

Coagulation and chlorination of NOM and algae in water treatment: A review

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Abstract: Due to health concerns of natural organic matter (NOM) and algae presence in surface water and difficulties encountered in their removal in the water treatment, this paper reviews coagulation and chlorination processes which are largely used in water treatment technology. In the conventional water treatment, coagulation and slow filtration treatments have better efficiency to reduce the NOM in water especially for the hydrophobic portion than the hydrophilic one. However, the pre-chlorination treatment for raw water has been proved to increase the dissolved organic carbon concentration due to the lysis of algae cells and disinfection by-products formation. The impact of water treatment processes on disinfection by-products formation remains complex and variable, as demonstrated by recent literature. It is concluded that no pre-, no inter-, only post-chlorination preceded by optimised coagulation for NOM and algae removal is the best available technology for the conventional water treatment which would be reinforced by at least adsorption on powdered activated carbon or nanofiltration in the short terms. Finally, the conventional water treatment will not remain a viable solution for drinking water from source waters containing NOM as their quality deteriorates and water quality standards become more difficult to achieve.

Keywords: Coagulation/Chlorination, Natural Organic Matter (NOM), Algae; Disinfection by-Products (DBPs), Water Treatment

1. Introduction

Coagulation and disinfection are the main units in the drinking water treatment technology in both developing and industrialised countries [1,2]. Coagulation is expected to eliminate particles and colloids via a coagulant, like alum or ferric chloride, while disinfection is applied to inactivate pathogens by disinfectants like aqueous chlorine (HOCl/OCl^-). During disinfection, chlorine can react with natural organic matter (NOM) and bromide in raw water to produce halogenated disinfection by-products (DBPs) [3-6]. Many halogenated DBPs have been verified to possess potential genotoxicity and carcinogenicity to human beings [7-11]. Therefore, improving removal efficiency of NOM through "enhanced coagulation", which is usually operated

by decreasing pH to ~ 6 and/or increasing coagulant dosage [11], has received great attention from the environmental community [12]. The United States Environmental Protection Agency (USEPA) specifies the required NOM removal in terms of total organic carbon (TOC) by enhanced coagulation under different TOC and alkalinity levels [13]. For instance, for raw waters with alkalinity levels of > 60-120 mg L⁻¹ as CaCO_3 and with dissolved organic carbon (DOC) levels of > 4.0-8.0 mg L⁻¹ as C, the required TOC removal is 35.0% [13].

Effects of coagulation or enhanced coagulation on DBPs formation during chlorination have been largely studied [14]. In drinking water treatment plants, trihalomethanes (THMs) are a common parameter to evaluate the effectiveness of

coagulation in controlling DBPs formation [13]. Due to the apolar nature of THMs, a decrease of THMs does not necessarily mean a decrease of polar or highly polar halogenated DBPs. More than 50% of total organic halogen (a parameter estimating collective halogenated DBPs) formed during chlorination has not been identified [15,16]. A large portion of unknown total organic halogen may be attributed to polar or highly polar halogenated DBPs [17,18]. It has been demonstrated that some polar or highly polar halogenated DBPs such as the class of haloacetic acids (HAAs) are more cytotoxic and genotoxic than the class of THMs [1,19].

On the other hand, algae, which are ubiquitous in rivers, reservoirs and lakes, may cause a series of problems in water treatment in algal blooming seasons [20]. This includes poor settling, clogging filters, breakthrough of small-size algae through sand filters, obnoxious taste and odours and the release of algal toxins [21,22]. In addition, algae can also serve as precursors to form DBPs during chlorination [20]. Among these DBPs, THMs and HAAs have drawn particular attention due to their dominant occurrence and potential carcinogenic effects [23,24]. The influences of chlorination condition (including reaction time, chlorine dosage and pH), algal species, algal growth phase, biochemical composition and extracellular organic matter on total DBPs formation, specific DBPs yields and DBPs species distribution have been extensively studied in drinking water treatment [25-28].

Due to health concerns of NOM and algae presence in surface water and difficulties encountered in their removal in the water treatment, this paper presents a review of the current knowledge concerning both coagulation and chlorination of NOM and algae.

Since surface water contains both NOM and algae one hand and the algae physicochemical dissociation to form more dissolved organic molecules in on the other hand, this manuscript is motivated to cover NOMs and algae together in one review.

2. Coagulation and Chlorination of NOM

Seasonal coagulation objectives for a typical North-China water treatment plant with micro-polluted and high alkalinity source waters are proposed by Zhan *et al.* [29]. These are based on a yearlong data collection period where raw water characteristics, trihalomethanes formation potential (THMFP) and coagulation features were investigated using a jar test procedure, resin absorption and ultrafiltration fractionations. Three approaches beyond simply increasing the coagulant dose were used to achieve optimised coagulation. One is coagulation by adjusting the pH of the raw water when metal salt coagulants (FeCl_3 and AlCl_3) are used. At pH levels of ~ 5.0 for FeCl_3 and ~ 5.8 for AlCl_3 , the highest removal of NOM was obtained, which is twice that without pH control. The second is enhanced coagulation through coagulant optimisation based on raw water characteristics. A high efficient composite polyaluminium chloride (HPACl) coagulant was developed for the water taking the advantages

of polyaluminium chloride (PACl) and other additives. HPACl exhibited 30% more efficiency than AlCl_3 , FeCl_3 and PACl in DOC removal and was also very effective in turbidity removal. The third is enhanced softening with coagulant addition. Higher removal of NOM is achieved by enhanced softening with coagulant addition conditions as compared with conventional coagulation at natural pH. Especially with PACl addition, it can enhance the formation of $\text{Mg}(\text{OH})_2$ precipitate and remove NOM efficiently at a relatively lower pH range ($\text{pH} < 10$). By this approach, the pH for enhanced softening can be decreased significantly into a practical operation pH range for high-hardness water at a treatment plant.

