modifications, e.g., by heat or inorganic/organic active compounds. Adsorptive properties of many bio-sorbents, such as chitosan, chitin, lignocellulose, algae, bacteria, and fungal biomass, etc., have recently been investigated in relation to the removal of both organic and inorganic pollutants from waters [21–23]. Additionally, some of these biosorbents have other applications, e.g., they can be used to produce effective energy storage devices (e.g., chitosan and alginate) [24,25].

This manuscript presents an overview of the latest developments (since 2019) in the use of various novel chitosan-based adsorption materials for the removal of hazardous contaminants such as metal and metalloid ions, pharmaceuticals, and synthetic dyes and for the recovery of valuable metal ions (e.g., rhenium) from aqueous solutions. Attention was paid to the main advantages and limitations of the developed methods, with particular emphasis on their potential impact on the sustainable development of the ecological environment. Although, due to the properties and potential applications of chitosan and its

derivatives as effective adsorbents, several review papers on this topic have been published in recent years, the subject of these works focused mainly on the sources, properties, and chemical modifications of chitosan and factors influencing the adsorption process or concerned the removal of other pollutants from aqueous solutions (e.g., phosphate and nitrate) [26,27].

2. Chitosan and Chitosan-Based Adsorbents

Chitosan, which is one of the intensively investigated materials used recently in many fields (e.g., engineering, biotechnology, and medicine), contains poly(2-amino-2-deoxy-d-glucopyranose) structural units connected by $\beta(1\rightarrow4)$ glycosidic bonds (Figure 1). Although the natural, biodegradable, and non-toxic chitosan dissolves in acidic aqueous solutions (it contains hydrophilic amino groups and hydroxyl groups), which limits the possibility of using this substance in adsorption processes, it is susceptible to modifications (e.g., chemical modifications) leading to the formation of desired insoluble derivatives that can be used in adsorption materials. Moreover, chitosan is a natural polysaccharide found in quite large quantities on Earth (e.g., in the shells of crayfish, crabs, etc.), and obtaining it from food processing by-products and using it for other applications (e.g., the removal of hazardous pollutants from water) is part of sustainable development and has a positive impact on the environment. An important advantage of chitosan-based materials is that they are also much cheaper than other established and commonly used adsorbents, such as activated carbon [28,29]. The properties of chitosan and its numerous advantages, including adsorption properties, availability, ease of modification, and relatively low costs (of acquisition and use), have led to an increase in the interest of scientists in chitosan-based adsorption materials and, consequently, the development of many new, effective adsorption methods intended for the removal of specific pollutants from different types of water solutions.

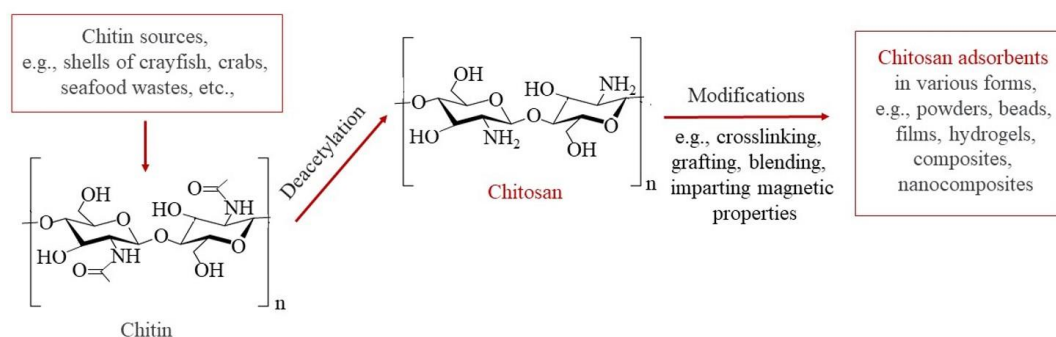


Figure 1. Simplified scheme for obtaining chitosan adsorbents (prepared based on references included in the text).

The utilization of unmodified chitosan (CS) in contaminated water purification processes, despite its adsorption abilities towards various chemical species (which result from the presence of various functional groups, e.g., amino and hydroxyl groups), is associated with numerous limitations. For example, chitosan in the form of flakes and powder is characterized by inappropriate porosity and specific surface area, is not thermally stable, is sensitive to pH changes, and has poor mechanical strength. Due to these disadvantages, it is necessary to modify chitosan to obtain adsorptive materials better suited for removing specific contaminants (e.g., metal/metalloid ions) from aqueous solutions [30].

2.1. Preparation of Chitosan and Chitosan-Based Adsorbents

Chitosan is typically obtained from chitin originated from natural sources (e.g., crustaceans, exoskeletons of insects, and fungal cell walls) by deacetylation processes through enzymatic or alkaline methods. Alkaline methods are usually based on three basic processes, i.e., demineralization (removal of mineral substances by the utilization of a hydrochloric

acid solution), deproteinization (removal of proteins by the use of a sodium hydroxide solution; *N*-acetyl groups within the polymer backbone are hydrolyzed), and decolorization (removal of pigments using organic solvents). Although the key step is deacetylation of chitin in 40–45% sodium hydroxide, proper preparation of the raw material (e.g., appropriate degree of grinding) as well as purification of the product have a significant impact on the quality of the obtained chitosan. With optimal process conditions, chitosan with a purity of >99.0% can be obtained [26,31]. Enzymatic methods are much less frequently used, mainly due to higher process costs (compared to alkaline methods). Enzymatic methods can be based, for example, on the utilization of specific strains of bacteria producing organic acids and enzymes needed for demineralization and deproteinization of crustacean shells [26,32]. However, it should be emphasized that unmodified chitosan obtained from various sources by application of alkaline methods may differ in molecular weight, degree of deacetylation (it depends on the reaction temperature, concentration of the alkaline solution, time of the process), and sequence of the acetamido and amino groups. The degree of CS deacetylation is one of the key parameters influencing the physicochemical properties and structure of chitosan. For example, increasing the degree of deacetylation contributes to an increase in the number of free amino groups on the chitosan polymeric chain, and because these groups may participate in the formation of intra- and inter-molecular hydrogen bonds, it can affect CS solubility. The distribution of the acetyl groups along the main chain affects the mechanical properties, swelling, and thermal degradation of chitosan [26]. Due to these differences, certain properties of chitosan derivatives obtained in similar processes from CS of different origins may also differ.

In recent years, many studies have been conducted on the possibility of modifying chitosan to give it specific functional properties, and the group of well-known modifications of CS that influence the physicochemical features of the obtained derivatives, including solubility in polar solvents (in a wide range of pH), comprise quaternization, *N*-alkyl modifications, *N*-acyl modifications, and C-6 oxidation [33]. In general, modifications of chitosan aimed at improving its adsorptive performance towards specific compounds may include, among others, changes of CS functional groups by crosslinking and graft modification, the generation of chitosan nanoparticles and hydrogels, or the integration of CS with other materials (e.g., graphene and zeolite) resulting in composite materials. Among the possible modifications of chitosan adsorbents, crosslinking, grafting, and imparting magnetic properties are playing an increasingly important role [30,34]. The magnetic properties of the chitosan-based adsorbents can be obtained by co-precipitation methods, crosslinking, or electrochemical methods [35]. Crosslinking strategy, which is used to improve specific properties of chitosan-based adsorbents (e.g., increasing the number of bioactive sites and adsorption efficiency, improving mechanical efficiency, and hydrophobicity of an adsorptive material), allows to connect chitosan chains and create a three-dimensional macromolecular network, but it requires the use of various substances facilitating such processes, i.e., crosslinking agents, containing various functional groups. Popular crosslinking agents, despite their availability and low price, are not always safe for the environment (e.g., toxic glutaraldehyde), which is why safer alternatives (e.g., citric acid and inorganic phosphates) are being utilized more often [33]. However, the toxicity of crosslinking agents is not the only problem, as some of these agents can negatively affect the adsorption capacity of CS by reducing the number of available functional groups (e.g., -OH and -NH₂). Therefore, proper selection of crosslinking agents may be crucial for the efficiency of the synthesized adsorption material. In recent years, chitosan hydrogels (soft and three-dimensional network polymers), whose inherent property is cross-linking, have gained great interest. Hydrogels can be obtained as a result of physical interactions or chemical cross-linking, where chemical cross-linking is permanent and the structure of the obtained product is very stable [36]. When grafting is used to modify chitosan, the backbone of CS is not altered in any way, just like in the case of crosslinking. Grafting new functional groups onto the chitosan backbone increases the number of adsorption sites, usually improves adsorption selectivity, changes the pH range of pollutant (e.g., metal

ion) adsorption, and consequently positively influences the capacity and efficiency of the modified adsorption material [37]. Many methods have been developed for the synthesis of crosslinked or grafted chitosan derivatives. They may differ significantly, both by the reagents used and by the process conditions; therefore, it is not possible to propose a single synthesis process scheme for obtaining such chitosan derivatives [38]. Additionally, for many CS derivatives, several different synthetic methods have been developed. For example, phenolic-grafted chitosan can be prepared using three different methods: free radical initiation, carbodiimide coupling, and enzyme catalysis [39]. However, it can be observed that whenever possible, attempts are made to develop the simplest methods possible, e.g., those in which the necessary ingredients are mixed under specific conditions (e.g., at elevated temperatures or under microwave-assisted heating) [28,29,40–42].

Often, in order to obtain an efficient adsorbent, both types of modifications are used, i.e., crosslinking and grafting. For crosslinked chitosan, the possibility of using grafting is of great importance because some CS adsorption sites can be lost as a result of crosslinking. Various chemical compounds can be used for grafting crosslinked chitosan (e.g., thiourea, triethylenetetramine, and acrylic acid); however, other substances that are more suitable for this purpose are still being sought [43,44]. As various (e.g., chemical and physical) modifications can be introduced into chitosan, it is possible to obtain various CS-based adsorption materials in different forms. As a result of modifications, more active groups can be formed on the chitosan chain, which improves the adsorption properties of the material but may also positively affect its selectivity and stability [45]. Figure 1 shows a simplified scheme for obtaining CS-based adsorbents.

2.2. Adsorption Mechanisms and Kinetics

The performance of biodegradable chitosan in adsorption processes mainly depends on the degree of deacetylation, particle size, and crystallinity. The molar mass of CS does not significantly affect the ability of the chitosan-based material to adsorb pollutants. Increasing the degree of deacetylation of chitosan results in the presence of a larger number of amino groups, an increase in the tensile strength and crystallinity of CS, and usually a shortening of the polysaccharide chain. A higher degree of CS deacetylation leads to a reduction in the number of acetyl side groups, which leads to a more regular packing of the polymer chains, which finally promotes crystallinity. The CS surface area and particle sizes (related to porosity, pore volume, and pore size distribution) are of key importance in adsorption processes since efficient adsorption of pollutants is possible with the appropriate number of accessible sites and porous structure. In general, larger particle sizes lead to reduced pollutant uptake due to the smaller specific surface area [26,46]. However, it should be emphasized that the mechanism of the adsorption process also depends on the properties of the removed pollutants and on the process conditions. Due to the number of factors influencing the adsorption processes, their mechanisms in many cases have not been fully elucidated. Typically, in the case of positively charged heavy metal ions, adsorption onto chitosan is related to the chelation with the primary amino groups and the hydroxyl groups. Therefore, the degree of chitosan deacetylation plays an important role in these processes (affecting the number of amino groups) [46,47]. However, it has also been shown that in the case of simultaneous adsorption of two different ions, the process mechanism may be more complex. For example, it has been shown that the adsorption of iron ions ($\text{Fe}^{2+}/^{3+}$) resulting from $(\text{FeSO}_4)_{\text{aq}}$ is related to the oxidative effect of $\text{Fe}^{2+}/^{3+}$ with the formation of orthorhombic $\alpha\text{-FeOOH}$ and $\gamma\text{-FeOOH}$ ([47], and references therein). Anions can be adsorbed to chitosan by hydrogen bonding and/or electrostatic forces and/or by the heavy metal ions adsorbed in the crystallization process [46]. In the case of the adsorption of dyes or pharmaceuticals, the structure and properties of the removed compounds, as well as the pH of the reaction environment, are important. For example, based on results of quantum chemical calculations and molecular dynamics, it was shown that in the case of CS adsorption of anionic dyes (e.g., tartrazine, sunset yellow, and brilliant blue) in an acidic medium, there was a strong inclination of chitosan to donate electrons. It indicated

that CS can be protonated at nitrogen atoms ($-NH_2$ groups) in an acidic solution, which can later serve as interaction sites for the anionic dyes [48]. The efficiency of the chitosan-based adsorption process can be controlled by changing parameters such as, among others, adsorbent dosage, removed compound concentration (e.g., metal ions, dyes, etc.), and pH of the reaction medium. The higher amount of adsorbent dosage may increase the adsorption rate of pollutants; however, a higher initial concentration of removed pollutants may result in lower adsorption (a result of an inadequate number of accessible sites for adsorption). In general, in the case of various pollutants adsorption (e.g., metal ions), cationic adsorption decreases at a low pH value, and anionic adsorption increases (the pH of a medium controls the magnitude of electrostatic charges that are imparted by the ionized molecules). In order to express the influence of the adsorption process parameters (e.g., pH, temperature, and initial concentration of the adsorbed substance) on the efficiency of this process (mass of the adsorbed substance), an adsorption isotherm can be used (e.g., Freundlich and Temkin isotherm equations) [49].

3. Application of Chitosan-Based Adsorbents to Remove Metal and Metalloid Ions from Aquatic Systems

A group of toxic heavy metals that can readily bioaccumulate in plant, animal, and human tissues and, due to their properties, pose a serious threat to human health and the environment include, among others, Hg(II), Pb(II), Cu(II), Cd(II), and Cr(III and VI) [50,51]. Under certain conditions, many metalloids (e.g., Sb (III and V), As (III and V)) pose a similar threat and also have an adverse effect on living organisms [52]. Therefore, it is very important to effectively remove these toxic pollutants from domestic and industrial sewage, and the application of appropriate techniques is a key challenge because methods used for such purposes, in relation to sustainable development, should not be expensive, complex, or cause secondary pollution. Adsorption methods, which typically meet these requirements, are increasingly being used to construct simple and low-cost platforms for high-efficiency removal of heavy metal and metalloid ions from wastewater [50,53]. Among the adsorbents used, natural chitosan (e.g., extracted from crustacean shells by partial deacetylation of acetamide groups using strong alkaline solutions) has been attracting interest for a long time because of its significant ability to bind various metal/metalloid ions, which consequently allows for their efficient removal from different matrices (e.g., wastewater, cigarette mainstream smoke, etc.) in adsorption processes [54].

3.1. Crosslinked Chitosan-Based Adsorbents

In recent research related to the development of new chitosan-based adsorbents intended for the removal of metal and metalloid ions from aqueous solutions, much attention has been paid to the possibility of using various crosslinking agents for CS modification. For this purpose, both known chemical compounds (with some changes to specific parameters of the adsorption processes) and new substances that had not been utilized for crosslinking before were applied. Typically, non-toxic compounds are sought that not only enable crosslinking of CS, but also provide additional benefits. For example, recently, Cheng et al. [55] reported that the application of tetrafluoroterephthalonitrile (TFT) as a crosslinking agent for chitosan leads to the formation of new functional groups ($-O=C=NH_2$) during CS-TFT preparation, the presence of which increases the adsorption capacity of this novel adsorption material, although it is known that hydroxy and amino groups play a key role in the chemical adsorption of Cr(VI) and U(VI). The maximum adsorption capacities of CS-TFT for Cr(VI) and U(VI) were 265.96 and 346.06 mg/g, respectively [55]. However, the efficiency of an adsorption process depends not only on chitosan derivatives' properties but also on many other factors, including the concentration of pollutants (e.g., metal/metalloid ions) in the aqueous solution, pH of such solution, adsorbent concentration, temperature, and process duration [33]. Therefore, crosslinked chitosan is usually synthesized in the first stage of research using various crosslinking agents, and then the conditions for the adsorption process of specific metal/metalloid ions

from a specific aqueous solution are optimized. For example, Kekes et al. [56] compared the efficiency of adsorption processes of toxic Cr(VI) ions using two different, novel chitosan-based adsorbents, i.e., beads containing plain chitosan crosslinked with emerging non-toxic sodium tripolyphosphate (STTP) and beads with chitosan and β -cyclodextrin crosslinked with STTP. In general, cyclodextrins (CDs) are cyclic polysaccharides that are able to chelate metal ions (containing hydroxyl groups). Moreover, modified (e.g., crosslinked) CD adsorbents usually provide higher adsorption [57]. The results obtained by Kekes and co-workers [56] indicated that under optimal conditions for the adsorption processes (initial adsorbent concentrations of 15 g/L (CS/STTP) and of 20 g/L (CS/ β -CD/STTP), pH = 4, and temperature of 15 °C), chitosan/ β -cyclodextrin containing beads provided higher Cr(VI) removal efficiency than the crosslinked plain chitosan beads (the maximum adsorption capacity was 555.56 mg/g and 400.00 mg/g, respectively). Importantly, in relation to environmental protection and sustainable development, all components of the innovative adsorption materials are non-toxic (environmentally safe), the adsorbents enabled efficient decontamination of aqueous solutions containing Cr(VI) exceeding acceptable levels, and they were also effectively used several times after regeneration (in four subsequent cycles of adsorption/desorption), which is important for environmental and economic reasons. Boudouaia et al. [58] synthesized novel adsorption materials (films) containing crosslinked chitosan using terephthaldehyde (TPA) and different crosslinking rates (0%, 0.1%, and 0.2%, respectively) and investigated their properties (swelling, Cr(VI) adsorption, thermodynamic properties) taking into account factors such as salinity and pH of the solution, temperature, and process duration. Their results indicated that the maximum adsorption capacity (60.53 mg/g) was obtained using 0.1% TPA, and this process was favorable, spontaneous, and exothermic. As reported by Cheng et al. [55], the efficiency of the adsorption process is also influenced by the presence of inorganic cations co-existing in the solution. Due to the number and complexity of factors influencing the adsorption of metal and metalloid ions from aqueous solutions, the use of similar chitosan-based adsorbents to remove the same ions, but under different experimental conditions, often leads to significantly different results. Therefore, each time a chitosan-based adsorption material is synthesized with a new crosslinking agent, it is necessary to carefully analyze under what conditions its performance is the best in terms of metal ion removal. Table 1 contains examples of the application of various crosslinked chitosan-based adsorbents (in different forms, i.e., beads, films, hydrogels, and membranes) intended for the removal of metal/metalloid ions or the recovery of precious metal ions (e.g., Au) from aqueous solutions.

