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Sewage Polluted Water Treatment via Chitosan: A Review

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Abstract

Due to the increasing scarcity of water, wastewater treatment and water conditioning are one of the major future issues. Together with the need to apply highly accessible abundant materials and the demand to replace fossil-based chemicals with sustainable compounds from renewable resources, chitosan (CS) provides some of the solutions to obtain these goals and combines both, abundance and sustainability. Hence, the focus of this review is on the application of CS in wastewater treatment providing advantages and drawbacks in using CS in contrast to chitin. We herewith present the application of CS for coagulation/flocculation purposes, whether as native compound, as functionalized molecule or as blend, respectively, composite. The heavy metal, respectively, dye removal is an additional theme to be addressed in the body of the text. The third topic of this review contains the application of CS blends or composites in order to prepare membrane materials for water purification or conditioning. Together with a summary of the recent study, we discuss these findings and possible consequences for future works. In addition, we provide some theoretical background of the processes that CS is involved in and state some mechanistic insights.

Keywords: adsorption, anionic dye, blends, composites, coagulation/flocculation, heavy metal removal, membrane, wastewater treatment, water conditioning

1. Introduction

There are different kinds of sewages derived from industrial production, agriculture, or directly emerging from the households. As a consequence, the three sectors generate high volumes of wastewaters containing inorganic and organic compounds of every description: dyes, heavy metal ions, antibiotics, hormones, feces, colloids, and further contaminants with a

broad structural variety. The removal of these pollutants from wastewater and the conditioning of the water are thus of major interest for the water conservancy. The major parameters that need to be considered and measured in municipal wastewater are as follows: total solids, suspended solids, dissolved solids, total organic carbon, chemical oxygen demand, conductivity, alkalinity, pH, nitrogen, phosphorus, and sulfate content [1]. Special wastewaters, for example, from pharmaceutical or mining industry, require further quantifications such as hormone or heavy metal cation content. According to this, the methods applied for water conditioning mainly depend on the kind of pollution that needs to be separated. In general, processes to purify wastewater include physical, mechanical, chemical, and biological methods with various technologies ranging from adsorption, filtration, biodegradation, oxidation and reduction, UV irradiation, and coagulation/flocculation [2]. However, at the end, qualitative and quantitative criteria required must be met after purification, whereas sustainability as modern key performance is pushed into the foreground. A further aspect concerns the availability and the efficiency of the materials used during conditioning of the wastewater. Chitin, or especially the acid-soluble derivative CS, as the second abundant polysaccharide after cellulose, is one of the polymers to be applied in the wastewater meeting the two requirements. CS has the benefit that it originates from fishery waste and is biocompatible, biodegradable as well as nontoxic and has thus a versatile application portfolio [3]. In contrast to the most naturally occurring polysaccharides, which are either anionic or neutral, such as cellulose, starch, or alginate, CS is a polycation. The free amine groups, which are responsible for the polycationic character, bear nonbinding electrons providing donor properties suitable for coupling to electrophiles, for example, for the formation of imines or amides [4, 5].

One question always arises concerning the application in wastewater treatment: Rather use CS than chitin? Chitin is a glycosidic polymer that has a high degree of polymerization, forms numerous intra- and intermolecular hydrogen bonds, is semi-crystalline, and almost completely acetylated. Chitin manufacturing benefits from known chemical or biotechnological production routes starting at fishery waste that provides a cheap and renewable source. Furthermore, the purification of chitin results in calcium carbonate- or protein-rich side streams that can be further processed supporting economics of chitin production [6]. CS is a derivative of chitin with commonly lower molecular weight and lower acetylation degree, predominantly produced by the chemical conversion of chitin. The conversion reaction includes the application of high concentrated alkaline solution at increased temperature providing thus a nonsustainable process. The harsh conditions are prerequisite due to the fact that the acetamido groups are arranged in a trans-configuration with regard to the hydroxyl group at C3 [7]. The enzymatic deacetylation of chitin at mild conditions is nowadays the content of numerous extensive studies so that the development of prospective economic conversion processes is expected. The prospect of an economic production process contributes to the prediction that CS has a more promising future than chitin in the wastewater treatment [8]. Younes and Rinaudo accordingly stated that CS has a wider range of application areas in comparison to chitin [9]. This is due to the high availability and accessibility of the amine groups, the lower intermolecular forces, and the solubility in acidic aqueous media. Chitin takes advantage of the poor solubility resulting in decreased leaching and thus repeated application in all media. On the other hand, there are processes and functionalizations described increasing

CS stability in acidic media: CS is applicable as powder, flakes, and gel, such as membranes or beads. Gel preparation processes comprise freeze-drying, ionotropic gelation, neutralization, crosslinking, and solvent evaporation method. At least the latter four methods include concluding steps resulting in a more robust CS derivative, composite, or blend [10]. However, CS could be applied as a concentrated solution in acidic media, and this offers the opportunity for homogeneous modification reactions or heavy metal adsorption at the free amine functionalities. The bulky acetyl groups of the chitin provide steric hindrance disabling the proper approximation of reagents to the nitrogen. The inefficient adsorption of heavy metal ions by chitin was already demonstrated [11]. Further, the higher the deacetylation degree, as in CS, the higher the density of the available primary amine groups mainly responsible for the electrostatic interaction. The higher proportion of amorphous regions increases accessibility, sorption capacity and makes it furthermore suitable to act as a flexible linker of different colloids as required for the application in coagulation/flocculation techniques [12].