To examine the effects of enhanced and conventional coagulation on the formation of polar halogenated DBPs during chlorination, Xiao *et al.* [1] employed precursor ion scans using electrospray ionisation-triple quadrupole mass spectrometry with or without ultra performance liquid chromatography pre separation. It is of interest that many new polar halogenated DBPs were generated as a consequence of enhanced or conventional coagulation, and a number of them were nitrogenous DBPs and/or had m/z values larger than 250. Some of the new polar halogenated DBPs showed up only in samples with enhanced coagulation but not in samples with conventional coagulation, although enhanced coagulation was better for controlling the overall DBP formation. The results suggest that the fraction of NOM resistant to be removed by coagulation should have a low reaction potential with halogens; after enhanced or conventional coagulation, halogens are forced to react with the remaining fraction of NOM, producing new polar (nitrogenous) halogenated DBPs. In addition, enhanced coagulation altered the speciation of halogenated DBPs by elevating the ratio of bromine-containing to chlorine-containing DBPs; this phenomenon was observed for both polar and apolar halogenated DBPs, but polar DBPs were more susceptible to be altered [1].

The removal of NOM by coagulation and adsorption on modified wheat straw (MWS) has been investigated [29]. Two types of inorganic polymer coagulants, polyferric chloride (PFC) and PACl, were used during experiments. The removal efficiency of NOM in terms of ultraviolet absorption (UV_{254}) and DOC increased with the dosage of coagulants and adsorbent increasing. Combined coagulation and adsorption showed better UV_{254} and turbidity removal efficiency (61.8 and 95.8% respectively for PFC-MWS, and 61.5 and 94.2% respectively for PACl-MWS) than individual treatment. The effects of combination sequences on DOC fractionation and residual chlorine decay were analysed and the chlorine data were fitted using a chlorine decay model. In general, the higher the molecular weight (MW) of NOM was, the better removal efficiency the combined treatment can achieve. MWS can enhance the removal of NOM with higher MW. The DBPs formation potential in the effluents from coagulation and subsequent adsorption was greater than that in the effluents from adsorption and subsequent coagulation.

With respect to the treatment of low specific UV

absorbance (SUVA) surface water, the effect of coagulant dose and pH on the coagulation behaviours of nano- Al_{13} polymer ($\text{Al}_{13}\text{O}_4(\text{OH})_{24}^{7+}$) has been studied [30]. The removal of fine particles and NOM was investigated under different coagulation conditions. PACl and alum ($\text{Al}_2(\text{SO}_4)_3$) were used for purpose of comparison. Floc size, strength and fractal structure were investigated under different coagulation conditions. The results showed that fine particles and hydrophobic (HPO) NOM with large MW could be easily removed by the three coagulants in a wide dose range (5–17 mg L^{-1}); while the proportion of hydrophilic (HPI) NOM in the removed dissolved organic matter (DOM) was larger in Al_m and Al_{13} species coagulation at low and moderate dose (lower than 11 mg L^{-1}). Neutral and alkaline pH facilitated the particle removal, while acidic pH contributed to better HPI NOM removal. The floc strength investigation indicated that the floc strength formed by Al_{13} under different coagulation conditions was in the following hierarchy: pH 6.5 (15 mg L^{-1}) > pH 4.0 (9 mg L^{-1}) > pH 8.0 (15 mg L^{-1}). For $\text{Al}_2(\text{SO}_4)_3$ coagulation, the order was as following: pH 4.0 (9 mg L^{-1}) > pH 6.5 (15 mg L^{-1}) > pH 8.0 (15 mg L^{-1}). Additionally, the fractal dimension of flocs indicated that Al_{13} species resulted in compact aggregates at low concentration and pH.

The effect of coagulation coupled with chlorination (i.e., pre-, inter-, and post-chlorination) on the formation of DBPs and the removal efficiency of DBPs precursors has been investigated [31]. Compared with coagulation coupling with pre-chlorination, coagulation coupled with inter-chlorination could lead a higher removal efficiency of DOC, SUVA and chloroacetic acids formation potential (CAAsFP). The CAAsFP/DOC value of residual DOC showed that coagulation with inter-chlorination has a beneficial effect on CAAs precursors removal. More DBPs were produced during inter-chlorination than that of pre-chlorination at pH 7.5, while less DBPs were produced during inter-chlorination than that of pre-chlorination at pH 5.5 [31]. These results may be explained by the fact that (1) coagulation process is more efficient in terms of DBPs precursors removal at pH 5.5 (i.e., enhanced coagulation) than 7.5 (i.e., conventional coagulation) and (2) pre-chlorination disturbs coagulation process in NOM removal by oxidising the organic molecules. These explanations are recently confirmed by Ji et al. [31] who found that pre-chlorination at 1.3 mg L^{-1} , the post-chlorination at 1, 2, 3, and 4 mg L^{-1} of chlorine contributed to high total trihalomethanes (TTHMs) values of 0.94, 1.65, 2.07, and 2.21, respectively. In addition, the precipitate of humic acid (HA) after coagulation was chlorinated to study the kinetics of chlorine decay. The results of Ji et al. [31] showed that coagulated-HA had a higher reactivity with chlorine than aqueous-HA at pH 7.5. Furthermore, the trends of zeta potential during coagulation process suggested that the distribution of chlorine species had significant influence on the removing of DBPs precursors by coagulation coupled with chlorination.