Table 1. Examples of the use of various crosslinked chitosan-based adsorbents for the removal of metal and metalloid ions.

| Adsorption Material Used | Metal/ Metalloid Removed | The Main Advantages of the Adsorption Process | Reference/ Year of Publication |
|---|--------------------------------|---|-----------------------------------|
| Glutaraldehyde-crosslinked chitosan beads | Cr(VI) | The maximum adsorption capacity was 28.65 mg/g. | [59], 2021 |
| Glutaraldehyde-crosslinked chitosan beads | Cr(VI) | After 90 min. of adsorption 100% of Cr(VI) has been removed. | [41], 2022 |
| Citrate-crosslinked chitosan salt microspheres | Cr(VI) | The maximum adsorption capacity was 172 mg/g in 30 min. of adsorption. | [42], 2020 |
| Polyamine-co-melamine crosslinked chitosan derivatives, MCS-4N and MCS-5N | Hg(II) | The highest adsorption capacities were 140.3 mg/g and 109.7 mg/g for MCS-4N and MCS-5N, respectively. | [60], 2021 |

Table 1. Cont.

| Adsorption Material Used | Metal/ Metalloid Removed | The Main Advantages of the Adsorption Process | Reference/ Year of Publication |
|--|--------------------------------|--|-----------------------------------|
| Chitosan, glutaraldehyde-crosslinked chitosan (GCS), crosslinked carboxymethyl-chitosan (CMCS) | Ni(II), Cd(II) | The maximum adsorption capacity for Ni(II) was 16.6 mg/g (for CS) and for Ni(II)/Cd(II) were 16.8/6.0 mg/g (for GCS) and 84.9/113.4 mg/g (for CMCS), respectively. | [61], 2019 |
| Glutaraldehyde-crosslinked chitosan with carbonaceous nano material (CS-GO) and with TiO ₂ (CS-TiO ₂) | Pb(II), V(V) | Novel adsorbents were characterized by high mechanical strength and showed excellent adsorption capacity for Pb(II) and V(V). | [62], 2022 |
| Pyridine-2,6-dicarboxylic acid crosslinked chitosan | Cu(II) | The maximum adsorption capacity was 2186 mmol/g, equilibrium was reached within 1 h, adsorption limit/efficiency depended strongly on temperature and pH. | [63], 2020 |
| Formaldehyde crosslinked chitosan–guanythiourea adsorbent (CS-GTU) | Au(III) | The maximum adsorption capacity was 695.63 mg/g, the adsorbent was selective toward Au(III) from multi-metallic solutions and could be efficiently regenerated. | [64], 2021 |
| Nano-titania-crosslinked chitosan beads (TiO ₂ -CS) | Sb(III/V), As(III/V) | The maximum adsorption capacities were 70.19, 25.32, 64.52 and 102.89 mg/g for Sb(III/V) and As(III/V), respectively. | [65], 2023 |
| Iminodiacetic acid crosslinked carboxymethyl chitosan hydrogel | Sr(II) | The maximum adsorption capacity was 144.73 mg/g, the gel showed high mechanical strength and is a promising material for radioactive wastewater treatment. | [66], 2022 |
| Azelaic acid crosslinked chitosan | Cu(II), Ag(I), Au(III) | The adsorbent has superior thermal stability and can be used even under harsh environmental conditions and increased temperatures, adsorption capacities depend on the ions' concentration and type. The maximum percentage of removal of Ag, Cu and Au ions was 40%, 30%, and 70%, respectively. The initial concentration of each metal ions was 1 mg/L. | [67], 2022 |

3.2. Grafted Chitosan-Based Adsorbents

Chemical compounds that are cheaper, more environmentally friendly (e.g., non-toxic and biodegradable), and that would improve the adsorption properties of the designed novel CS-based adsorbents are also being systematically sought for grafting. For example, it was demonstrated that melamine, which contains three amine groups and a triazine ring with lone pair electrons, can be successfully applied for this purpose. A comparison of chitosan and a novel adsorption material containing chitosan grafted with melamine (GMCS, obtained with glutaraldehyde utilized as a crosslinker between CS and melamine) used for the adsorption of Pb(II), Hg(II), Ni(II), Cu(II), Cd(II), and Co(II) ions from aqueous solutions showed that GMCS had a significantly higher selectivity and uptake for the adsorption of lead and mercury ions than CS (in the case of GMCS, the maximum adsorption capacities were 618.2 mg/g for Pb(II) and 490.7 mg/g for Hg(II), at pH 5 and 6, respectively). It was also shown that the adsorption process depends on experimental conditions (e.g., the

presence of other ions, pH, etc.) and that the new adsorbent can be successfully used in five consecutive adsorption/desorption cycles, and its efficiency decreases in the last cycle only by approximately 20%. The GMCS adsorbent's high capacity and efficient regeneration indicate that, potentially in the future, this eco-material can be used on a larger scale to remove lead and mercury metal ions from aqueous solutions [44]. Moreover, in chitosan modification processes, easily accessible and inexpensive substances with well-known chelating properties are increasingly used, such as ethylenediaminetetraacetic acid (EDTA), which contains six binding sites (four carboxyl groups and two tertiary amine groups). For example, Zhuang et al. [68] used EDTA-grafted chitosan (obtained by acylation reaction) to adsorb Co(II) and Sr(II) ions from both single-component systems and multi-component solutions containing various metal ions and reported that adsorption affinity depended on the nature of EDTA fragments used for grafting and the remaining CS fragments. The maximum adsorption capacities were 61.0 mg/g for Co(II) and 8.8 mg/g for Sr(II) in single-component solutions. In a multi-component solution, the following order of removal efficiency was observed: Cd(II), Cu(II), Pb(II) (about 100%) > Co(II) (about 95%) > Ni(II) (about 80%) > Fe(III) > Al(III) > Mg(II), Sr(II) (0%). In addition to its high efficiency, this novel material is characterized by relatively low preparation costs; the adsorption process is also not expensive (it does not require the use of complicated devices or expensive reagents) and is relatively simple and fast. This means that the developed method can be potentially used on a larger scale in the future (e.g., for the removal of metal ions from radioactive wastewater) as an economical solution consistent with sustainable development. Recently, EDTA has been used for grafting of chitin/chitosan, and the obtained biosorbent showed high adsorption efficiency towards Cu(II) (above 99% removal rate, 223.70 mg/g adsorption capacity) and reusability. Thanks to these new chitin-based adsorbents (using crustacean shell wastes) being obtained in facile and green ways, as well as the possibility of their effective use to remove copper ions, this method has great potential for environmental restoration [69]. Due to the increased interest in chitosan-based bio-adsorbents, numerous research results have been published on the utilization of various chemical compounds for grafting CS. Examples of selected grafted chitosan adsorbents and their applications are presented in Table 2.

Table 2. Examples of the application of various grafted chitosan-based adsorbents for the removal of metal/metalloid ions.

| Adsorption Material Used | Metal/ Metalloid Removed | The Main Advantages of the Adsorption Process | Reference/ Year of Publication |
|---|--------------------------------|--|-----------------------------------|
| Aniline-grafted chitosan (A-CS) | Cu(II) | The maximum adsorption capacity was 106.6 mg/g; A-CS can be used repeatedly (in 5 cycles); in aqueous solution, A-CS exhibits fluorescence emissions that undergo quenching in the presence of low levels of Cu(II). | [70], 2020 |
| 5-Hydroxymethyl-furfural-grafted chitosan (HMF-CS) | Ni(II), Hg(II), Ba(II) | The maximum adsorption capacities in optimal experimental conditions were 147 mg/g for Ni(II), 107 mg/g for Hg(II), and 64 mg/g for Ba(II). | [71], 2021 |
| 5-Hydroxymethyl-furfural-grafted chitosan (HMF-CS) modified by cross-linking | Cu(II), Cd(II) | The efficiency of the adsorption process strongly depended on grafting (%), pH, temperature, and contact time; ten reuse cycles were successfully carried out without significant loss of adsorption ability. The removal efficiency of the CS-HMF after 1 and 10 cycles was decreased by 11% and 62% for Cu ²⁺ (from 75 to 66.75%) and Cd ²⁺ (from 96 to 34%) ions, respectively. | [72], 2020 |

Table 2. Cont.

| Adsorption Material Used | Metal/ Metalloid Removed | The Main Advantages of the Adsorption Process | Reference/ Year of Publication |
|---|--------------------------------|--|-----------------------------------|
| Poly(<i>N</i> -vinylimidazole)- grafted chitosan (PNVI-CS) | Hg(II) | The maximum adsorption capacity was 112.35 mg/g. | [73], 2020 |
| 2,5-Dimercaptothiadiazole- grafted chitosan (DMTD-CS) | Hg(II) | The maximum adsorption capacity was 628.09 mg/g; DMTD-CS has very good selectivity for Hg(II) and was effective after six adsorption/desorption cycles (80%). | [74], 2023 |
| 2-Hydroxyethylmethacrylate (HEMA) and 4-sodium styrene sulphate (SSS)-grafted chitosan (HEMA-Co-SSS)-CS and ungrafted CS | As(V) | The maximum adsorption capacity was 16.8 mg/g for (HEMA-Co-SSS)-CS and 1.78 mg/g for CS. | [75], 2021 |
| 2-Hydroxyethylmethacrylate (HEMA) and 4-sodium styrene sulfonate (SSS)-grafted chitosan in a fixed-bed column (HEMA-Co-SSS)-CS | As(V) | The maximum removal of As(V) was about 95%; the maximum reusability of grafted chitosan was 8 cycles. | [76], 2021 |
| Sulfhydryl groups (SH)-grafted chitosan SH-CS | As(III) | Removal efficiency was over 99%; the maximum adsorption capacity was 21.01 mg/g; after regenerating the SH-CS, its efficiency was over 80% (in two subsequent cycles). | [77], 2021 |
| Chitosan grafted by a mixture of itaconic acid, methacrylamide, and bentonite | Pb(II) | The maximum adsorption capacity in optimal conditions was 520 mg/g; the adsorbent has also been successfully used to remove lead ions from industrial effluents. | [78], 2022 |
| Bayberry tannin-grafted chitosan microfibers (BT-CS) | Pb(II) | The adsorption capacity was strongly pH-dependent (e.g., 4.5 mg/g in pH = 2.5; 21.7 mg/g in pH = 5.5); BT-CF was applicable for continues adsorptive removal of Pb(II) at the low concentration of 2.0 mg/L. | [79], 2021 |
| Polypyrrole-grafted chitosan biodegradable copolymer | Cr(VI) | The maximum removal was 98%; the maximum adsorption capability is 128 mg/g; novel adsorbent is environmentally friendly and allows for the removal of negatively charged pollutants from water resources. | [80], 2023 |

Research relating to the possibility of using crosslinked and/or grafted chitosan was mainly related to the possibility of obtaining efficient, selective, and resistant (e.g., to pH changes) adsorption materials with suitable mechanical strength, which are also economical and safe for the environment. In order to obtain novel crosslinked/grafted CS-based materials, various chemical compounds can be used, both those with simple structures (e.g., alanine) and more complex ones (e.g., poly(*N*-vinylimidazole) [70,73]. However, the possibility of using non-toxic substances of natural origin (e.g., tannins) [79] is increasingly being explored to create adsorptive materials that will not pose a threat to the aquatic environment if they are used on a larger scale. An important advantage of (crosslinked/grafted) CS-based adsorbents in the context of sustainable development is the

possibility of their regeneration and repeated use. It has been shown that an appropriate selection of desorption conditions usually enables the reuse of a CS adsorbent, and in many cases, it is possible to carry out several adsorption/desorption cycles without significant loss of adsorption ability [72,74,76]. In the last five years, there has also been an increasing interest in CS-based materials that are characterized by additional, useful properties (apart from the ability to efficiently adsorb metal/metalloid ions), e.g., fluorescence emission, and such materials may potentially be utilized in solutions as new sensing materials. For example, Vafakish and Wilson [70] reported that aniline-grafted chitosan (A-CS) adsorbent has a strong fluorescence emission that undergoes quenching in aqueous solution in the presence of copper(II) ions (linear relation). They found that such properties of A-CS enable quick detection of Cu(II) ions in aqueous solutions, even in small amounts. Therefore, novel A-CS material is not only a good adsorbent for copper(II) ions that can be regenerated and utilized several times, but it can also be used as a responsive material for the detection of Cu(II). Xiong et al. [81] used [2,6-bis-[4-formylthiophene]]-1,3,5,7-tetramethyl-8-phenyl-4,4-difluoroborazaindoloene as a crosslinking agent for the formation of a series of chitosan–fluoroboron dipyrrole–chitosan-based fluorescent hydrogels with large Stokes shifts and reported that such hydrogels can be successfully used for Cu(II) ion detection. Moreover, the properties of these novel materials, such as hydrophilicity, thermal stability, and swelling ability, were better those of the original chitosan used to produce hydrogels. Bejan et al. [82], who utilized luminescent xerogel prepared by chitosan crosslinking with a phenothiazine luminogen to detect and remove fifteen environmentally relevant metals (e.g., Cu(II), Ni(II), Co(II), Mn(II), Hg(II), Cr(III), Eu(III), Cd(II), Na(I), K(I), and Ba(II)), found that this novel material was effective for sensing and adsorption of mercury(II) ions. Additional advantages of the developed material are related to its safety (both chitosan and phenothiazine precursors are non-toxic), as well as to its easy manufacture process (it is possible to produce xerogel foils that show a fast, selective, and sensitive response to Hg(II) ions). As the authors noted, this solution may have great potential for the construction of portable sensors for on-site and real-time Hg(II) detection in the future. As chitosan, due to its properties and availability, is currently one of the most frequently applied functionalizing agents used in various materials, both for the removal of metal and metalloid ions (which constitute a major part of aquatic pollution) and for sensing them, it has been recently called “the miracle biomaterial” [83].

