

REVIEW OF CHITOSAN NANOMATERIALS FOR METAL CATION ADSORPTION

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Abstract

Polysaccharides are polymers of long chains of monosaccharide units linked via glycosidic bonds. Starch, cellulose, chitin and their derivatives, such as chitosan, are examples of polysaccharides. Chitin is the second most common natural polysaccharide in the world (after cellulose). Chitin and chitosan are amino polysaccharides. Chitosan is often obtained by chemical, or sometimes enzymatic, deacetylation of chitin. These compounds are increasingly being modified to the nanometric scale. New engineering nanomaterials show better chemical, biological, mechanical, thermal, electrical and sorption properties than the primary materials. In this paper, the methods of chitosan nanomaterials synthesis and their adsorption properties of metal cations are discussed. As it is shown, the selected chitosan nanomaterials have promising adsorption properties of metal cations.

Keywords: *chitosan; nanochitosan; nanomaterials; adsorption; metal cations*

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1. Introduction

Chitin and its derivative, chitosan, are natural amino polysaccharides that have been frequently described in the literature [1–7]. Chitin is a linear polymer composed of β -(1→4)-linked 2-acetamido-2-deoxy- β -D-glucose (*N*-acetylglucosamine) (Fig. 1) [3, 4]. Several natural sources of chitin are known, for instance shells of shrimp, crabs, krill, crayfish and other crustaceans [5]. Chitosan has also the linear structure, which is built of glucosamine and *N*-acetyl glucosamine units linked via β -(1-4)-glycosidic bonds (Fig. 1) [3, 6]. The number of *N*-acetyl units and *D*-acetyl units is calculated from the following formula (1) [5, 13]:

$$DD = \frac{N_{\text{NH}_2}}{N_{\text{NH}_2} + N_{\text{NHCO}}}, \quad (1)$$

where DD is the degree of deacetylation, N is the number of specific units (structural units) in the polymer, N_{NH_2} is the number of amine groups in the polymer and N_{NHCO} is the number of amide group in the polymer. The numbers and location of amine and amide groups in the polymer chain affects its physicochemical properties, e.g. solubility, crystallinity and susceptibility to degradation [5].

Chitosan is obtained by chemical or enzymatic deacetylation of chitin [1–7]. In these processes, acetyl groups are removed partially or completely from the acetylamino groups of chitins. The production of chitosan from natural chitin via **chemical deacetylation of chitin** is shown in Scheme 1. It consists of three basic phases: demineralization, deproteinization and deacetylation [1, 6, 7].

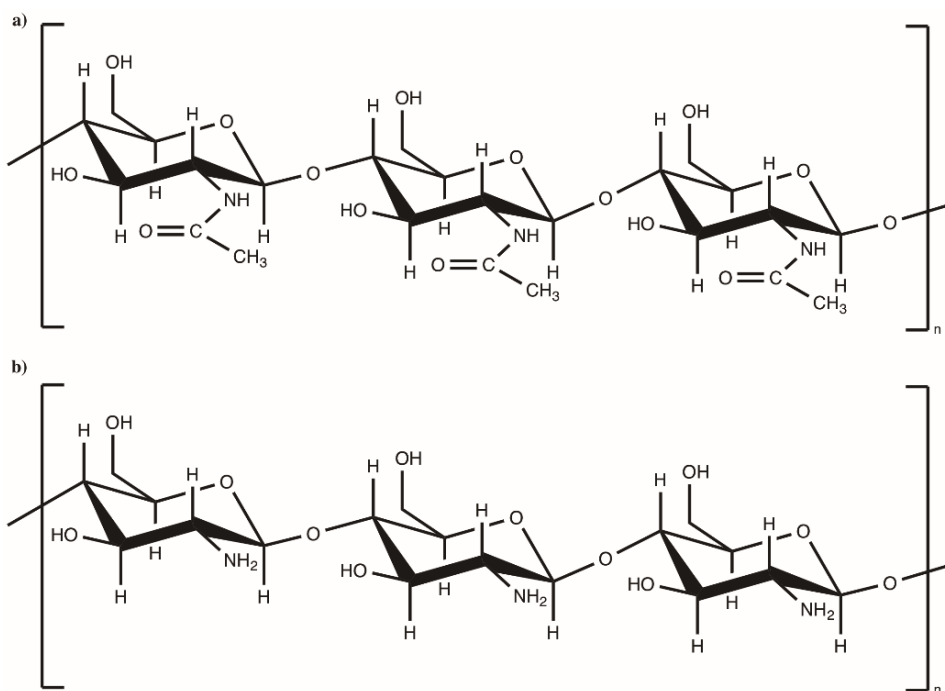
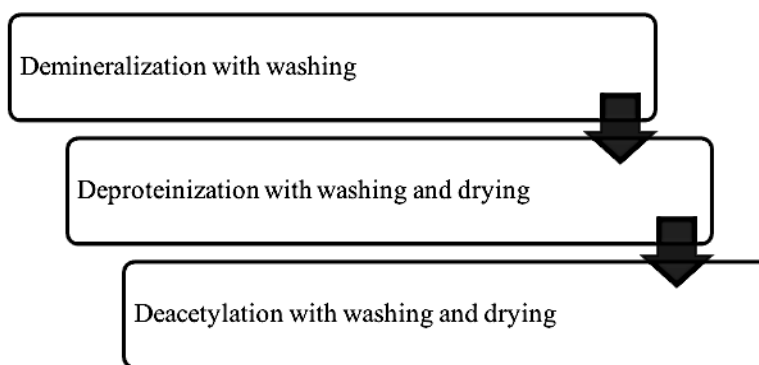