Water from the three reservoirs, Min-ter, Li-yu-ten and Yun-hoshen (Taiwan), for concentration of chlorophyll-*a*,

UV_{254} , fluorescence intensity, concentration of DOC, and fractionation of dissolved molecules by MW has been examined [21]. The water samples were collected over the change from spring to summer (May to July but before the typhoon season) when the water temperature and extent of eutrophication increase. Analytical results indicate that the concentration of DOC is proportional to the concentration of chlorophyll-*a*, but not to the values of UV_{254} and fluorescence intensity. Therefore, eutrophication, extraneous contaminants of small molecules, and the extracellular products of algae cause an increase in DOC, but a decrease in the proportion of large organic molecules such as of humic substances. The fraction of DOC with a MW of less than 5000 Da increases with the concentration of chlorophyll-*a*. All these data suggest that changes in the quality of water after eutrophication make the treatment of drinking water more difficult. The results of Cheng and Chi [21] demonstrate that the efficiency of DOC removal falls as the degree of eutrophication increases. When the percentage of DOC with small molecules excreted by algae increased by 1%, the efficiency of DOC removal decreased by approximately 1%, implying that enhanced coagulation is not able to remove the DOC excreted by the algae during eutrophication, and resulting an increased concentration of THMs formation in water disinfections process.

The effects of coagulation processes with two different coagulants (PACl and alum) on aldehydes formation during oxidation with common oxidants (ozone, chlorine and chlorine dioxide) in a particular groundwater source in Northern Banat region, Yugoslavia, have been studied [32]. Aldehydes concentrations in coagulated water were lower than in raw water. In contrast, obtained results showed that specific contents of these DBPs ($\mu\text{g mg TOC}^{-1}$) showed an increase after coagulation processes in a number of samples. Results indicate that the choice of the coagulant-oxidant combination may be important as well as the type of filtration bed, retention time, and filter washing regime in the removal of aldehydes from water.

DOM in a filtered river water was isolated and fractionated into six different fractions [33]. THMs and HAAs formed from these isolated DOM fractions during chlorination and chloramination were determined. Results show that the HPO acid, HPI acid, HPI base and HPO neutral are major precursors of THMs and HAAs. There exist good correlations between the values of SUVA at 254 nm of the individual DOM fractions and their DBPs formation potential, indicating that aromatic moieties are responsible for DBPs formation for both HPO and HPI DOM fractions. Chloramination of the DOM fractions yields much less THMs and HAAs than chlorination. For the dominant DOM fraction (i.e. HPO acid) in the water, the yields of THMs and HAAs increase more significantly in chlorination than those in chloramination with the increase of disinfectant dosage, contact time and DOC content.

The effectiveness of alum and PACl as coagulants for the treatment of surface water with low DOC (2.1–2.4 mg L^{-1}) and at two alkalinity–hardness levels was evaluated [34].

Effectiveness was evaluated by measurement of DOC, UV₂₅₄, and different THMFP tests. PACl showed higher removal efficiency for all the analysed variables and under both high and low alkalinity–hardness conditions. Results also showed that alum coagulation is more sensitive to operational conditions, especially pH. Maximum differences between coagulants were observed in the removal of final THMFP with average values ($n = 48$) being 48 and 31%. This difference was maximum when coagulation/flocculation was carried out at pH 8.0. Comparison of full scale plant data and jar test data revealed that optimisation based on DOC and UV₂₅₄ removal does not ensure optimum results for THMs precursors removal. Solution pH above 6.0 units ensures acceptable residual levels of dissolved aluminium ($< 0.2 \text{ mg Al}^{3+} \text{ L}^{-1}$). Precursor removal optimisation did not compromise residual aluminium requirements. After treatment a noticeable increase in the contribution of low MW molecules to the THMFP was observed. Under high alkalinity–hardness conditions bromine incorporation factor of treated water is much more sensitive to the type of coagulant used. Results of bromine incorporation factor suggest that at higher alkalinity–hardness levels HPI NOM is better removed. Finally, the relationship between removal of UV absorbance and removal of THMFP was investigated. Results suggest that this relationship is more accurate and more reliable when PACl is used.

Laboratory and pilot scale tests were conducted to compare the effectiveness of enhanced coagulation with the more advanced technologies of ozone and granular activated carbon in treating a range of clean, eutrophic and industrially polluted waters [35]. Particular attention was paid to the removal of DBP precursors, organics and micropollutants that could be achieved using the various types of treatment. Reductions of up to 50% THMFP and between 40 and 70% organic carbon and colour were obtained using enhanced coagulation, which compared favourably with the advanced treatment processes. The more sophisticated processes were especially effective in the removal of micropollutants, this generally being in excess of 70%, which was not achievable using enhanced coagulation. pH depression using acid addition allowed for increases in organics removal at lower coagulant doses and inorganic coagulants were found to be more effective than the polymeric coagulants for organic matter removal. It was shown that the advanced treatment processes became more cost effective for larger plants and as water quality deteriorates, but for smaller water works, enhanced coagulation is cheaper.

Xue *et al.* [36] studied the THMFP and structural characteristics of DOM in the secondary effluent from the Wenchang Wastewater Treatment Plant (Harbin, China) and evaluated the alterations in structural and chemical compositions of the DOM during chlorination. Using XAD-8 and XAD-4 resins, DOM was fractionated into 5 fractions: HPO acid (HPO-A), HPO neutral (HPO-N), transphilic acid (TPI-A), transphilic neutral (TPI-N) and HPI fraction. Results showed that HPO-A and HPI dominated in the secondary effluent, collectively accounting for more than

66% of the DOM as DOC, and 70–84% of the THMFP of DOM was converted from the reaction of chlorine with HPOA and HPI. Fourier-transform infrared analysis illustrated that the functional groups involved in the chlorination reaction were aromatic C=C, C–O, C=O, C–Cl and amide functional groups. Proton nuclear magnetic resonance analysis indicated that HPO-A, HPO-N, TPI-A and TPI-N had significantly decreased aromatic protons after chlorination. Although HPO-A, HPO-N, TPI-A and TPI-N exhibited different fluorescence changes during chlorination, the wavelength that corresponded to the position of the normalised emission band at its half-intensity ($\lambda_{0.5}$) for the four fractions decreased as a result of chlorination.