3.3. Chitosan Composites

A group of efficient and durable adsorbents increasingly used to remove metal and metalloid ions from aqueous solutions consists of various types of chitosan composites. Typically, composites are generated to provide an adsorption material with additional beneficial characteristics. For example, Liu et al. [84] formulated a novel biomimetic SiO₂@CS composite that, due to the presence of SiO₂, was characterized by good mechanical strength and stable chemical properties but additionally effectively counteracted agglomeration of the adsorbent. Nanoparticles of chitosan coated on SiO₂, due to the presence of a large number of active sites, enabled the adsorption of metal/metalloid ions. The obtained results show that SiO₂@chitosan composites can be successfully applied for the removal of Hg(II) and As(V) ions with maximum adsorption capacities of about 204 mg/g and 199 mg/g for mercury and arsenic, respectively. Moreover, the adsorption process was very fast, as the removal efficiency reached over 60% within only 2 min. The authors concluded that the SiO₂@chitosan composite has promising potential for drinking water purification. Generally, SiO₂, due to its properties (e.g., uniform pore structure, large specific surface area, and good pore size), is quite often used to produce less or more complex composites containing chitosan intended for metal/metalloid ion removal. For example, Billah et al. [85] compared the effectiveness of chitosan and CS-based composites developed by incorporating silica (CS-Si) and both silica and hydroxyapatite (CS-Si-Hap) towards hexavalent Cr(VI) ions and reported that maximum monolayer adsorption capacities were about 55 mg/g, 64 mg/g, and 213 mg/g for CS, CS-Si, and CS-Si-Hap, respectively. The

developed composites were not only more efficient towards Cr(VI) than chitosan and could be reused for three consecutive regeneration cycles; moreover, they were also effective in the presence of coexisting ions (Cl^- , NO_3^- , and SO_4^{2-}). Chitosan–silica composites can be used not only to remove common metal/metalloid ions but also to adsorb valuable metal ions that are found in small amounts on Earth, such as rhenium. Re, which is one of the least abundant elements, presently plays a key role in the fields of aerospace and defense. As the sources of Re are ores containing other metals (e.g., Mo, Cu, and Pb) and various types of waste (secondary sources), developing an effective technology for obtaining this element is important both in relation to national security, sustainable development, and environmental protection. Adsorption is not only a “green” and efficient technique but also has the potential to recover Re from low- or ultra-low-concentration solutions [86]. Chitosan–silica-based adsorbents intended for Re(VII) recovery are usually efficient, easy to prepare, relatively inexpensive, and can often be used several times. For example, Shan et al. [87] reported that the utilization of sodium silicate as a silica precursor for the sol–gel reaction (one-pot method) allows for the preparation of a mesoporous chitosan–silica composite that exhibits highly efficient adsorption towards Re(VII) ions (206.31 mg/g) and is characterized by good reusability. The results of experiments performed by Cui et al. [88], who prepared functionalized mesoporous chitosan–silica composites (one-pot microwave-assisted synthesis method) and used them for Re(VII) recovery, showed that the maximum adsorption capacity for rhenium ions was very high in the case of this novel material with the optimal composition (261.81 mg/g) and that the outstanding adsorption performance was related to the chelation between $\text{C}=\text{N}$ and ReO_4^- . The possibility of using this composite in eight consecutive cycles (after regeneration) without a significant decrease in its efficiency allows us to assume that this adsorbent may potentially be used in the future for the recovery of Re(VII) from real industrial effluents. Xiong et al. [89] synthesized three-dimensional molybdenum-imprinted chitosan/mesoporous silica composites using a one-step method (with glutaraldehyde and chitosan as crosslinking agents and monomers and tetraethyl orthosilicate as a silicon source) and found that the obtained material has an adsorption capacity towards Re(VII) ions as high as 368.8 mg/g. They used MoO_4^{2-} , which has a similar radius to ReO_4^- , as template ions to overcome the cost problem (the market price of molybdenum is over 20 times lower than the price of rhenium), and showed that the much cheaper template ions can be easily recovered and recycled. Additionally, after applying density functional theory (DFT) to verify the mechanism of Re(VII) ion-binding processes using the synthesized adsorbent, they discovered that three N atoms from the adsorbent were coordinated with three oxygen atoms from ReO_4^- . Based on the examples of these novel chitosan-based composites, it can be concluded that more and more attention is being paid to the development of methods enabling the synthesis of effective adsorbents “in one pot”, and there is also an increasing interest in the possibility of using imprinting technology. Computational chemistry methods (e.g., DFT) that enable the understanding of the mechanisms of binding of particular metal/metalloid ions by specific components of chitosan composites are also playing an increasingly important role. A better understanding of the adsorption mechanism consequently leads to the development of better-performing composites. For example, quantum mechanics calculations have been successfully used, *inter alia*, to explain the adsorption mechanisms of chitosan–vermiculite–lignin ternary composite used for effective removal of uranyl ions [90], to analyze the interactions between chitosan/cellulose composite and Mn(VII) ions [91], or to investigate molecular mechanisms of pyrophosphate-mediated selective adsorption of Ni(II) by polyamine-grafted chitosan–wood flour composite [92].

Much of the research conducted in recent years also concerns the possibility of using nanocomposites to remove various metal/metalloid ions from aqueous solutions. For example, Ahmed et al. [93] synthesized complex composites containing green nano-zerovalent copper (GnZVCu), activated carbon (AC), chitosan, and alginate (ALG) and used GnZVCu/AC–CS–alginate and AC–CS–alginate adsorbents for the removal of Cr(VI) ions from polluted solutions. The ingredients of both nanocomposites were carefully

selected (activated carbon is often used in environmental treatments because of its high surface area, green nZVCu is characterized by special catalytic activity, alginate and chitosan are biopolymers characterized by hydrophilicity and biocompatibility, plus all these components are non-toxic); thus, the obtained adsorbents were extremely mesoporous and enabled a very efficient adsorption of Cr(VI) ions, i.e., 97.5% and 95% for GnZVCu/AC-CS-alginate and AC-CS-alginate, respectively. El Aziz et al. [94] reported that nanocomposites consisting of chitosan grafted by various monomers (e.g., acrylamide, acrylic acid, 4-styrene sulfonic acid) and hybrid nanoparticles of graphene oxide/titanium dioxide nanoparticles (GO@TiO₂-NPs) are efficient adsorbents for both lead(II) ions and basic-red 46 dye (in optimal conditions, the adsorption was about 79% for Pb(II) ions and about 80% for the synthetic dye). The development of adsorption methods enabling simultaneous removal of various contaminants (e.g., metal ions, dyes) from wastewater is important because polluted waters usually have a very complex composition. Recently, Hassan et al. [95] found that the combination of chitosan and CaCO₃ nanoparticles enables the formation of a nanocomposite that is stable, mechanically strong, and characterized by high adsorption efficiency in relation to Cd(II), Cu(II), Pb(II), Zn(II), Cr(III), and Ni(II) ions (98.0%, 94.8%, 99.0%, 97.9%, 97.4%, and 98.3% removal, respectively). Various types of waste are also increasingly used as components of chitosan-based nanocomposites. Such solutions implemented on a larger scale may have a significant positive impact on sustainable development and environmental protection in the future. For example, nanocomposite beads prepared by using chitosan and paper sludge, which contains a lot of fiber and inorganic salts, used for the removal of Cu(II) and Cr(III) ions from wastewater enabled efficient adsorption of these pollutants (adsorption capacity of 114.6 mg/g for copper and 110.3 mg/g for chromium ions). Moreover, it has been shown that this cheap and easily available sludge–chitosan material has good regenerative properties [96]. Also, chitosan–carbon nanocomposites containing carbon nanoparticles (C-NPs) resulting from the treatment of agricultural wastes turned out to be much more efficient adsorbents than CS in the process of removing various metal ions (e.g., Cr, Cu, Zn, Ni, Cd, and Pb) from aqueous solutions [97].

An important group of adsorbents are magnetic chitosan composites (MCSC), consisting of magnetic particles dispersed in a chitosan polymer matrix. In general, they are characterized by great versatility, and their significant advantages, apart from their usually high efficiency, are the possibility to easily separate them from the aqueous environment by using an external magnetic field and the possibility of their repeated use after regeneration [98]. However, it should be emphasized that the composition of chitosan-based magnetic composites intended for the removal of specific metal ions may be significantly different. For example, chitosan matrix embedding magnetite/maghemite was developed for the removal of Cu(II), Pb(II), and Ni(II) ions [98], magnetic rectorite/humic acid/chitosan composite was used to remove Cu(II), Cd(II), and Pb(II) ions [99], and a composite containing magnetic chitosan (with Fe₃O₄ as the core and glutaric dialdehyde as the crosslinking agent) and bismuth tungstate coated by silver (MCS-Ag/Bi₂WO₆) was utilized for enhanced adsorption/photocatalytic removal of Cu(II) ions from wastewater [100]. The last example shows that not only new complex composites based on chitosan are being developed, but also modifications are being introduced to the adsorption process to increase efficiency, e.g., the application of photo-assisted adsorption. An important group of chitosan-based adsorbents are metal-modified CS materials (e.g., Pb(II)-modified chitosan), which are usually characterized by efficient metal ion adsorption capacity, selectivity, and the possibility of reuse [101].

In conclusion, the field related to the designing and use of chitosan-based adsorbents for the removal of metal and metalloid ions from aqueous solutions is developing dynamically due to, among others, the possibility of various modifications of synthesis and functionalization of CS (e.g., through physical, chemical, and biological methods), the possibility of forming chitosan adsorbents in various forms (e.g., powder, fibers, films, composites, beads, hydrogels, etc.), and different mechanisms of adsorption processes for specific metal ions (e.g., chelation, electrostatic interaction, ionic exchange, etc.) [102]. All

this means that attempts are being made to design “tailor-made” adsorbents, i.e., intended to remove specific metal ions under specific conditions. However, such research is usually time-consuming and labor-intensive, as it is necessary to consider many different factors. Research is also undertaken to produce efficient and stable chitosan-based adsorbents containing non-toxic ingredients derived from various types of waste, which may have a significant impact in the future on both sustainable development and environmental protection.

4. Removal of Pharmaceuticals from Aqueous Solutions by Adsorbents Based on Chitosan

As pharmaceuticals are usually not completely removed or degraded in wastewater plants, they exit the plants with the treated wastewater, then find their way to ponds, rivers, and lakes, and eventually get into potable water. The group of pharmaceuticals contains, among others, human drugs, such as, for example, non-steroidal anti-inflammatory drugs, antibiotics, painkillers, psychotropic medicines, anticonvulsant medicines, β -blockers, hormones, etc., and veterinary drugs, which, after use, are excreted from the animal's body in their original or derived form and then, via various routes, get into the water [103]. The main source of ground and surface water pollution by pharmaceuticals is municipal, hospital, and process wastewater. Moreover, wastewater sludge containing such pollutants applied to agricultural land causes soil contamination, additionally influencing the purity of groundwater and surface water [104].

Typically, wastewater and drinking water treatment processes are not designed mainly to focus on reducing or eliminating pharmaceuticals. Advanced wastewater treatment processes can provide high removal rates for pharmaceutical compounds, but most of them involve high costs and generate undesirable by-products. However, among the purification methods used, the adsorption processes seem to be a promising cost-effective technique suitable for the effective removal of these environmentally hazardous substances [105]. Chitosan-based adsorbents have shown many advantageous properties, such as, for example, high adsorption efficiency, low swelling, and high stability over a wide temperature and pH range; therefore, they have recently been widely used to remove various pharmaceuticals from wastewater [103]. Due to the possibility of various modifications of chitosan (obtained from different sources), the number of developed CS-based adsorbents intended for the removal of certain pharmaceuticals from aqueous solutions is impressive. Tables 3 and 4 show examples of the application of various CS adsorption materials for the removal of different pharmaceuticals.

To remove pharmaceuticals, such as antibiotics and non-steroidal anti-inflammatory drugs, from aqueous solutions, and wastewater chitosan or chitosan-based adsorbents can be used. For example, pure chitosan was used by Sharin et al. to remove rifampicin, streptomycin, and ibuprofen from wastewater. Chitosan was synthesized by deacetylation of chitin isolated from mud crab shells. The adsorption capacity of RIF, STM, and IBU onto chitosan was 66.91 mg/g, 11.00 mg/g, and 24.21 mg/g, respectively. The results show that after the adsorption process, the molecular structure of chitosan was not altered, i.e., the pharmaceuticals adsorbed onto the biopolymer by dipole-dipole intermolecular force interaction via hydrogen bonding [106].

Table 3. Examples of the application of chitosan-based adsorbents intended for removal of non-steroidal anti-inflammatory drugs and antibiotics.

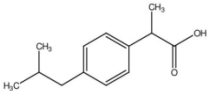
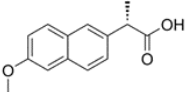
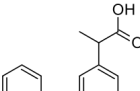
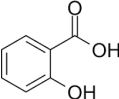
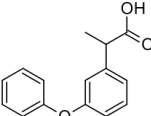
| Non-Steroidal Anti-Inflammatory Drugs | | | | | |
|--|--------------------------|---|----------------------------|--|-------------------------------|
| Drug | Adsorbent | Preparation of Adsorbent | Adsorption Capacity [mg/g] | Additional Information | Reference/Year of Publication |
|  Ibuprofen (IBP) | CS | Deacetylation of chitin, which was isolated from mud-crab shells | 24.21 | The IBP was adsorbed as a multilayer on the chitosan surface. | [106], 2023 |
| | GC/MGO-SO ₃ H | The chitosan/graphene oxide-SO ₃ H composite adsorbent was cross-linked with genipin | 138.16 | The removal of IBP increased as solution pH values increased from 2 to 6. At pH levels higher than 6, IBP became negative, resulting in a decrease in q_e for IBP. | [107], 2019 |
| | CS/Fe/MIP | The chemical synthesis of chitosan with ibuprofen-imprinted monoliths (MIP) and microparticles (MIPmp) | 79.41 | The adsorption process was through adsorbent-ibuprofen interactions in functional groups of chitosan, iron(III) hydroxide, and cavities of polymers adapted to IBP molecules. | [108], 2023 |
| | CGC-MOF200 | The aerogel was synthesized by direct mixing of components and then freeze-drying | 5.96 | CGC-MOF200 aerogel could be used after five adsorption-desorption cycles (56.17% and 68.24% removal of IBP and NPX, respectively); the decrease in its effectiveness resulted from the loss of the material during successive regeneration cycles. | [109], 2023 |
|  Naproxen (NPX) | CGC-MOF200 | The aerogel was synthesized by direct mixing and then freeze-drying | 7.07 | | |
|  Diclofenac (DCF) | PVA/CS nanofibers | The solution used to produce nanofibers (spray base electrospinning) was obtained in a volume ratio of PVA to CS of 70:30 | 1666.6 | The removal efficiency of the PVA/CS nanofibers was decreased by 8–10% for all cycles, and after three cycles was very poor. | [110], 2022 |
| | GO-CS | Mechanical mixing method without any heat treatment and usage of chemical crosslinkers | 1250 | | |
| | AGO-CS | | 58.21 | The adsorbents can be reused in three consecutive cycles; in the third cycle, hydrogel was partially destroyed. | [111], 2021 |
|  Salicylic acid (SA) | PVA/CS nanofibers | The solution used to produce nanofibers (spray base electrospinning) was obtained in a volume ratio of PVA to CS of 70:30 | 27.85 | | [110], 2022 |
|  Fenopropfen (FPF) | | | 166.6 | | |

Table 3. Cont.

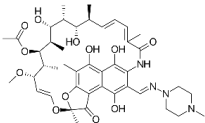
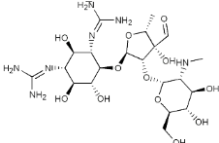
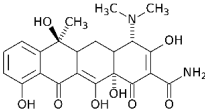
| Non-Steroidal Anti-Inflammatory Drugs | | | | | |
|---|------------------------------------|---|----------------------------|---|--------------------------------|
| Drug | Adsorbent | Preparation of Adsorbent | Adsorption Capacity [mg/g] | Additional Information | Reference/ Year of Publication |
| Antibiotics | | | | | |
|  Rifampicin (RIF) | CS | Deacetylation of chitin, which was isolated from mud-crab shells | 66.91 | The RIF was homogeneously adsorbed as a monolayer on the chitosan surface. | [106], 2023 |
|  Streptomycin (STM) | | Deacetylation of chitin, which was isolated from mud-crab shells | 11.00 | The STM was adsorbed as a monolayer on the chitosan surface. | |
|  tetracycline (TC) | GC/MGO-SO ₃ H | Genipin-crosslinked chitosan | 556.28 | The maximum sorption capacity (q _e) for TC was obtained at pH 10. Increasing the pH caused a gradual increase of GC/MGO-SO ₃ H q _e and led to GO surface functional groups becoming negatively charged. | [107], 2019 |
| | CTM@Fe ₃ O ₄ | The chemical synthesis of magnetic nanocomposite using chitosan, thiobarbituric acid, malondialdehyde, and Fe ₃ O ₄ nanoparticles | 215.31 | The nanocomposite can be used repeatedly in 6 cycles of adsorption–desorption processes. | [112], 2020 |

Table 4. Examples of the application of chitosan-based adsorbents intended for the removal of selected psychotropic medicines, anticonvulsant medicines, β -blockers, and hormones.

