Chitosan-Containing Composite Materials for Adsorption and Catalysis

Composite materials including organic–inorganic systems have drawn special attention due to their enhanced properties such as adsorbents and heterogeneous catalysts. At the same time, large-scale production of environmentally benign functionalized biopolymers, such as chitosan (CS), allows for constantly developing new materials, since CS reveals remarkable properties as a stabilizing agent for metal-containing compounds and enzymes and as an adsorbent of organic molecules.

Keywords: chitosan ; organic–inorganic composites ; adsorbents ; catalytic supports

1. Introduction

Chitosan (CS) is a natural polysaccharide composed of 2-amino-2-deoxy-D-glucose residues connected via 1,4-glycosidic bonds, which is obtained by deacetylation of chitin (**Figure 1**)—the main component of the exoskeleton of crustaceans, insects and the cell walls of fungi [1][2][3].
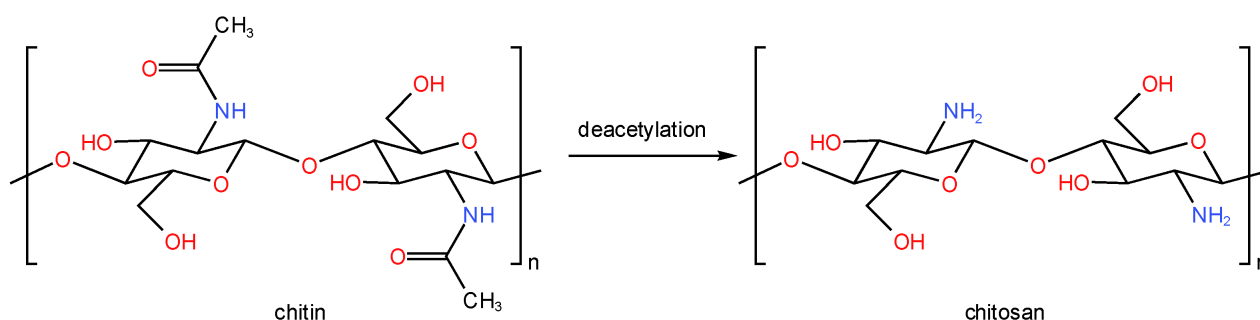
Figure 1. Deacetylation of chitin.

CS is a unique biopolymer that contains primary amines as well as hydroxyl groups and has exceptional properties and wide application. The high adsorption capacity of CS is used for the capture of cations, anions, organic dyes and pharmaceutical ingredients from wastewater. It is noteworthy that CS-based materials are also used as carriers for drug delivery. In addition, various CS-based metal-containing nanocomposite materials have been effectively used in catalytic reactions. CS can be also used for the development of promising inexpensive materials for the agricultural industry. The constant demand for effective adsorbents for the removal of pollutants can be met by fine-tuning the structural properties of CS using appropriate crosslinking agents or additives. Thus, the development of CS-based materials is a constantly growing field requiring continuous research [1][2][4], which also causes the corresponding growth of the CS market [5]. There is a large number of synthetic polyamines, such as polyaniline (PANI) [6][7][8][9], polyalkylamines [10][11], polylysine [12] [13] and polyornithine [14], which can be applied in adsorption, catalysis or medicine. Synthetic materials reveal excellent antibacterial and adsorption properties. However, CS-based materials are still promising due to the low cost, biocompatibility and biodegradability.

CS can be divided into the following types: technical, industrial, food and medical. This division depends on the CS solubility in diluted solutions of organic acids (acetic, lactic and malic acids) and its characteristics such as viscosity, molecular weight and deacetylation degree (DD). The most valuable for practical use is CS with high DD, low molecular weight and high solubility, which make it a structure-forming agent and effective sorbent. Lowmolecular weight CS can be produced using variety of methods, among which are oxidative depolymerization, plasma process, ultrasound treatment, acid hydrolysis and enzymatic hydrolysis [15][16][17][18][19][20][21].

