



Natural organic matter removal by coagulation during drinking water treatment: A review

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ABSTRACT

Natural organic matter (NOM) is found in all surface, ground and soil waters. An increase in the amount of NOM has been observed over the past 10–20 years in raw water supplies in several areas, which has a significant effect on drinking water treatment. The presence of NOM causes many problems in drinking water and drinking water treatment processes, including (i) negative effect on water quality by causing colour, taste and odor problems, (ii) increased coagulant and disinfectant doses (which in turn results in increased sludge volumes and production of harmful disinfection by-products), (iii) promoted biological growth in distribution system, and (iv) increased levels of complexed heavy metals and adsorbed organic pollutants. NOM can be removed from drinking water by several treatment options, of which the most common and economically feasible processes are considered to be coagulation and flocculation followed by sedimentation/flotation and sand filtration. Most of the NOM can be removed by coagulation, although, the hydrophobic fraction and high molar mass compounds of NOM are removed more efficiently than hydrophilic fraction and the low molar mass compounds. Thus, enhanced and/or optimized coagulation, as well as new process alternatives for the better removal of NOM by coagulation process has been suggested. In the present work, an overview of the recent research dealing with coagulation and flocculation in the removal of NOM from drinking water is presented.

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Abbreviations: AOPs, Advanced oxidation processes; APAMs, Anionic polyacrylamides; BAC, Biological activated carbon; BDOC, Biodegradable dissolved organic carbon; COD, Chemical oxygen demand; CPAMs, Cationic polyacrylamides; DBP, Disinfection by-product; DBPFP, Disinfection by-product formation potential; DOC, Dissolved organic carbon; EC, Electrocoagulation; GAC, Granular activated carbon; HAAs, Haloacetic acids; HMM, High molar mass; HPAC, Composite polyaluminium chloride; HPSEC, High performance size exclusion chromatography; IPFs, Inorganic polymer flocculants; LMM, Low molar mass; MCBR, Submerged UF membrane coagulation bioreactor; MF, Microfiltration; MIEX, Magnetic ion exchange resin; MWD, Molecular weight distribution; NF, Nanofiltration; NOM, Natural organic matter; PAA, Polyacrylamide; PAC, Powdered activated carbon; PACI, Polyaluminium chloride; PAF-SiC, Poly-aluminium-ferric-silicate-chloride; PAS, Polyaluminium sulphate; PASiC, Poly-aluminium-silicate-chloride; PDADMAC, Polydiallyldimethyl ammonium chloride; PFC, Polyferric chloride; PFS, Polyferric sulphate; PFSiS, Polyferric silicate sulphate; PICl, Polymeric iron chloride; PSF, Polysilicate ferric; RO, Reverse osmosis; SUVA, Specific UV absorbance; THMFP, Trihalomethane formation potential; THMs, Trihalomethanes; TOC, Total organic carbon; UF, Ultrafiltration.

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1. Introduction

Natural organic matter (NOM) is defined as a complex matrix of organic materials present in all natural waters. As a result of the interactions between the hydrological cycle and the biosphere and geosphere, the water sources used for drinking water purposes generally contain NOM. Thus the amount, character and properties of NOM differ considerably in waters of different origins and depend on the biogeochemical cycles of the surrounding environments [1]. Moreover, the range of organic components of NOM may vary also on the same location seasonally [2–4], due to for example rainfall event, snowmelt runoff, floods or droughts. Floods and droughts are the main impacts of climate change on water availability and quality. It has been suggested that these changes may be the reason for an increase in the total amount of NOM [5,6], which has been noted to occur on several areas around the world during the past 20 years [6–10]. Besides the quantity of NOM, the quality of NOM has been noted to alter as well, since other important characteristics of NOM, e.g. specific UV absorbance (SUVA), have also increased [7]. The changes in NOM quantity and quality have a significant influence on selection, design and operation of water treatment processes.