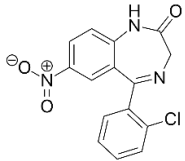
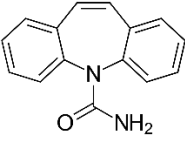
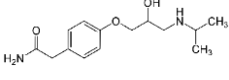
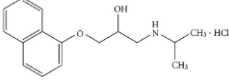
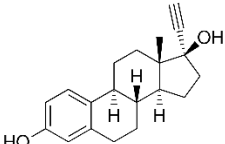
| Psychotropic Medicines | | | | | |
|--|------------|---|----------------------------|--|-------------------------------|
| Drug | Adsorbent | Preparation of Adsorbent | Adsorption Capacity [mg/g] | Additional Information | Reference/Year of Publication |
|  Clonazepam (CZP) | CS-3TiCN | The synthesis of the TiNT nanoparticles was carried out by hydrothermal reaction. | 3.31 | Adsorption percentages of CZP for the CS-3TiCN powders and CS-3TiCN coating after four reuse cycles have decreased by approx. 16 and 3%, respectively. | [113], 2023 |
| Anticonvulsant medicines | | | | | |
|  Carbamazepine (CBZ) | CXL-CS-ZEO | The fixed-bed column | 41.24 | The cross-linked chitosan/zeolite could be applied for at least seven cycles with high removal efficiency. | [114], 2019 |
| | MC-CS | A magnetic cellulose–chitosan gel mixture was added dropwise to the precipitation bath to form beads. | 291 | The magnetic cellulose–chitosan could be reused for 10 cycles to remove CBZ ($q_e > 250$ mg/g). | [115], 2021 |
| β -blockers | | | | | |
|  Atenolol (ATN) | MC-CS | A magnetic cellulose–chitosan gel mixture was added dropwise to the precipitation bath to form beads. | 340 | The MC-CS could be reused for 10 cycles to remove ATN ($q_e > 150$ mg/g). | [115], 2021 |
|  Propranolol hydrochloride (PRP) | | | 308 | The MC-CS could be reused for 10 cycles to remove PRP ($q_e > 200$ mg/g). | |

Table 4. Cont.

| Psychotropic Medicines | | | | | |
|--|-----------|--|----------------------------|---|-------------------------------|
| Drug | Adsorbent | Preparation of Adsorbent | Adsorption Capacity [mg/g] | Additional Information | Reference/Year of Publication |
| Hormones | | | | | |
|  Ethinylestradiol (EE) | CS-n | Commercial chitosan nanoparticles with a purity of >98%, molecular weight of 150–300 kDa, and deacetylation percentage of >85% were used | 5.79 | The removal efficiency of EE was 98.34% and 74.81% after 1 and 10 cycles, respectively. | [116], 2023 |

Modified CS has been utilized, for example, by Liu et al. [107], who used a genipin-crosslinked chitosan/graphene oxide-SO₃H (GC/MGO-SO₃H) magnetic composite as an adsorbent for the removal of pharmaceutical contaminants, namely ibuprofen and tetracycline. They found that the GC/MGO-SO₃H composite could be an efficient adsorbent for these drugs. The adsorption capacities depended on the process temperature and increased from 113.27 to 138.16 mg/g for ibuprofen and from 473.25 to 556.28 mg/g for tetracycline with the increase in temperature from 298 to 313 K. Moreover, it was reported that tetracycline can be removed by a magnetic nanocomposite that contains chitosan, thiobarbituric acid, malondialdehyde, and Fe₃O₄ nanoparticles (CTM@Fe₃O₄). The highest adsorption capacity of 215.31 mg/g was achieved using a 0.05 g adsorbent dose and 60 mg/L of TC. The results show that CTM@Fe₃O₄ nanocomposite is an efficient superparamagnetic adsorbent. Its superparamagnetic properties enabled the recovery of adsorbent from an aqueous solution using an external magnet in successful industrial applications [112]. In a different study, Stachowiak et al. prepared composite chitosan/molecularly imprinted polymer hydrogel beads doped with iron(III) hydroxide (CS/Fe/MIP) to selectively eliminate ibuprofen from aqueous solutions. The maximum adsorption capacity, i.e., 79.41 mg/g, was obtained for beads containing monoliths printed with ibuprofen, while for chitosan beads without polymers, it was 39.42 mg/g. The adsorption of ibuprofen molecules was probably caused by the interactions between them and the imprinted cavities, chitosan functional groups, and iron hydroxide [108]. It was also reported that for the removal of ibuprofen and naproxen, a thermally activated gelatin–chitosan and amine-functionalized metal–organic framework (UiO-66-NH₂) aerogel (CGC-MOF) can be used as an adsorbent. The maximum theoretical adsorption capacity was 5.96 mg/g for IBP and 7.07 mg/g for NPX, and the removal efficiency for IBP and NPX was 99.28% and 96.39%, respectively [109]. In another study, synthesized nanofibers from a blend of chitosan and poly(vinyl alcohol) (PVA) were used to remove acidic drugs such as acetylsalicylic acid, naproxen, fenopropfen, and diclofenac from wastewater. Before using the prepared PVA/CS nanofibers for the adsorption of drugs from water systems, they were crosslinked using thermal treatment to reduce their solubility in water. Using ultrapure water, the maximum adsorption capacity was calculated with the Langmuir isotherm to be 27.85, 1666.66, 166.6, and 1250 mg/g for acetylsalicylic acid, naproxen, fenopropfen, and diclofenac, respectively [110]. To remove diclofenac from water, Mahmoodi et al. [111] utilized hydrogel adsorbents prepared on the basis of graphene oxide–chitosan (GO-CS) and amino graphene oxide–chitosan (AGO-CS) using mechanical stirring. Based on these experiments, it was found that the optimum GO-to-CS mass ratio was 2:5, and the same ratio was used for AGO and CS to assess the influence of amino functionalization on the effectiveness of DCF removal. For the optimum parameters of adsorption, i.e., pH = 5, 100 ppm of DCF, and an adsorbent dose of 1.5 g/L, 90.42% and 97.06% of DCF were removed with GO-CS and AGO-CS, respectively. It was found that the adsorption was more spontaneous with AGO-CS hydrogels, and the tested adsorbent was effective in three sorption cycles.

Additionally, other pharmaceuticals such as psychotropic drugs, anticonvulsant medicines, beta-blockers, and hormones can be removed using chitosan-based adsorbents (Table 4).

In the case of some pharmaceuticals, it is necessary to use a combination of various methods (including adsorption) or complex adsorbents to effectively remove them from aqueous solutions. For example, clonazepam can be removed by an adsorption/photocatalysis-conjugated method using H₂TiO₇ (TiNT) nanotubes functionalized with 1 (1TiCN), 5 (2TiCN), or 10 (3TiCN) wt.% of chitosan. The obtained results show that 2TiCN in powder form (83.3%) had better adsorption efficiency than immobilized nanotubes of 2TiCN (80.79%). It was determined that the main oxidizing substances were OH[•] ions and that the surface area of 2TiCN (168.6 m²/g) was two times bigger than that of TiNT. On the other hand, the 3TiCN sample (CS-3TiCN) with the highest chitosan content showed the highest adsorption capacity ($q_e = 3.12$ mg/g) after 180 min of the process in comparison to the TiNT sample ($q_e = 1.46$ mg/g) [113]. Vakili et al. [114] used a crosslinked chitosan/zeolite (CXL-

CS/ZEO) as a fixed-bed column for carbamazepine removal from an aqueous solution. They removed approximately 1.4724 mg/L (i.e., 90.0%) of CBZ at pH 5.1 when the initial concentration of CXL-CS/ZEO was 1.636 mg/L. To optimize the drug removal, an artificial neural network (ANN) was used. In a different study, it was reported that a magnetic cellulose–chitosan (MC–CS) nanocomposite (containing $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ and $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$) can be an effective adsorbent for the removal of two β -blockers, atenolol and propranolol, and an anticonvulsant medicine—carbamazepine. At pH 7.0, the maximum adsorption capacity was 308 mg/g for propranolol hydrochloride, 340 mg/g for atenolol, and 291 mg/g for carbamazepine, respectively. The percentage removal of ATN, PRP, and CBZ was from 85 to 98%. Additionally, it was reported that the hydrogel can be used even ten times, retaining the removal effectivity of over 80% [115]. In another study, to remove ethinylestradiol (EE) as an exemplary estrogen from an aqueous solution, chitosan nanoparticles (CS-n) were used. It was found that optimum conditions for the removal of EE (92.50%) onto chitosan nanoparticles were 1.45 g/L of adsorbent and an initial concentration of estrogen of 5.7 mg/L, with the process being conducted for 220 min at pH 7.3 [116].

Due to the diverse properties of substances belonging to the group of pharmaceuticals, their removal from aqueous solutions is usually not easy and requires not only the proper design and preparation of CS-based adsorbents but also a thorough examination of the optimal conditions for the adsorption processes. It is also important to analyze and understand the mechanisms of the adsorption processes (in the case of removing different compounds, they may differ significantly), as this allows for a better selection of adsorbent components and the determination of optimal experimental conditions, consequently obtaining better-performing adsorbents. Due to the threat posed by pharmaceuticals and their transformation products to the natural environment and the effectiveness of chitosan-based adsorbents in removing these pollutants, it can be assumed that there will continue to be a search for materials that are even better suited for this purpose that are more environmentally friendly, cheaper, and suitable for repeated use after regeneration.

5. Removal of Dyes by Adsorbents Based on Chitosan

Dyes are complex organic compounds, usually soluble in water and oil, that selectively absorb electromagnetic radiation in the visible range. In the textile industry, there are three main groups of utilized dyes: acid, basic, and reactive. The basic dyes, otherwise known as cationic dyes (i.e., they are positively charged), make the color more bright and vivid. Whereas the acid dyes, or anionic dyes, produce bright and vivid colors. They have a negative charge on their molecules and may bind with fabric fibers in an acidic environment [117]. In neutral to alkaline conditions, reactive dyes (which are generally bright and durable) can form covalent bonds with hydroxyl groups on cellulose fibers and protein fibers, as well as with amino groups on polyamide fibers, combining into one whole “dye-fiber” entity [118]. Reactive dyes have an anionic character, and since cotton fibers have an anionic surface charge in water, there is an electrostatic repulsion between them, which consequently results in a limited dye exhaustion. To overcome this problem, large quantities of electrolyte are added [119].

Various textile dyes introduced into the environment significantly deteriorate water and soil quality. Some of them may increase biochemical and chemical oxygen demand, inhibit plant growth, enter the food chain, cause resistance and bioaccumulation, and promote toxicity, mutagenicity, and carcinogenicity. Due to the threat posed by many synthetic dyes and the dynamic development of the textile industry around the world, the development of water treatment strategies allowing for the effective removal of these pollutants is extremely important in order to ensure the sustainability of the environment [120]. Among the methods currently used for the removal of various dyes from aqueous solutions, adsorption methods based on the use of adsorbents containing chitosan or its derivatives are attracting increasingly more attention. Various CS-based adsorbents enable the removal of certain cationic dyes, such as, *inter alia*, methylene blue (MB), crystal violet (CR), brilliant green (BG), and rhodamine B (RhB), which are commonly used. For example, Jyothi et al. [121]

prepared MnFe_2O_4 -impregnated chitosan microspheres (CMMS) as an adsorbent for the removal of methylene blue from an aqueous solution. They found that the adsorption capacity of the novel adsorbent increased with the increase in the initial concentration of MB, which created a higher driving force for the MB solution to overcome the mass transfer resistance that existed between the water phase and the adsorbent. At first, the dye molecules present in the aqueous solution move to the exterior surface of the CMMS and then into the pores of this surface. Due to the availability of excess active sites on the investigated biopolymer, a higher percentage removal of MB was observed at the initial stages of the adsorption process. Then it remained at a constant level, which was caused by a smaller number of active sites available (constant adsorbent dose). The maximum adsorption capacity of CMMS was 85.25 and 371.7 mg/g for the initial MB concentration of 671.36 and 3235.9 mmol/L, respectively [121]. Kaoul et al. [122] prepared a self-assembled nanocomposite by incorporating graphene oxide (GO) nanosheets into the polymer network of carboxymethyl cellulose (CMC) and chitosan (CMC-GO-CS). The synthesis did not use any initiator or crosslinker systems. The nanocomposite was used for the removal of selected cationic dyes (MB and BG) from wastewater. The highest percentage removal was 97.9% for brilliant green and 100% for methylene blue in 7 h or 1.5 h during the adsorption process, respectively. Moreover, to eliminate MB and methyl orange (MO) from wastewater, it is possible to use a β -cyclodextrin–chitosan-based crosslinked (NTA- β -CD-CS) adsorbent. The maximum adsorption capacities for MB and MO were 162.6 and 132.5 mg/g, respectively. It was found that the adsorption of MB occurred through the host–guest inclusion due to MB being surrounded by β -CD cavities, while MO was adsorbed by the other functional groups, i.e., hydroxyl, carboxyl, and amino, groups (i.e., adsorption active sites for MO) [123]. Another cationic dye, rhodamine B, can be removed from aqueous solutions using chitosan-derived Schiff base (CS-SB). A condensation reaction was used to prepare chitosan modified with 2,3-dihydroxybenzaldehyde, which was utilized to remove RhB from aqueous solutions. It was found that percentage extraction depended on the pH of the solution and the adsorbent dose. By increasing the pH of the solution from 3 to 10 and the adsorbent dose from 0.2 to 2 g/L, a higher percentage removal of the dye was achieved. The maximum adsorption capacity of RhB was 233.4 mg/g at pH 8 and 298 K [124]. In another study, a magnetized adsorbent (magsorbent) of chitosan-based polypyrrole (MCS/Ppy) was used to remove cationic dyes, such as crystal violet, as well as anionic dyes, e.g., methyl orange, from wastewater. The maximum percentage removal of CV and MO was 88.11% at pH 8 and 92.89% at pH 4, respectively. At 303 K, the maximum sorption capacity of MCS/Ppy composite was 62.893 for CV and 89.286 mg/g for MO. The MCS/Ppy adsorbent can be reused efficiently in three consecutive adsorption and desorption cycles [125]. The ability to regenerate the adsorption material and the possibility of its repeated use after regeneration without a significant drop in efficiency are important advantages, both for economic reasons and in the context of sustainable development.

Huo et al. [126] reported that effective elimination of anionic dyes, e.g., MO, from aqueous solutions can be achieved by the application of cellulose nanofiber/chitosan (CNF/CS) composite films. The prepared composite films had low swelling and acid-proof properties; thus, it was possible to reduce the risk of adsorbent destruction after the adsorption process. Strong hydrogen bonding and good compatibility between cellulose nanofiber and chitosan confer a water-resistant structure to the prepared films. The maximum adsorption capacity of methylene orange onto CNF/CS film was 655.23 mg/g. In a different experiment, a glutaraldehyde-crosslinked chitosan support and catalysts obtained after loading Ag metal on chitosan (Ag/CS) were prepared and used for the adsorption and elimination of phenol red dye in an aqueous solution. The catalytic reduction and adsorption of phenol red dye onto Ag/chitosan and crosslinked chitosan were carried out under ambient conditions. The reduction of phenol red (PR) was conducted with sodium borohydride (NaBH_4) as the reducing agent. It was found that PR reduction depended on the amount of catalyst, concentration of NaBH_4 , Ag metal loading, reaction temperature, PR concentration, and initial pH of the dye solution. The use of solutions with an almost neutral pH (6.4) allowed

for efficient dye adsorption, while the utilization of acid ($\text{pH} = 4$) and basic ($\text{pH} = 8, 11$, and 13.8) solutions exhibited incomplete or no dye adsorption [127]. Khushbu and Jindal [128] prepared an amphoteric adsorbent based on chitosan and sodium alginate (ALG) nanocomposite modified with graphene oxide and bentonite (BN) with both positive and negative charges, which were used for the removal of a cationic dye, methylene blue, and an anionic dye, xylenol orange (XO). With a 0.5 g dose of adsorbent and at a neutral pH , the maximum adsorption capacity of XO onto CS/ALG/GO nanocomposite was 85% , whereas onto CS/ALG/BN it was 93% . For MB, the removal onto CS/ALG/GO and CS/ALG/BN nanocomposite was 91% and 96% , respectively. The maximum adsorption capacity was observed on the CS/ALG/BN nanocomposite; for MB, it was 0.731 mg/g , and for XO, it was 0.195 mg/g . Importantly, the adsorbent used was not only efficient but also contained non-toxic, environmentally safe ingredients, which is also important for environmental protection [127]. Moreover, Congo Red (CR) can be removed from aqueous solutions using chitosan modified by activated charcoal (AC). The highest adsorption capacity of CS-AC for Congo Red was 5.99 mg/g [129]. The synergistic effect of activated carbon and chitosan consists of increasing the pore volume and surface area of the adsorbent, which results in an increase in adsorption capacity [130]. The synergic effect of active carbon and chitosan was also used to remove cationic dyes, e.g., thionine (TH). The thionine was removed by the chitosan-activated charcoal (CS-AC) composite, obtaining the maximum adsorption capacity of 56.7 mg/g at 303 K . The adsorption probably occurred as a result of electrostatic interactions, hydrogen bonding, and π - π interactions [131]. Moreover, Jawad et al. also used different CS-based adsorbents to remove TH, i.e., the mesoporous crosslinked chitosan-epichlorohydrin/activated charcoal composite (CS-ECH/AC). The maximum adsorption capacity of TH in the case of the application of CS-ECH/AC was 60.9 mg/g at 303 K [132].