Figure 1. The structure of (a) chitin and (b) chitosan.



Scheme 1. The production of chitosan from natural chitin via chemical deacetylation of chitin.

- **First phase** – demineralization; it is used to remove the mineral salt contents in the skeleton of crustacean and inorganic compounds, which are insoluble in water, e.g. calcium carbonate. This process is carried out using acids, mainly 5%–10% hydrochloric acid at room temperature, for 1–3 h. The solid-to-solvent ratio is usually 1:10 [7] or 1:15 (w/v) [1]. After treating the sample with the acid solution under certain conditions, it must be rinsed with distilled water (pH 7).

- **Second phase** – deproteinization; the proteins and lipids are removed from the sample. Deproteinization of chitin is carried out by alkaline treatment. The sample is dissolved in 5% sodium hydroxide (1:10 or 1:20 (w/v) [1]) at room temperature, for 1–12 h [1] or longer [7]. After deproteinization, the sample is rinsed with distilled water (pH 7) and dried at 80°C for about 15 h.

- **Third phase** – deacetylation; the resulting chitin is converted to chitosan by chemical deacetylation. This process removes the acetyl groups. Deacetylation is carried out in alkali solution (40%–60% NaOH [1, 6] in a 1:10 (w/v) ratio [1]) at 80–140°C for 30 min [6] or longer, e.g. even for 4 h [1]. The chitosan is then washed to pH 7 (using boiled distilled water) and is dried for a shorter time at a higher temperature or a longer time at a lower temperature. Finally, dry flakes of chitosan are obtained.

The chemical deacetylation of chitin to chitosan is still under investigation and modification. Due to economic and ecological reasons, scientists are striving to reduce the concentration of sodium hydroxide and lower the reaction temperature [1, 6, 8]. **Enzymatic deacetylation of chitin** has been frequently studied by scientific institutions since the 1980s [6, 8–12]. Chitin deacetylase is used in this reaction. Enzymatic deacetylation of chitin leaves no changes in the structure of the resulting polymer and is easier to control than the chemical process [12].

2. Physicochemical Characteristics of Chitosan

Chitin and chitosan are polysaccharides with a different deacetyl component [1, 3, 5–7]. The amount of this ingredient is known as the degree of deacetylation [1, 3, 5–7, 13]. Several physicochemical parameters also characterize the obtained chitin and chitosan, e.g. molecular weight, viscosity, solubility and crystallinity [1, 3, 5–7]. The basic methods for determining the physicochemical parameters of chitosan are presented in Table 1.

Table 1. Basic methods for determining the physicochemical parameters of chitosan.

