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Progress, challenges, and opportunities in enhancing NOM flocculation using chemically modified chitosan: a review towards future development

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Natural organic matter (NOM) occurs ubiquitously in water bodies and this can greatly affect feed or raw water quality (taste, colour, odour, bacterial growth). Furthermore, it reduces the performance of the coagulation-based water treatment process. Because the NOM content and its chemical complexity are increasing throughout the world, the removal of NOM from water has become a major challenge in supplying the required amounts of good quality water. The coagulation–flocculation process is widely used for purifying urban water supplies. However, it is not always sufficiently successful in removing the augmented NOM in the feed water, mostly because the polyelectrolytes currently used as coagulants/flocculants cannot effectively interact with all the NOM components consisting of different functional groups, molecular weights, charges, and hydrophobicity. Within the class of polyelectrolytes, chitosan (Cs), which is produced by the deacetylation of abundantly available chitin, has been tested in removing NOM. The effectiveness of Cs can be further improved by chemically modifying the abundant free amino and hydroxyl groups along the Cs chain backbone. This will provide new functional groups that can increase the positive charges, molecular weight, and allow for solubility over a wider pH range, as well as introduce tailored groups which interact in an optimised way with NOM, thereby reducing the solubility of the formed complexes. This paper critically reviews the chemistry of the formed polyelectrolyte/NOM complexes and provides information on how this can be taken advantage of, to identify modified chemical structures of Cs to improve NOM removal in water treatment strategies.

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Water impact

Natural organic matter (NOM) generally affects feed or raw water quality and increases complexity in water treatment processes. This paper critically reviews the current methods of enhancing NOM removal by the coagulation/flocculation process using chemically modified bio-flocculant, chitosan. Based on current knowledge in the colloid and surface chemistry field, this process is analysed, and we propose structural modifications of chitosan for optimising NOM removal.

1. Introduction

The coagulation–flocculation process is a widely used method for purifying urban and industrial wastewaters because it can

effectively remove contaminants, is simple to operate and low cost. Coagulation is the process of destabilisation of small colloidal particles by reducing the repulsion between similarly charged particles. They can form microflocs, whereas flocculation brings together the coagulated particles and microflocs to form larger macroscopic flocs which settle as a result of sedimentation and can be easily removed.^{1–4} In recent years, research has implemented the coagulation–flocculation process to wastewaters, mainly industrial waters containing suspended particles. These include, for example clay particles, metal oxy-hydroxides, dyes, and metals.^{1,2,5–9} It has not, however, dealt sufficiently enough with the removal of natural organic matter (NOM), especially from a fundamental colloid science point of view of complexing an

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anionic macromolecule by a polycation. Natural organic matter, which arises from the decomposition of plants and microorganisms, is ubiquitous in water bodies.^{10–12} It causes colour, taste and odour problems and acts as a substrate for bacterial growth. It is a major contributor to disinfection by-product (DBP) formation which is tightly regulated.

Changes in the concentration and composition of the heterogeneous NOM in the feed attributed to climate change have impacted on coagulation-based water treatment plants' performance.¹³ This has often reduced the treatment capacity of direct filtration in the water treatment plants. Because NOM concentrations in raw water are continuously rising (e.g. in Australia¹⁴), its comprehensive removal has become increasingly more difficult to achieve. It has also been reported that numerous water utilities in the UK and USA have been experiencing operational difficulties due to the increase in dissolved organic carbon (DOC – a measure of NOM) levels during autumn and winter periods.¹⁵ Whitehead *et al.*¹⁶ reported that throughout the UK, NOM concentration in surface waters has increased progressively from the 1980's to 2003, in fact almost doubled, presumably due to climate change. Rising NOM concentrations in raw drinking waters of Nordic countries due to climate change were also reported.¹⁷ The raw water used in water treatment works in the UK had a strong seasonal variation in DOC concentration ranging from 4.3 mg L⁻¹ in September to 14.5 mg L⁻¹ in December, with this variation the DOC components ratio also changed.¹⁵ This variation was also observed in other temperate climate countries and it was generally ascribed to changes in temperature and hydrology.¹⁸ Yet nonetheless it is very important to retain high water quality and meet the stringent drinking water standards required by legislation and demanded in order to have safe water supplies. The topic of NOM in water has been comprehensively discussed in a recent book.¹⁹

As polyelectrolytes, polycations have mainly been employed as a coagulant–flocculant due to their high complexing tendency for opposite charged NOM.^{3–7} Naturally the strength and type of interaction between the NOM and polyelectrolytes will depend largely on the latter's molecular architecture and the strength of interaction. Accordingly, a number of different polyelectrolytes (both inorganics and organics) are employed here. Although inorganic coagulants (Al³⁺, Fe³⁺ and polymeric versions) have been used for a long time, they have some disadvantages.²⁰ Firstly, a large amount of coagulant is required, and this generates large quantities of sludge which have disposal problems. Secondly, in the case of alum the process is very sensitive to pH. Thirdly, they are difficult to tailor for optimised removal, *i.e.* to adjust them specifically to various types of NOMs and thereby achieve as much NOM removal as possible. For these reasons, organic polyelectrolytes (e.g. poly diallyl dimethyl ammonium chloride (PDADMAC)) with enhanced abilities to flocculate NOM even when added in small quantities have been developed in the last few decades.^{10,11}

Organic polyelectrolytes can be synthetic or natural. The advantage of using natural polyelectrolytes is that typically

they are biodegradable, and mostly obtained from natural wastes or resources. Within the class of natural polyelectrolytes, chitosan (Cs), which is produced by the deacetylation of chitin, plays a leading role in effectively removing NOM.^{4,21} It has many uses in many fields including cosmetics, food, wine, pharmaceutical, wood and agrochemical industry as well as in water treatment.^{5,22} In water treatment the use of Cs is concentrated mostly on the removal of dyes, microorganic pollutants, heavy metals and inorganic colloidal particles and humic acid. The initial investigations concentrated on unmodified Cs, whose applicability is largely restricted to pH values below 6.5, as above it becomes insoluble. However, the effectiveness of Cs can be tuned and further improved by chemical modification to provide new functional groups, to modify its water solubility, and to enhance synergistic interaction with the NOM that needs to be removed. The modifications can be easily done due to the presence of abundant free amino and hydroxyl groups along the Cs chain backbone. A recent review article highlighted the easy chemical modifications of Cs resulting in a wide range of physico-chemical and biological properties of the modified Cs that have opened-up new opportunities for its application in many industries.²² Some modifications reported for Cs in the literature are:

- (i) Enhancement of its solubility in a wider pH range.
- (ii) Increasing the number of positive charges for stronger interaction with the negatively charged NOM.
- (iii) Increasing molecular weight (M_w) for effective bridging with NOM.^{1,2,23–28}

Such modifications have been made to improve the Cs' adsorption capacity/flocculation properties to remove mainly pollutants such as heavy metals, clay minerals, microorganic compounds and dyes.^{1,2,5,9,27} Recent reviews have summarised the results obtained with chitosan-based flocculants for removing a variety of pollutants in water.^{2,22} However, the precise role of modified Cs (and also of other polycations) in the removal of NOM is still not currently well understood. As well, previous reviews did not comprehensively consider the necessary Cs modifications and possibility of removing all components of NOM, notably the more hydrophobic components. Furthermore, a central aspect here is the strength of interaction between the polyelectrolyte and NOM, which for the anionic NOM and cationic polyelectrolyte largely results from the electrostatics involved and the release of the counterions. However, other factors including hydrophobic interactions, van der Waals forces, and H-bonding may play an important role. In colloid science such systems of oppositely charged colloids/polymers have been studied to quite an extent over the last 30 years regarding thermodynamics, structures present and kinetics of their formation.²⁹ Yet, only some aspects of the concept may have been transferred to the realm of water treatment.