The effect of pH on coagulation performance and floc characteristics with respect to the treatment of HA solution using PFC as coagulant was investigated [37]. Ultrafiltration was used after coagulation to further remove organics under three pH conditions. The subsequent effects on chlorine decay were studied using a first decay model and AQUASIM modelling software. The results indicated that PFC had different coagulation mechanisms in different pH regions. Charge neutralisation was the dominant mechanism in acidic region, while *sweep* was the predominant mechanism at pH > 6.0. HA was effectively removed in acidic region and turbidity removal efficiency was higher in neutral and alkaline regions. The median equivalent volumetric diameter (d_{50}) of flocs formed in coagulation process in acidic region was larger than that of flocs formed at pH 9.0. The flocs formed at pH 5.0 were more compact because larger floc fractal dimension (D_f) was observed. Floc breakage behaviour showed that flocs formed at different pH values gave different floc strength and recovery ability, and the strength and recovery factors of the flocs varied in the following order: pH 5.0 > 4.0 > 9.0. The treated water at pH 5.0 possibly contained the minimal amount of DBPs precursors due to the minimal reacting compounds present in the treated water. DBPs precursors were probably prone to be removed by coagulation process during which flocs with larger strength factor, recovery factor and D_f were formed.

The influence of pH, chloride or bromide concentration on the formation of THMs from carbohydrates was studied [38]. It was observed that THMs are not formed at acidic pH, while basic pH values only increase slightly the THM content, although the consumption of chlorine increases up to 100% with respect to pH 8. The presence of chloride in ppm increases the THM formation from carbohydrates without influence of the chlorine consumption. In the same manner, the presence of bromide ions in ppb also increases remarkably the THMs formed upon chlorination of saccharides. Even more, they have observed that at bromide concentrations below 100 ppb, complete incorporation of bromide in THMs occurs. Overall, the results obtained show that saccharides widely present in natural waters can give rise to significant THM concentrations in the disinfection process by chlorine.

The relationship between chlorine decay and the formations of DBPs, including trichloromethane (TCM) and

CAA in the presence of four model compounds, i.e., resorcinol, phloroglucinol, *p*-hydroxybenzoic acid, and *m*-hydroxybenzoic acid was investigated [39]. The chlorine degradation in model compounds with OH and/or COOH functional groups were rapid after chlorination. The TCM yields of carboxylic group substituted compounds (3-hydroxybenzoic acid [3-HBA], 4-hydroxybenzoic acid [4-HBA]) were found to be lower than that of the *m*-dihydroxy substituted compounds. Phloroglucinol, with one more OH substitution group than resorcinol, tends to form significant amounts of CAA after chlorination. However, it was observed that with the COOH substitution of 3-HBA and 4-HBA tend to exhibit more CAAsFP than resorcinol. The developed parallel second and first-order reaction model for chlorine demand has been successfully utilised for TCM, CAA and DBP formation modelling. A high correlation between CAA and TCM was observed for the model compounds.

Thirty organic compounds to investigate their chloroform formation characteristics during chlorination with sodium hypochlorite at pH-values 7.0 and 8.0 were selected [40]. These experiments were conducted under conditions similar to those applied on the chlorination of raw water. The results indicated that the chloroform concentrations occurred by the all tested compounds was in the ppm range. The maximum levels of chloroform (11-13 mg L⁻¹) were determined during the reaction of resorcinol and phloroglucinol at pH-value 8.0.

3. Coagulation and Chlorination of Algae

It is known that some metal compounds (e.g., iron and manganese), which are considered to be indispensable microelements in the growth of algae, are generally detected in source water, especially in eutrophic lakes and reservoirs [41-43]. For example, total iron and manganese concentrations were reported to range from 0.28 to 0.89 mg L⁻¹ and from 0.20 to 0.56 mg L⁻¹, respectively in Taihu Lake of China [20]. Furthermore, the water supply pipes are commonly made with metal materials, e.g., iron and copper. The inner surface of metal pipe can be eroded gradually by active algal cells, which might further lead to the variation of DBPs formation in chlorination.

The role of iron and manganese on the formation of HAAs when algae are chlorinated at different pHs was investigated [20]. The results showed that both iron and manganese can reduce the yields of dichloroacetic acid (DCAA) and trichloroacetic acid (TCAA) on chlorinating green alga *Chlorella vulgaris* (*C. vulgaris*) at a pH range of 6.0–9.0, and the decline of DCAA and TCAA was shown to be more significant at the low pH range. At pH 6.0, DCAA and TCAA yields decreased by 44.5 and 57.3%, respectively with the addition of 0.5 mg L⁻¹ iron, and decreased 39.5 and 49.4%, respectively with the addition of 0.5 mg L⁻¹ manganese. The main reason for decreasing the yields of HAAs as shown by scanning electron microscope (SEM) is that Fe(OH)_{3(am)} or MnO_{2(am)} coat the algal cells, which then improves their agglomeration of algal cells which is also revealed by the

laser particle size analysis [20].