2. Chitosan Modifications

In protonated form CS is capable of interacting with negatively charged molecules, nanoparticles (NPs) and cells [4][22]. In general, CS is able to participate in four main types of interaction: ionic, hydrogen, hydrophobic and complex formation. This opens numerous methods of CS modification. The reactive groups of CS (primary amino groups, primary and secondary hydroxyl groups (C_6, C_3), glycosidic bonds and acetamide groups).

Chemical transformations of CS include the formation of ethers (methyl, ethyl, carboxymethyl, hydroxyethyl) and esters of both inorganic (nitrates, sulfates, xanthogenates) and organic (acetates) acids. Physical, chemical and mechanical properties of CS-based polymers can be significantly improved by mixing, inclusion of solid fillers, grafting (insertion of other functional groups), crosslinking and binding to other macromolecular chains, impregnation, interpenetration and ion imprinting methods [2].

2.1. Grafting of Functional Groups

Grafting of additional functional groups can noticeably increase the number of adsorption sites in a CS molecule and, consequently, its adsorption capacity [23]. Recently, Olshannikova et al. [24] synthesized 2-(4-acetamido-2-sulfanilamide) chitosan (**Figure 2**)—water soluble derivatives with molecular weights of 200, 350 and 600 kDa. 2-(4-Acetamido-2-sulfanilamide)-CS was synthesized with high yield (75–83%) through the reaction of CS with 4-acetylsulfanilchloride in DMSO medium. A synthesized CS derivative was used for the successful immobilization of different cysteine proteases: ficin, papain and bromelain.
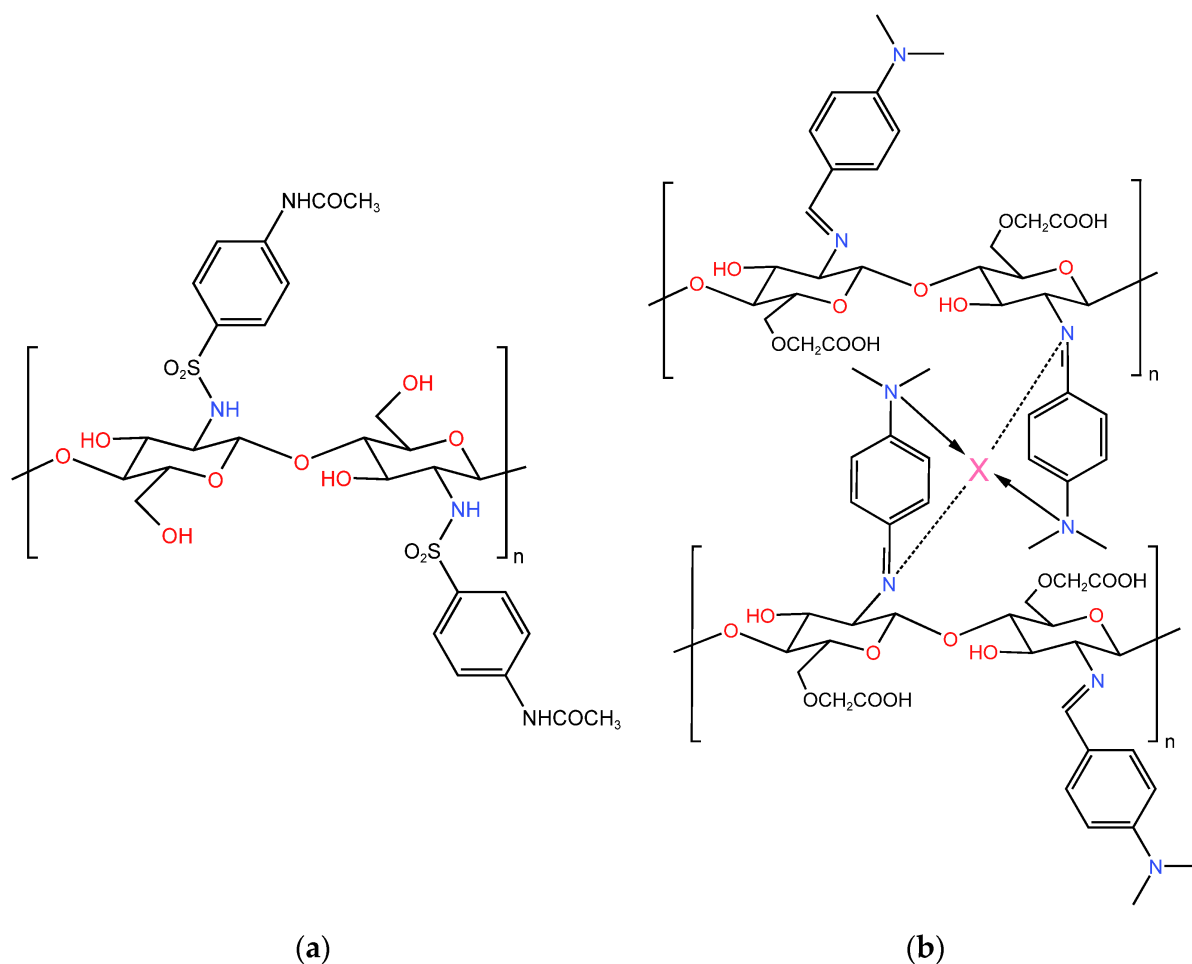
Figure 2. Structure of 2-(4-acetamido-2-sulfanilamide)chitosan (**a**) [24] and carboxymethyl CS/p-dimethylaminobenzaldehyde metal complex (**b**) [25].