This paper critically reviews the current methods and mechanisms of coagulation/flocculation used to remove NOM with a special emphasis on employing chemically modified Cs to promote the formation of polyelectrolyte



complexes with NOM. New modifications based on the knowledge garnered from colloid stabilisation studies applied to industrial applications such as drug delivery, cosmetics, food and packaging, and paper manufacture that have the potential for the enhanced removal of NOM, are suggested.^{9,22,23,30–33} Some of the modifications suggested previously may not be applicable to the removal of NOM due to the removal mechanism being different from those for other chemical compounds. For example, it was reported that the molecular weight of Cs needs to be reduced by chemical modification so that Cs is better utilised in some commercial applications.²² In contrast, the molecular weight of Cs needs to be increased for the effective removal of NOM by the bridging mechanism. The novelty of this paper is: firstly, critically reviewing the mechanisms for removing NOM using polyelectrolytes and secondly, identifying the chemical modifications of Cs that are suitable for NOM removal based on the unique properties of NOM and its flocculation mechanisms.

2. Natural organic matter (NOM) characteristics

Understanding the characteristics of NOM is essential in selecting the most suitable coagulation/flocculation process for its removal. However, it is difficult to assess the characteristics of NOM in thorough detail because of the heterogeneous size (wide molecular weight distribution), structure (different structural motifs contained), and the functional chemistry of its constituents. The NOM characteristics are broadly classified based on hydrophobicity/hydrophilicity, M_w , and charge of the functional groups, mainly using operationally defined procedures such as resin adsorption, size exclusion chromatography (SEC), nuclear magnetic resonance (NMR) spectroscopy, and fluorescence spectroscopy. One study reviewed the methods available for its characterisation several years ago, demonstrating the highly complex nature of NOM.³⁴

Natural organic matter in decreasing order of size consists of zooplankton, phytoplankton, bacteria, viruses, clay-humic acid complexes, humic acids, proteins, polysaccharides, fulvic acids, and very small molecules such as fatty acids, carbohydrates, amino acids, and hydrocarbons.³⁵ Of these, humic acids and fulvic acids constitute the largest amounts in most NOM, typically accounting for 53–68% of the dissolved organic carbon (DOC) in natural water bodies.³⁶ In one procedure called the rapid fractionation procedure, NOM is classified according to hydrophobicity, hydrophilicity, and charge, into four fractions: (i) very hydrophobic (VHA) or hydrophobic acid (HPA); (ii) slightly hydrophobic (SHA) or transphilic acid (TPA); (iii) hydrophilic charged (CHAR); and (iv) hydrophilic neutral (NEUT) by using adsorption of NOM on various ion exchange resins.^{35,37} The hydrophilic fractions are composed mostly of aliphatic carbon and nitrogenous compounds, for example carboxylic acids, carbohydrates, and

proteins.¹⁰ The hydrophobic fractions are rich in aromatic carbon, phenolic structures and conjugated double bond.^{10,38} The various NOM fractions exhibit different properties in terms of treatability by coagulation, coagulant demand, and DBP formation potential.¹⁰

Another important aspect of the characterisation of NOM is the molecular weight distribution, which can be determined using high performance size exclusion chromatography (HPSEC) analysis.^{39–41} The chromatographic peaks correspond to 50 000 Da (organometallic colloids and biological residues), 1900 Da (high M_w humic substances), 800–1200 Da (low molecular weight humics), 500 Da (building blocks), and 300 Da (low M_w acids and nitrogen containing aromatics).^{39,42} Coagulation studies with repeated applications of alum to a surface water revealed that the HPSEC profiles having high molecular weight peaks were readily removed with the first addition of alum. Conversely the low molecular weight peaks (800–1200 Da) were still present even after five applications of alum. Both the 500 Da and 300 Da remained unchanged.³⁹ This then obviously constitutes a major problem since these lower M_w components are not removed in this treatment.

In general, one can state that from a colloid science point of view the challenge is to achieve strong complexation of the NOM, which are in general anionic macromolecules comprising of carboxylic and phenolic groups and contain a relatively high percentage of aromatic groups, therefore being macromolecules with a relatively low degree of flexibility.

3. Mechanisms of organic polyelectrolyte coagulation/flocculation of NOM

In the coagulation/flocculation processes, the polyelectrolyte acts as a secondary coagulant, after the use of hydrolysed coagulants (Al^{3+} and Fe^{3+}), *via* a charge neutralisation-precipitation mechanism (therefore working best at stoichiometric conditions),⁴³ and is an agent for floc growth. The basic mechanism of this process is the binding of the oppositely charged cationic polyelectrolyte to the negatively charged NOM, where the main driving force is of an entropic nature and arises largely from the counterions' release.^{44–46} However, the counterions release is most effective for the case of counterions being condensed into the polyelectrolyte. According to Manning,⁴⁷ counterion condensation takes place if the spacing between the polyelectrolyte and the counterion becomes smaller than the Bjerrum length L_B and is controlled by the Manning parameter $\zeta_M = L_B/b$. The Bjerrum length is defined as:

$$L_B = \frac{e_0^2}{\epsilon \cdot k_B \cdot T} \quad (1)$$

and is the distance at which the electrostatic energy between two elementary charges (e_0) in a medium (characterised by the permittivity ϵ) reaches the value of the thermal energy



$k_B T$, L_B is 0.714 nm for water at 25 °C. Only if ξ_M is larger than 1 counterions are condensed and their fraction is $(1 - 1/\xi_M)$. According to this basic argument, complexation due to counterion release will mostly become effective for polyelectrolytes which have their charged units closer than 0.714 nm and the strength of binding will increase with rising charge density. This agrees well with the experimental observation that polyelectrolytes with high charge density are typically more effective in coagulation/flocculation.

Such complex formation is generically observed for the interaction of polycations with oppositely charged colloids, for example micelles, nanoparticles, clays, proteins, other polyelectrolytes, *etc.*, or in compaction in biological systems which leads to the formation of hierarchically structured complexes above a critical charge ratio²⁹ (Fig. 1). Their size and stability depend on the colloid to be complexed, the effectiveness of the interaction with the polyelectrolyte, and then largely on the M_w of the polyelectrolyte employed. They increase in size as the M_w of the polyelectrolyte increases. Typically, around charge neutralisation, precipitation is observed but the range of mixing ratios where precipitation occurs depends for a given colloid largely on the type and M_w of the polyelectrolyte.⁴⁸ Of course, the aim of enhanced NOM removal is to make the biphasic range as large as possible, and at the same time reduce the colloidal stability of such complexes as much as possible. This means the aim emphasises the thermodynamic aspect, so that strong attractive interactions will favour phase separation and at the same time in the range of colloidal kinetics to create conditions where this phase separation takes place quickly and efficiently. The waiting times in water treatment, due to the large quantities being treated, need to be kept in the range of some minutes. However, this may constitute a limitation to the polyelectrolytes applied as colloidal metastable complexes may be formed that precipitate only too slowly for a practical application.

3.1. Complexation by polyelectrolyte – coagulation

Basically, it is possible to describe the coagulation process as depicted in Fig. 1 as one where the polyelectrolyte interacts

with a multi-valent macroion (as for instance would be the case for humic acid). The many counterions released during binding as well as released water molecules drive the complexation process.⁴⁹ However, this means that the main thermodynamic driving potential is already released within the initial complexation process, while further growth of these structures is not necessarily much favoured. In addition, one has to consider the fact that by complexation the macromolecules lose translational entropy, but this effect becomes less prominent with increasing M_w , therefore explaining why larger M_w both on the side of the NOM and on the side of the added polyelectrolyte facilitate precipitation. In addition, computer simulations,⁵⁰ have shown that complexation is exothermic for weakly charged polyelectrolytes and endothermic for highly charged polyelectrolytes. Recent experiments by isothermal titration calorimetry (ITC) on complexes of carboxymethyl cellulose (CMC) and lentil protein isolate, confirmed these predictions. In addition, light scattering showed the formation of smaller aggregates with increasing charge density and decreasing M_w of the CMC.⁵¹ It is also important to note that the architecture of the charged macromolecules plays an important role with respect to the electrostatic contribution to the free energy, facilitating complexation for linear polyelectrolytes and suppressing it for comb-like ones.⁵² However, H-bonding will also be an important contributor to the free energy, either directly or water-mediated,⁵³ as well as hydrophobic interactions.