Flocculation/coagulation is an abundant, efficient, cheap and thus one of the most important processes for the treatment of effluents [13]. The removal of the suspended solids or colloids is mandatory in order to perform the succeeding purification steps. This is one of the processes carried out with inorganic metal salts and/or polyelectrolytes, as CS is. The majority of the CS publications and patents in wastewater treatment focuses on this field of application. Hence, section 2.1 of this chapter elucidates the CS usage in coagulation and flocculation. The specific removal of heavy metals or anionic dyes is a topic that needs to be considered in special effluents as derived from mining or textile industries. CS showed promising results within this field of application and is thus content of section 2.2 of this chapter. The last section has the application of chitin and CS in membrane materials for a theme. Membrane-assisted approaches become more and more important due to their efficiency, improved process controls, and the opportunity for a directed compounding of different materials. Within these applications, CS takes the role of not only a structural substance but also a functional compound as it is the case for adsorption as well as coagulation and flocculation.

2. Main body

2.1. Chitosan as coagulating and flocculating agent

Water quality is commonly diminished by the presence of colloids or smaller organic substances resulting in a high chemical oxygen demand (COD) and high turbidity. The removal of the majority of these compounds is predominantly performed via coagulation and flocculation. Though coagulation and flocculation are used interchangeably, they represent two distinct processes: coagulation is the act of destabilizing a suspension, whereas flocculation means either the spontaneous or polymer-induced formation of large agglomerates succeeding destabilization [14]. The technique transforms colloidal particles or solutes with settling times of years to flocculated or precipitated particles with settling times between seconds and hours. Furthermore, the moisture content of the resulting slurry from up to 99% can be reduced to 65–85% enabling succeeding processing [15]. In general, different organic and

inorganic coagulants and organic flocculants were used. Often, ferric chloride, lime, or alum as agents of choice are applied as the primary coagulant for the destabilization of suspensions due to their availability, efficacy, and their little cost [16]. However, residual concentrations of alum bear environmental risks to the whole aquatic biota [17, 18]. Synthetic polymeric flocculants, as polyacrylamide, are currently used based on the ability to improve flocculation despite their application is associated with lack of biodegradability and the release of degradation products [19]. A decrease or substitution of these reagents by the addition of biopolymers would be beneficial regarding sustainability, ecology, and health. One of the polymers focused on within the investigations was CS. An overview of the recent studies concerning the usage of CS for coagulation and flocculation purposes with original wastewaters rather than model solutions can be obtained from **Table 1**.

The experiments summarized in the table were carried out with different kinds of wastewaters and with native crab shell CS rather than the modified one. Economic viability would be greatly decreased if CS modification is essential to ensure a high efficiency of such a low-cost unit operation even if several investigations were performed with grafted or modified CS [27]. The results revealed that the CS could significantly reduce COD (>60%) and turbidity of the treated solutions (>80%) applied to all kinds of wastewaters and at different conditions. Regarding this, the authors stated that CS has approved to be efficient, concerning the coagulation of suspended matter in wastewater even at low temperatures and low doses [28].

Wastewater from	Effect	Notes	Refs.
Textile treatment	72.5% COD and 94.9% of nephelometric turbidity units (NTO) reduction	Optimum performance at pH 4–6 and 30 mg/L chitosan	[20]
Pulp and paper mill industry	90% turbidity reduction and 60% COD reduction	$FeCl_3$ as coagulant, CS as auxiliary, improves sedimentation and compaction, heterogeneous photocatalysis succeeded	[21]
Olive oil and wine production	80–94% turbidity reduction, 81–94% decrease of total suspended solids, and 73% COD decrease	Best performance at actual pH of wastewater (olive oil wastewater) or no significant influence of pH (wine production wastewater)	[22]
Catfish farming	>99% of microalgae removal efficiency, significant NTU reduction and 80% of the microalgae recovered	CS could be used for both removal recovery of biomass and the overall reduction of the microbial community	[23]
Cardboard industry	Turbidity lowered more than 85% and COD more than 80%	Higher efficiencies than polyaluminum chloride; additionally decreases heavy metal, removes colored compounds	[24]
Tequila industry	CS was the most efficient biopolymer removing 84% of COD	Catalytic oxidation succeeds coagulation/flocculation process	[25]
Rural domestic water treatment	Turbidity reduction of at maximum 99%	Unmodified chitin was used in comparison to alum and sago	[26]

Table 1. An overview about latest results obtained applying CS for coagulation/flocculation purposes with "real" effluents.

The independence of the CS flocculation efficacy from different environment conditions, as temperature, is mandatory since the proposed application is likely to be carried out in non-temperated outdoor sewage plants or in open aquatic systems. The application in aquatic systems for fish or shrimp farming reasons on the requirements to reduce the high nutrient loading and to prevent the accumulation of toxic substances. Synthetic polymers or inorganic compounds mentioned before are not adequate to perform this since they are commonly not biocompatible and biodegradable. For the same reason, CS was successfully applied in accelerating the sedimentation of microalgae. The authors reported differing flocculation efficiencies depending on the pH and dosage but approved that CS can be successfully applied to harvest microalgae [29]. Hence, the application of CS to induce biofloc formation with microorganisms for clarification purposes or reducing harmful nutrient contents would be suitable. This could on one hand increase the water quality in aquatic systems, on the other hand, the resulting flocs can be easily removed or uptaken by the marine animals [23, 30]. However, it can be expected that the growth of different bacterial strains is decreased due to the antibacterial characteristics of the CS constraining the application to eukaryotic microorganisms that are used for this process [31]. Since the antibacterial property is dependent on the amount of amine functionalities, chitin usage in aquatic systems is worth trying out. Native chitin was also successfully applied to decrease COD and turbidity of surface water, but it has to be considered that high concentrations of chitin (>0.1 g/L) were applied. At the same time, surface water contains a lower amount of contaminants in comparison to industrial or municipal effluents [26]. This reduces the amount of flocculant or "active" sites necessary, possibly enabling the application of chitin.