Another example of the utilization of CS-based adsorbents for dye removal is the application of Schiff base-crosslinked chitosan-glutaraldehyde (CS-GLA) modified with 25% and 50% TiO_2 nanoparticles for the adsorption of reactive red 120 dye (RR120). It has been shown that CS-GLA/TNC-25 exhibited better adsorptive properties for RR120 dye in an aqueous solution than CS-GLA and CS-GLA/TNC-50, probably due to the excellent balance between the surface area and the available amino groups (NH_2) in the composite. The maximum adsorption capacity of CS-GLA/TNC-25 for RR120 dye was 103.1 mg/g at 303 K [133]. Regarding RR120, there was also an experiment in which a zwitterion composite adsorbent of chitosan-epichlorohydrin/zeolite (CS-ECH/ZL) was used to remove two types of dyes: one cationic dye, MB, and one anionic reactive dye, RR120, from an aqueous solution. The highest adsorption capacities of CS-ECH/ZL were 156.1 and 284.2 mg/g for MB and RR120, respectively, at temperatures from 303 to 323 K and $\text{pH} = 4$ – 10 , with the dose of the adsorbent in the ranges of 0.02 to 0.5 g . The mechanism of investigated dye adsorption onto the CS-ECH/ZL indicates various types of interactions: electrostatic interaction, hydrogen bonding, and Yoshida H-bonding, in addition to n - π interaction [134]. Karmaker et al. [135] used chitosan 8B (80% deacetylated chitin) to remove reactive red 239 dye (RR239) from an aqueous solution. The maximum adsorption capacity of RR239 onto chitosan 8B (CS-8B) was $163.93 \text{ }\mu\text{mol/g}$ at $45 \text{ }^\circ\text{C}$. RR239 was bound by chitosan 8B via surface sorption and intraparticle diffusion. It was found that dye adsorption onto chitosan 8B was spontaneous and endothermic. Additionally, it has been shown that the desorption process can be successfully carried out in a NaOH solution. Jaafari et al. [136] synthesized magnetic chitosan (MC) with $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ and $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ (magnetic compounds) and used it to eliminate two reactive dyes, reactive red 141 (RR141) and reactive yellow 14 (RY14), from water solutions. Under optimum conditions, the maximum adsorption capacity of RR141 onto the MC adsorbent was 98.8 mg/g and the adsorption efficiency was 99.2% , while the removal of RY14 was 92.7% and its highest adsorption capacity was 89.7 mg/g . Moreover, magnetic chitosan-polyvinyl alcohol (m-CS-PVA) was used as an effective bio-adsorbent to remove reactive orange 16 (RO16) from aqueous solutions. The adsorption process was described using Box-Behnken Design (BBD)

surface methodology, and with a statistical method (ANOVA), it was shown that there were significant interactions between the adsorbent dose and the dye at the solution pH and process temperature. In this context, the highest percentage removal of RO16 (90.3%) was observed with chitosan–poly(vinyl alcohol)/fly ash (m-CS–PVA/FA) adsorbent dose of 0.06 g at 30 °C and pH 4 with a contact time of 17.5 min. $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ and $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ were responsible for the magnetic properties of m-CS–PVA/FA. The highest adsorption capacity of RO16 was 123.8 mg/g at 30 °C. The tested adsorbent can be recovered using a magnetic field [137]. In another study, a multi-functional adsorbent based on chitosan with nanosized MgO (CS/MgO) was used as an effective adsorbent to remove reactive blue 19 dye (RB19). The maximum adsorption capacity of CS/MgO was 512.82 mg/g at 38 °C, and the minimum adsorption capacity was 408.16 mg/g at 18 °C. The optimum contact time of RB19 with CS/MgO was 120 min, and the adsorption was endothermic and spontaneous [138]. RB19 was also successfully removed by Mohamadi et al. [139], who used composite chitosan–graphene oxide (CS–GO). The maximum percentage removal of RB19 from a water solution during a 60 min adsorption process was 99% (pH = 4, 20 mg/L of RB19, and 1 g/L dose of the adsorbent). As the presented results show, recently various types of CS-based composites (including magnetic composites) were successfully used to remove different dyes from aqueous solutions and wastewater. However, as shown in many reports, the adsorption processes also depend to a large extent on the conditions of the experiments (e.g., the concentration of the dye in the solution, temperature, pH, process duration, etc.). Table 5 presents information summarizing achievements related to the application of chitosan-based adsorbents intended for the removal of selected dyes (cationic, anionic and reactive).

In conclusion, currently, increased textile production produces huge amounts of industrial wastewater, which contains various types of dyes dissolved therein. Therefore, textile wastewater purification is necessary and must be done in a stringent and cost-effective way to ensure sustainable development of the industry and the environment [140]. Based on the conducted analysis of the literature from the last 5 years, it was found that bio-adsorbents based on chitosan were not only selective but also effective in the removal of various types of dyes from water and wastewater. Moreover, these materials are very well in line with “green chemistry”, according to which it is not enough to remove pollutants from water and wastewater—it should be conducted with natural, non-toxic, and environmentally friendly separation methods. Green chemistry should be treated as one of the strategies aimed at reducing threats to the natural environment.

Table 5. Examples of the application of chitosan-based adsorbents intended for the removal of selected dyes (cationic, anionic, and reactive dyes).

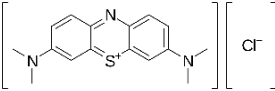
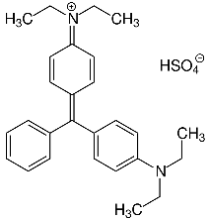
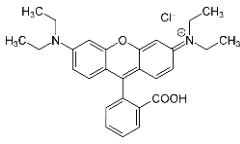
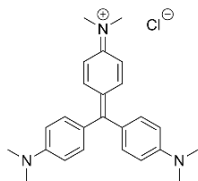
| Cationic Dyes | | | | |
|--|-------------|--------------------|--|-------------------------------|
| Dyes | Adsorbent | Removal Efficiency | Additional Information | Reference/Year of Publication |
|  MB | CMMS | 371.7 mg/g | CMMS can be applied in the adsorption process, followed by magnetic separation and regeneration. CMMS can be reused. | [121], 2019 |
| | CMC-GO-CS | 122.1 mg/g | The adsorption capacity after five reuse cycles declined to 63.3% from 100%. | [122], 2019 |
| | NTA-β-CD-CS | 162.6 mg/g | NTA-β-CD-CS can be reused after four adsorption–desorption cycles. | [123], 2021 |
| | CS/ALG/GO | 91% | The removal efficiency of MB was 90% and 45.6% after 1 and 5 cycles, respectively. | [128], 2023 |
| | CS/ALG/BN | 0.731 /g (96%) | The removal efficiency of MB was 93% and 44.53% after 1 and 6 cycles, respectively. | |
| | CS-ECH/ZL | 156.1 mg/g | The percentage removal raises from 3.3% to 88.1% with the increase in the quantity of the CS-ECH/ZL dosage from 0.02 g to 0.2 g. | [134], 2020 |
|  GB | CMC-GO-CS | 1.8975 g | The adsorption capacity after five reuse cycles declined to 65.7% from 97.9%. | [122], 2019 |
|  RhB | CS-SB | 233.4 mg/g | The maximum dosage of adsorbent was 50 mg (removal efficiency was about 80%). | [124], 2021 |
|  CV | MCS/Ppy | 88.89 mg/g | The removal efficiency of CV was 62.36% and 61.60% after 1 and 3 cycles, respectively. | [125], 2020 |

Table 5. Cont.

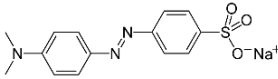
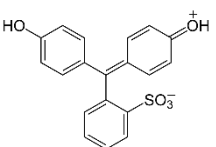
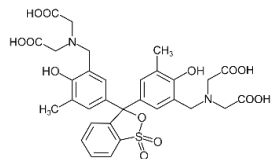
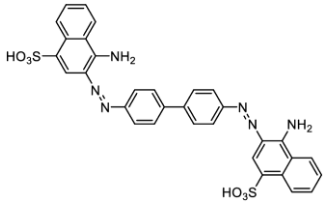
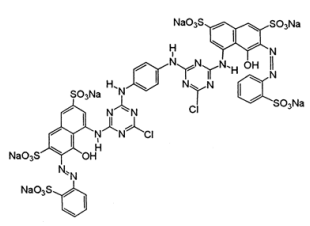
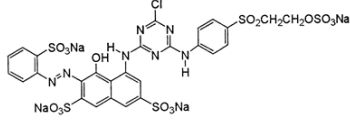
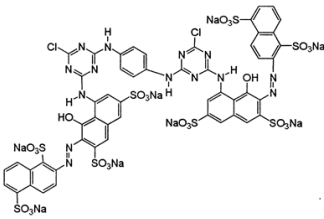
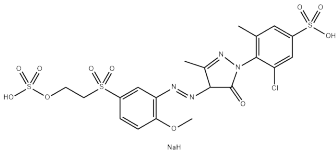
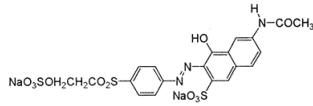
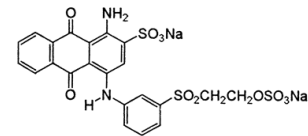
| Anionic Dyes | | | | |
|--|---------------|------------------|--|-------------|
|  MO | NTA-β-CD-CS | 132.5 mg/g | The NTA-β-CD-CS can be used in the four cycles of adsorption–desorption processes. | [123], 2021 |
| | MCS/Ppy | 92.89 mg/g | The removal efficiency of MO was 69.02% and 54.42% after 1 and 3 cycles, respectively. | [125], 2020 |
|  PR | CNF/CS | 655.23 mg/g | The removal efficiency of PR was 96.50% and 89.65% after 1 and 6 cycles, respectively. | [126], 2021 |
| | Ag/CS | - | The 6.7 wt.% Ag/chitosan catalyst was recycled five times, showed identical activity, and no losses of Ag metal were observed. | [127], 2023 |
|  XO | CS/ALG/GO | 85% | The removal efficiency of XO was 81% and 46.76% after 1 and 3 cycles, respectively. | [128], 2023 |
| | CS/ALG/BN | 0.195 mg/g (93%) | The removal efficiency of XO was 85% and 50.3% after 1 and 4 cycles, respectively. | |
|  CR | CS-AC | 5.99 mg/g | The CS-AC composite can be used as an economical adsorbent for the removal of 75–80% CR from wastewater. | [129], 2023 |
| Reactive Dyes | | | | |
|  RR120 | CS-GLA-TNC-25 | 103.1 mg/g | The sorption capacity of the CS-GLA-TNC-25 increased from 8.6 to 97.2 mg/g as the initial dye concentration increased (from 30 to 400 mg/L). | [133], 2020 |
| | CS-ECH/ZL | 284.2 mg/g | The percentage removal rose from 7.8% to 90.5% with the increase in the quantity of the adsorbent dosage from 0.02 g to 0.2 g. | [134], 2020 |
|  RR239 | CS-8B | 163.93 μmol/g | The CS-8B can be reused, after desorption processes was released 89% of RR239. | [135], 2019 |

Table 5. Cont.

| Reactive Dyes | | | | |
|---|-------------|-------------------|--|-------------|
|  RR14 | MC | 98.8 mg/g (99.2%) | The percentage removal of RR14 was 89% after five cycles. | [136], 2020 |
|  RY14 | MC | 89.7 mg/g (92.7%) | The removal efficiency of RY14 was 85% after five cycles. | |
|  RO16 | m-CS-PVA/FA | 123.8 mg/g | The removal efficiency of RO16 was increased with the lowering pH from 17.4% to 90.3%. | [137], 2021 |
|  RB19 | CS/MgO | 79.82% | The percentage removal of RB19 was increased slightly from 58.70% to 59.82% as the MC/MgO dosage increased from 0.14 g to 0.16 g. | [138], 2020 |
| | CS-GO | 99.1% | The removal efficiency of RB19 was from 5 to 98.85% from 10 to 60 min. The highest percentage removal of RB19 was 99.1% in 90 min and at pH 9. | [139], 2019 |

6. Limitations and Future Perspectives

The United Nations Sustainable Development Goals (UN SDGs) are a major policy achievement for assessing environmental, social, and economic development. Governments around the world have committed to protecting ecosystems, promoting equality, and focusing on sustainable development, while simultaneously recognizing the interconnectedness of these objectives for achieving human wellbeing [141]. One of the sustainable development goals is to ensure that, through sustainable resource management, all people have access to water and sanitation (Goal 6) [104]. The improvement of water quality can be achieved by halving untreated wastewater and increasing recycling and safe reuse of water around the world [142]. Therefore, it is extremely important to properly treat wastewater (e.g., municipal, industrial, and agricultural wastewater) by removing pollutants, such as pharmaceuticals, synthetic dyes, and metal and metalloid ions, and maintaining the appropriate quality of ground and surface waters. Adsorption methods using selected adsorption materials and belonging to the so-called “green” techniques, play an increasingly important role in wastewater treatment processes [143]. Many modern adsorption materials are based on chitosan, which not only effectively adsorbs various pollutants but is characterized by its natural origin, biodegradability, non-toxicity, relatively easy modification (e.g., by crosslinking, grafting, composite forming, etc.), and the fact that it can be used in various forms (e.g., powder, beads, microfibers, etc.). Figure 2 shows the main advantages and disadvantages of chitosan-based adsorbents.

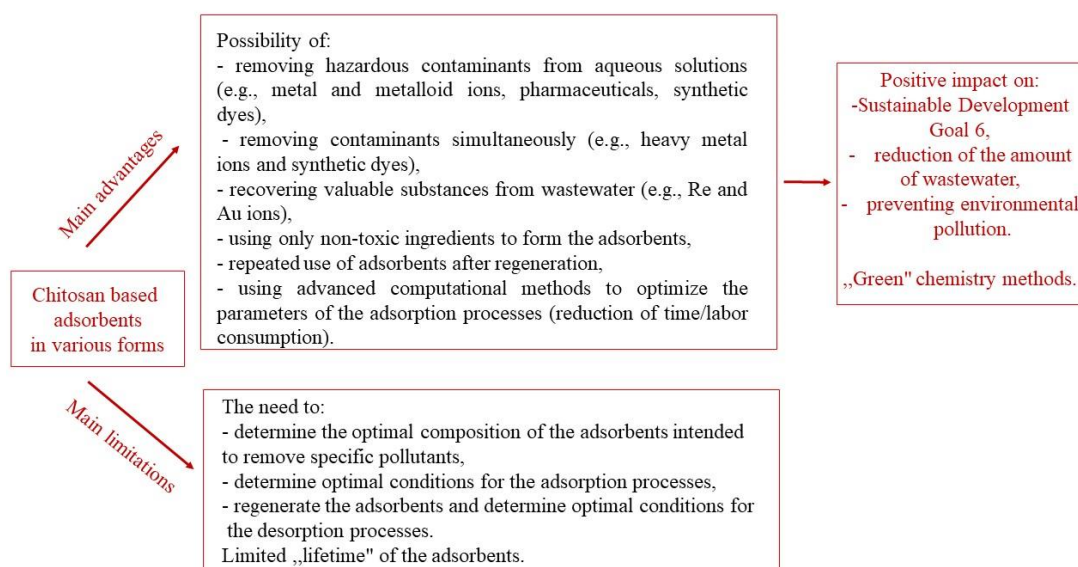


Figure 2. Simplified scheme regarding the main advantages and limitations of chitosan-based adsorbents intended for the removal of hazardous pollutants from aqueous solutions (prepared based on references included in the text).

Despite the many advantages of chitosan and chitosan-based materials intended for the removal of various hazardous contaminants from aqueous solutions, the use of these adsorbents, especially on a larger industrial scale, may be associated with certain limitations. In the case of some chitosan-based adsorbents, the adsorption efficiency is not always satisfactory; they may partially dissolve in certain solutions, and additionally, such materials do not always have adequate mechanical strength. A significant problem may also be the lack of selectivity of some CS-based adsorbents with respect to the removed pollutants. Currently, many studies are being carried out on increasing the selectivity of various adsorbents, for example, through surface modification [144]. Limitations may also result from the need to develop efficient and cheap methods for recycling such adsorbents.

7. Conclusions

In recent years, many novel chitosan-based adsorption materials with excellent adsorption capacity and selectivity that can be repeatedly used have been developed. Usually, the main criterion for their development was sorption performance, but also the low cost of the adsorbent formation and the possibility of utilizing eco-friendly technology [145]. Chitosan-based adsorbents fit into the future trend of eco-friendly adsorbent preparation (Figure 3) and regeneration. Moreover, they can also potentially be applied on a larger scale in the future (for economic and ecological reasons).

The number of new adsorbents containing modified chitosan described in the literature is impressive, but certain trends related to sustainable development can be observed. For example, there have been some attempts to use mainly by-products from the food/agricultural industry or biological wastes as chitosan sources and to produce CS-based adsorbents utilizing only environmentally safe, non-toxic ingredients (e.g., replacing toxic glutaraldehyde crosslinking agents with safe citric acid, using natural Bayberry tannin for chitosan grafting, etc.). In research related to the development/application of novel CS-based adsorbents intended to remove specific pollutants from aqueous solutions, the possibility of reducing costs (e.g., associated with labor, consumption of energy, or chemical reagents) is also important. In this context, solutions such as, inter alia, “one pot” adsorbent synthesis methods or computational chemistry methods (e.g., DFT) used to investigate the binding mechanisms between pollutants and CS-based adsorbents, which consequently enable faster determination of the optimal conditions for the adsorption process, may play a key role in the future. In relation to both sustainable development and potential applica-

tions of CS-based adsorbents on a larger scale (e.g., for removing hazardous contaminants from wastewater), the possibility of repeated use of most of these novel chitosan adsorbents is of significant importance. As many studies have shown, their effectiveness does not decrease significantly in subsequent cycles (after regeneration). Moreover, the regeneration process (adsorption/desorption cycles) usually does not require the use of any complicated equipment or toxic reagents. Finally, modern adsorption materials containing chitosan can be successfully used not only to remove pollutants (e.g., toxic heavy metal ions, metalloids ions, synthetic dyes, etc.) but also to recover valuable substances (e.g., Re and Au ions) from aqueous solutions; therefore, they can have a positive impact on both the sustainability and development of many crucial (e.g., electronic and defense) industries.