Studies have shown that the negative charge on NOM molecules can be effectively neutralised by the cationic polymer, facilitating agglomeration.⁵⁴ The best removal occurs when the particles' zeta potential is close to zero and they carry approximately net zero charge. At this point, basically no electrostatic colloidal stabilisation is possible and phase separation is principally favoured. In jar tests on synthetic and natural waters of low turbidity and moderate to high colour, cationic polymers having high charge density can effectively remove the organics responsible for colour.⁵⁵ Cationic polyelectrolytes have a distinct advantage over the metal salts which are commonly used in this procedure, because they affect charge neutralisation without the

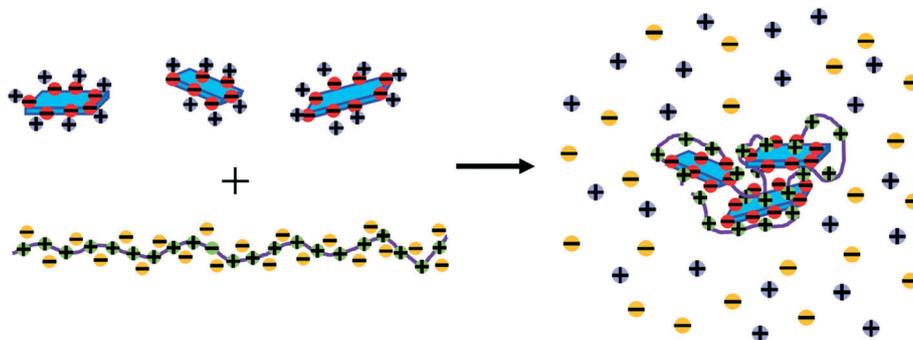


Fig. 1 Complexation of NOM molecules (depicted as blue plates) by an oppositely charged polyelectrolyte, resulting in a compacted complex and released counterions.



formation of additional solids in the form of metal hydroxide precipitate. This is quite logical since: firstly, polyelectrolytes naturally form bigger complexes than the low M_w inorganic compounds; and secondly, these bigger complexes are subsequently more likely to lead to faster and potentially more robust floc formation. The M_w of the complexes typically increases with the M_w of the polyelectrolyte, as similarly observed for complexing oppositely charged surfactant micelles.⁵⁶

3.2. Flocculation

The properties of complexes of oppositely charged polyelectrolyte and colloid/macromolecule become further complicated as the process of precipitation (coagulation/flocculation) may depend largely on the detailed composition of the system. Sometimes it occurs immediately, while in other cases hours, days, or even weeks may be required before macroscopic phase separation takes place.^{57,58} For water treatment, one is, of course, aiming at fast precipitation in order to make the process efficient. In any case, further growth of the initially formed nanometric complexes is required. The stability or metastability of these primary complexes (Fig. 1) is naturally linked to the remaining charge of the formed complexes (as measured by the zeta potential), but also largely to the question of how easily they can grow further (to larger flocs), provided there is a thermodynamic driving force and no kinetic hindrance. Here the polyelectrolyte, if not fully neutralized, may be counter-productive and function as a stabiliser, due to protruding uncomplexed chains that are highly hydrophilic. In that context, long chains (high M_w) typically lead to larger complexes but these may also invoke enhanced colloidal stability. Fig. 2 depicts the further growth (flocculation) process and this will largely depend on two things: firstly, attractive forces between the initially formed complexes; and secondly, how easily they can rearrange to form more compacted agglomerates (flocs). Here, especially hydrophobic interactions may play an important role, as typically simple electrostatic interactions were already largely reduced in the primary coagulation step.

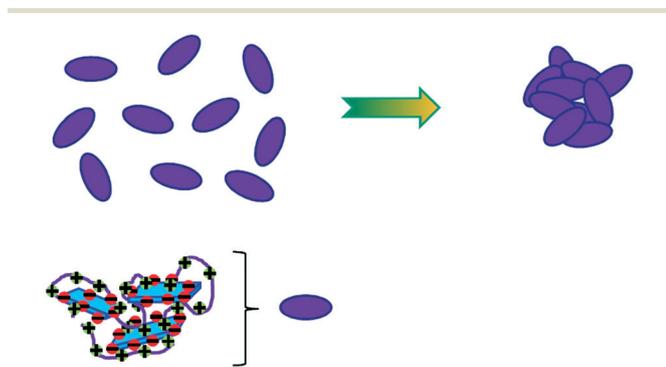


Fig. 2 Flocculation of initially formed complexes of NOM/polyelectrolyte, to form larger agglomerates (flocs).

In a review of the literature on flocculation and flocculants, Sharma *et al.*²⁰ reported that flocculation of NOM with polyelectrolytes may occur through a bridging mechanism. Such a polyelectrolyte bridging mechanism of flocculation was similarly presented by Bolto and Gregory.¹¹ Here segments of a polyelectrolyte chain adsorb on more than one particle, thereby linking them together. The polyelectrolyte adsorbed to NOM has portions of the molecule not bonded to the NOM extending into the solution as loops and tails; they also extend to some distance from the NOM surface into the solution. Their ends suspend and are adsorbed by another NOM molecule forming a bridge between them. The length of the polyelectrolyte chain is crucial for effective bridge formation with linear polyelectrolytes having long chains being the most effective. The bridging mechanism's relevance has also been confirmed due to the fact that intense flocculation takes place long before the isoelectric point is reached, as seen for the flocculation of bentonite and kaolin by polycations.⁵⁹

If excess polyelectrolyte is added the particles are restabilised by surface saturation, *i.e.* an appropriate dosage is required as only in the range of compensating the NOM charges by polyelectrolyte precipitation can be expected (as pointed out above). From a practical point of view this dosage range should be as wide as possible, meaning that the addition of the polycation should render the solubility of formed complexes as low as possible. For instance, one model study on flocculating silica particles by cationic polymer of different M_w and charge density indicated that low charge density facilitates bridging, while high charge density favours the patch flocculation mechanism.⁶⁰ This so-called 'electrostatic patch' mechanism is related to the bridging mechanism and makes it possible to explain flocculation of positively charged polyelectrolyte and negatively charged NOM. In the patch mechanism, a high charge density polyelectrolyte adsorbs on the negatively charged NOM having fairly low density of charges and neutralises the charges on NOM. However, because the distance between the charged sites in NOM is greater than the charged segments in the polyelectrolyte, positive charges between uncoated negative charges of NOM occur as patches. These positively charged patches are electrostatically attracted to the negatively charged areas in another particle and hence the particles become attached to form flocs.

In addition to the above electrostatic and bridging modes of coagulation/flocculation mechanisms, there are other mechanisms where the segments of polyelectrolyte are attached to NOM. They involve H-bonding, hydrophobic interaction, van der Waals force attraction and π - π stacking interactions^{11,24} and will depend largely on the detailed molecular architecture of the NOM. The nature of the flocculation process by polymers has been reviewed and discussed comprehensively some years ago.⁶¹



4. Natural polyelectrolyte (biofloculant) – chitosan (Cs)

As already indicated most commercial organic polyelectrolytes are derived from petroleum-based raw materials, as is the case for the typically employed PDADMAC or alternatives like cationic polyacrylamides, ionenes, or epichlorohydrin/dimethylamine polymers in NOM removal. Compared with those polyelectrolytes, biofloculants produced from natural materials are typically better biodegradable and mostly obtained from natural organic wastes. However, the overwhelming number of biopolyelectrolytes are polyanions, which are of limited use if one wants to precipitate/remove anionic NOM. As cationic biopolyelectrolytes that can act as primary flocculants, one mainly has cationic starch,^{62–64} which has been employed in paper modification,⁶⁵ or Cs. Other alternatives are cationic polypeptides, such as polylysine or polyarginine, which for instance have proved to be quite effective in flocculation of cohesive clay suspensions.⁶⁶

For the application as biofloculant, Cs appears to be the most promising one, since it is available in large quantities at low cost and has already been shown to be a versatile flocculant in water treatment.² Applications of chitin and chitosan derivatives for the detoxification of water and wastewater were reviewed a decade ago.⁶⁷ It was shown that they can remove a large range of contaminants, for example metal ions, dyes, phenol derivatives, and many other pollutants quite effectively from aqueous solution.⁶⁷ Here modifications of Cs can improve the general performance substantially, as has been reviewed recently.^{5,22} However, literature on their use in the removal of NOM from water is scarce. Most of the available literature on this describes the removal of synthetic humic acid as a model representative of NOM. Utilising chitosan hydrogel beads for pollutant adsorption demonstrated that humic acid can become effectively bound to the beads by complexation in the pH 5 to 7.5 range.⁶⁸ In general, Cs has emerged as an attractive option to other polyelectrolytes and therefore the literature on this natural polyelectrolyte that is relevant for water treatment will be discussed in this paper.