In addition to functional groups, other polymers can be grafted to CS as well. For example, Rostami et al. [26] grafted cellulose to CS using EDTA (**Figure 3**). The CS-EDTA-cellulose network contained both acidic and basic sites on the surface and was used as a multifunctional organocatalyst for the synthesis of 2-amino-4*H*-pyran derivatives with high yields (85–96%) at room temperature via a one-pot reaction between ethyl acetoacetate aromatic aldehydes and malononitrile in EtOH as a green solvent. The CS-EDTA-cellulose nanocatalyst was easily recovered from the reaction mixture by using filtration and reused at least five times without any significant decrease in its catalytic activity.
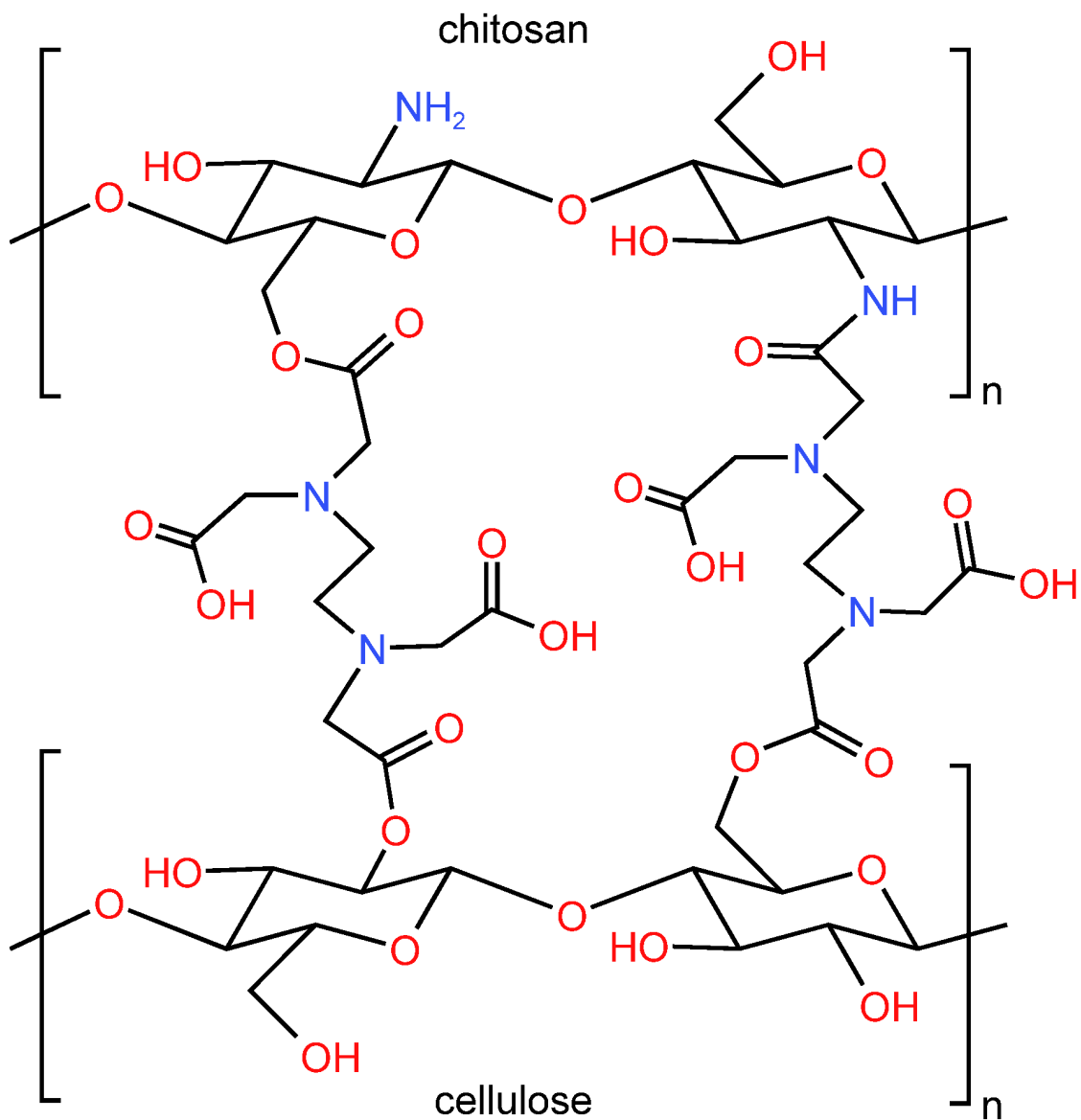
Figure 3. Structure of CS–EDTA–cellulose [26].