In contrary to the findings of the authors summarized in **Table 1**, it was proposed several years ago that the effectiveness of flocculants based on biopolymers is low compared to synthetic polymers [27]. It is also obvious that a combination of CS with other techniques seems to be favored rather than the direct application as flocculant [21]. The addition of CS could significantly lower the amount of coagulant required or enhance floc formation, approved for the flocculation of a model system with clay or bentonite, the conditioning of groundwater or for clarification of pulp and paper mill wastewater [21, 32, 33]. Such a process is exemplary provided for the synergistic action with Fe salts shown in **Figure 1**.

In **Figure 1**, ferric chloride is applied as a primary coagulant to destabilize the system, and the so-called perikinetic flocculation due to Brownian motion under vigorous stirring succeedingly occurs. This results in a formation of smaller flocs. The polyelectrolyte activity initiating a large floc formation (orthokinetic flocculation) is not only based on one mechanism. For cationic polymers, such as CS, two main mechanisms can be postulated which occur coincidently: (a) Bridging by the adsorption of one polymer to adjacent colloids (bridging model). This applies also to polymers bearing the same charge as the colloid. (b) Reduction of the electronic repulsion between adjacent colloids by electrostatic interaction, adsorption, and charge neutralization of a polymer with opposite charge (patch mechanism) [14]. The interaction of the CS with the colloids leads to the formation of flocs having low settling times. The performance of floc formation and turbidity removal is withal dependent from the CS dosage, thereby approving the contribution of the patch mechanism. First, increasing CS dosage fosters turbidity decrease; further CS addition concludes in a contrary effect based on the
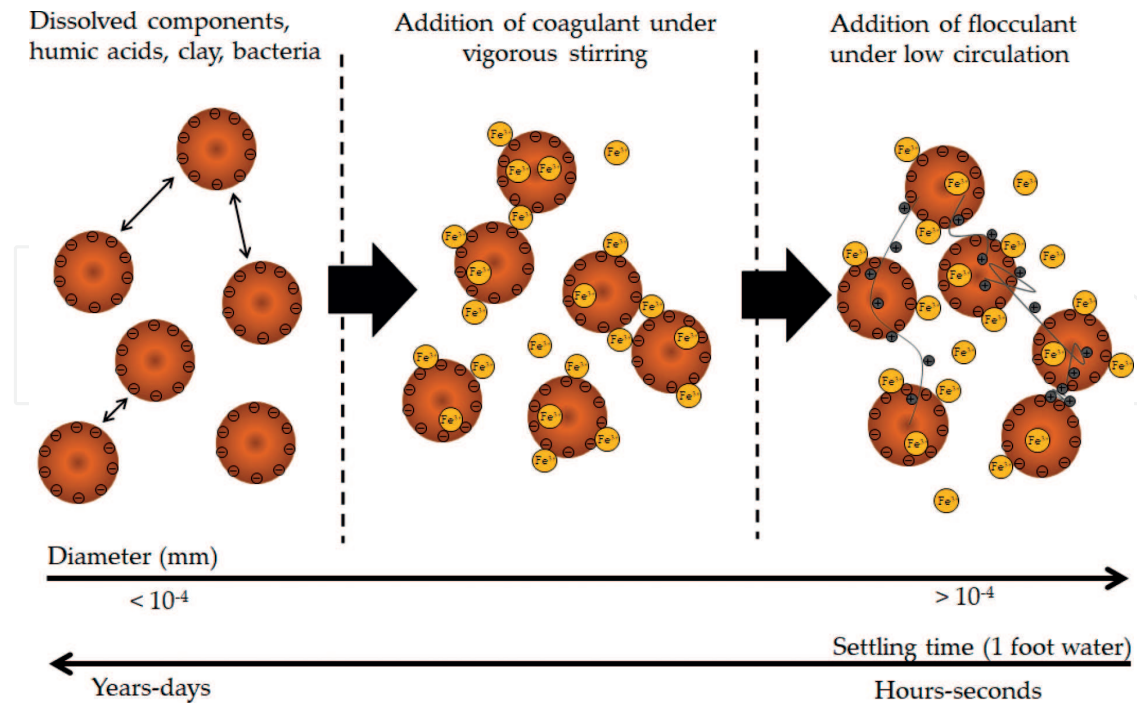
Figure 1. Mechanism for coagulation/flocculation of colloids or solutes with a ferric chloride-CS system. The mechanism is exemplarily shown for Fe^{3+} salts (yellow circles) as primary coagulant and CS (gray line) as flocculant auxiliary. The size relations are not representative.

repulsion of the excess CS adsorbed to the colloids [34]. The size or molecular weight of the polysaccharide provides a further influencing factor. Investigations revealed a higher efficacy of the turbidity removal with increasing CS molecular weight. This approves that bridging also contributes to the effect, but only in tap water, determining the importance of the ionic strength for the mechanism [14, 35]. Guibal et al. stated that the effect of the deacetylation degree was not very significant except at nearly neutral pH values and low ionic strength suspensions. This confirms that a variance analysis with only one independent factor to optimize the flocculation process with CS is not expressive without coincident consideration of other relevant parameters [36].

Based on the results, CS was approved to be an efficient flocculant auxiliary but needs to be applied at an optimum dosage and as a polymer bearing physical-chemical characteristics suitable for the application. Furthermore, the performance is greatly influenced by the pH of the reaction medium [37]. The pH dependency of the CS is linked to the charge density, as confirmed by several authors, providing a double-edged sword [38, 39]. The pH of an effluent can scarcely be adapted due to the commonly high volumes of wastewater generated. This applies not only to the application as flocculant but the more for the usage as adsorbent which is highly sensitive for pH changes.