Physicochemical parameters	Methods	Reference(s)
Degree of deacetylation	Nuclear magnetic resonance ¹ H NMR and ¹² C NMR	[14, 17, 19]
	Spectroscopy UV-Vis	[15, 17]
	Fourier transform infrared spectroscopy	[16, 17, 19]
	Potentiometric titration (PT)	[17]
	Conductometric titration (CT)	[14]
	Pyrolysis-gas chromatography-mass spectrometry (PyGC/MS)	[18]
	Gel permeation chromatography (GPC)	[19]
Molecular weight	Gel permeation chromatography (GPC)	[19]
	Viscometry (indirect method)	[20, 21, 23]
	Light scattering	[22]
Viscosity	Gel permeation chromatography (GPC)	[19]
	Viscometry	[23]
Solubility	Group contribution methods (GCM)	[24]
Crystallinity	X-rays diffraction (XRD)	[27]

Viscometry is the most popular method for determining the molecular weight of chitosan, but its result is a correlation between the values of intrinsic viscosity and molecular weight [1, 23]. Commercial chitosan has a molecular weight ranging from 10,000 to 1,000,000 Da [1]. The molecular weight of chitosan increases with its viscosity and concentration.

The **degree of deacetylation** determines the biological and physicochemical properties of chitosan and influences its application. Potentiometric titration (PT) and nuclear magnetic resonance (NMR) are the most commonly used methods for its determination [1, 13]. The degree of deacetylation also increases as viscosity increases [25]. Researchers have shown that as the time of chemical deacetylation of chitin decreases, chitosan is obtained with lower degree of deacetylation, higher molecular weight and higher shear viscosity [1, 6].

The important physicochemical parameter is **solubility**. Chitosan solubility depends on the degree of deacetylation [1,26]. This is due to amount of protonated amino groups in the polymeric chain. A higher degree of deacetylation value determines its higher solubility and vice versa [26].

Crystallinity is another physicochemical parameter of chitosan [1, 27]; it is determined by X-ray diffraction [27].

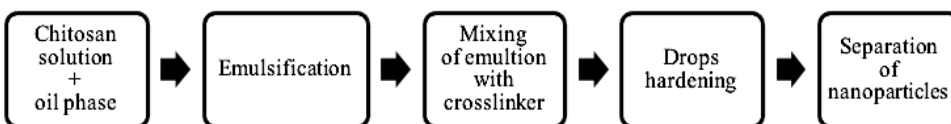
3. Methods for the Preparation of Chitosan Nanomaterials

Chitosan nanomaterials might have nanochitosan particles, other nanoadditives or nano-sized polymer chains (1–100 nm) [5, 28, 29]. Many methods of chitosan modification have been reported in the literature [29]. There are three common chitosan modification methods to generate nanomaterials [6, 29–36]:

- emulsion crosslinking;
- the ionic gelation method; and
- the reverse micellar method.

There are also other methods of nanoparticle synthesis, e.g. emulsion-droplet coalescence method, sieving method or spray drying [6, 30, 38].

Emulsion crosslinking is shown in Scheme 2 [6, 30–33]. Functional chitosan groups react with aldehyde groups of the crosslinker. The emulsion (W/O, water in oil) is formed by emulsifying the acidic aqueous solution of chitosan in the oil phase. Water drops are stabilized by surfactant solutions. Glutaraldehyde is added to the emulsion to harden the drops. The resulting nanoparticles are filtered and washed in *n*-hexane and alcohol and then dried. The size of the formed droplets in emulsion affects the size of the nanoparticles [30].



Scheme 2. The emulsion crosslinking method to synthesize chitosan nanoparticles

The **ionic gelation method** allows synthesis of nontoxic and stable chitosan nanoparticles without using organic solvent [6, 30, 34, 35]. This method is based on the phenomenon of complexation between oppositely charged particles. Through replacing chemical crosslinking with physical crosslinking with electrostatic interaction, the toxic reagents and side reactions can be avoided. Chitosan is dissolved in aqueous acetic acid. As a result, chitosan cations are formed. Then, drops of this solution at a constant stirring speed are added to the solution containing polyanions of tripolyphosphate (TPP). There is interaction between chitosan cations and TPP anions. As a result, chitosan undergoes ionic gelation and chitosan nanoparticles are formed.

The most popular method for nanoparticle synthesis is **reverse micellar** (Scheme 3) [6, 30, 36]. In this method, synthesized nanoparticles are thermodynamically stable and monodisperse, and they are isotropic reverse micelles. The nanoparticles can have a wide range of diameters: 50–100 to 200 nm. Surfactant is dissolved in organic solution, forming reverse micelles.