2.2. Gelation

Gelation is one of the most widely used methods of CS modification [27]. Polymer hydrogels are hydrophilically crosslinked macromolecular systems capable of retaining significant amounts of water, while preserving the properties inherent in solids (certain shape, mechanical properties of the material during tensile and shear deformations). This combination of properties determines a wide range of their applications: sorbents, gas separation and ion-exchange membranes, structure-forming agents for food industry, drug carriers, artificial tissues and materials for soft and intraocular lenses [28] [29].

Gels that meet these requirements can be obtained through physical interactions, which include electrostatic, hydrogen and van der Waals bonds arising between polymer chains [30][31][32].

2.3. Formation of Nanoparticles

It has been proven that CS derivatives are especially effective while in the form of NPs [33]. NPs are used as a method of integration and storage of active substances and consist of macromolecular and/or molecular structures in which active substances (drugs, enzymes, metal ions) are dissolved, stored, encapsulated or even adsorbed, or maintained at the outer interface [34]. Methods of CS NP synthesis include ionotropic gelation, emulsification and cross-linking, complexation with PE, self-assembly and drying processes. Below are some peculiarities of these methods.

## 3. Chitosan-Containing Materials and Composites as Adsorbents

CS is known to be an environment-friendly and cost-efficient adsorbent for dyes and inorganic ions from wastewater. However, CS has some drawbacks, including dissolution in anacidic environment and poor mechanical properties,

resulting in unsatisfactory adsorption performances. Crosslinking allows for the enhancement of the mechanical properties and pH-stability of CS. At the same time, the grafting of CS with functional groups is an effective way ofimproving its adsorption performance [35].