2.2. Chitosan as sorbent

The coagulation/flocculation mechanism is also effective with regard to the removal of anionic compounds and positively charged heavy metal ions via solid–liquid separation. Besides the

destabilization of dispersions and the removal of the formed floccules, CS can also act as a specific adsorbent although both processes, coagulation/flocculation and adsorption, cannot be investigated separately and occur in general simultaneously. In this section, we focus on the adsorption of the mentioned contaminants present in the effluents. This is especially the case for effluents generated by metal finishing, textile dyeing, or board manufacturing, resulting in wastewaters with high concentrations of toxic heavy metal ions and anionic dyes. Native and derivatized CS demonstrated to separate both compounds with a high effectivity [40]. The capacity of the native CS to adsorb dyes or heavy metals ions is in general dependent from various parameters as deacetylation degree, the particle size, the physical state of the CS, the pH value, and the temperature [41–44]. According to different studies, deacetylation grade is the most relevant parameter and thus the primary amine groups [7]. It has to be stated that the total amount is not relevant but the accessible amount of amine groups is, depending on crystallinity and diffusional properties [45].

Native CS is able to interact with other compounds via free primary alcohol or free primary amine groups depending on the system conditions. In comparison to the application as flocculant, it is widely accepted to modify or combine the CS in order to modulate the stability, rigidity, and viscosity [46]. Crosslinking as one of the most prominent modification procedures prevents leaching of CS at acidic pH and gives additionally the opportunity to recycle, respectively, reuse, the resin [40]. Furthermore, modification is carried out to increase sorption capacity as well as selectivity to adsorb specific compounds as can be inferred from **Table 2**. There are two general modification processes described here for CS: the linkage to reactive molecules and thus the insertion of functional groups, named as grafting, or the crosslinking reactions to form a dense network of CS chains conferring stability to the resin [47]. For derivatized CSs, crosslinking method, crosslinking grade, and the kind of derivatization are crucial for the performance. There are several techniques, covalent and ionic, to crosslink the CS [48]. A third opportunity besides the crosslinking and grafting is the formation of composites or blends to combine the benefits of CS and other materials or better, to develop synergistic effects [40, 49]. Here, the type of compound used and the content greatly alter the functionality and efficiency.

Common to all experiments is that the majority of compounds applied in combination or used to derivatize CS are non-sustainable materials (polyacrylamide and epichlorhydrin). To become the benefits important and to pursue a holistic sustainable approach, materials from renewable resources have to be applied in combination with CS, focusing investigations concerning the removal efficiency with different effluents. All investigations, summarized in **Table 2**, were performed with aqueous solutions spiked with model substances. Although this is only a short overview of the current study, it is obvious that there is a lack of experiments carried out with "real" wastewaters as it is shown in **Table 1** for the coagulation/flocculation studies. Studies with model solutions are suitable for an estimation of the prospective potential and application field but cannot substitute the experiments with effluents. This bases on an activity and stability reduction that has to be expected in a complex matrix. However, results revealed the effective removal of heavy metal ions or dyes from model solutions. Especially the dye removal based on the polycationic character of CS seems to be promising indicated by the high removal efficiencies.

Substrate	Agents	Adsorption characteristics	Notes	Refs.
Synthetic heavy metal solutions	CS dianhydride (ChD)and ChD amine (ChDA)	>66% removal of Cu^{2+}, Pb^{2+}, Ca^{2+}, Ni^{2+}, Zn^{2+}, Cd^{2+}, and Cr^{3+}	Binding constants from 10^4 to 10^5 M^{-1}; ChDA sedimentation velocity 20* higher than native CS	[50]
	Native CS, polyethylene-imine-CS	146 mg/g Cu^{2+} capacity	Desorption with alkaline EDTA; capacity of native CS lower	[51]
	Carboxymethyl CS-hemicellulose	Up to 909 mg/g Cd^{2+} and 333 mg/g Cu^{2+}	Desorption with EDTA; covalent bond via thermal crosslinking	[52]
	Glycine or chloroacetic acid reacted CS	280 mg/g Cu^{2+}, 99% removal of Cu^{2+} and Co^{2+}	Modification does not significantly enhance properties; pH 9 adsorption works best	[53]
Synthetic dye and heavy metal solution	Carrageenan/ CS-microspheres	212 mg/g for dyes and 20 mg/g for Cu^{2+}	Ampholytic microspheres with magnetic Fe_3O_4 core were applied	[54]
	CS-lignin composites	>95% removal and 111 mg/g for RBBR, >95% removal and 20 mg/g of Cr(VI)	The composites exhibit better performance than CS and lignin, no significant pH effect	[55]
Synthetic dye solutions	Carboxymethyl CS grafted polyacrylamide	>93% removal of dyes	Effective removal of anionic and cationic dyes also results in flocculation of dyes	[56]
	CS crosslinked with sulfonates and epichlorohydrin	>90% removal of dyes	Ampholytic character enables the removal of different dyes with one crosslinked CS	[57]
	CS/PVA-blends	130 mg/g capacity for RR	Desorption by pH increase, Langmuir model fits best	[49]
	Nano-ZnO/CS composite beads	76% removal, adsorption capacity of 190 mg/g for RB5	Langmuir model fits best, pH 4 suitable for adsorption	[58]

RBBR: Remazol Brilliant Blue R; RB5: Reactive Black 5; RR: Reactive Red.

Table 2. Abstract of the current research and results concerning the application of native and derivatized CS in dye and heavy metal removal.