Cs is an amino-based polysaccharide consisting of a linear copolymer of D-glucosamine and N-acetyl-D-glucosamine (Fig. 3).^{4,5} It is a readily available biopolymer derived *via* deacetylation of chitin, the second most abundant polysaccharide in nature after cellulose. Chitin is present in

many insects, diatoms, and marine animals. Steps involved in the extraction of chitin from fishery wastes (carapace of crustaceans and shellfish) were described elsewhere.^{22,33} It is positively charged in acidic conditions due to the protonation of the amino groups (Fig. 3).^{1,27} Naturally derived Cs is typically a linear copolymer, but its branched version has also been synthesised for the purpose of modifying and improving material properties.⁶⁹

The structure and morphology of Cs depends on available functional groups, the degree of deacetylation, molecular weight, and the functional group's ionisation state.¹ The effective pK_a value of Cs is ~6.5, depending on its degree of deacetylation. At pH values below ~6.2–6.4, Cs is water-soluble but it becomes insoluble at higher pH,^{1,70} thereby restricting its potential applications in native form substantially. However, in addition to its high biodegradability, low cost, and non-polluting nature, the functional groups (hydroxylic, amino, and acetylic groups) can be easily modified to improve its molecular properties and overcome these limitations,^{71–73} for instance to address this solubility issue at higher pH. This can be done by introducing permanent charges, and also the control of hydrophobicity is interesting, which can be done *via* the amounts of acetylated groups contained and in addition by introducing additional hydrophobic moieties. Consequently, one controls the degree of hydrophobicity of the polymer.

Guibal *et al.*²¹ demonstrated that Cs can be used as a primary coagulant as well as a flocculant after coagulation: it has characteristics of both coagulants and flocculants. The addition of small amounts of Cs (for example 0.25 mg L⁻¹) to kaolin + humic acid suspension was sufficient to diminish the amount of alum required to halve the original value (from 24 to 12 mg L⁻¹). Interestingly, this study also indicated no effect of the Mw of the Cs on the coagulation/flocculation of humic acid. The mechanism of coagulation and flocculation of Cs was considered, to be charge-neutralisation (including electrostatic patch), inter-particle bridging, and precipitative coagulation (entrapment of NOM by excess of Cs). In treating drinking water, Cs was found to be very effective in removing turbidity but not very efficient in DOC removal.⁷⁴ In removal of humic substances, Cs was found having a significantly higher maximum extent of flocculation in comparison to other conventional polycations like cationic polyacrylamide.⁷⁵

As Cs is considered to have much potential for use as a coagulant/flocculant, much attention in recent years has

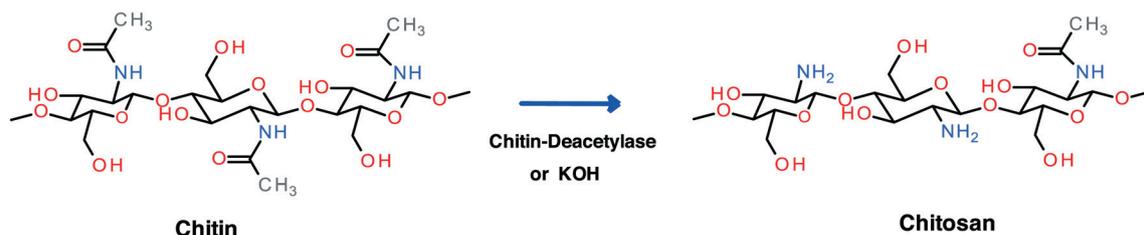


Fig. 3 Process of forming chitosan from chitin; in the industrial process concentrated KOH solution is employed.^{4,5,22}



focused on developing even more efficient products by chemical modification of Cs. The aim here is to have modified Cs tailor-made for a specific demand and in our study, this is NOM removal, and this requires a strong tendency for complexation and subsequent growth of strong flocs.

4.1. Chitosan modification

The three most important aspects of Cs which reduce its effectiveness as a coagulant/flocculant for more widespread use are:

- Poor water solubility at high pH (low solubility at pH > 6), while water treatment typically takes place at higher pH.
- Often too low molecular weight.
- Low charge density at neutral and alkaline pHs.

Chemical modifications can be done to overcome these limitations, which mostly use the high chemical reactivity of the amino group that is obtained by deacetylation of chitin (Fig. 3).

The simplest and most straightforward way to render chitosan soluble irrespective of pH is direct quaternisation of its amino group, thereby transforming the pH-dependent charge on the amine to a permanent one on a quaternary amine (see Fig. 4). Quaternisation of the amino groups to increase the solubility of Cs and its derivatives at higher pHs is also an advantage in cosmetics, medicine and food industries.³³ Two other major methods of chemical modifications used to increase the number of positive charges of Cs at a wider pH range are grafting quaternary ammonium and amino acid groups. Along with increasing positive charges the solubility and molecular weight can also be increased. The quaternisation of the Cs amino group also allows for a parallel hydrophobic modification possible, which then leads to forming a markedly amphiphilic Cs derivative. These methods are discussed below in more detail and we focus here, only on modifications that can be

considered to be interesting for enhanced NOM removal, which are mainly the control of:

- The charge.
- The molecular weight.
- Hydrophobic modification.
- Solubility of the Cs backbone, *e.g.* controlled *via* O-methylation.

It should be noted that the chemistry of Cs modification is still much richer and has been discussed at length in the literature⁷³ and this also determines their potential applications as biomaterials.^{76,77}

4.1.1. Direct quaternisation of chitosan (q-Cs). Pure Cs has little application value for NOM removal because it becomes insoluble at pH values larger than 6.2–6.4 and at the same time less and less charged, while a strong positive charge is required for electrostatically binding to the humic and fulvic acids of the NOM as main targets at high pHs. Therefore, a simple Cs modification for NOM coagulation and flocculation is quaternisation of the Cs amino group to introduce additional and permanent positive charges. Cs is positively charged at pH < 6.5, whereas q-Cs is positively charged even above pH 6.5.²² The formed quaternised Cs (q-Cs) is not only much more water-soluble, especially at higher pH where NOM removal typically takes place (pH 8–9), but also the charge density can be directly adapted to the needs of binding to humic and fulvic acids.