3.1. Structured Chitosan Materials

The general method for preparation of CS beads consists of the dissolution of CS in acid medium and its subsequent dripping in alkaline medium. There are many beading parameters (CS molecular weight and concentration, acid concentration, NaOH concentration, temperature), which are the subject of optimization. Additionally, the subsequent crosslinking of CS beads with various agents allows for further increase in their permeability, stability and adsorption ability.

Diepoxyoctane (DEO)-crosslinked CS beads modified with spermine (SP) were synthesized (**Figure 4**) [36]. SP was chosen as an amination agent for the enhanced adsorption of Cr(VI) from aqueous solutions. As can be seen from **Figure 4**, DEO can interact with either $-CH_2OH$ or $-NH_2$ groups of CS; thus, free $-CH_2OH$ groups can further interact with ECH and then with SP. Optimal CS–DEO–SP beads were prepared using 1.5 mg/L of SP for 5 h at 50 °C. The prepared beads exhibited heterogeneous and porous surfaces. The obtained CS–DEO–SP beads were macroporous and had increased surface area, pore volume and pore size by 4.9, 7.1 and 1.4 times, respectively, in comparison with initial CS beads. The experimental data revealed that the adsorption of Cr(VI) ions on the CS–DEO–SP beads was extremely dependent on the solution's pH level. A maximum adsorption capacity of 352 mg/g was found at acidic condition (pH 2.0). Regeneration of CS–DEO–SP was successfully performed via treatment with NaOH solution (1.0 mol/L). Regenerated CS–DEO–SP beads allowed for the achievement of an adsorption capacity of 192.31 mg/g after five cycles of repeated use. Thus, high adsorption capacity, acid stability and reusability render the CS–DEO–SP beads a promising and effective adsorbent for eliminating Cr(VI) from metal plating wastewater.
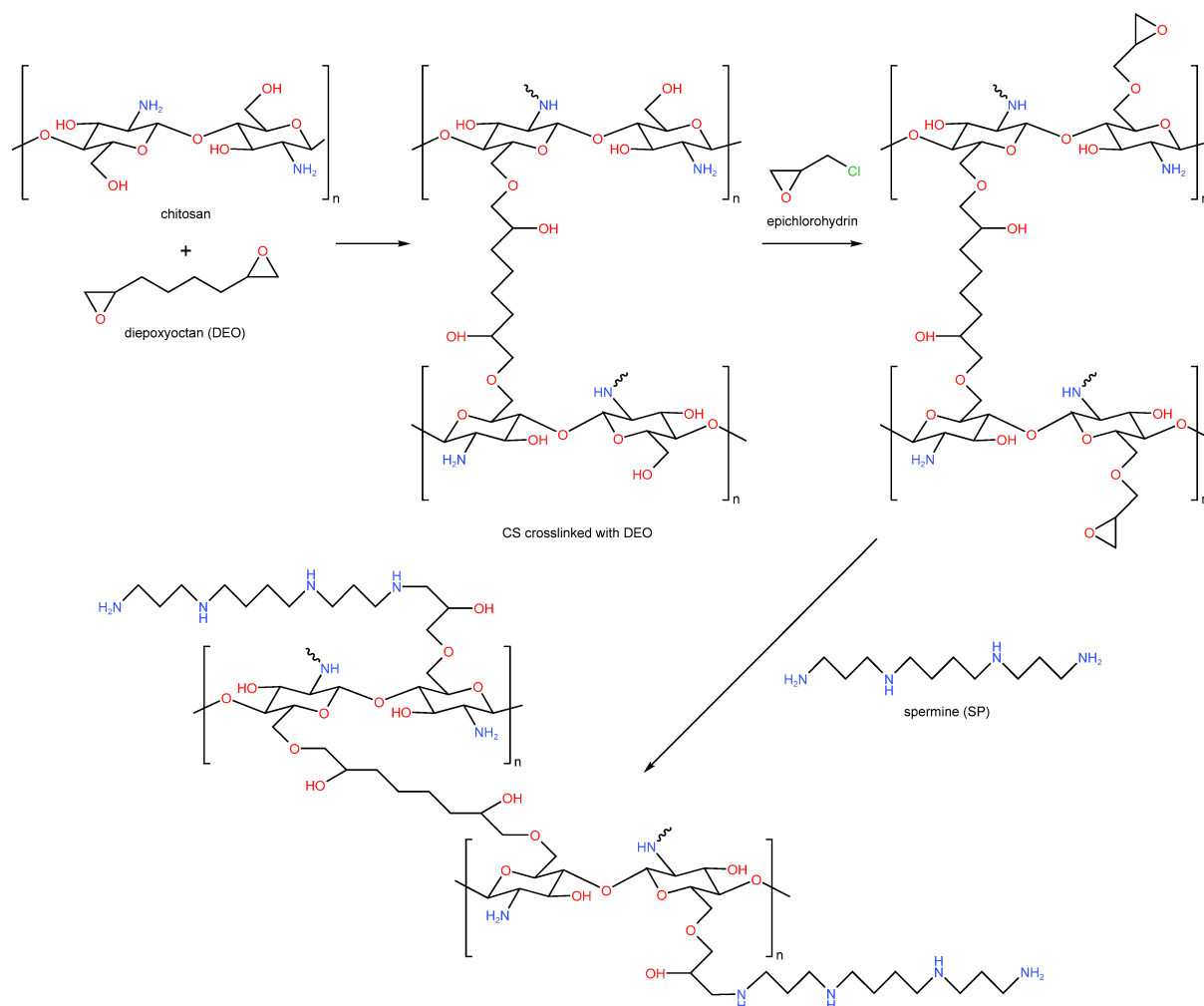
Figure 4. Synthesis of CS–DEO–SP beads [36].