2.2.1. Adsorption of dyes

Dyes as adsorbate are usually classified with regard to their charge, succeeding dissolution in water. There are cationic (basic) dyes, reactive (acidic dyes), and non-ionic (dispersed) dyes. The adsorption of anionic dyes is a property originally derived by native CS due to the cationic character at low pH values. Electrostatic interactions play thus the major role with regard to the adsorption of the dyes. The modification of the CS is commonly carried out to improve stability or to extend the adsorbate spectrum. Herrera-González et al., for example,

crosslinked the CS with epichlorohydrin and subsequently grafted the modified polymer with sulfonates resulting in the ability to capture positive-charged dyes [57]. In general, to capture a broader spectrum of dyes and to overcome the hurdle that they show inert properties, CS composites, as CS/bentonite, CS/montmorillonite, or CS/activated clay, were stated as promising materials. As an additional feature, the materials provide an increased stability at low pH values [40]. The compounds to form the composite resins implement new properties resulting in a variety of further interactions between dyes and adsorbent and thus in stronger bonds [55]. Bond strength between adsorbent and adsorbate can be assessed by thermodynamic measurements. The adsorption of reactive dyes with crosslinked CS or CS composites revealed enthalpic values from −53 to 46 kJ/mol. This determines that the enthalpy values are highly dependent on the crosslinking agent and the other compounds the CS is applied with. This is not the case for the Gibbs energy showing low negative values for all investigations and thus exhibiting a spontaneous reaction [58–60].

Rashid et al. bridged the gap between heavy metal removal and dye adsorption. They applied a mixed Fe^{3+}- and Cu^{2+}-CS complex for the efficient removal of Reactive Black 5 [61]. The separation of both, dyes and heavy metal ions, is the content of several investigations using composites. It has to be stated that the adsorption capacity of the materials is decreased (~20 mg/g) in respect to materials developed for the recovery of one compound class alone even if the simultaneous separation was not in the focus of these experiments. Hence, the adsorption of heavy metals should be focused using other CS grafts, blends, or composites.

2.2.2. Remediation of heavy metal pollutants/contaminants

Heavy metal contaminations constitute a severe risk for the environment and also for humans. Not least because they are at the top of the food chain, humans will inevitable uptake and accumulate heavy metals released. An adsorptive removal directly at the source of formation would thus be advantageous in minimizing exposition potential. Based on many studies, CS provides an adsorbent to accomplish this task.

Since the term "heavy metal" is inconsistently defined in the scientific literature [62], we refer to toxic metals with a high density and their oxyanions. The majority of investigations thus focuses on Al^{3+}, Cu^{2+}, Pb^{2+}, Hg^{2+}, Ni^{2+}, Zn^{2+}, Cd^{2+}, Cr^{3+}, and Fe^{3+}, demonstrating the successful application of CS for the removal of these metal ions. On the other hand, CS does not tightly adsorb alkali and alkaline earth metals according to the HSAB (hard soft acid base) principle [63].

As it is the case for the dye removal, the combination of CS with other compounds was in the scope of recent investigations: the hydroxyapatite/CS nanostructures were efficient concerning the removal of Pb^{2+} from wastewater, revealing a higher adsorption capacity than comparable sorbents [64]. The same applies to CS-tannic acid modified biopolymers being able to adsorb Pb^{2+} and Al^{3+} [65]. Blending lignin and CS provides a sustainable material for the removal of metal ions, whereas not only interpolymeric interactions exist but also synergistic effects to capture the adsorptive. The authors state several adsorption sites for one adsorptive based on the interactions derived from hydrogen bridge bonds [55]. All together is that the CS additionally provides a backbone for modifications with functional molecules, improving the chelation of metal ions. However, the results also indicate that the CS itself significantly contributes to the adsorption of these compounds [53].

Investigations approved the high affinity for different metal cations, as, for example, Fe^{3+} to CS by an equilibrium constant of 9.49×10^5 M^{-1} determining that the equilibrium is strongly shifted toward the CS-heavy metal complex [66]. These findings were confirmed by thermodynamic measurements revealing highly negative Gibbs free energy values (−37 kJ/mol) and negative enthalpic values (−41 kJ/mol) [67]. In contrast to that, Negm et al. claimed that the adsorption of copper and cobalt ions is endothermic and entropy-driven, likely reasoning on the different conditions and the functionalization of shrimp shell CS with glycine/chloroacetic acid greatly altering the sorption mechanism [53]. Summarizing the CS-metal ion equilibrium systems revealed that particularly the Langmuir isotherm was the isotherm of choice to analyze the equilibrium data in over 30 systems since they provided a very good fit to the data. However, the authors mentioned that there is a lack of comparable results with other isotherms [68].

Although the detailed mechanism of metal sequestration remains unclear, in general, the removal of metal ions by the action of CS can occur via coprecipitation, chelation, coordination of amine groups as well as ligand exchange or electrostatic interactions with protonated amine groups [69, 70]. The majority of the complexation and chelation studies were performed using Cu^{2+} which is particularly reasoned by the fact that copper ions provide the highest affinity towards CS (up to 1.2 mmol/g) [43]. According to the HSAB model of Pearson, nitrogen as the hard base is appropriate, donating electrons to a borderline acid such as Cu^{2+} [71].