Such q-Cs has already been prepared many years ago and is considered to have high potential for drug delivery purposes.³² The simplest version for its synthesis is the reaction with a methylating agent, such as methyl iodide and this reaction is well documented.^{22,73,78,79} However, any such electrophilic agent may not only react with the amino group but also have a propensity for reacting with the abundantly present OH-groups of the polysaccharide. The degree of O-methylation (see Fig. 4) as a side reaction will then have very significant relevance for the properties of the final q-Cs

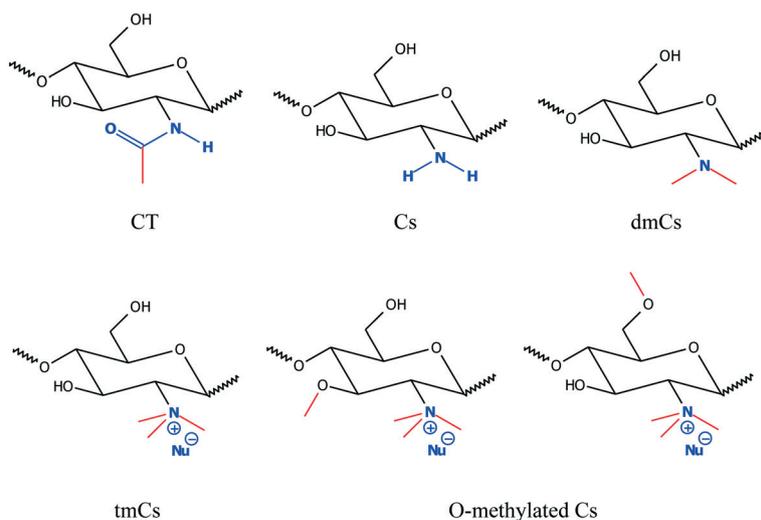


Fig. 4 Typical structural motifs present in quaternised chitosan: CT: chitin, Cs: chitosan, dmCs: dimethylated chitosan, tmCs: trimethylated chitosan, and O-methylated chitosan (Nu⁻: anionic counterion).



and its occurrence depends markedly on the conditions chosen for the methylation procedure. For instance, *O*-methylation reduces the water solubility.⁷⁹ Direct quaternisation with a methylation agent like methyl iodide typically leads to a high degree of *O*-methylation of 0.1–0.6, depending on the degree of quaternisation utilised, which in turn depends on how much methylation agent is employed. However, the advantage of this reaction is that it is a “one-pot” synthesis and is consequently a simpler and more economical procedure. Yet, having good control over the degree of *O*-methylation is critical because it modifies the solution properties of the modified Cs, and this also affects its interaction with humic acid. In one study, an optimised solubility of modified Cs was claimed for an intermediate degree of quaternisation of ~40%. However, for higher quaternisation also a higher degree of *O*-methylation was present, and this may have been responsible for this observation.⁸⁰

By using a two-step reaction in which one first obtains the tertiary amine by an Eschweiler–Clarke reaction (reacting with an excess of formaldehyde and formic acid) and then in a second step quaternises the tertiarised Cs by a Menshutkin reaction, one can largely suppress *O*-methylation, while still achieving high levels of quaternisation.⁸¹ This final quaternisation stage may also be conducted with an alkyl iodide instead of methyl iodide, thereby allowing a hydrophobically modified Cs to form (hm-Cs, see sub-section 4.1.2). In addition, also a “one pot” synthesis of highly *N*-substituted trimethyl chitosan has been described.⁸²

Being typically very biofriendly, Cs and its derivatives represent a very appealing choice for NOM removal. After quaternisation (yielding q-Cs) one is left with a rather complex polymer containing a variety of different monomeric units (see Fig. 4). Apart from the aimed for quaternised unit (tmCs) one will still have some units of chitin (CT) or Cs present, as well as a dimethylated product (dmCs). There may also be a smaller monomethylated product. Their presence may potentially even be desired as these units would then still show pH-dependence and have the capacity of H-bonding, while the tmCs has a pH-independent charge and no ability to form H-bonds. Furthermore, by not quaternising all of the amino units, the charge density along the backbone can still be varied, which is an additional control parameter for the electrostatic interactions with the NOMs. Of course, one always starts with a certain degree of acetylation (DA), which during the reaction is retained and determines the percentage of CT units in the final product, and thereby also the potential charge density along the Cs chain. The CT units themselves have some hydrophobic characteristics⁸³ and will affect the properties of the q-Cs as well. This is also the case concerning the amount of *O*-methylated monomeric units.

4.1.2. Hydrophobically modified chitosan (hm-Cs). While quaternisation aims to make Cs soluble in aqueous solution and provide a larger number of positive charges, hydrophobisation of Cs also needs to be considered,

particularly for removing the hydrophobic components of NOM. This process will reduce its solubility but at the same time allow for more intense hydrophobic interactions with other components, which for applications like NOM removal may be desired. Such a modification typically is a hydrophobic side chain attached to the amino group, which may vary in alkyl chain length (or even be other than straight alkyl groups, *i.e.* containing branched chains, aromatic groups, or functional organic moieties⁸⁴) and one may vary the percentage of hydrophobic modifications present. By introducing such a group, one forms hydrophobically modified Cs (hm-Cs) or if one has the same quaternisation taking place, a hydrophobically modified quaternised Cs (hm-q-Cs) is produced. The general chemical transformation scheme for forming hm-(or hm-q-) Cs is given in Fig. 5 (of course, the initial degree of acetylation (DA) is retained in the final product).

The hydrophobic interactions in solution become pronounced once the alkyl chain used for hydrophobic modification of the free amino group of the Cs has a length of at least 6 C atoms, and then leads to a substantially higher viscosity for concentrations of hm-Cs about 1 g L⁻¹ (ref. 85) and can even be tuned to gel-like behaviour.⁸⁶ Based on the fluorescence experiments the presence of hydrophobic aggregates has been deduced both for hm-Cs and normal Cs, but for the hm-Cs an additional type of hydrophobic aggregation takes place.⁸⁷ Accordingly, self-assembled aggregates will be formed that may be employed for instance for drug delivery purposes.⁸⁸ hm-Cs will also associate with other amphiphilic moieties, as for instance shown for the case of linking surfactant vesicles and thereby forming a gel.⁸⁹ Additionally, the hydrophobic modification makes the chitosan surface active.⁹⁰ Referring to water treatment the hydrophobic modification is attractive because in addition to the already present electrostatic interaction, one can introduce additional hydrophobic interactions⁹¹ of the modified chitosan with the NOM. This may be important not only for interacting with the more hydrophobic parts of the NOM, but also help floc growth and building stronger flocs.

The most common approach for alkylation has been a two-step reaction in which first the free amino group of the Cs is reacted with an aldehyde and subsequent hydrogenation to yield a monoalkylated amino group, thereby yielding hm-Cs (Fig. 6).⁸⁵ Then this hm-Cs (Fig. 7, left) can become quaternised by a methylation reaction, thereby yielding hm-q-Cs (Fig. 7, right). Here full quaternisation or only partial quaternisation can be considered, thereby retaining some protonable amino groups (and thus pH-sensitivity). An alternative is to produce a tertiarised Cs (*N*-dimethylchitosan) obtained by an Eschweiler–Clarke reaction, which then becomes in a next step alkylated and quaternised with a longer alkyl chain.⁸¹ The hydrophobic modification cannot only be done for introducing alkyl chains but similarly aromatic moieties can be introduced *via* a Schiff base. This is formed by the reaction of the 2-amino group of the chitosan with an aromatic aldehyde and subsequent



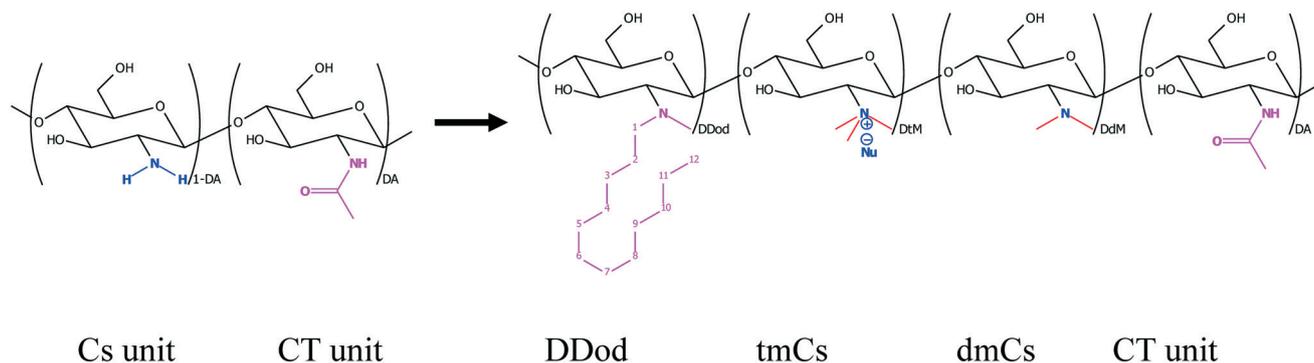


Fig. 5 Generic reaction scheme for preparing hydrophobically modified (quaternised) Cs (hm-Cs) suitable for NOM removal in the case of a dodecyl modification as an example. DDod: dimethylated-dodecylate Cs (as a special case of a hm-Cs).