3.2. Chitosan-Based Organic/Inorganic Composite Adsorbents

In most cases, composite CS-based materials represent the combination of CS with inorganic compounds such as metal oxides. Such CSoxide composites typically are obtained via preliminarily mixing CS solution with solid inorganic particles

and the subsequent gelation of the resulting composite material.

A composite adsorbent made of CS and bentonite clay was prepared [37] and used for the adsorption of Cr(VI) ions from aqueous solutions. A composite CS–bentonite clay was obtained by mixing bentonite with CS solution in 2% acetic acid with further dripping in NaOH solution to form composite CS capsules, which underwent crosslinking with GA. The effects of pH, adsorbent dosage, adsorbate concentration, temperature and contact time were studied in batch mode. The experimental data were well-fitted to a Scatchard adsorption isotherm and the adsorption capacity was calculated from theisotherm model. It was found that bentonite clay had a maximum adsorption capacity of 11,076 mg/g, while the composite revealed an almost ten times higher maximum adsorption capacity (106.444 mg/g) for the removal of Cr(VI) ions at 25 °C, pH 2 and a contact time of 60 min. The mechanism of adsorption included ion exchange, electrostatic interaction and complexation.

3.3. Magnetically Separable Chitosan Composites

Magnetically separable composites based on various biopolymers are widely used for removal of different heavy metals from aqueous solutions [38]. Incorporating magnetic materials into the CS matrix and shaping CS in various forms such as beads, membranes, hydrogels, etc., greatly boosts the separation problem of CS [39].