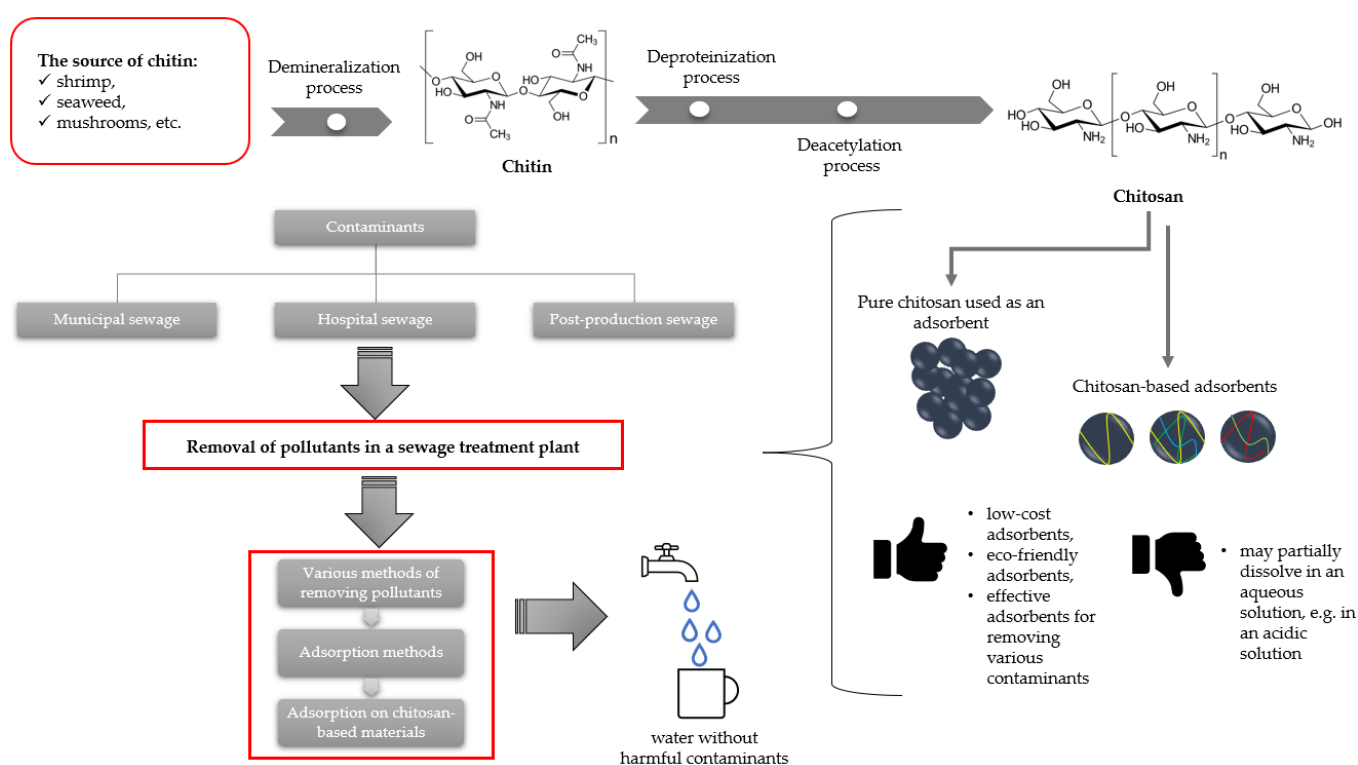


Figure 3. Simplified scheme summarizing the possibility of using chitosan and chitosan-based adsorbents to remove contaminants from sewage (prepared based on references included in the text).

In conclusion, both chitosan, which is called a “miracle molecule”, and chitosan-based adsorbents, which can be described as “versatile” due to their properties and possible application range, are of interest to scientists and have great potential in the field of adsorption removal of various pollutants and recovery of valuable substances from aqueous solutions. Moreover, the use of CS-based adsorption methods is consistent with the idea of sustainable development and is beneficial for environmental and economic reasons.

Author Contributions: Conceptualization, M.A.K. and D.B.; resources, M.A.K. and D.B.; writing—original draft preparation, M.A.K. and D.B. writing—review and editing, M.A.K. and D.B. All authors have read and agreed to the published version of the manuscript.

Funding: This research received no external funding.

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: Data are contained within the article.

Conflicts of Interest: The authors declare no conflicts of interest.

References

1. Aziz, K.H.H.; Mustafa, F.S.; Omer, K.M.; Hama, S.; Hamarawf, R.F.; Rahman, K.O. Heavy metal pollution in the aquatic environment: Efficient and low-cost removal approaches to eliminate their toxicity: A review. *RSC Adv.* **2023**, *13*, 17595–17610. [CrossRef] [PubMed]
2. Ramírez-Malule, H.; Quiñones-Murillo, D.H.; Manotas-Duque, D. Emerging contaminants as global environmental hazards. A bibliometric analysis. *Emerg. Contam.* **2020**, *6*, 179–193. [CrossRef]
3. Kaczorowska, M.A.; Bożejewicz, D.; Witt, K. The Application of Polymer Inclusion membranes for the removal of emerging contaminants and synthetic dyes from aqueous solutions—A mini review. *Membranes* **2023**, *13*, 132. [CrossRef] [PubMed]
4. Li, C.; Xia, W.; Wang, L. The transfer mechanism of pollution industry in China under multi-factor combination model—Based on the perspective of industry, location, and environment. *Environ. Sci. Pollut. Res.* **2021**, *28*, 60167–60181. [CrossRef] [PubMed]
5. Wieser, A.A.; Scherz, M.; Passer, A.; Kreiner, H. Challenges of a healthy built environment: Air pollution in construction industry. *Sustainability* **2021**, *13*, 10469. [CrossRef]
6. Waithaka, S. Effects of Agriculture on the Environment. *Int. J. Agric.* **2023**, *8*, 10–20. [CrossRef]
7. Hien, B.T.; Chi, N.T.K. Green innovation in agriculture development: The impact of environment awareness, technology spillover, and social networks. *Int. J. Sustain. Agric. Manag. Inform.* **2023**, *9*, 56–73. [CrossRef]
8. Saravanan, A.; Senthil Kumar, P.; Jeevanantham, S.; Karishma, S.; Tajsabreen, B.; Yaashikaa, P.R.; Reshma, B. Effective water/wastewater treatment methodologies for toxic pollutants removal: Processes and applications towards sustainable development. *Chemosphere* **2021**, *280*, 130595. [CrossRef]
9. Wu, Y.; Zhao, S. Status quo and change characteristics of groundwater resources pollution in the Hami region based on sustainable development strategies. *Water Supply* **2023**, *23*, 1478–1494. [CrossRef]
10. Lichtfouse, E.; Morin-Crini, N.; Bradu, C.; Boussouga, Y.A.; Aliaskari, M.; Schäfer, A.I.; Das, S.; Wilson, L.D.; Ike, M.; Inoue, D.; et al. Methods for selenium removal from contaminated waters: A review. *Environ. Chem. Lett.* **2022**, *20*, 2019–2041. [CrossRef]
11. Available online: <https://www.epa.gov/ground-water-and-drinking-water/national-primary-drinking-water-regulations> (accessed on 5 January 2024).
12. Malik, L.A.; Bashir, A.; Qureashi, A.; Pandith, A.H. Detection and removal of heavy metal ions: A review. *Environ. Chem. Lett.* **2019**, *17*, 1495–1521. [CrossRef]
13. Adam, A.M.; Saad, H.A.; Atta, A.A.; Alsawat, M.; Hegab, M.S.; Altalhi, T.A.; Refat, M.S. An Environmentally friendly method for removing Hg(II), Pb(II), Cd(II) and Sn(II) heavy metals from wastewater using novel metal-carbon-based composites. *Crystals* **2021**, *11*, 882. [CrossRef]
14. Li, L.; Guo, W.; Zhang, S.; Guo, R.; Zhang, L. Electrospun Nanofiber Membrane: An Efficient and Environmentally Friendly Material for the Removal of Metals and Dyes. *Molecules* **2023**, *28*, 3288. [CrossRef] [PubMed]
15. Burakov, A.E.; Galunin, E.V.; Burakova, I.V.; Kucherova, A.E.; Agarwal, S.; Tkachev, A.G.; Gupta, V.K. Adsorption of heavy metals on conventional and nanostructured materials for wastewater treatment purposes: A review. *Ecotoxicol. Environ. Saf.* **2018**, *148*, 702–712. [CrossRef] [PubMed]
16. Xu, H.; Sun, H.; Zhang, J.; Cao, H.; Li, G.; Ni, Z. Construction and ReO_4^- adsorption of ionic covalent organic frameworks by solvothermal synthesis based on Zincke reaction. *Sep. Purif. Technol.* **2024**, *333*, 125895. [CrossRef]
17. Peydayesh, M.; Boschi, E.; Donat, F.; Mezzenga, R. Gold Recovery from E-Waste by Food-Waste Amyloid Aerogels. *Adv. Mater.* **2024**, 2310642. [CrossRef] [PubMed]
18. Siddique, A.B.; Amr, D.; Abbas, A.; Zohra, L.; Irfan, M.I.; Alhoshani, A.; Ashraf, S.; Amin, H.M.A. Synthesis of hydroxyethylcellulose phthalate-modified silver nanoparticles and their multifunctional applications as an efficient antibacterial, photocatalytic and mercury-selective sensing agent. *Int. J. Biol. Macromol.* **2024**, *256*, 128009. [CrossRef]
19. Yang, J.; Chen, X.; Zhang, J.; Wang, X.; Wen, H.; Xie, J. Role of chitosan-based hydrogels in pollutants adsorption and freshwater harvesting: A critical review. *Int. J. Biol. Macromol.* **2021**, *189*, 53–64. [CrossRef]
20. Ababneh, H.; Hameed, B.H. Chitosan and chitosan composites for oil spills treatment: Review of recent literature. *J. Water Process Eng.* **2023**, *55*, 104193. [CrossRef]
21. Tran, V.S.; Ngo, H.H.; Guo, W.; Zhang, J.; Liang, S.; Ton-That, C.; Zhang, X. Typical low cost biosorbents for adsorptive removal of specific organic pollutants from water. *Bioresour. Technol.* **2015**, *182*, 353–363. [CrossRef]
22. Singh, J.; Yadav, P.; Mishra, V. *Inorganic Pollutants in Water, Chapter 11-Low-Cost Bio-Adsorbent for Emerging Inorganic Pollutants*; Devi, P., Singh, P., Kansal, S.K., Eds.; Elsevier: Amsterdam, The Netherlands, 2020; pp. 205–220.
23. Zare, E.N.; Mudhoo, A.; Khan, M.A.; Otero, M.; Bundhoo, Z.M.A.; Navarathna, C.; Patel, M.; Srivastava, A.; Pittman, C.U.; Mlsna, T.; et al. Water decontamination using bio-based, chemically functionalized, doped, and ionic liquid-enhanced adsorbents: Review. *Environ. Chem. Lett.* **2021**, *19*, 3075–3114. [CrossRef]
24. Ramkumar, R.; Minakshi, M. Fabrication of ultrathin CoMoO_4 nanosheets modified with chitosan and their improved performance in energy storage device. *Dalton Trans.* **2015**, *44*, 6158–6168. [CrossRef] [PubMed]
25. Wickramaarachchi, K.; Sundaram, M.M.; Henry, D.J.; Gao, X.P. Alginate Biopolymer Effect on the Electrodeposition of Manganese Dioxide on Electrodes for Supercapacitors. *ACS Appl. Energy Mater.* **2021**, *4*, 7040–7051. [CrossRef]
26. da Silva Alves, D.C.; Healy, B.; Pinto, L.A.d.A.; Cadaval, T.R.S., Jr.; Breslin, C.B. Recent Developments in Chitosan-Based Adsorbents for the Removal of Pollutants from Aqueous Environments. *Molecules* **2021**, *26*, 594. [CrossRef]

27. Eltaweil, A.S.; Omer, A.M.; El-Aqapa, H.G.; Gaber, N.M.; Attia, N.F.; El-Subruiti, G.M.; Mohy-Eldin, M.S.; Abd El-Monaem, E.M. Chitosan based adsorbents for the removal of phosphate and nitrate: A critical review. *Carbohydr. Polym.* **2021**, *274*, 118671. [\[CrossRef\]](#)
28. Dos Santos, C.C.; Mouta, R.; Junior, M.C.C.; Santana, S.A.A.; Silva, H.A.D.S.; Bezerra, C.W.B. Chitosan-edible oil based materials as upgraded adsorbents for textile dyes. *Carbohydr. Polym.* **2018**, *180*, 182–191. [\[CrossRef\]](#)
29. Wang, Y.; Wang, S.; Li, R.; Wang, Y.; Xiang, O.; Qiu, S.; Xu, W.; Bai, Y. Synergistic effect of corn fiber gum and chitosan in stabilization of oil in water emulsion. *LWT* **2022**, *154*, 112592. [\[CrossRef\]](#)
30. Zhang, Y.; Zhao, M.; Cheng, Q.; Wang, C.; Li, H.; Han, X.; Fan, Z.; Su, G.; Pan, D.; Li, Z. Research progress of adsorption and removal of heavy metals by chitosan and its derivatives: A review. *Chemosphere* **2021**, *279*, 130927. [\[CrossRef\]](#)
31. Yuan, Y.; Chen, L.; Shi, W.; Wang, Z.; Zhang, H. Insight into physicochemical, rheological, and antibacterial properties of chitosan extracted from antarctic krill: A comparative study. *Molecules* **2020**, *25*, 4074. [\[CrossRef\]](#)
32. Benchamas, G.; Huang, G.; Huang, S.; Huang, H. Preparation and biological activities of chitosan oligosaccharides. *Trends. Food Sci. Technol.* **2021**, *107*, 38–44. [\[CrossRef\]](#)
33. Brasselet, C.; Pierre, G.; Dubessay, P.; Dols-Lafargue, M.; Coulon, J.; Maupeu, J.; Vallet-Courbin, A.; de Baynast, H.; Doco, T.; Michaud, P.; et al. Modification of Chitosan for the Generation of Functional Derivatives. *Appl. Sci.* **2019**, *9*, 1321. [\[CrossRef\]](#)
34. Sheth, Y.; Dharaskar, S.; Khalid, M.; Sonawane, S. An environment friendly approach for heavy metal removal from industrial wastewater using chitosan based biosorbent: A review. *Sustain. Energy Technol. Assess.* **2021**, *43*, 100951. [\[CrossRef\]](#)
35. Shaumbwa, V.R.; Liu, D.; Archer, B.; Li, J.; Su, F. Preparation and application of magnetic chitosan in environmental remediation and other fields: A review. *J. Apply. Polym. Sci.* **2021**, *138*, e51241. [\[CrossRef\]](#)
36. Thirupathi, K.; Raorane, C.J.; Ramkumar, V.; Ulagesan, S.; Santhamoorthy, M.; Raj, V.; Krishnakumar, G.S.; Phan, T.T.V.; Kim, S.-C. Update on chitosan-based hydrogels: Preparation, characterization, and its antimicrobial and antibiofilm applications. *Gels* **2023**, *9*, 35. [\[CrossRef\]](#) [\[PubMed\]](#)
37. Zhang, D.; Crini, G.; Lichtfouse, E.; Rhimi, B.; Wang, C. Removal of mercury ions from aqueous solutions by crosslinked chitosan-based adsorbents: A Mini Review. *Chem. Rec.* **2020**, *20*, 1220–1234. [\[CrossRef\]](#)
38. Woźniak, A.; Biernat, M. Methods for crosslinking and stabilization of chitosan structures for potential medical applications. *J. Bioact. Compat. Polym.* **2022**, *37*, 151–167. [\[CrossRef\]](#)
39. Zhang, X.; Liu, J.; Qian, C.; Kan, J.; Jin, C. Effect of grafting method on the physical property and antioxidant potential of chitosan film functionalized with gallic acid. *Food Hydrocoll.* **2019**, *89*, 1–10. [\[CrossRef\]](#)
40. Alanazi, K.D.; Alhammari, B.H.; SheejAhmad, O.A.; Aljohani, M.M.; Alsharif, H.H.; Al-Bagawi, A.H.; Alsehli, A.H.; El-Metwaly, N.M. Citric acid-cross linked with magnetic metal-organic framework composite sponge for superior adsorption of indigo carmine blue dye from aqueous solution: Characterization and adsorption optimization via Box-Behnken design. *J. Mol. Struct.* **2024**, *1299*, 137131. [\[CrossRef\]](#)
41. Torres-Badajoz, S.G.; Rodríguez-Núñez, J.R.; López-Ramírez, E.; Peña-Caballero, V.; Villa-Lerma, A.G.; Madera-Santana, T.J.; Rodríguez-Carrillo, M.G.; Castillo, O.S. Kinetic and equilibrium studies of Cr(VI) adsorption using glutaraldehyde-crosslinked chitosan beads. *Iran. J. Sci. Technol. Trans. Sci.* **2022**, *46*, 147–160. [\[CrossRef\]](#)
42. Zhang, N.; Zhang, H.; Li, R.; Xing, Y. Preparation and adsorption properties of citrate-crosslinked chitosan salt microspheres by microwave assisted method. *Int. J. Biol. Macromol.* **2020**, *152*, 1146–1156. [\[CrossRef\]](#)
43. Hamza, S.F.; El-Sawy, M.M.; Alian, N.A.; Shaker, N.O. Synthesis and evaluation of performance characteristics green composites from sustainable fatty chitosan graft copolymer with acrylic acid for wastewater treatment. *Egypt. J. Chem.* **2021**, *64*, 6007–6015. [\[CrossRef\]](#)
44. Ge, H.; Du, J. Selective adsorption of Pb(II) and Hg(II) on melamine-grafted chitosan. *Int. J. Biol. Macromol.* **2020**, *162*, 1880–1887. [\[CrossRef\]](#)
45. Liu, X.; Zhao, X.; Liu, Y.; Zhang, T. Review on preparation and adsorption properties of chitosan and chitosan composites. *Polym. Bull.* **2022**, *79*, 2633–2665. [\[CrossRef\]](#)
46. Weißpflog, J.; Gündel, A.; Vehlou, D.; Steinbach, C.; Müller, M.; Boldt, R.; Schwarz, S.; Schwarz, D. Solubility and selectivity effects of the anion on the adsorption of different heavy metal ions onto chitosan. *Molecules* **2020**, *25*, 2482. [\[CrossRef\]](#)
47. Weißpflog, J.; Boldt, R.; Kohn, B.; Scheler, U.; Jehnichen, D.; Tyrpekl, V.; Schwarz, S. Investigation of mechanisms for simultaneous adsorption of iron and sulfate ions onto chitosan with formation of orthorhombic structures. *Colloids Surf. A Physicochem. Eng. Asp.* **2020**, *592*, 124575. [\[CrossRef\]](#)
48. Khnifira, M.; Boumya, W.; Attarki, J.; Mahsoun, A.; Abdennouri, M.; Sadiq, M.; Kaya, S.; Barka, N. Elucidating the adsorption mechanisms of anionic dyes on chitosan surface in aqueous medium by quantum chemical and molecular dynamics. *Mater. Today Commun.* **2022**, *33*, 104488. [\[CrossRef\]](#)
49. Bakar, S.A.; Mohamed, R.M.S.R.; Al-Gheethi, A.; Khamidun, M.H.; Musa, S.; Soon, C.F. Kinetics and isotherms of heavy metals removal from laundry greywater by chitosan ceramic beads. *Environ. Adv.* **2023**, *13*, 100391. [\[CrossRef\]](#)
50. Ru, J.; Wang, X.; Wang, F.; Cui, X.; Du, X.; Lu, X. UiO series of metal-organic frameworks composites as advanced sorbents for the removal of heavy metal ions: Synthesis, applications and adsorption mechanism. *Ecotoxicol. Environ. Saf.* **2021**, *208*, 111577. [\[CrossRef\]](#) [\[PubMed\]](#)
51. Kim, S.H.; Bae, S.; Hwang, Y.S. Comparative bioaccumulation, translocation, and phytotoxicity of metal oxide nanoparticles and metal ions in soil-crop system. *Sci. Total Environ.* **2023**, *856*, 158938. [\[CrossRef\]](#) [\[PubMed\]](#)