To efficiently remove algae from drinking water, a strengthening process or combined process of coagulant (alkaline aluminium chloride) and chlorine, and with the dosage of potassium permanganate 0.3 mg L⁻¹ was investigated on three selected water supply and purification plants during the algae outbreak period [44]. The results show that the algae density increases with the increase of water temperature. When the algae density in raw water is less than 1.0 × 10⁶ cells L⁻¹, more than 98% of algae can be removed with a coagulant dosage of 13 mg L⁻¹. When the algae density is increased to more than 10 × 10⁶ cells L⁻¹, i.e. during algae outbreak period, 96% or more algae can be removed using the coagulant and chlorine of dosages of approximately 20 and 4.0 mg L⁻¹, respectively [44].

The roles that algal populations, as sources of DOC, and water quality play in DOC removal during ozonation and coagulation processes were examined [45]. Algal monocultures were grown as suspensions in continuous-flow reactors to simulate bloom conditions and to provide a distinct type of DOC for treatment experiments. Jar tests were conducted with and without preozonation to assess DOC removal as a function of algal source, coagulant type and dose, pH and bicarbonate concentration. Overall, algal-derived DOC was difficult to remove; high coagulant doses were required and removal was strongly influenced by solution pH and algal source.

The use of sonication to improve the removal by coagulation of *Microcystis aeruginosa*, a common species of toxic algae was investigated [46]. The results show that sonication significantly enhances the reduction of algae cells, solution UV₂₅₄, and chlorophyll-*a* without increasing the concentration of aqueous microcystins. The main mechanism involved the destruction during ultrasonic irradiation of gas vacuoles inside algae cells that acted as ‘nuclei’ for acoustic cavitation and collapse during the “bubble crush” period, resulting in the settlement of cyanobacteria. Coagulation efficiency depended strongly on the coagulant dose and sonication conditions. When the coagulant dose was 0.5 mg L⁻¹, 5 s of ultrasonic irradiation increased algae removal efficiency from 35 to 67%. As further sonication enhanced the coagulation efficiency only slightly due to better mixing, optimal sonication time was 5 s. The most effective sonication intensity was 47.2 W cm⁻², and the highest removal ratio of *M. aeruginosa* was 93.5% by the sonication–coagulation method. Experiments with reservoir water showed that this method could be successfully applied to natural water containing multiple species of algae.

Fang et al. [47] investigated formation of carbonaceous disinfection by-products (C-DBPs), including THMs, HAAs, halo ketones (HKs), chloral hydrate (CH), and nitrogenous disinfection by-products (N-DBPs), including haloacetonitriles and trichloronitromethane (TCNM) from chlorination of *M. aeruginosa* under different conditions. Factors evaluated include contact time, chlorine dosages, pH, temperature, ammonia concentrations and algae growth stages. Increased reaction time, chlorine dosage and

temperature improved the formation of the relatively stable CDBPs (e.g., THM, HAA, and CH) and TCNM. Formation of dichloroacetonitrile followed an increasing and then decreasing pattern with prolonged reaction time and increased chlorine dosages. pH affected DBP formation differently, with THM increasing, HKs decreasing, and other DBPs having maximum concentrations at certain pH values. The addition of ammonia significantly reduced the formation of most DBPs, but TCNM formation was not affected and 1,1-dichloropropanone formation was higher with the addition of ammonia. Most DBPs increased as the growth period of algal cells increased. Chlorination of algal cells of higher organic nitrogen content generated higher concentrations of N-DBPs (e.g., haloacetonitriles and TCNM) and CH, comparable DCAA concentration but much lower concentrations of other C-DBPs (e.g., THM, TCAA and HKs) than did NOM.

A state of the art on cyanotoxins in water and their behaviour towards chlorination was presented [48]. Chlorination efficiency on cyanotoxins alteration depends on pH, chlorine dose and oxidant nature. Microcystins and cylindrospermopsin (CS) are efficiently transformed by chlorine, with respectively 6 and 2 by-products identified. In addition, chlorination of microcystins and CS is associated with a loss of acute toxicity. Even though they have been less investigated, saxitoxins and nodularins are also altered by chlorine. For these toxins, no by-products have been identified, but the chlorinated mixture does not show acute toxicity. On the contrary, the fact that anatoxin-*a* has a very slow reaction kinetics suggests that this toxin resists chlorination.

The effectiveness of chlorination as a water treatment procedure for CS degradation was studied [49]. The results demonstrate that relatively low chlorine doses ($< 1 \text{ mg L}^{-1}$) are sufficient for degradation of CS, when the DOC content is low. However, if organic matter other than CS is present in the solution, the effectiveness of chlorine for CS degradation is reduced as other organic matter present consumes chlorine. Under the experimental conditions using samples with a solution pH of 6-9, a residual chlorine concentration of 0.5 mg L^{-1} was sufficient to degrade $> 99\%$ of CS. Toxin degradation via chlorination occurs within the first minute and no difference was observable between degradation in an open system and in a closed system. With a decrease of the pH from 6 to 4 a reduction in the efficiency of chlorine for degradation of CS was observable, a possible indication that CS is more stable to chlorine degradation at lower pH. However, in normal water treatment this is not relevant since the pH is consistently higher than 6.