Scheme 3. The reverse micellar method for chitosan nanoparticle synthesis.

An aqueous chitosan solution is added to an oil solution. During stirring, solidification solution also must be added. The sample is dispersed in water, and after adding this salt, it precipitates, separating the surfactant. Wet nanoparticles are formed after sedimentation by centrifugation. The nanoparticles must be dried.

The key is choosing of the right technology to obtain nanoparticles in accordance with the principle of sustainable development and product lifecycle management (PLM) [37]. The chosen method of chitosan nanomaterial synthesis should be as simple as possible, inexpensive in all phases of PLM and should allow obtaining nanoparticles with an expected morphology and a small size distribution [28, 37]. PLM of chitosan nanomaterials is shown in Fig. 2 [28].

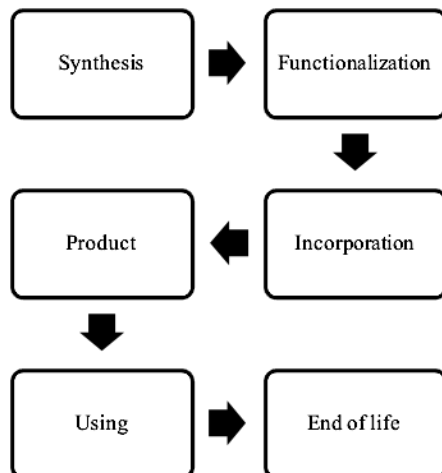


Figure 2. Project lifecycle management of chitosan nanomaterials.

4. Selected Chitosan Nanomaterials With the Ability to Adsorb Metal Cations

Metal cations can be adsorbed by chitosan via chelation on amine groups. These metal cation-chitosan interaction may have potential impacts on new applications of chitosan polymers in material engineering. Chitosan materials have been applied for the adsorption and removal of metal cations as coagulants for water treatment; they are used in cosmetics, medical materials and in various other industries [38, 39]. These materials are also used to adsorb dyes [39–43] and metal anions or phenol products [39,40]. The effectiveness of traditional materials used in water purification has been recently enhanced by the use of nanoparticles or composites. Chitosan, nanochitosan and its nanomaterials exhibit high adsorption activity for a variety divalent metal ions, e.g. copper(II) (Cu^{2+}), nickel(II) (Ni^{2+}), cadmium(II) (Cd^{2+}), zinc(II) (Zn^{2+}), lead(II) (Pb^{2+}) and mercury(II) (Hg^{2+}) in acidic or nonacidic conditions [4, 30, 38, 39, 44–58]. Chitosan nanomaterials are also known as compounds for removal of higher valence metal ions, such as chromium(III) (Cr^{3+}) [47, 56], chromium(VI) (Cr^{6+}) [56, 57] and selenium(IV) (Se^{4+}) [58]. Table 2 presents a comparison of the metal cation adsorption properties for selected chitosan nanomaterials.

Vijayalahshimi's group synthesized biopolymer with beads of nanochitosan (NCS)/sodium alginate (SA)/microcrystalline cellulose (MC) (NCS/SA/MC) [44]. The NCS was prepared by ionic gelation. The author's studies this polymer as a removal system of divalent metal ions, namely Cu^{2+} . The effect of adsorbent dose on the Cu^{2+} ion adsorption was evaluated in the solution of the synthesized NCS/SA/MC beads (prepared in a 2:8:1 ratio), with an amount that ranged from 1 to 6 g and a constant concentration of divalent ions at pH 5. In the beginning, the removal percentage of Cu^{2+}

increased as the adsorbent dose increased (from 1 to 4 g). In the range from 4 to 6 g, there was approximately 80% Cu^{2+} ion removal. This process had better efficiency at higher concentration of the adsorbent. The 4 g dose exhibited the maximum ion removal percentage (about 82%). The effect of initial metal ion concentration decreased from 87% (62.5 mg/L Cu^{2+}) to 43% (10,000 mg/L Cu^{2+}) with an increase in the initial Cu^{2+} concentration. The adsorbent dose and metal ion concentration influenced the removal of Cu^{2+} ions. These NCS/SA/MC beads could be used to water treatment to remove copper(II) ions.

Table 2. Comparison of the metal cation adsorption properties of selected chitosan nanomaterials with adsorption properties.