52. Dutta, S.; Datta, A.; Zaid, A.; Bhat, J.A. Metalloids and Their Impact on the Environment. In *Metalloids in Plants*; Wiley: Hoboken, NJ, USA, 2020; pp. 19–26.
53. Gupta, K.; Joshi, P.; Gusain, R.; Khatri, O.P. Recent advances in adsorptive removal of heavy metal and metalloid ions by metal oxide-based nanomaterials. *Coord. Chem. Rev.* **2021**, *445*, 214100. [\[CrossRef\]](#)
54. Zhou, W.; Xu, Y.; Wang, D.; Zhou, S. Chitosan removes toxic heavy metal ions from cigarette mainstream smoke. *J. Ocean Univ. China* **2013**, *12*, 509–514. [\[CrossRef\]](#)
55. Cheng, P.; Wei, Z.; Arbid, Y.; Fu, T.; Liu, X.; Monfort, O. Insights into the performance and mechanism of Cr(VI) and U(VI) removal in water using innovative cross-linked chitosan adsorbent. *J. Environ. Chem. Eng.* **2024**, *12*, 111731. [\[CrossRef\]](#)
56. Kekes, T.; Kolliopoulos, G.; Tzia, C. Hexavalent chromium adsorption onto crosslinked chitosan and chitosan/ β -cyclodextrin beads: Novel materials for water decontamination. *J. Environ. Chem. Eng.* **2021**, *9*, 105581. [\[CrossRef\]](#)
57. Syeda, S.E.Z.; Nowacka, D.; Khan, M.S.; Skwierawska, A.M. Recent Advancements in Cyclodextrin-Based Adsorbents for the Removal of Hazardous Pollutants from Waters. *Polymers* **2022**, *14*, 2341. [\[CrossRef\]](#) [\[PubMed\]](#)
58. Boudouaia, N.; Bendaoudi, A.A.; Mahmoudi, H.; Saffaj, T.; Bengharez, Z. Swelling and adsorption properties of crosslinked chitosan-based films: Kinetic, thermodynamic and optimization studies. *Desalin. Water Treat.* **2022**, *255*, 56–67. [\[CrossRef\]](#)
59. Watwe, V.; Kulkarni, P. Evaluation of Cr(VI) adsorption on glutaraldehyde crosslinked chitosan beads using cyclic voltammetry employing gold electrode. *J. Anal. Sci. Technol.* **2021**, *12*, 37. [\[CrossRef\]](#)
60. Shen, W.; Fang, Y.; Azeem, M.; Gao, Y.; Li, X.; Zhao, P.; Ali, A.; Li, M.; Li, R. Chitosan crosslinked with polyamine-co-melamine for adsorption of Hg^{2+} : Application in purification of polluted water. *Int. J. Biol. Macromol.* **2021**, *181*, 778–785. [\[CrossRef\]](#)
61. Moreira, J.V.I.; Sousa, R.B.; Morais, L.N.; Borba, R.D.; Xavier, G.R.; Signini, R. Evaluation of the Adsorption of Nickel(II) and Cadmium(II) Ions in Chitosan, Crosslinked Chitosan and Crosslinked Carboxymethyl chitosan. *Rev. Virtual Quim.* **2019**, *11*, 237–254. [\[CrossRef\]](#)
62. Chen, M.; Yu, M.; Kang, R.; Sun, H.; Zhang, W.; Wang, S.; Wang, N.; Wang, J. Removal of Pb(II) and V(V) from aqueous solution by glutaraldehyde crosslinked chitosan and nanocomposites. *Chemosphere* **2022**, *297*, 134084. [\[CrossRef\]](#)
63. Bisiriyu, I.O.; Meijboom, R. Adsorption of Cu(II) ions from aqueous solution using pyridine-2,6-dicarboxylic acid crosslinked chitosan as a green biopolymer adsorbent. *Int. J. Biol. Macromol.* **2020**, *165*, 2484–2493. [\[CrossRef\]](#) [\[PubMed\]](#)
64. Zhao, M.; Li, X.; Huang, Z.; Wang, S.; Zhang, L. Facile cross-link method to synthesize chitosan-based adsorbent with superior selectivity toward gold ions: Batch and column studies. *Int. J. Biol. Macromol.* **2021**, *172*, 210–222. [\[CrossRef\]](#)
65. Long, X.J.; Wang, T.N.; He, M.C. Simultaneous removal of antimony and arsenic by nano-TiO₂-crosslinked chitosan (TA-chitosan) beads. *Environ. Technol.* **2023**, *44*, 2913–2923. [\[CrossRef\]](#)
66. Ding, Y.; Liu, D.; Luo, D.; Sun, X.; Mei, J.; Wang, S.; Li, Z. Rapid one-step preparation of a carboxymethyl chitosan gel with a novel crosslinker for efficient adsorption of Sr^{2+} . *Colloids Surf. Physicochem. Eng. Asp.* **2022**, *641*, 128576. [\[CrossRef\]](#)
67. Radwan-Pragłowska, J.; Janus, Ł.; Sierakowska, A.; Piątkowski, M.; Galek, T.; Szajna, E.; Tupaj, M.; Radomski, P.; Bogdał, D. Ecofriendly chitosan-based super sorbent obtained under microwave radiation for valuable metals recovery from wastewater. *Polym. Test.* **2022**, *112*, 107629. [\[CrossRef\]](#)
68. Zhuang, S.; Zhang, Q.; Wang, J. Adsorption of Co^{2+} and Sr^{2+} from aqueous solution by chitosan grafted with EDTA. *J. Mol. Liq.* **2021**, *325*, 115197. [\[CrossRef\]](#)
69. Ge, Y.M.; Zhang, L.; Zhang, Y.; Ge, Y.M.; Zhang, L.; Zhang, Y.; Yang, J.S.; Gao, H.M.; Li, S.J.; Liu, J.Z. Effective Removal of Aqueous Cu(II) Pollution by a Novel Readily Prepared Porous Biomaterial Using Crab Shell Wastes. *Water Air Soil Pollut.* **2023**, *234*, 254. [\[CrossRef\]](#)
70. Vafakish, B.; Wilson, L.D. Cu(II) Ion Adsorption by Aniline Grafted Chitosan and Its Responsive Fluorescence Properties. *Molecules* **2020**, *25*, 1052. [\[CrossRef\]](#) [\[PubMed\]](#)
71. Liakos, E.V.; Mone, M.; Lambropoulou, D.A.; Bikiaris, D.N.; Kyzas, G.Z. Adsorption evaluation for the removal of nickel, mercury, and barium ions from single-component and mixtures of aqueous solutions by using an optimized biobased chitosan derivative. *Polymers* **2021**, *13*, 232. [\[CrossRef\]](#) [\[PubMed\]](#)
72. Mone, M.; Lambropoulou, D.A.; Bikiaris, D.N.; Kyzas, G. Chitosan Grafted with Biobased 5-Hydroxymethyl-furfural as adsorbent for copper and cadmium ions removal. *Polymers* **2020**, *12*, 1173. [\[CrossRef\]](#) [\[PubMed\]](#)
73. Labidi, A.; Salaberria, A.M.; Fernandes, S.C.M.; Labidi, J.; Abderrabba, M. Microwave assisted synthesis of poly (*N*-vinylimidazole) grafted chitosan as an effective adsorbent for mercury(II) removal from aqueous solution: Equilibrium, kinetic, thermodynamics and regeneration studies. *J. Dispers. Sci. Technol.* **2020**, *41*, 828–840. [\[CrossRef\]](#)
74. Ma, M.; Chen, R.; Feng, L. Efficient and selective removal of mercury ions from aqueous solution by 2,5-dimercaptothiadiazole covalently grafted chitosan derivative. *Int. J. Biol. Macromol.* **2023**, *251*, 126272. [\[CrossRef\]](#)
75. Vijayasri, K.; Tiwari, A. Detoxification of arsenic from contaminated water using chitosan and radiation-induced grafted chitosan: A comparative study. *Chem. Ecol.* **2021**, *37*, 323–341. [\[CrossRef\]](#)
76. Vijayasri, K.; Tiwari, A.; Chaudhari, C.V. Mitigation of toxic arsenic(V) from aqueous solution in fixed-bed column using functionally modified bio-polymer. *Inorg. Nano-Met. Chem.* **2021**, *51*, 780–791.
77. Ye, Y.; Zhang, T.; Lv, L.; Chen, Y.; Tang, W.; Tang, S. Functionalization of chitosan by grafting sulfhydryl groups to intensify the adsorption of arsenite from water. *Colloids Surf. Physicochem. Eng. Asp.* **2021**, *622*, 126601. [\[CrossRef\]](#)
78. Azizinezhad, F. Surface adsorption of Pb^{2+} ions from aqueous solutions using chitosan grafted with a mixture of IA-MAm/bentonite. *Int. J. Environ. Anal. Chem.* **2022**, *104*, 624–640. [\[CrossRef\]](#)

79. Peng, Y.; Huang, H.; Wu, Y.; Jia, S.; Wang, F.; Ma, J.; Liao, Y.; Mao, H. Plant tannin modified chitosan microfibers for efficient adsorptive removal of Pb^{2+} at low concentration. *Ind. Crops Prod.* **2021**, *168*, 113608. [\[CrossRef\]](#)
80. Cabuk, M.; Oztas, M.; Gode, F.; Unal, H.I.; Yavuz, M. Effects of zeta-potential on enhanced removal of hexavalent chromium by polypyrrole-graft-chitosan biodegradable copolymer. *Colloids Surf. Physicochem. Eng. Asp.* **2023**, *676*, 132104. [\[CrossRef\]](#)
81. Xiong, S.; Sun, W.; Chen, R.; Yuan, Z.; Cheng, X. Fluorescent dialdehyde-BODIPY chitosan hydrogel and its highly sensing ability to Cu^{2+} ion. *Carbohydr. Polym.* **2021**, *273*, 118590. [\[CrossRef\]](#) [\[PubMed\]](#)
82. Bejan, A.; Doroftei, F.; Cheng, X.; Marin, L. Phenothiazine-chitosan based eco-adsorbents: A special design for mercury removal and fast naked eye detection. *Int. J. Biol. Macromol.* **2020**, *162*, 1839–1848. [\[CrossRef\]](#) [\[PubMed\]](#)
83. Biswas, S.; Biswas, R. Chitosan—The miracle biomaterial as detection and diminishing mediating agent for heavy metal ions: A mini review. *Chemosphere* **2023**, *312*, 137187. [\[CrossRef\]](#) [\[PubMed\]](#)
84. Liu, J.; Chen, Y.; Han, T.; Cheng, M.; Zhang, W.; Long, J.; Fu, X. A biomimetic SiO_2 @chitosan composite as highly-efficient adsorbent for removing heavy metal ions in drinking water. *Chemosphere* **2019**, *214*, 738–742. [\[CrossRef\]](#) [\[PubMed\]](#)
85. Billah, R.E.K.; Khan, M.A.; Park, Y.-K.; AM, A.; Majdoubi, H.; Haddaji, Y.; Jeon, B.-H. A Comparative Study on Hexavalent Chromium Adsorption onto Chitosan and Chitosan-Based Composites. *Polymers* **2021**, *13*, 3427. [\[CrossRef\]](#) [\[PubMed\]](#)
86. Zhao, B.; Wang, Y.; Zhang, H.; Deng, L.; Li, G.; Cao, Y. Recent progress and advances of adsorption for Re recovery from solution. *J. Ind. Eng. Chem.* **2023**, *132*, 22–35. [\[CrossRef\]](#)
87. Shan, W.; Zhang, D.; Wang, X.; Wang, D.; Xing, Z.; Xiong, Y.; Fan, Y.; Yang, Y. One-pot synthesis of mesoporous chitosan-silica composite from sodium silicate for application in Rhenium(VII) adsorption. *Microporous Mesoporous Mater.* **2019**, *278*, 44–53. [\[CrossRef\]](#)
88. Cui, J.; Li, W.; Song, X.; Zhang, Z.; Yu, H.; Shan, W.; Xiong, Y. Microwave-assisted one-pot rapid synthesis of mesoporous silica-chitosan composites for efficient recovery of rhenium(VII). *Sep. Purif. Technol.* **2021**, *277*, 119497. [\[CrossRef\]](#)
89. Xiong, Y.; Xie, L.; Zhu, L.; Wang, Y.; Shan, W.; Lou, Z.; Cui, J.; Yu, H. Superior adsorption of Re(VII) by anionic imprinted chitosan-silica composite: Adsorption performance, selectivity and mechanism study. *J. Ind. Eng. Chem.* **2022**, *108*, 344–355. [\[CrossRef\]](#)
90. Şenol, Z.M.; Kaya, S.; Şimşek, S.; Katin, K.P.; Özer, A.; Marzouki, R. Synthesis and characterization of chitosan-vermiculite-lignin ternary composite as an adsorbent for effective removal of uranyl ions from aqueous solution: Experimental and theoretical analyses. *Int. J. Biol. Macromol.* **2022**, *209*, 1234–1247. [\[CrossRef\]](#) [\[PubMed\]](#)
91. Mohamed, H.S.; El-Mageed, H.R.A.; Ali, H.S.; Mahmoud, T.R.; Ahmed, S.A.; Soliman, N.K. Adsorption of Mn^{+7} ions on chitosan/cellulose composite: Experimentally and theoretically approaches. *J. Dispers. Sci. Technol.* **2022**, *43*, 1525–1542. [\[CrossRef\]](#)
92. Ling, C.; Wang, Z.; Song, Y.; Fu, L.; Zhang, Y.; Wang, W.; Xing, W.; Han, J. Molecular mechanisms of pyrophosphate-mediated selective adsorption of Ni(II) by polyamine-grafted chitosan–wood flour composite from alkaline plating wastewater: EXAFS investigation and theoretical calculations. *Appl. Surf. Sci.* **2023**, *632*, 157591. [\[CrossRef\]](#)
93. Ahmed, I.A.; Hussein, H.S.; Ragab, A.H.; Al Masoud, N.; Ghfar, A.A. Investigation the Effects of Green-Synthesized Copper Nanoparticles on the Performance of Activated Carbon-Chitosan-Alginate for the Removal of Cr(VI) from Aqueous Solution. *Molecules* **2021**, *26*, 2617. [\[CrossRef\]](#)
94. Abd El-Aziz, M.E.; Youssef, A.M.; Kamal, K.H.; Kelnar, I.; Kamel, S. Preparation and performance of bionanocomposites based on grafted chitosan, GO and TiO_2 -NPs for removal of lead ions and basic-red 46. *Carbohydr. Polym.* **2023**, *305*, 120571. [\[CrossRef\]](#) [\[PubMed\]](#)
95. Hassan, A.S.M.; El-Aziz, M.E.A.; Fayez, A.E.; Kamel, A.H.; Youssef, A.M. Synthesis and characterization of bio-nanocomposite based on chitosan and $CaCO_3$ nanoparticles for heavy metals removal. *Int. J. Biol. Macromol.* **2024**, *255*, 128007. [\[CrossRef\]](#) [\[PubMed\]](#)
96. Xu, K.; Li, L.; Huang, Z.; Tian, Z.; Li, H. Efficient adsorption of heavy metals from wastewater on nanocomposite beads prepared by chitosan and paper sludge. *Sci. Total Environ.* **2022**, *846*, 157399. [\[CrossRef\]](#) [\[PubMed\]](#)
97. Fayez, A.E.; Kamel, A.H.; Hassan, A.S.M.; Abd El-Aziz, M.E.; Youssef, A.M. Development and Utilization of Chitosan/Carbon Nanocomposite for Heavy Metal Removal from Wastewater. *Egypt. J. Chem.* **2022**, *65*, 559–569.
98. Peralta, M.E.; Nisticò, R.; Franzoso, F.; Magnacca, G.; Fernandez, L.; Parolo, M.E.; León, E.G.; Carlos, L. Highly efficient removal of heavy metals from waters by magnetic chitosan-based composite. *Adsorption* **2019**, *25*, 1337–1347. [\[CrossRef\]](#)
99. Zhu, X.; Tang, Y.; Chen, F.; Shi, Y.; Wang, X. Synthesis of magnetic rectorite/humic acid/chitosan composite for removal of heavy metal ions from water. *Desalin. Water Treat.* **2019**, *163*, 155–165. [\[CrossRef\]](#)
100. Yang, L.; Peng, Y.; Qian, C.; Xing, G.; He, J.; Zhao, C.; Lai, B. Enhanced adsorption/photocatalytic removal of Cu(II) from wastewater by a novel magnetic chitosan@ bismuth tungstate coated by silver (MCTS-Ag/ Bi_2WO_6) composite. *Chemosphere* **2021**, *263*, 128120. [\[CrossRef\]](#)
101. Zhang, L.; Zeng, Y.; Cheng, Z. Removal of heavy metal ions using chitosan and modified chitosan: A review. *J. Mol. Liq.* **2016**, *214*, 175–191. [\[CrossRef\]](#)
102. Gamage, A.; Jayasinghe, N.; Thiviya, P.; Wasana, M.L.D.; Merah, O.; Madhujith, T.; Koduru, J.R. Recent Application Prospects of Chitosan Based Composites for the Metal Contaminated Wastewater Treatment. *Polymers* **2023**, *15*, 1453. [\[CrossRef\]](#)
103. Liu, Y.; Nie, P.; Yu, F. Enhanced adsorption of sulfonamides by a novel carboxymethyl cellulose and chitosan-based composite with sulfonated Graphene oxide. *Bioresour. Technol. Part B* **2021**, *320*, 124373. [\[CrossRef\]](#)