The contribution of major biomolecules, including protein, carbohydrates and lipids, in predicting DBPs formation upon chlorination of algal cells was investigated [25]. Three model compounds, including bovine serum albumin, starch and fish oil, as surrogates of algal-derived proteins, carbohydrates and lipids, and cells of three algae species, representing blue-green algae, green algae, and diatoms, were chlorinated in the laboratory. The results showed that bovine serum albumin

($27 \text{ } \mu\text{g mg C}^{-1}$) and fish oil ($50 \text{ } \mu\text{g mg C}^{-1}$) produced more than nine times higher levels of chloroform than starch ($3 \text{ } \mu\text{g mg C}^{-1}$). For the formation of HAAs, bovine serum albumin was shown to have higher reactivity ($49 \text{ } \mu\text{g mg C}^{-1}$) than fish oil and starch ($5 \text{ } \mu\text{g mg C}^{-1}$). For the algal cells, *Nitzschia sp.* (diatom) showed higher chloroform yields ($48 \text{ } \mu\text{g mg C}^{-1}$) but lower HAA yields ($43 \text{ } \mu\text{g mg C}^{-1}$) than *Chlamydomonas sp.* (green algae) (chloroform: $34 \text{ } \mu\text{g mg C}^{-1}$; HAA: $62 \text{ } \mu\text{g mg C}^{-1}$) and *Oscillatoria sp.* (blue-green algae) (chloroform: $26 \text{ } \mu\text{g mg C}^{-1}$; HAA: $72 \text{ } \mu\text{g mg C}^{-1}$). The calculated chloroform formation of cells from the three algal groups, based on their biochemical compositions, was generally consistent with the experimental data, while the predicted values for HAAs were significantly lower than the observed ones. As compared to humic substances, such as humic and fulvic acids, the algal cells appeared to be important precursors of DCAA.

Cyanobacterial growth in semi-closed water areas such as reservoirs brings about a coagulation inhibition in a drinking water treatment system, but the inhibitory substances and mechanisms involved have yet to be elucidated. Takaara *et al.* [50] isolated proteins having a high affinity with PACl from organic substances produced by *M. aeruginosa* with the affinity chromatography technique. Both extracellular organic matter and cellular organic matter disturbed the flocculation of suspended kaolin with PACl, but it was likely that nonproteinous substances in extracellular organic matter cause the reduction of coagulation efficiency. In contrast, proteins in cellular organic matter were obtained as possible inhibitory substances for the coagulation with PACl. These proteins could consume PACl in the coagulation process due to the formation of chelate complexes between these inhibitory proteins and the coagulant. The consumption of PACl by cyanobacterial proteins could be one of the important causes of the increase in coagulant demand.

Henderson *et al.* [51] characterised the algogenic organic matter (AOM) originating from four algae species (*C. vulgaris*, *M. aeruginosa*, *Asterionella formosa* and *Melosira sp.*) using techniques including DOC, SUVA, zeta potential, charge density, hydrophobicity, protein and carbohydrate content, MW and fluorescence. All AOM was predominantly HPI with a low SUVA. AOM had negative zeta potential values in the range pH 2–10. The stationary phase charge density of AOM from *C. vulgaris* was greatest at 3.2 meq g^{-1} while that of *M. aeruginosa* and *Melosira sp.* was negligible. Lower charge density was related to higher hydrophobicity, while it was related in turn to increasing proteins $> 500 \text{ kDa}$:carbohydrate ratio. This demonstrates that AOM is of a very different character to NOM.

Ho *et al.* [52] chlorinated four microcystin analogues in two treated waters and two of the analogues in deionised water. The oxidation of the microcystins was related to the chlorine exposure (CT) of the sample waters with the ease of oxidation following the trend: microcystin-YR $>$ microcystin-RR $>$ microcystin-LR \geq microcystin-LA. This trend was in agreement with published data on model compounds and free amino acids. Values of CT of up to 25 mg min L^{-1} were required for oxidation of all microcystin

analogues to below the World Health Organisation guideline value of $1.0 \mu\text{g L}^{-1}$. Results from this study indicate that for some water resources it is important to determine the speciation of the microcystin analogues to optimise chlorination practices.

Crane et al. [53] utilised three species of marine algae representing major taxonomic groups of phytoplankton, *Isochrysis galbana* (Chrysophyceae), *Carteria* sp. (Chlorophyceae), and *Thalassiosira pseudonana* (Bacillariophyceae), to investigate the potential of naturally occurring chlorophyll-*a* of living algae to produce THMs during the chlorination of saline waters. Chlorination of filtered natural estuarine water (salinity = 23 ppt) from the North Edisto River, South Carolina, results in rapid formation of 201–221 $\mu\text{g L}^{-1}$ THMs comprised mainly of bromoform (CHBr_3) and chlorodibromomethane (CHBr_2Cl). In the presence of 10^6 cells mL^{-1} *Isochrysis galbana*, chlorination of filtered estuarine water with sodium hypochlorite (NaOCl) to a nominal 10 mg L^{-1} chlorine increased the total THM concentration by an average of 41% ($N = 6$). The presence of *Thalassiosira pseudonana* resulted in an average 24% decrease ($N = 6$) while *Carteria* sp. did not produce a statistically significant effect upon the total THM concentration formed. The absence of any significant statistical correlations between the chlorophyll-*a* content of algal cultures and THM concentrations causes us to discount chlorine-chlorophyll-*a* interactions as a source of these compounds. However, THM concentrations produced from the chlorination of algal culture media, after removal of algal populations, suggests instead that the observed trends in THM production are mainly due to chlorines reaction with the by-products of algal metabolism.

Brooks and Liptak [54] demonstrated that the Lake Michigan phytoplankton showed a significant loss of chlorophyll-*a* and permanent reduction of carbon uptake rates after exposure for 30 min to concentrations of total residual chlorine at or above 1 mg L^{-1} . At this level the photosynthetic system of the algae was irreversibly destroyed. Below 0.1 mg L^{-1} residual chlorine only slight changes in chlorophyll-*a* were noted, and, following an initial decrease, carbon uptake rates exhibited nearly complete recovery after 24 h.

The chlorination of four cyanobacteria species and three cyanotoxins and their analogues in natural water and bloom samples was studied [55]. They quantified the DBPs formation due to chlorination of cell-bound material and water matrix. They concluded that (1) pre-chlorination of natural water containing cyanobacteria cell numbers below 200,000 cells mL^{-1} for different treatment purposes is an efficient operational option and (2) the water background quality is the key factor in DBPs formation potential independent of cyanobacteria cell-bound material.