In contrast to the removal of anionic dyes, it is stated that the adsorption of heavy metal ions decreases due to protonation. A chelation process would be efficient at increased pH values since the adsorption of different metal cations is mainly attributed to the unprotonated amine groups of the CS acting as ligands of the metal ion [72]. In the year 1986, the bridge model was one of the first trials to propose a coordination geometry emphasizing the relevance of the amine groups for adsorption [73]. Schlick suggested a square planar structure of the CS-Cu^{2+} complex with four nitrogen ligands derived from the primary amine groups of CS. An octahedral coordination geometry (coordination number: 6) is formed by the arrangement of axial water molecules (see **Figure 2a**) [74]. However, there are investigations suggesting the C3-hydroxyl group as further ligand for complexation substantiated by thermodynamic data that led to the development of refined models (**Figure 2b**) [67]. Further investigations supposed a neutral complex (see **Figure 2c**) consisting of two nitrogen ligands and two hydroxide ions coordinating the copper ion occurring at high Cu^{2+} loadings and pH values of >5.5 [75, 76]. The structures illustrated in **Figures 2a–c** can be described as "bridge model "since they involve the chelation of the Cu^{2+} by nitrogen atoms from different glucosamine units in an inter- or intramolecular fashion [77]. The structure depicted in **Figure 2d** is called the "pendant model "and is up to date the most prominent model describing the interaction between Cu^{2+} and CS supported by potentiometry and circular dichroism data [78]. The model developed by Ogawa et al. in the year 1993 based on X-ray studies assumes the chelation of different heavy metal cations by one amino group only [79]. On the other hand, several authors stated that at least a degree of polymerization of four is required to affect an efficient chelation, the consequence being that not only one glucosamine unit is responsible for chelation [80]. However, the truth probably lies somewhere in between these models based on the dependency of the heavy-metal ion-CS ratio and pH [75]. Some amine functions may be inaccessible for chelation, and others suffer from steric hindrance to form a regular coordination geometry. This is based on the fact that CS provides a natural polysaccharide with all its heterogeneities.
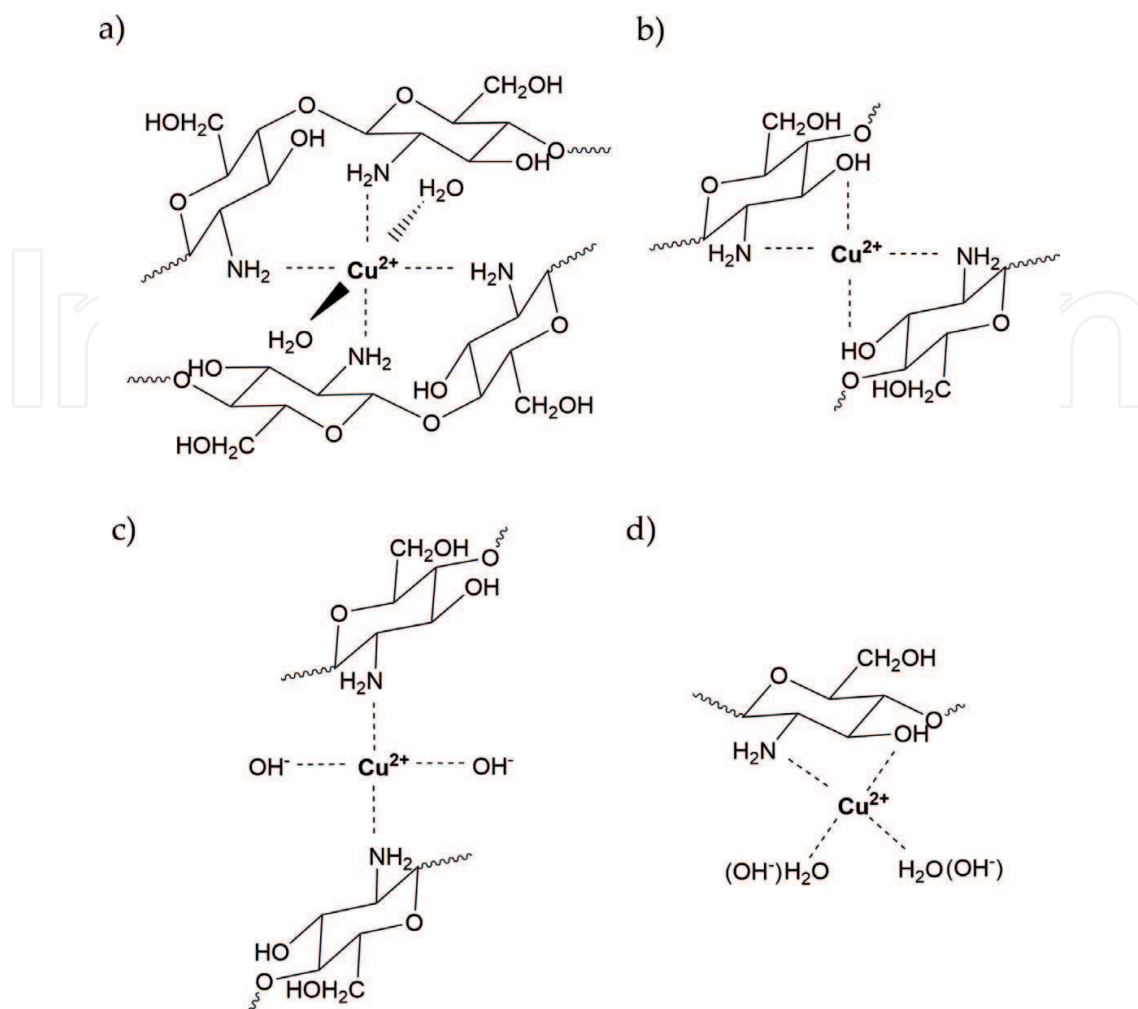
Figure 2. Different chelation mechanisms between CS and metal ions using the example of copper ions: (a) octahedral coordination geometry of the CS-Cu^{2+} complex with four amine and two axial water ligands; (b) Cu^{2+} chelation mechanism utilizing the C3-hydroxyl groups of two glucosamine units; (c) neutral complex with two nitrogen ligands and two hydroxide ions coordinating the Cu^{2+}; (d) "pendant model", chelation of Cu^{2+} by one amino group and the C3-hydroxyl group of one glucosamine unit.

The desorption of metal cations succeeding the adsorption onto CS is scarcely described in the studies. The desorption of the metal ions was either performed by the application of ammonium chloride, potassium iodide, or by EDTA [81]. Shifting pH represents the most suitable method for elution. For example, a pH decrease resulted in a 94% cadmium ion desorption, whereas 8.3 mM H$^+$ per gram of beads was adsorbed to substitute the bound metal ion [82].