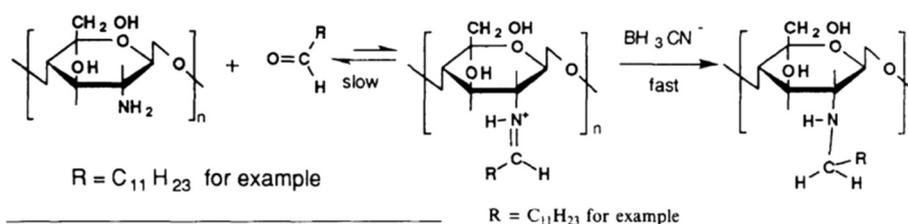


Fig. 6 Alkylation of chitosan by reacting with an aldehyde to yield the imine, which subsequently becomes hydrogenated to yield the alkylated chitosan (taken from Desbrières *et al.*⁹⁴).

reduction with cyanoborohydride.⁹² In a similar way, heterocyclic Cs derivatives have been produced.⁹³

However, one can also achieve direct alkylation of the amino group by reaction with an ω -bromo-alkyl trimethyl ammonium salt in basic aqueous solution, which then leads to an additional cationic charge on the end of the added chain. Alternatively, one can combine both approaches to produce two different alkyl chains within one Cs derivative.⁹⁵ Due to the increased hydrophobic interaction the hydrophobic modification of Cs should be advantageous for removing NOM which contains many hydrophobic fractions, for example very hydrophobic (VHA) or hydrophobic acid (HPA), and slightly hydrophobic (SHA) (see section 2).

4.1.3. Quaternary ammonium group grafting and carboxymethylation. In contrast to quaternisation where the primary amine group in the Cs structure is converted into a

quaternary amine group (as discussed in the preceding section), in quaternary ammonium group grafting, a grafting reaction is done on the primary amine of the Cs. Carboxymethylation can increase the solubility range of Cs to alkaline pH; however, it will also produce negative charges which cause repulsion of the negatively charged turbidity particles including NOM, thus affecting coagulation.²⁶ To solve this problem, Yang *et al.*²⁶ firstly, introduced quaternary ammonium groups into the carboxymethylated Cs (CMCs) to increase the number of positive charges; and secondly, grafted polyacrylamide branches to increase the molecular weight of the product. This was achieved by grafting poly(2-methacryloyloxyethyl)trimethyl ammonium chloride (PDMC) to the CMCs (CMCs-g-PDMC) at a weight ratio of PDMC to CMCs of 2.51.

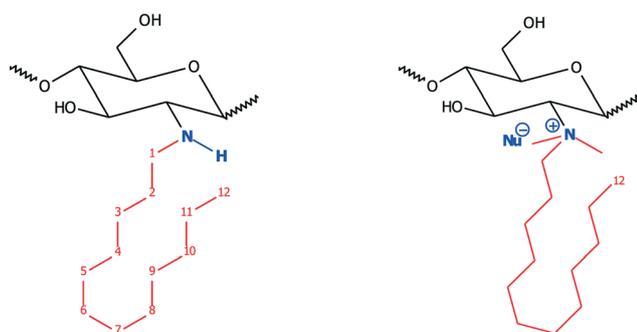


Fig. 7 Structure of hydrophobically modified Cs (hm-Cs, left) and dimethylated-dodecylate Cs (hm-q-Cs, right).

Yang *et al.*²⁶ compared the flocculation performance of CMCs-g-PDMC with poly-aluminium chloride (PACl) under acidic, neutral, and alkaline conditions on suspensions of kaolin and humic acid (HA), which are commonly found in real surface water. Zeta potential measurements explained the flocculation performance; floc size was found to be much higher at higher pH. They found that the zeta potential of Cs was positive at pH lower than 8.0 because amine groups were present.²⁶ In contrast, CMCs indicated much lower zeta potential values with an isoelectric point of approximately 5.5. However, when PDMC was grafted onto CMCs, the



Table 1 Comparison of chemically modified Cs (CMC-g-PDMC) with poly aluminium chloride (PACl) in the removal of humic acid (50 mg L⁻¹) from synthetic wastewater at different pHs (ref. 26)

pH	Polyelectrolyte	Optimum dose (mg L ⁻¹)	Residual humic acid (%)	Floc size (µm)
4	CMC-g-PDMC	20	1.13	167
	PACl	75	5.97	160
7	CMC-g-PDMC	22	1.29	201
	PACl	100	4.33	144
11	CMC-g-PDMC	75	2.26	502
	PACl	—	—	—

CMCs-g-PDMC was found to be positively charged in the entire measured pH range and the amounts of positive charges were also higher than those of Cs.

The CMCs-g-PDMC had lower optimal dosage, superior humic acid removal efficiency, wider pH applicability range, and larger floc size, in comparison with inorganic PACl (Table 1). This difference in performance between flocculants was more prominent at the natural water pH of 7 rather than at the acidic pH of 4.

The CMCs-g-PDMC's better flocculation performance was ascribed to two structural advantages, specifically, increased number of positive charges and molecular weight.²⁶ The increased number of positive charges was caused by the introduction of the positively charged quaternary NH₄ group into the Cs. They did occur as seen in the increase in zeta potential values. The increased molecular weight resulted from the grafting of polyacrylamide branches to Cs in order to extend the chain length of Cs, provided more sites for bridging and patching with the humic acid molecules in solution. Charge neutralisation and patching were reported to be the predominant mechanisms of flocculation. If the net charge on the flocs (as indicated by the zeta potential) was close to zero at the optimal dosage, charge neutralisation contributed largely to the flocculation. If the net charge at the optimal dosage was still negative and away from zero as observed at high pHs, patching was reported to be dominant. Charge neutralisation resulted in flocs with relatively weak strength whereas patching produced strong ones.

Based on CMCs, one can also produce amphoteric Cs, which has been done by reacting with 3-chloro-2-hydroxypropyl trimethyl ammonium chloride (CTA), thereby yielding CMCs-CTA. The amphoteric CMCs-CTA demonstrated excellent flocculation performance in water treatment and this occurred in a wider pH range than Cs and with a lower optimal dosage than that of traditional flocculants.⁹⁶ Modification with polyacrylamide (PAM) allows for the formation of CMCs-PAM which was tested for flocculating kaolin. Here patching was claimed to be the main mechanism at acidic conditions and bridging the dominant mechanism for neutral and alkaline conditions.²⁸

Li *et al.*²⁵ prepared a Cs-based cationic polyacrylamide flocculant (Cs-g-PAMA) with enhanced function of sterilisation and flocculation by copolymerisation of a cationic quaternary ammonium salt (methacrylamide propyl

trimethyl ammonium chloride, MAPTAC) and acrylamide monomer and tested it on the treatment of a series of simulated wastewater containing *Escherichia coli*. The Cs dissolved in water only below pH 3.0, whereas Cs-g-PAMA was soluble at pHs up to 13, which indicated that the largely improved solubility resulting from the modification should enhance its flocculation performance and broaden the pH range of its application. Li *et al.*²⁵ compared the flocculation and sterilisation performance of Cs-g-PAMA, PAMA and PAM using *Escherichia coli* suspension. Their analysis showed that Cs-g-PAMA led to a relatively better flocculation and sterilisation outcome and was less affected by pH compared to PAMA and PAM. The positively charged Cs-g-PAMA was reported to be adsorbed on the negatively charged cytoderm of *Escherichia coli*, reducing the repulsion between cells and causing cell destabilisation. The unstable cells were reported to have formed large and dense bacteria flocs through the bridging and netting effect. Simultaneously, excess Cs-g-PAMA was said to have destroyed cell membranes through the quaternary ammonium group, thereby helping sterilisation.