The impact of algal properties and pre-oxidation on solid-liquid separation of algae is presented by Henderson et al. [56]. Moreover, algae, cyanotoxins, and NOM removal by coagulation/flocculation are also discussed [57,58].

4. Optimisation of NOM and Algae Removal before Chlorination

The use of chlorine only at the end of the water treatment permits a great reduction of THM formation [59]. A low THM level may be obtained by the optimisation of each treatment step. Coagulants such as Al^{3+} and Fe^{3+} remove significant concentrations of TOC and THM precursors which, in actual practice tends to range from 40 to 70%. Further, Fiessinger et al. [59] concluded that pre-chlorination should be abandoned; algal growth may be controlled with chloramines or coverage of open sedimentation basins; and chlorine can be maintained as a final disinfectant if organic precursors are sufficiently removed.

Several authors have proposed that removal of DBP precursors must be accomplished prior to disinfection such as [60–62]. Kristiana et al. [62] investigated the impact of the addition of powdered activated carbon (PAC) to an enhanced coagulation treatment process at an existing water treatment plant on the efficiency of NOM removal, the disinfection behaviour of the treated water, and the water quality in the distribution system. As a result of the PAC addition, the removal of NOM improved by 70%, which led to a significant reduction (80–95%) in the formation of DBPs. The water quality in the distribution system also improved, indicated by lower concentrations of DBPs in the distribution system and better maintenance of disinfectant residual at the extremities of the distribution system. The efficacy of the PAC treatment for NOM removal was shown to be a function of the characteristics of the NOM and the quality of the source water, as well as the PAC dose. PAC treatment did not have the capacity to remove bromide ion, resulting in the formation of more brominated DBPs. Since brominated DBPs have been found to be more toxic than their chlorinated analogues, their preferential formation upon PAC addition must be considered, especially in source waters containing high concentrations of bromide.

Preoxidation of the algal cell with chlorine must be avoided, because it frequently causes toxin release from algae and produce THMs during water treatment [63]. Recently, Lin and Wang [64] concluded that, in conventional water treatment process, coagulation and slow filtration treatments have better efficiency to reduce the NOM in water especially for the HPO portion. However, the pre-chlorination treatment for raw water increased the DOC concentration due to the lysis of algae cells. HPO acids portion is the most sensitive portion of NOM to $\text{UV}/\text{H}_2\text{O}_2$ and conventional treatment processes. THMFP tests showed that HPO acids portion is also the main contributor to THMs formation after chlorination process.

It was concluded that the impact of water treatment processes on N-DBP formation is complex and variable [65]. While coagulation and filtration are of moderate efficacy for the removal of N-DBP precursors, such as amino acids and amines, biofiltration, if used prior to disinfection, is particularly successful at removing cyanogens halide

precursors. Oxidation before final disinfection can increase halonitromethane formation and decrease N-nitrosodimethylamine, and chloramination is likely to increase cyanogen halides and N-nitrosodimethylamine relative to chlorination.

The effect of conventional water treatment processes using alum on the integrity of cells of toxic *M. aeruginosa* using both jar tests and pilot plant studies was studied [66]. Removal of *M. aeruginosa* cells by alum flocculation using a jar test apparatus indicated all cells were removed without damage to membrane integrity. Thus the chemical treatment and mechanical action did not damage the cultured *M. aeruginosa* cells and, more importantly, did not result in additional release of cell metabolites above background concentrations. For pilot plant experiments, which consisted of coagulation/flocculation-sedimentation-filtration, most of the cells were removed intact and no additional microcystin was found in the finished water.

The variability of the occurrence of HAAs during the treatment process in two facilities where surface water is pre-chlorinated before being treated by conventional physico-chemical processes was investigated [67]. The investigation focused on both seasonal and point-to-point fluctuations of HAAs. In both facilities, samples were collected weekly

during 1 complete year at four points in order to generate robust data on HAAs and on complementary parameters. The results showed that the initial formation of HAAs was the highest and the most variable in the plant where levels of DBP precursor indicators and the pre-chlorination dose were both higher and more variable. Subsequent formation of HAAs from the pre-chlorination point until the settled water occurred due to remaining levels of residual chlorine and DBP precursors. However, HAA levels and in particular DCAA (the preponderant HAA species in the waters under study) decreased dramatically during filtration, very probably because of biodegradation within the filter. The effect of filtration on DCAA fate was season-dependant, with the highest degradation in warm water periods and practically no variation during winter. Statistical modelling was applied to empirically identify the operational factors responsible for HAA formation and fate. Model performance to identify HAA variability in waters following pre-chlorination was much better than for water following filtration, which is due to the lack of information on mechanisms and conditions favouring DCAA degradation.

Fig. 1 shows how coagulation mechanisms for microcystin-LR removal are highly dependent on time and charge species distribution.