Moreover, Fan et al. [40] used two methods for the preparation of magnetic CS beads. The first method (embedding method) was based on the most widespread approach—preliminarily synthesis of Fe_3O_4 NPs, mixing of magnetic NPs with CS solution, and dripping of Fe_3O_4–CS solution in NaOH solution with further crosslinking with GA. The second method (chemical coprecipitation method) was based on the dissolution of CS and precursors of magnetic particles (Fe(II) and Fe(III)salts) in 3% acetic acid with subsequent dripping of this mixture in NaOH solution and crosslinking with GA. Thus, two series of magnetic CS beads with different Fe_3O_4/CS mass ratios were prepared.

Synthesized magnetic CS beads were used for the adsorption of Ag^+, Cu^{2+}, Hg^{2+}, Cr^{3+} and Cr^{6+} from aqueous solutions and recovery studies. Compared to the adsorption recovery index, the effort vector data visualization was more straightforward and easier to use. While comparing the two magnetic CS bead synthesis methods based on the proposed effort vector data visualization, it was found [40] that both synthesis methods allow for similar efficiency of heavy metal adsorption and data distribution. Independent of the synthesis method, CS beads containing 0.3 g of CS and 0.7 g of Fe_3O_4 NPs revealed best performance for the adsorption of the chosen heavy metal ions.

Though most researchers prefer to synthesize CS-based materials in the form of beads, which possess low flow resistance and are hence convenient for continuous mode operation, for special applications, CS films and coatings can be obtained.

CS nanocomposite films were prepared [41] using in situ precipitation of magnetic particles. The method of synthesis was based on the above-described chemical coprecipitation. The difference was in the shaping of the resulting material: a film was obtained by pouring the mixture (CS and iron salts) into Teflon Petri dishes and subsequently drying and rinsing it with NaOH solution; no crosslinking agents were added.

4. Chitosan as Catalytic Support

4.1. Catalytic Metal–Chitosan Composites

The lives of NPs can be divided into three stages: preparation, storage and application. The stabilization of particles' physical and chemical characteristics is critical and must be carefully controlled [42]. Metal deposition on CS is a promising area of research in the field of catalysis, since CS is a source of various functional groups that can effectively bind metal ions or NPs [43][44]. In the resulting catalytic materials, CS can serve as a reducing agent (due to the presence of hydroxymethyl and amino groups) and stabilizer as well, which is able to control the sizes of metal NPs to some extent.

Any modifications to CS influence the concentration of functional groups and contribution of different interactions (hydrogen bonds, electrostatic interactions, π–π stacking interactions, etc.). For example, it was found that the DD and molecular weight of CS influences the sizes of Au NPs. At low CS concentration (0.005% and 0.01% (*w/v*)), individual spherical Au NPs with a mean diameter of about 10 nm were obtained regardless of chitosan DD and Mw, while anisotropic Au NPs were obtained at a concentration above 0.05% (*w/v*) [45].

The growth of larger polygonal Au NPs was promoted as the higher concentration and lower DD CS was used. Chitooligomers (2.4 kDa, DD 94%) showed the highest reduction ability for Au(III) and the synthesized Au NPs exhibited

aggregation. In general, it was concluded that the DD and concentration of CS is more important than Mw [45].

4.2. Chitosan-Containing Composite Biocatalysts

CS is widely used for the immobilization of enzymes as a part of support for covalent binding or encapsulation [46][47][48][49] [50][51]. The ability of CS to shape beads/microspheres, microcapsules, fibers, membranes, coatings, sponges and gels has expanded its applicability as a support for the immobilization of a wide range of biomolecules and enzymes [52]. However, despite the advantages of using CS as a support for enzyme immobilization, CS beads and fibers are quite fragile and mechanically unstable [53][54].