Algae and its metabolites in water sources can seriously damage the quality of drinking water, for example by producing unpleasant tastes and odours, formation of DBD and toxins from cyanobacteria. Dong *et al.*⁹⁷ prepared a quaternised carboxymethyl chitosan (q-CMCs) and determined the flocculation properties and mechanisms of coagulation/flocculation of algal turbid water (turbidity of 10–40 NTU). They also examined the formation, breakage and regrowth of algal flocs using q-CMCs in comparison with aluminium sulphate (Al₂(SO₄)₃). Cs had the narrowest solubility pH region (pH < 5), indicating its poor solubility. Although CMCs elicited better solubility than Cs, it was still insoluble or partially soluble in slightly acidic water (pH = 4–7). Compared with Cs and CMCs, q-CMCs demonstrated remarkably improved solubility and are soluble almost in the whole pH range and only showed partial insolubility near its isoelectric point at around pH 9.2.

The flocculation performance of modified and unmodified Cs and several conventional coagulants/flocculants, such as Al₂(SO₄)₃, FeCl₃ and PAM, were investigated by Dong *et al.*⁹⁷ at different pH values for comparison. q-CMCs consistently revealed the best flocculation performance amongst all five coagulants/flocculants and indicated both the lowest optimal dosage (OD) and highest turbidity removal efficiency (TRE) at both pH 5 and 9 (Table 2). This is due to the higher molecular weight of q-CMC and larger number of positive charges on q-CMC as shown by the higher positive zeta potential than the other coagulants/flocculants in the study. The optimum doses of the inorganic coagulants were 40–200 times higher than that of q-CMC. The floc strength for q-CMCs was also stronger than that for Al₂(SO₄)₃ under each flocculation condition, because the algal cells adsorbed onto q-CMCs molecule chains with much stronger physical or chemical forces (charge neutralisation, hydrogen bonding, and extensive strong bridging due to higher molecular weight).



Table 2 Optimal dosages (OD) and corresponding algal turbidity removal efficiencies (TRE) of various flocculants/coagulants⁹⁷

Flocculant/coagulant	Price (US \$ per kg)	pH 5, OD (mg L ⁻¹)	pH 5, TRE (%)	Cost (US \$ per m ³)	pH 9, OD (mg L ⁻¹)	pH 9, TRE (%)	Cost (US \$ per m ³)
Chitosan	51.2	0.4	94.7	0.02	5.5	85.3	0.28
QCMCs	368.2	0.1	96.3	0.04	0.6	95.8	0.22
PAM	22.1	3.0	94.1	0.07	8.0	86.5	0.18
Al ₂ (SO ₄) ₃	5.8	20.0	89.2	0.12	35.0	88.2	0.20
FeCl ₃	3.7	15.0	93.4	0.06	25.0	91.2	0.09

4.1.4. Amine group grafting. Instead of introducing quaternary ammonium groups to increase positive charges on Cs as described in the preceding section, Jia *et al.*²⁴ modified Cs by grafting two amino acids with aromatic rings (*L*-tryptophan and *L*-tyrosine with aromatic rings) to provide increased positive surface charges on Cs and facilities for π - π bonding for the removal of three antibiotics in the presence of kaolin and humic acid (HA, a representative of NOM) by flocculation. They found that the optimum dose for the removal of humic acid, kaolinite and antibiotics was lower for the amine grafted Cs than unmodified Cs and poly aluminium chloride. The removal mechanisms were explained using charge neutralisation, π - π interaction, and H-bonding. The amino acid modification increased the zeta potential of Cs (thus increased number of positive charge density) which is favourable for the flocculation of the negatively charged kaolin and HA at neutral pH. The aromatic rings in the amino acids were deemed to further improve flocculation through π - π stacking interaction (electron donor-acceptor effect) with the aromatic rings in the antibiotics and those of the humic acid.

The coexistence of kaolin particles and HA (both negatively charged at slightly acidic pH) plays a positive role in the removal of antibiotics, as parts of antibiotic molecules (with positively charged amine groups (R₃N⁺)) were reported to be adsorbed onto kaolin and the NOM by electrostatic attraction, hydrogen bonds (antibiotic-kaolin/HA), π - π stacking (two of the antibiotics-HA) or charge attraction (two of the antibiotics-HA/kaolin). In contrast, kaolin and HA alone without adding flocculants did not remove much of the antibiotics.

4.1.5. Other possible modifications. It might be noted that Cs can also be modified enzymatically, for instance by grafting with phenol and using tyrosinase.⁹⁸ More interestingly still, several modifications (grafting and cross-linking) at the amino and hydroxyl positions in Cs were reported to improve Cs's adsorptive removal of pollutants.⁵ Some of these modifications can be tested to determine their suitability for improving the efficiency of coagulation/flocculation of NOM.

Bhalkaran and Wilson¹ reported the following modified Cs: glycidyl-trimethyl ammonium chloride, poly(2-methacryloyloxyethyl) trimethyl ammonium chloride-grafted Cs (Cs-g-PDMC), Cs sulphate, Cs-graft-polyacrylamide, 3-chloro-2-hydroxypropyl trimethyl ammonium chloride-modified carboxymethyl Cs; to have higher flocculation

efficiency than unmodified Cs in removing turbidity, clay mineral suspension, biological cells, or anionic and cationic dyes. The potential of these modifications in flocculating NOM, still has to be explored more thoroughly in future studies.

4.2. Perspectives of using modified Cs in NOM removal

When looking at the above abundant options for chemically modifying Cs, Cs emerges as an interesting starting molecule to construct optimised modified versions for NOM removal and water treatment in general. Since the backbone is retained, good biodegradability and biocompatibility is given and by being able to play with the charge density, hydrophobic modification, and ability for H-bonding and specific interactions, there is a wide field for optimising its ability to strongly interact with NOMs. Looking at Fig. 5 and 7, one may think in particular about the following parameters to be varied:

- Molecular weight (M_w) of the Cs to be achieved by a higher degree of polymerisation of its backbone or grafting of side chains where especially grafting appears interesting as for instance for starch it was shown to be rendering it much more efficient in removing humic acid by flocculation.⁹⁹
- Degree of acetylation (DA).
- Degree of quaternisation (tm-Cs, or hm-q-Cs) and thereby also the amount of primary, secondary, and tertiary amines still contained.
- Type of hydrophobic modification.
- Percentage of hydrophobic modification.

This is a rather large parameter space and one that cannot easily be explored in its fullest extent. However, in general, it has been found that: firstly, high M_w of the flocculating polyelectrolyte is preferred; and secondly, relatively high charge densities of the polyelectrolyte are expected to be required for strong binding to humic and fluvic acids. For instance, bentonite was more effectively coagulated and flocculated by Cs of higher M_w .¹⁰⁰ Much less clear and not really in great depth is the importance of specific binding *via* H-bonds, aromatic groups, or hydrophobic interactions. This may determine whether one prefers to have a completely quaternised Cs or still retain some amino groups. In this respect, additionally, the degree of *O*-methylation as well as the degree of acetylation (DA) might be important parameters.



Accordingly, the first and principal parameter to be explored is the effect of the charge density on the quaternised Cs in conjunction with using Cs having different DA. For binding and especially flocculation then an optimised hydrophobic modification (or a series thereof) could be important; here one can have electrostatic binding and binding *via* hydrophobic interactions at the same time. In that context the relevance of hydrophobic interactions is often underestimated, but the transfer of a dodecyl group from aqueous to hydrophobic environment releases about 15 kT in free energy, while coupling to elementary charges in aqueous solutions typically just releases about 3–5 kT. The latter especially may also be important for building up flocs. With reference to the type of hydrophobic modification one can be flexible in terms of chemistry, as that can be straight or branched aliphatic chains, or also contain aromatic moieties. In principle one is also not restricted to having just one type of hydrophobic modification on the amino group but could also react a second or third hydrophobic group on it (or on different amine groups along the Cs backbone). Furthermore, their content in the modified Cs can be varied, where most likely values up to 10 mol% modification are most likely to be relevant for NOM removal. In general, modified Cs is an interesting type of flocculant, as at the same time it offers the opposite charge to humic/fluvic acid and hydrophobic chains that may allow for additional interaction. On this basis it may be speculated to be most effective in flocculation.