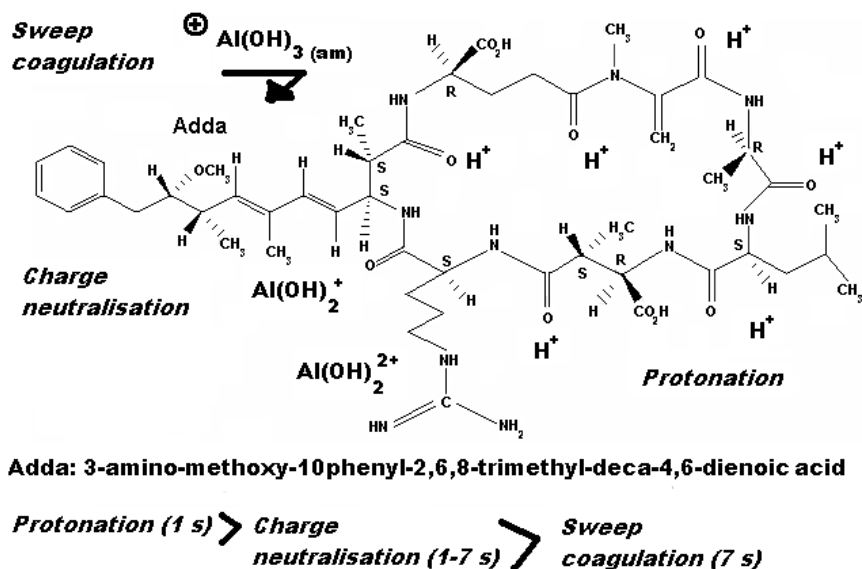


Fig 1. Coagulation mechanisms for microcystin-LR removal [11].

5. Future Trends of Conventional Drinking Water Treatment

As seen above, the removal of algae and NOM is important, as for example the reactions with chlorine-based disinfectants lead to the formation of DBPs. For waters that are rich in NOM, coagulants such as aluminium and iron play a key but insufficient role in removing the organic levels [68]. There has been recent interest in alternatives to the coagulation process such as advanced oxidation processes (AOPs), adsorption on PAC [62], ozone, biotreatment and

nanofiltration [69-73], and electrocoagulation [74].

Bond *et al.* [75] presented an excellent Table (Table 1) about the selectivity of NOM removal processes and focused on the fact that the removing of NOM is through a variety of principally electrostatic mechanisms. In the same point of view, *sweep* flocculation as a second form of charge neutralisation is also discussed [76]. Recently, Badawy *et al.* [77] concluded that using pre-ozonation/enhanced coagulation/activated carbon filtration treatment train appears to be the most effective method for reducing DBPs precursors in drinking water treatment.

Table 1. Selectivity of NOM removal processes [75].

Process	Mechanism/s	Selectivity	Least treatable
Coagulation	Adsorption onto flocs and charge neutralisation/colloid destabilisation. Sweep flocculation	Large, anionic molecules	Neutral molecules
Anion exchange	Ion exchange (electrostatic), also adsorption (hydrophobic) and hydrogen bonding	Small, anionic molecules	Neutral molecules
Membranes	Size exclusion, differing diffusion rates across membrane. Electrostatics for charged membranes	Species > MWCO	Hydrophobic molecules < MWCO
Activated carbon	Reversible physical adsorption by non-specific forces	Small, neutral, hydrophobic molecules	Hydrophilic charged molecules
Biotreatment	Enzyme-controlled microbial degradation and adsorption	Low MW polar molecules (e.g. amino acids, aldehydes)	Large & hydrophobic molecules
AOPs	OH reactions : electron transfer, H abstraction and OH addition	Relatively unselective	
Ozone	Electrophilic addition : oxidation and bond cleavage,. Also OH radicals	Aromatic compounds and amines	Saturated compounds

As remembered by Simate et al. [78] and Ghernaout et al. [79-81], we recommend that any chemical used in, on, or near drinking water sources, or used during the treatment of drinking water should, (1) not present a public health concern, and (2) not result in the chemical, its by-products, or any contaminants exceeding drinking water guideline values as provided by the WHO [78].

6. Conclusions

This paper discusses both NOM and algae coagulation and chlorination. The following conclusions may be drawn:

1. A low THM level may be obtained by the optimisation of each treatment step. Coagulants such as Fe^{3+} and slow filtration treatments remove significant concentrations of TOC and THM precursors especially the HPO portion. Pre-chlorination should be abandoned due to the lysis of algae cells, algal growth may be controlled with more frequent cleaning of the basins especially in summer periods and coverage of open sedimentation basins would be avoided to benefit from solar radiation disinfection and oxygen diffusion from the air, and chlorine can be maintained as a final disinfectant if organic precursors are sufficiently removed.
2. Finally, it remains doubtful that the conventional water treatment (clarification + filtration + chlorination) will continue to be a viable solution for drinking water from source waters containing NOM as their quality deteriorates and water quality standards become more difficult to achieve.

Abbreviations

AOPs	Advanced Oxidation Processes
AOM	Algal Organic Matter
CAA	Chloroacetic Acid
CAAsFP	Chloroacetic Acids Formation Potential
C-DBPs	Carbonaceous Disinfection By-products
CH	Chloral Hydrate
CS	Cylindrospermopsin

DBPs	Disinfection By-products
DCAA	Dichloroacetic Acid
DOC	Dissolved Organic Carbon
DOM	Dissolved Organic Matter
HA	Humic Acid
HAAs	Haloacetic acids
HKs	Haloketones
HPI	Hydrophilic
HPACl	High efficient composite Polyaluminium Chloride
HPO	Hydrophobic
HPO-A	HPO Acid
HPO-N	HPO Neutral
MW	Molecular Weight
MWCO	Molecular Weight Cut-off
MWS	Modified Wheat Straw
N-DBPs	Nitrogenous Disinfection By-products
NOM	Natural Organic Matter
PAC	Powdered Activated Carbon
PACl	Polyaluminium Chloride
PFC	Polyferric Chloride
SUVA	Specific Ultraviolet Absorbance
TCA	Trichloroacetic Acid
TCM	Trichloromethane
TCNM	Trichloronitromethane
THMFP	Trihalomethane Formation Potential
THMs	Trihalomethanes
TOC	Total Organic Carbon
TPI-A	Transphilic Acid
TPI-N	Transphilic Neutral
TTHMs	Total Trihalomethanes
USEPA	United States Environmental Protection Agency
UV ₂₅₄	Ultraviolet Absorption

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