As previously mentioned, the mechanical properties of CS-based materials can be increased via covalent crosslinking (i.e., with GA or ECH). However, the cytotoxicity of the aforementioned crosslinking agents may hinder the use of CS hydrogels for pharmaceutical and biomedical applications. Thus, in contrast to CS-based adsorbents and metal-containing catalysts, toxic GA is replaced with the safer TPP at the crosslinking stage. For example, Ji et al. [55] used CM prepared by dripping of CS acid solution in the solution of sodium TPP (crosslinking agent) for further co-immobilization of 7α- and 7β hydroxysteroid dehydrogenases (HSDH). It is noteworthy that the immobilization of these enzymes was carried out by preliminary activation of CM with GA that is common for enzyme deposition on heterogeneous supports. CM-immobilized HSDHs were used for the conversion of taurochenodeoxycholic acid (a component of chicken bile). The catalytic reaction reached equilibrium within 4 h. The yield of reaction product (tauroursodeoxycholic acid) was about 62% after equilibrium and the content of tauroursodeoxycholic acidin the reaction product was as high as 33.16% [55]. A similar procedure was applied by Singh et al. [56] for the immobilization of extracellular inulinase from *Kluyveromyces marxianus* on CS beads. Under the optimized conditions, a maximum yield 65.5% of immobilized inulinase was obtained. The maximum hydrolysis of inulin—84.5%—was observed at 125 rpm after 4 h using an immobilized enzyme. The developed immobilized biocatalyst was successfully used for the hydrolysis of inulin for 14 batches.

De Freitas et al. [57] immobilized β-galactosidase produced by the yeast *Kluyveromyces lactis* NRRL Y1564 and delivered an enzymatic activity of 4418.37 U/g_{cell} after 12 h of processing on the CS particles without any crosslinker (CS was dissolved in 2% acetic acid, and then coagulating agent (KOH) was added during stirring). After coagulation, CS particles were activated with GA, ECH or glycidol. GA was chosen as an optimal activating agent. The biocatalyst obtained by immobilization in CS–GA allowed for the effective hydrolyzation lactose of milk (42.8% of conversion) and produced lactulose (17.32 g/L).

5. Conclusions

CS provides a number of opportunities for the production of environmentally friendly adsorbents and catalytic supports due to the existence of functional groups andthe ability to form different shapes (fibers, membranes, beads, NPs, etc.).

For adsorption purposes, the general trend is the use of crosslinking agents (preferably covalent crosslinking) and grafting of functional groups, resulting in a noticeable increase in thenumber of adsorption sites. However, this approach (CS modification) is rarely used in catalysis, especially inthe development of biocatalysts, since the high adsorption ability of CS with respect to both inorganic and organic components may have a negative influence on the biocatalysts' efficiency. Thus, in the case of biocatalysts, CS can be used as a surface modifier of solid supports in an amount of less than 1 wt.%. This also contributes to the maximum availability of active centers of the immobilized enzymes.

At the same time, in the case of metal-catalyzed catalytic reactions, the high adsorption ability of CS can be used for the development of catalytic systems, in which the inorganic part entrapped by CS is a catalytically active phase while organic adsorbate is the subject of catalytic transformation. Thus, modified (grafted), CS-based materials are promising catalytic supports. In the composition of catalytic supports, crosslinking agents are typically not used, as well as certain shaping at a macro-level of the resulting catalytic materials.

The use of CS in biocatalytic processes is based primarily on its excellent gel-forming ability and the presence of amino groups available for interactions in its composition. Thanks to gelation, it is possible to synthesize various stable forms of solid supports for the immobilization of enzymes. Amino groups of CS are used for the covalent crosslinking of enzymes via activating agents due to the formation of Schiff's bases (GA) or amide bonds (carbodiimides), as well as the crosslinking of CS itself in order to form particles of a certain shape. The combination of these properties allows for the achievement of high activity and the operational stability of synthesized biocatalytic systems. CS is most widely used for the immobilization of oxidoreductases (peroxidases, LACs and GOxs) and hydrolases (e.g., LIPs).

Magnetically separable catalysts/biocatalysts obviously have the advantage of easy separation from the reaction mixture, but most of these catalysts have the limitation of sensitivity to low pH. Thus, the further improvement of magnetically separable CS-based composites is a promising area of research.

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