Nanomaterials	Adsorbed metal ions	Reference(s)
Nanochitosan/sodium alginate/microcrystalline cellulose	Cu^{2+} and Pb^{2+}	[44, 45]
Nanochitosan	Zn^{2+}	[46]
Chitosan/sporopollenin microcapsules	Cu^{2+} , Cd^{2+} , Cr^{3+} , Ni^{2+} and Zn^{2+}	[47]
Electrospun chitosan/polyethylene oxide nanofibres	Cu^{2+}	[48]
Magnetic chitosan nanocomposites	Cu^{2+} , Cd^{2+} and Pb^{2+}	[49]
Chitosan-poly(maleic acid)	Hg^{2+}	[50]
Fe_3O_4 @Chitosan- <i>p</i> SDCalix	Hg^{2+}	[51]
Chitosan- <i>crosslinked</i> -poly(aliginic acid)	Cr^{6+}	[52]
ZnO @Chitosan core-shell nanocomposite	Cu^{2+} , Cd^{2+} and Pb^{2+}	[53]
Granular composites, composed of metal oxyhydroxide–chitosan nanostructures	Fe^{2+} , Pb^{2+} and As^{5+}	[54]
Chitosan- Fe^0 nanoparticles	Cr^{3+} , Cr^{6+} and Fe^{3+}	[56]
Magnetically recoverable $\text{ZrO}_2/\text{Fe}_3\text{O}_4$ /chitosan nanocomposite	Cr^{6+}	[57]
Chitosan spun hollow fibre with iron oxide nanoparticles	Se^{4+}	[58]

Vijayalahshimi's group also studied NCS/SA/MC as a removal agent for Pb^{2+} [45]. The optimum conditions for adsorption were pH 6, a 4 g adsorbent dose and an initial Pb^{2+} concentration of 62.60 mg/L. These results were very similar to the removal of Cu^{2+} .

Seyedmohammadi's group studied the removal of Zn^{2+} from a water source [46]. Zn is a heavy metal and is an important environmental problem; its accumulation in tissues leads to numerous disorders and diseases. The authors used chitosan and nanochitosan to adsorb Zn^{2+} ions. The effect of the initial metal ion concentration on Zn^{2+} adsorption during metal ion removal via chitosan and nanochitosan was examined in the range of 10 to 1000 mg/L of metal ions and 2 g/L of adsorbent. Chitosan at pH 7 and nanochitosan at pH 5 were studied. The percentage of metal ion removal decreased with an increase in the initial concentration of metal ions. The highest removal percentages

for both compounds at 2 g/L occurred at an initial 10 mg/L Zn^{2+} concentration: 91% for chitosan and 99% for nanochitosan. In general, the nanochitosan had better properties than chitosan. The adsorption properties were better for removing Zn^{2+} by chitosan and nanochitosan than for removing Cu^{2+} ions by NCS/SA/MC. The Langmuir isotherm model for both experiments was correct.

Sargin and Arslan synthesized chitosan/sporopollenin microcapsules via a crosslinking method [47]. They examined their adsorption activity towards ions such as Cu^{2+} , Cd^{2+} , Cr^{3+} , Ni^{2+} and Zn^{2+} . The sorption capacity of this compound increased according to the relation: Ni^{2+} (0.58 mmol/g) < Zn^{2+} (0.71 mmol/g) < Cd^{2+} (0.77 mmol/g) < Cr^{3+} (0.99 mmol/g) < Cu^{2+} (1.34 mmol/g). Plain chitosan beads had higher affinity for Cu^{2+} (1.46 mmol/g), Cr^{3+} (1.16 mmol/g) and Ni^{2+} (0.81 mmol/g). Plain chitosan beads adsorbed less Cd^{2+} (0.15 mmol/g) and Zn^{2+} (0.25 mmol/g). The addition of sporopollenin to chitosan microcapsules resulted in an increase the sorption capacity of Zn^{2+} and Cd^{2+} ions.

Lakhdhar's group synthesized electrospun chitosan(CS)/polyethylene oxide (PEO) nanofibres (CS/PEO nanofibres) to remove Cu^{2+} from aqueous solutions [48]. The optimal adsorption (94.7%), from an initial 100 mg/L Cu^{2+} concentration, was obtained by using 75 mg of CS/PEO nanofibres at pH 5.5.