Oxyanions like chromate or vanadate can be adsorbed by protonated amine groups at lower pH values due to electrostatic interactions resulting in an exothermic reaction [67, 83]. The simultaneous recovery of oxyanions and metal cations is described in a further study. In common, protonation reduces the adsorption capacity for metal cations but increases the effectivity of metal anion adsorption. The authors performing the experiments take advantage of the distribution of deprotonated and protonated amine groups in a pH range of 5–6. Deprotonated amine groups enable the formation of chelate complexes with Ni^{2+}, Cu^{2+}, and Fe^{2+}, the metal anions were attracted by electrostatic interaction [84]. The optimum pH removing majority of

metal anions by electrostatic attraction is in the range of 2 and 4. At lower pH values, competitive pressure by other anions derived from the acid for pH adjsutement for binding sites on CS is drastically increasing [77]. The decreased adsorption capacity of metal anions in the presence of, for example, high chloride, sulfate, or nitrate concentrations is based on the same effect. A further option to remove toxic oxyanions as selenite or arsenite was provided by Yamani et al. The group demonstrated that the chelation of copper ions leads to the formation of electron-accepting "anion" adsorption sites which did not exist previously, enabling the directed binding of these oxyanions. The bimetallic complex connected via oxygen linker offers the separation of both even in the presence of phosphate at high concentrations [76]. According to this, it was approved that Fe-crosslinked CS enables the adsorption of chromate. The adsorption mechanism is suggested to be a ligand exchange substituting an anion by the chromate in the coordination sphere of the iron ion, resulting in an uptake of Cr(VI) (295 mg/g at pH 4.8) [85].

Resuming the study and investigation results, CS is a valuable sorbent for dyes and heavy metals. However, an efficient simultaneous removal of both compound classes with native CS is unlikely due to the pH dependency of both processes. A successful removal can be expected if the solute containing media has a suitable pH for adsorption. CS solubilization can be prevented by crosslinking, functionalization, or blending, additionally resulting in an increased performance of the resin, widening pH range for optimum sorption and creating synergies between the compounds as for CS-functionalized membranes.

2.3. Chitosan-functionalized membranes

The previously mentioned wastewater treatments, adsorption and coagulation/flocculation, require the direct physical-chemical interaction of the effective agent with the contaminant in the effluent. The intention is to remove the compounds from the bulk solution to achieve effluents for further processing steps. By way of contrast, membrane-assisted applications are commonly applied to enable the purification or conditioning of water with regard to physical rather than chemical properties. The composition of the membrane and the quantity of the materials contained are of great importance to provide selectivity for membrane permeation. In common use, membrane materials consist of synthetic polymers and their composites or blends. Green and sustainable compounds as membrane components are highly demanded for well-known reasons. According to Dobosz et al., biopolymers could additionally reduce biofouling which is crucial for the lifetime, increasing the time span between sanitization cycles of the membrane [86]. Especially CS with its antibacterial activity is thus predestined for the production of membranes sensitive to fouling. Carboxymethyl CS membranes, for example, were applied during a 6-week protein separation process within which no fouling or deterioration in the membrane flux was recorded [87]. Weng et al. approved the antimicrobial activity of a cellulose/CS membrane against *Escherichia coli* in disc diffusion experiments [88]. Studies concerning CS-coated polyacrylonitrile hollow fiber membranes approved the antimicrobial and antibiofouling effect in respect to Gram-positive and Gram-negative bacteria [89, 90]. Another aspect to consider is the hydrophilicity of the membranes, which is a major requirement in water-conditioning applications to obtain membrane permeability. CS provides a high hydrophilicity allowing especially water from aqueous solutions to permeate. Together with a high salt rejection efficiency, this is also the relevant property for the main application fields of CS membranes which can be obtained from **Table 3**.

As can be inferred from the table, CS is content of reverse osmosis (RO), forward osmosis (FO) and nanofiltration membranes. Nanofiltration membranes differ from the other mentioned in the ability to separate particles in the size of 2–5 nm and thus enable permeation of minerals, which would be separated by osmosis membranes. In contrast to FO, RO processes work against the osmotic potential demanding membranes produced to resist high pressure. Both together have the need for semi-permeable membranes revealing high salt rejection grades and high water permeability, approving high efficiencies at moderate costs.

Research and innovation activities concerning the utilization of CS in the three membrane processes are mainly rooted in the countries in North Africa and the Arabian Peninsula. This originates from the access to seawater, resulting in a high availability of crustacean-derived chitin/CS and water deficiency leading to an increased demand for conditioning of water. Seawater is scarce, whereas saltwater is ubiquitous. Hence, in the majority of studies, synthetic monovalent salt solutions were applied, and the results revealed that removal by the CS-containing membranes is

Application	Membrane material	Effect/notes	Refs.
Reverse osmosis (RO) with NaCl solutions	Polyamide-6/CS	Salt rejection increases with the addition of CS as additive up to 52%	[91]
	CS crosslinked graphene oxide (GO)/titania hybrid lamellar membrane	Rejection rate is ~30% at 7.2–14.3 LMH/bar	[92]
	Thin film composite RO membranes covalently linked to CS	>90% salt rejection at LMH/bar >3	[93]
Forward (FO) and pressure-retarded RO with NaCl and Na_2SO_4 solutions	Polymerization of CS with trimesoyl chloride on the surface of SPES/PES support layer	95% NaCl rejection with up to 4.6 LMH/bar permeability, higher CS concentration revealed lower water permeabilities, but higher salt rejections	[94]
FO with synthetic salt and sucrose solution	Membrane consisting of layer-by-layer assembly of CS and GO nanosheets on a sulfonated polyethersulfone (SPES)/PES support layer	>90% Na_2SO_4 rejection at 3 LMH/bar, 2–4 orders of magnitude higher water flux compared to polyamide membrane on sulfonated PES/PES support	[95]
Nanofiltration with synthetic mineral saltwater	CS crosslinked buckypaper membranes	Rejection rates: 80–95% $MgCl_2$, 21–63% for NaCl, 18–37% $MgSO_4$ and 6–14% for Na_2SO_4; water permeability of 0.2–0.9 LMH/bar	[96]
Nanofiltration, retention of basic, neutral and acidic dyes	Polyurethane foam membrane filled with humic acid-CS crosslinked gels	Rejection efficiency >60% for all dye types, >99% for the anionic dyes, adsorption of dyes at the membrane	[97]
Nanofiltration, synthetic emulsion and dye solution	Coating layer with CS and silver nanoparticles, alginate nanofibers as midlayer and nonwoven as mechanical support	Nanoparticle retention >98%, oil removal >93%	[98]
Nanofiltration, humic acid retention	Carboxymethyl CS was blended with polyvinylidene fluoride	>97% humic acid retention; low irreversible fouling, good permeability, durability and stability	[99]