4.3. Cost effectiveness, secondary water pollution and sludge management

One of the major impediments restricting the use of modified Cs in practical application is their cost. Even the cost of unmodified chitosan is higher than that of the inorganic coagulants/flocculants. The cost of modified Cs would further increase because expensive chemicals are used for modification purposes. Dong *et al.*⁹⁷ reported that the cost of the modified Cs (US\$368 per kg) was much higher than that of the inorganic Al/Fe coagulant (US\$4–6 per kg) and unmodified Cs (US\$51) (Table 2). However, the optimum dose for the removal of algal turbidity was much lower, turning the modified Cs into a competitive and feasible coagulant in terms of cost per unit volume of water treated.

Furthermore, the smaller dose of modified Cs necessary to coagulate NOM implies that a smaller amount of sludge will be produced for disposal. This benefits water treatment plants because it can greatly reduce sludge handling costs.²⁶ Also, the flocs produced have larger size and denser structure with rapid settling velocity.^{26,97} This too is beneficial to water treatment plants leading to reduction in operational cost.^{4,97}

Although the beneficial effects of modified Cs have been demonstrated in laboratory studies, no large-scale production of these coagulants/flocculants has been reported for practical use in water treatment plants. However, the global production of the raw material, chitin for chitosan

production is increasing. Brasselet *et al.*²² reported that globally 10^{10} tons of chitin are produced annually, and the global market is very highly valued at US\$1205 million in 2015 and this was predicted to more than double by 2022. Such developments make it likely that the cost of modified Cs will become substantially reduced due to larger scale production of chitin.

Secondary water pollution is a concern when polyelectrolytes are used. Chitosan is a bio-organic polyelectrolyte and therefore it is not expected to be toxic to humans and animals. Chemically modified chitosan compounds are used in wine and food industries, but no toxicity has been reported.^{2,4,22} Yang *et al.*²⁶ conducted acute toxicity assays on water treated with the chemically modified CMC-g-PDMC (see section 4.13) and PACl using *Daphnia magna*. They found that the former had no effect on the immobilisation of *Daphnia magna*, whereas PACl produced a certain degree of toxicity. This would also indicate that the sludge produced after coagulation/flocculation using Cs based materials could be disposed of with less impact on the environment, which is important because legislation in this field is expected to become much more punitive over time.

5. Conclusions and outlook

Coagulation–flocculation followed by sedimentation is a widely used process to remove NOM. This treatment process currently provides healthy drinking water. However, the effectiveness of this process depends on the characteristics of the NOM and whether the selected coagulant and flocculant are efficient, and cost-effective.

Organic polyelectrolytes (synthetic and natural) that have marked abilities to flocculate NOM have been developed and employed in the last few decades. Polyelectrolytes have a distinct advantage over the Al and Fe salts which are commonly used in this process. This is because they affect coagulation/flocculation without the formation of additional solids in the form of metal hydroxide precipitate. Also, much smaller dosages of polyelectrolytes can be used to produce stronger flocs and are less pH dependent. However, there is the danger that when overdosed, they may restabilise a dispersion of NOMs.

As NOMs are anionic in nature, cationic polyelectrolytes are frequently used as primary coagulants or coagulation aids. Anionic and non-ionic polyelectrolytes are mainly used as either coagulation aids, flocculants, flocculant aids, or filter aids, but they have shown synergistic effects when employed together with a polycation. In particular, the mechanisms of these cationic polyelectrolytes' coagulation/flocculation are assumed to be charge neutralisation, electrostatic patch formation, and bridging. Charge neutralisation was reported to create flocs with relatively weak strength whereas patching and bridging of polyelectrolytes produced strong ones. A detailed mechanistic understanding in terms of molecular and mesoscopic changes is still largely missing in this field – and challenging



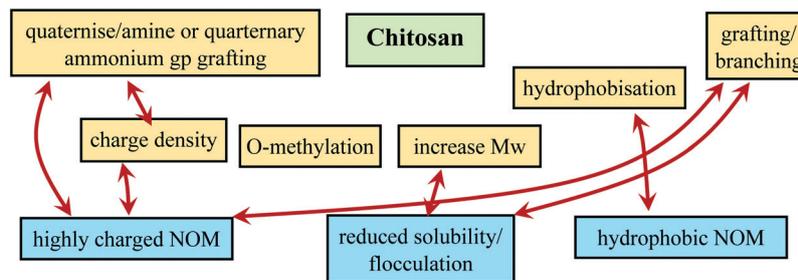


Fig. 8 Scheme for modifying chitosan for enhanced NOM removal.

due to the complex chemical nature of NOM. In principle, the interaction of NOM with polycations is just one version of complexes of polyelectrolytes with colloids, which have been much studied in colloid science but mostly with the focus on forming soluble complexes.^{49,101–103} However, in contrast to the many studies of polyelectrolyte/colloid complexes, for the case of polyelectrolyte/NOM complexes information about the thermodynamics of complexation (for example, obtainable by isothermal titration calorimetry)^{104,105} as well as a detailed characterisation of the mesoscopic structure, for instance to be done by scattering methods,²³ is largely missing. This is, despite the fact, that this information is very important for understanding their properties. It includes for example, designing conditions with polyelectrolytes like Cs for a tailored removal of organic compounds.¹⁰⁶ Finally, also theoretical modelling and computer simulations may give additional insights into this topic. All such fundamental studies are still largely missing for the case of NOM and these are very important for gaining a thorough understanding needed to optimise NOM removal by polycations.

Biofloculants produced from natural materials are safe, biodegradable and less expensive. Of the possible biofloculants, chitosan (Cs) has become a promising and attractive option to other polyelectrolytes. The strength of the Cs as a scaffold for an optimised polycation for water treatment is the relatively high flexibility in chemical modification. Its functional groups (especially the amino group, but also the hydroxylic and acetylic groups) can be easily modified in order to increase its solubility over a wider pH range, increase its molecular weight, provide additional positive charges, and one may also include additional hydrophobic moieties that may enhance binding of some NOM components *via* hydrophobic interactions. Accordingly, one can tune the extent of electrostatic and hydrophobic interaction but also the ability to form H-bonds. Due to the complex chemical nature of the NOMs one can expect that such high flexibility in terms of being able to interact with the NOMs is required in order to facilitate effective binding of the Cs to the NOMs. In addition, the intrinsically high extent of chain–chain interactions in Cs solutions (as evidenced by the rather high viscosity of its aqueous solution) is another advantage. Such interactions are certainly helpful in floc growth and forming strong flocs.

Intrinsically Cs has a rather poor solubility in water (as evidenced by its chain–chain attraction), which would be good for coagulation/flocculation. However, it also limits its usage to only low pH and therefore chemical modifications are needed to enhance its solubility. A straightforward modification of Cs is the direct quaternisation of the amino groups in Cs that introduces a permanent positive charge to the polymer. This can be coupled to hydrophobic modification of Cs which may improve the coagulation/flocculation properties of NOM. Two other major methods of chemical modifications used to increase the number of positive charges at wider pH range are grafting quaternary ammonium groups and amino acids. Chitosan modifications used in other processes such as adsorptive removal of pollutants and surfactants interactions can be explored for use in improved coagulation/flocculation processes. One aspect that is little explored with reference to Cs is the chain architecture. For cationic starch it has been found that the removal of HA improved substantially by having strongly cationic branch chains present in the molecule.⁹⁹ This has been ascribed to more efficient charge neutralisation and bridging flocculation,¹⁰⁷ and one may expect this to be similar for Cs and its derivatives. In general, the chemical architecture of an optimised Cs should be such that it has a strong interaction with humic substances, while at the same time not having been rendered too water soluble. Key parameters in that respect should be the charge density and *O*-methylation, which largely control the solubility. The different options for modification of Cs are summarised in Fig. 8 together with their main effects in terms of interaction with NOM and the coagulation/flocculation process.

With this “construction kit” depicted in Fig. 8 and ongoing synthetic advances in modification of Cs it is to be expected that further research on Cs-based flocculants is required. Doing so, should especially take into account all relevant aspects of fundamental colloid science, from mesoscopic structure and thermodynamics of interactions. These should make a substantial impact on a much-improved NOM removal in the water purification process.

Conflicts of interest

The authors declare no conflict of interest.



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