104. Kumar, A.; Rana, A.; Sharma, G.; Naushad, M.; Dhiman, P.; Kumar, A.; Stadler, F.J. Recent advances in nano-Fenton catalytic degradation of emerging pharmaceutical contaminants. *J. Mol. Liq.* **2019**, *290*, 111177. [CrossRef]
105. Khalil, A.M.E.; Memon, F.A.; Tabish, T.A.; Salmon, D.; Zhang, S.H.; Butler, D. Nanostructured porous Graphene for efficient removal of emerging contaminants (pharmaceuticals) from water. *Chem. Eng. J.* **2020**, *398*, 125440. [CrossRef]
106. Shahrin, E.W.E.S.; Narudin, N.A.H.; Shahri, N.N.M.; Nur, M.; Lim, J.-W.; Bilad, M.R.; Mahadi, A.H.; Hobley, J.; Usman, A. A comparative study of adsorption behavior of rifampicin, streptomycin, and ibuprofen contaminants from aqueous solutions onto chitosan: Dynamic interaction, kinetics, diffusion, and mechanisms. *Emerg. Contam.* **2023**, *9*, 100199. [CrossRef]
107. Liu, Y.; Liu, R.; Li, M.; Yu, F.; He, C. Removal of pharmaceuticals by novel magnetic genipin-crosslinked chitosan/Graphene oxide-SO₃H composite. *Carbohydr. Polym.* **2019**, *220*, 141–148. [CrossRef] [PubMed]
108. Stachowiak, M.; Cegłowski, M.; Kurczewska, J. Hybrid chitosan/molecularly imprinted polymer hydrogel beads doped with iron for selective ibuprofen adsorption. *Int. J. Biol. Macromol.* **2023**, *251*, 126356. [CrossRef] [PubMed]
109. Kim, M.; Njaramba, L.K.; Yoon, Y.; Jang, M.; Park, C.M. Thermally-activated gelatin-chitosan-MOF hybrid aerogels for efficient removal of ibuprofen and naproxen. *Carbohydr. Polym.* **2024**, *324*, 121436. [CrossRef] [PubMed]
110. Niragire, H.; Kebede, T.G.; Dube, S.; Maaza, M.; Nindi, M.M. Chitosan-based electrospun nanofibers mat for the removal of acidic drugs from influent and effluent. *Chem. Eng. Commun.* **2023**, *210*, 1485–1507. [CrossRef]
111. Mahmoodi, H.; Fattahi, M.; Motevassel, M. Graphene oxide-chitosan hydrogel for adsorptive removal of diclofenac from aqueous solution: Preparation, characterization, kinetic and thermodynamic modeling. *RSC Adv.* **2021**, *11*, 36289. [CrossRef] [PubMed]
112. Ahamad, T.; Naushad, M.; Al-Shahrani, T.; Al-Hokbany, N.; Alshehri, A.M. Preparation of chitosan based magnetic nanocomposite for tetracycline adsorption: Kinetic and thermodynamic studies. *Int. J. Biol. Macromol.* **2020**, *147*, 258–267. [CrossRef]
113. Castillo, P.C.H.; Castro-Velázquez, V.; Rodríguez-González, V. Adsorption and photocatalytic-conjugated activity of a chitosan-functionalized titanate coating for the removal of the drug clonazepam from drinking water. *Environ. Sci. Pollut. Res.* **2023**. [CrossRef]
114. Vakili, M.; Mojiri, A.; Kindaichi, T.; Cagnetta, G.; Yuan, J.; Wang, B.; Giwa, A.S. Cross-linked chitosan/zeolite as a fixed-bed column for organic micropollutants removal from aqueous solution, optimization with RSM and artificial neural network. *J. Environ. Manag.* **2019**, *250*, 109434. [CrossRef]
115. Mashile, P.P.; Nomngongo, P.N. Magnetic cellulose-chitosan nanocomposite for simultaneous removal of emerging contaminants: Adsorption kinetics and equilibrium studies. *Gels* **2021**, *7*, 190. [CrossRef]
116. Davarnejad, R.; Sarvmeili, K.; Safari, Z.; Kennedy, J.F. Estrogen adsorption from an aqueous solution on the chitosan nanoparticle. *Int. J. Biol. Macromol.* **2023**, *237*, 124224. [CrossRef]
117. Rehman, M.U.; Taj, M.B.; Carabineiro, A.S.C. Biogenic adsorbents for removal of drugs and dyes: A comprehensive review on properties, modification and applications. *Chemosphere* **2023**, *338*, 139477. [CrossRef] [PubMed]
118. Liu, Q. Pollution and treatment of dye waste-water, 4th International Symposium on Resource Exploration and Environmental Science. *IOP Conf. Ser. Earth Environ. Sci.* **2020**, *514*, 052001. [CrossRef]
119. Available online: <https://textilevaluechain.in/in-depth-analysis/articles/textile-articles/electrolyte-free-dyeing-of-textiles-with-cationic-reactive-dyes/> (accessed on 10 February 2024).
120. Lellis, B.; Fávoro-Polonio, C.C.; Pamphile, J.A.; Polonio, J.A. Effects of textile dyes on health and the environment and bioremediation potential of living organisms. *BIORI* **2019**, *3*, 275–290. [CrossRef]
121. Jyothi, M.S.; Angadi, V.J.; Kanakalakshmi, T.V.; Padaki, M.; Geetha, B.R.; Soontarapa, K. Magnetic nanoparticles impregnated, cross-linked, porous chitosan microspheres for efficient adsorption of methylene blue from pharmaceutical waste water. *J. Polym. Environ.* **2019**, *27*, 2408–2418. [CrossRef]
122. Kaur, K.; Jindal, R. Self-assembled GO incorporated CMC and chitosan-based nanocomposites in the removal of cationic dyes. *Carbohydr. Polym.* **2019**, *225*, 115245. [CrossRef]
123. Usman, M.; Ahmed, A.; Yu, B.; Wang, S.; Shen, Y.; Cong, H. Simultaneous adsorption of heavy metals and organic dyes by β -cyclodextrin-chitosan based cross-linked adsorbent. *Carbohydr. Polym.* **2021**, *255*, 117486. [CrossRef] [PubMed]
124. Alakhras, F.; Ouachtak, H.; Alhajri, E.; Rehman, R.; Al-Mazaideh, G.; Anastopoulos, I.; Lima, E.C. Adsorptive removal of cationic rhodamine b dye from aqueous solutions using chitosan-derived Schiff Base. *Sep. Sci. Technol.* **2022**, *57*, 542–554. [CrossRef]
125. Mashkoo, F.; Nasar, A. Facile synthesis of polypyrrole decorated chitosan-based magsorbent: Characterizations, performance, and applications in removing cationic and anionic dyes from aqueous medium. *Int. J. Biol. Macromol.* **2020**, *161*, 88–100. [CrossRef]
126. Huo, M.-X.; Jin, Y.-L.; Sun, Z.-F.; Ren, F.; Pei, L.; Ren, P.-G. Facile synthesis of chitosan-based acid-resistant composite films for efficient selective adsorption properties towards anionic dyes. *Carbohydr. Polym.* **2021**, *254*, 117473. [CrossRef]
127. Siciliano, C.C.; Dinh, V.M.; Canu, P.; Mikkola, J.-P.; Khokarale, S.G. Efficient adsorption and catalytic reduction of phenol red dye by glutaraldehyde cross-linked chitosan and its Ag-loaded catalysts: Materials synthesis, characterization and application. *Clean Technol.* **2023**, *5*, 466–483. [CrossRef]
128. Khushbu; Jindal, R. Sodium alginate and chitosan based amphoteric nanocomposites modified with graphene oxide and bentonite as an efficient adsorbent for both anionic and cationic dyes. *J. Polym. Environ.* **2023**, *31*, 264–286. [CrossRef]
129. Jayaseelan, C.H.; Kaur, M.; Sem, M. Activated carbon modified chitosan beads: An effective method for removal of Congo Red dye. *Mater. Today Proc.* **2023**. [CrossRef]
130. de Freitas, F.P.; Carvalho, A.M.M.L.; Carnerio, A.C.O.; de Magalhães, M.A.; Xisto, M.F.; Canal, W.D. Adsorption of neutral red dye by chitosan and activated carbon composite films. *Heliyon* **2021**, *22*, e07629. [CrossRef] [PubMed]

131. Jawad, A.H.; Abdulhameed, A.S.; Surip, S.N.; Sabar, S. Adsorptive performance of carbon modified chitosan biopolymer for cationic dye removal: Kinetic, isotherm, thermodynamic, and mechanism study. *J. Environ. Anal. Chem.* **2020**, *102*, 6189–6203. [\[CrossRef\]](#)
132. Jawad, A.H.; Abdulhameed, A.S.; Mastuli, M.S. Mesoporous crosslinked chitosan-activated charcoal composite for the removal of thionine cationic dye: Comprehensive adsorption and mechanism study. *J. Environ. Polym. Degrad.* **2020**, *28*, 1095–1105. [\[CrossRef\]](#)
133. Jawad, A.H.; Mubarak, N.S.A.; Abdulhameed, A.S. Tunable Schiff's base-cross-linked chitosan composite for the removal of reactive red 120 dye: Adsorption and mechanism study. *Int. J. Biol. Macromol.* **2020**, *142*, 732–741. [\[CrossRef\]](#) [\[PubMed\]](#)
134. Jawad, A.H.; Abdulhameed, A.S.; Reghioua, A.; Yassen, Z.M. Zwitterion composite chitosan-epichlorohydrin/zeolite for adsorption of methyle blue and reactive red 120 dye. *Int. J. Biol. Macromol.* **2020**, *163*, 756–765. [\[CrossRef\]](#) [\[PubMed\]](#)
135. Karmaker, S.; Sintaha, F.; Saha, T.K. Kinetics, isotherm and thermodynamic studies of the adsorption of reactive red 239 dye from aqueous solution by chitosan 8B. *Adv. Biol. Chem.* **2019**, *9*, 89691. [\[CrossRef\]](#)
136. Jaafari, J.; Barzanouni, H.; Mazloomi, S.; Farahani, N.A.A.; Sharafi, K.; Soleimani, P.; Haghighat, G.A. Effective adsorptive removal of reactive dyes by magnetic chitosan nanoparticles: Kinetic, isothermal studies and response Surface methodology. *Int. J. Biol. Macromol.* **2020**, *164*, 344–355. [\[CrossRef\]](#) [\[PubMed\]](#)
137. Malek, N.N.A.; Jawad, A.H.; Ismail, K.; Razun, R.; ALOthman, Z.A. Fly ash modified magnetic chitosan-polyvinyl alcohol blend for reactive orange dye removal: Adsorption parametric optimization. *Int. J. Biol. Macromol.* **2021**, *189*, 464–476. [\[CrossRef\]](#) [\[PubMed\]](#)
138. Nga, N.K.; Chau, N.T.T.; Viet, P.H. Preparation and characterization of a chitosan/MgO composite for the effective removal of reactive blue 19 dye from aqueous solution. *J. Sci. Adv. Mater. Devices* **2020**, *5*, 65–72. [\[CrossRef\]](#)
139. Mohamadi, M.B.; Ejazi, H.; Azadbakht, F. Using composite chitosan-graphene oxide to eliminate reactive blue 19 from water solution: The study of adsorption kinetics and reaction thermodynamics. *Desalin. Water. Treat.* **2019**, *155*, 341–349. [\[CrossRef\]](#)
140. Mandeep; Shukla, P. Microbial nanotechnology for bioremediation of industrial wastewater. *Front. Microbiol.* **2020**, *11*, 590631.
141. Coscieme, L.; Mortensen, L.F.; Anderson, S.; Ward, J.; Donohue, I.; Sutton, P.C. Going beyond gross domestic product as an indicator to bring coherence to the sustainable development goal. *J. Clean. Prod.* **2020**, *248*, 119232. [\[CrossRef\]](#)
142. Tortajada, C. Contributions of recycled wastewater to clean water and sanitation sustainable development goals. *Clean Water* **2020**, *3*, 22. [\[CrossRef\]](#)
143. Omer, A.H.; Dey, R.; Eltaweil, A.S.; Abd El-Monaem, E.M.; Ziora, Z.M. Insights into recent advances of chitosan-based adsorbents for sustainable removal of heavy metals and anions. *Arab. J. Chem.* **2022**, *15*, 103543. [\[CrossRef\]](#)
144. Amin, S.; Sher, M.; Ali, A.; Rehman, M.F.; Hayat, A.; Ikram, M.; Abbas, A.; Amin, H.M.A. Sulfonamide-functionalized silver nanoparticles as an analytical nanoprobe for selective Ni(II) sensing with synergistic antimicrobial activity. *Environ. Nanotechnol. Monit. Manag.* **2022**, *18*, 100735. [\[CrossRef\]](#)
145. Wang, W.; Wang, A. Perspectives on green fabrication and sustainable utilization of adsorption materials for wastewater treatment. *Chem. Eng. Re. Des.* **2022**, *187*, 541–548. [\[CrossRef\]](#)

Disclaimer/Publisher's Note: The statements, opinions and data contained in all publications are solely those of the individual author(s) and contributor(s) and not of MDPI and/or the editor(s). MDPI and/or the editor(s) disclaim responsibility for any injury to people or property resulting from any ideas, methods, instructions or products referred to in the content.