Table 3. An overview of the application fields of chitinous membrane materials and the thereof obtained results.

successfully carried out but with swaying rejection rates (30–90%) [91–93]. Separation efficiencies of nanofiltration membranes are significantly higher considering low-molecular weight organic compounds (>60%) grounding on larger molecular weight differences between the molecules to be separated and thus higher selectivity. Hence, it is not necessary to build high-density networks, which can be produced by utilizing the amine functions of CS as anchor points for modifications. In common, CS is not applied as native but as crosslinked polymer embedded in a matrix or coated on a support layer in order to introduce and combine the advantages of several compounds, or to compensate their weaknesses. Researchers report on the incorporation of modern and innovative components in CS, such as metal-organic frameworks, developing synergies of the two materials, resulting in $MgCl_2$ rejection efficiencies of 93% [100]. As already mentioned, the hydrophilicity of the membrane is the relevant factor for the water flux commonly determined by measuring the contact angle. CS coating of membranes indicated a significant higher water flux than the native membranes and thus resulted in a decreased pressure and energy demand in the process [101].

Swelling of CS is one of the properties to be compensated for the adequate application in membrane technology. As swelling is tantamount to a high water content, this greatly affects the water permeability as well as the mechanical strength of the membrane. Investigations revealed that the ability to swell must be controlled to create membranes that enable a selective separation of water and salt whatever, simultaneously guaranteeing a high water flux [102]. Decreasing the swelling of CS-based membranes means to constrain the movement of the CS chains especially in solvents in which the CS can be solubilized [103]. Further properties affecting the swelling behavior are the pH of the medium and the resulting electrostatic repulsion of CS chains at low pH values [104]. Crosslinking is thus a suitable tool to control this phenomenon as several researchers reported a significant decrease in swelling by crosslinking or modification of the CS up to 300% [96, 105].

Finally, CS seems to be a promising material with regard to the application as a membrane component. Its antibacterial activity in combination with the functionality of the amine groups provides a suitable tool to prevent fouling and coincidently adapts the network to the substrates to be filtrated. The challenges to be mastered are the reduction of swelling of these membranes while approving a high water permeability predominantly in drinking water purification. In addition, further investigations concerning osmosis membranes have to test real saltwater samples not lacking all other natural occurring compounds than sodium chloride as is the case for the synthetic model solutions.

3. Conclusion/summary

Within this publication, we reviewed the purification of effluents with native and modified CS as well as the application of CS-containing membranes for filtration purposes. Crosslinking, derivatization, and the production of composites or blends with other natural and synthetic polymers as well as low-molecular weight compounds are the main type of application described in the study rather than the usage of native CS. It seems to be appropriate to introduce new functionalities, to prevent leaching, or to foster the beneficial properties. Due to these manifold-positive properties in combination with other compounds, the preconditions are favorable for the implementation of CS in wastewater treatment. CS represents a compound to be effective as coagulant/flocculant in

the native state, whereas the addition as flocculant auxiliary decreasing the amount of inorganic coagulants required for the process seems to be promising. The good overall performance adsorbing heavy metal ions and dyes is stated in several investigations, enabling CS to be applied in the treatment of special wastewaters, such as textile and mining effluents. The simultaneous adsorption of both is limited due to the necessity to adjust the pH in order to protonate/deprotonate the CS, effectively removing the single compounds, respectively. Investigations concerning CS-containing membranes showed that a biopolysaccharide could also contribute to more sophisticated water conditioning processes. The water permeability and the selectivity have to be evaluated especially considering the swelling behavior. It can be assumed that CS can also be implemented to produce switchable membranes, which means membranes altering the properties due to pH shifts. However, the investigations concerning the application of CS and its derivatives suffer from several drawbacks not adequately addressed in the past, aggravating the market accessibility (1) cost factors were not considered; (2) experiments limited to lab scale; (3) only batch experiments were carried out; (4) mechanical strength should be increased; (5) studies have to be performed with actual wastewaters; (6) regeneration of the materials was not investigated; (7) swelling behavior of CS needs to be limited, and (8) the heterogeneity of different CS batches is not considered, yet [47, 106]. The heterogeneity particularly derives from the origin of the CS, the crab shells being exposed to varying environmental conditions. Not only the CS derived from fishery waste can be applied for wastewater treatment, but also the CS isolated from fungi or insects for the provision of more homogeneous batches. Since the production of fungal biomass or insect-based protein is already industrially established, a higher quantity and quality of fungal- or insect-based CS can be assumed and could be applied in a prospective effluent purification. For example, Adnan et al. successfully applied commercial fungal CS to purify a synthetic kaoline solution and palm oil mill effluent. They stated that in contrast to crab shell and shrimp shell CS, the fungal CS is available all over the year. Further, it has a narrow molecular weight based on the controlled production process, opposing the argument that the heterogeneity of CS limits its application. The authors assume therefore that prospective works will focus on fungal- and insect-based CS, increasing the opportunity to develop profitable products with improved properties [107].

Conflict of interest

The authors declare that there is no conflict of interest.

Appendices and nomenclature

CS   chitosan

FO   forward osmosis

LMH   liters per m^2 per hour

RO   reverse osmosis

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