Liu et al. [49] obtained magnetic chitosan nanocomposites. These compounds were based on amine-functionalized magnetite nanoparticles. The authors investigated the removal efficiency of Cu^{2+} , Cd^{2+} and Pb^{2+} ions from water. The adsorption capacity for the tested metal ions was Cu^{2+} < Cd^{2+} < Pb^{2+} . They concluded that the magnetic chitosan nanocomposites could be used to compounds for removal of metal ions.

Ge and Hua [50] received chitosan-poly(maleic acid) nanomaterial (PMACS) and examined its sorption of Hg^{2+} . The maximum adsorption of PMACS was 1,044 mg/g at pH 6.0. This result was similar to other known sorbents.

Bhatti's group also studied new $Fe_3O_4@Chitosan-pSDCalix$ hybrid nanomaterial for removal of Hg^{2+} from aqueous media [51]. The adsorption capacity was 0.043 mmol/g.

Sharma's group studied new chitosan based nanohydrogel, chitosan-*crosslinked*-poly(aliginic acid), which was prepared by co-polymerization method [52]. This compound was used to remove higher valence metal ions, Cr^{4+} from aqueous acid solutions. In 20 ppm Cr^{4+} solution, the highest adsorption was in the 85%. After addition of ionic salts, the results were decreased, e.g. $CaCl_2$ (78.4%) < $MgCl_2$ (79.6%) < KCl (81.4%) < $NaCl$ (82.1%). The smaller ions easily penetrated the pores of the adsorbent, so adsorption increased.

Saad et al. [53] investigated $ZnO@Chitosan$ core-shell nanocomposite (ZOCS) to remove Cu^{2+} , Cd^{2+} and Pb^{2+} from polluted water. The optimum removal efficiency for tested ions was at pH 4.6 and 6.5. The metal ions adsorption capacity increased as follows: Cu^{2+} (117.50 mg/g) < Cd^{2+} (135.10 mg/g) < Pb^{2+} (476.10 mg/g). The results showed that the renovated ZOCS might be used many times without significant efficiency loss.

Granular composites, composed of metal oxyhydroxide-chitosan nanostructures, were studied for their ability to remove iron(II) (Fe^{2+}), Pb^{2+} and arsenic(V) (As^{5+}) as part of a water treatment protocol [54]. All tested solutions were purified with final concentrations of metal ions below the permitted regulations. The researchers confirmed the usefulness of nanotechnology to provide safe drinking water [54, 55].

Geng et al. [56] prepared chitosan- Fe^0 nanoparticles. They studied the effect of initial Cr^{6+} and other factors on the reduction of Cr^{6+} on the surface of this nanomaterial. Geng's group suggested that the complete disappearance of Cr^{6+} might be caused initially by the physical adsorption of these ions and then reduction of Cr^{6+} to Cr^{3+} ions.

This study revealed the chelating properties of chitosan against iron(III) (Fe^{3+}) ions, which inhibited Fe^{3+} - Cr^{3+} precipitation with chitosan- Fe^0 nanoparticles.

Kumar's group used a magnetically recoverable $\text{ZrO}_2/\text{Fe}_3\text{O}_4$ /chitosan nanocomposite (ZFC) to treat carcinogenic Cr^{6+} [57]. ZFC photoreduced Cr^{6+} by 84.70% after 2 h of exposure to solar light.

Dorraj et al. [58] investigated the removal of Se^{4+} from water by chitosan-based nanocomposite. This nanomaterial was prepared via impregnation of Fe_3O_4 nanoparticles on dry-wet spun chitosan hollow fibres. The adsorption capacity was 15.62 mg/g.

5. Conclusions

Chitin and chitosan are commonly used in a wide variety of applications. These compounds are examples of biopolymers from natural sources. Chitosan has good physicochemical properties and is characterized by a polycationic structure with positively charged groups. It consists of two very important, reactive units: amino and hydroxyl groups. The modification of chitosan to nanochitosan is becoming more popular. These derivatives have better properties than chitosan. Chitosan, nanochitosan and chitosan-based nanomaterials are often used as plant protection products (based on their antibacterial activities) or as adsorbents that remove metal ions during water treatment. Chitosan nanomaterials have promising metal cation adsorption properties. As the literature has shown, the effectiveness of metal ion adsorption in the water purification process is higher for chitosan nanomaterials than for chitosan alone.

6. References

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