To understand the role of NOM in water treatment, the characterization of NOM in the raw water should be done. Dissolved organic carbon (DOC), chemical oxygen demand (COD), UV_{254} , pH, turbidity and colour are common water quality parameters assessed by water treatment facilities in their quality control, however, they do not give information about the character of NOM such as molar mass (MM) or hydrophobicity. The characterization of the NOM can be made e.g. by high performance size exclusion chromatography (HPSEC) analysis, where the molecular weight distribution (MWD) of NOM can be determined [11,12], or by fractionation techniques where the mixture of organic compounds of NOM are divided into hydrophilic and hydrophobic fractions with resins [2,13]. The hydrophilic fractions of NOM are composed mostly of aliphatic carbon and nitrogenous compounds, such as carboxylic acids, carbohydrates and proteins. Hydrophobic NOM primarily consists of humic and fulvic acids (humic substances) and is

rich in aromatic carbon, phenolic structures and conjugated double bonds [14]. The humic substances generally account over half of the total organic carbon (TOC) content in water [15]. Humic substances can be regarded as natural anionic polyelectrolytes, with anionic charge at pH values higher than 4. A hypothetical molecular structure of humic acid is shown in Fig. 1, where important functional groups are illustrated [16]. Another approach to define hydrophobicity is to determine the SUVA value (i.e. UV_{254} absorbance divided by the TOC concentration). High SUVA value indicates that the organic matter is largely composed of hydrophobic, high MM organic material. Low SUVA value indicates that water contains mainly organic compounds which are hydrophilic, of low MM and have low charge density [2,13,17]. The different NOM fractions exhibit different properties in terms of treatability by coagulation, coagulant demand, chlorine and ozone reactivity and disinfection by-product formation potential (DBPFP) [1,2,13,18].

NOM affects significantly many aspects of water treatment, including the performance of the unit processes, application of water treatment chemicals and biological stability of water. As a result, NOM acts upon potable water quality by contributing to annoying colour, taste and odour problems, and as a carrier of metals and hydrophobic organic chemicals. In addition, NOM is responsible for the majority of the coagulant and disinfectant use in water treatment. It has a tendency to interfere with removal of other contaminants, it is responsible for fouling of membranes and it contributes to corrosion and acts as a substrate for bacterial growth in the distribution system [19]. Moreover NOM has been noted to be the major contributor to the disinfection by-product (DBP) formation.

DBPs have become a focus of attention in water treatment, since they have been reported to have adverse health effects [20]. More than 600 compounds of DBPs have been identified, among which trihalo-methanes (THMs) and haloacetic acids (HAAs) are the most common [21]. The hydrophobic and HMM fraction of NOM is considered to be the more important source of DBP precursors than the hydrophilic fraction and LMM compounds. However, also hydrophilic compounds are found to contribute to the formation of DBPs, especially in low humic waters, and in addition, bromine and iodine are noticed to be highly reactive

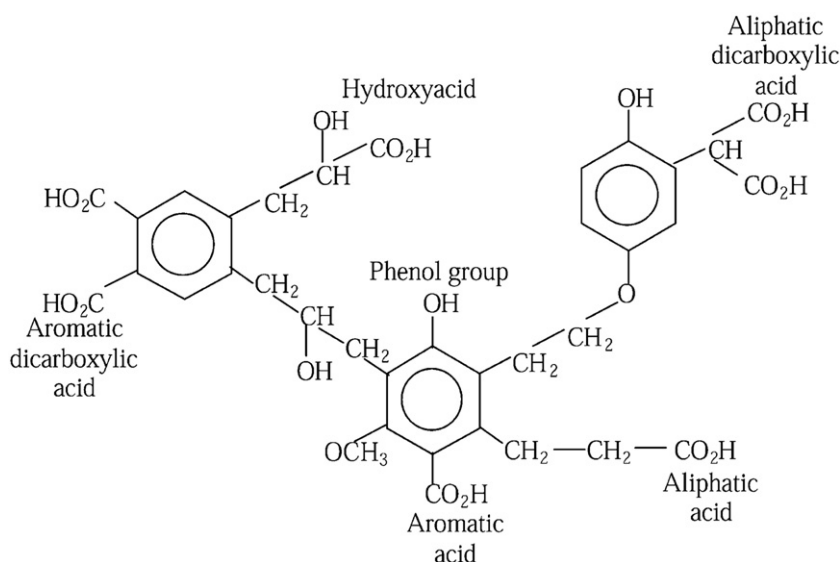


Fig. 1. Hypothetical molecular structure of humic acid (adapted from Duan and Gregory [16]).

Table 1

Overview of the different coagulants used in recent research studies.

Coagulant type	Features	Positive	Negative	References
Inorganic salts <i>Alum, Aluminium chloride</i>	Trivalent aluminium ions are released into a solution from the respective salt. They are hydrolysed and form soluble complexes possessing high positive charges. Coagulation efficiency depends on e.g. coagulant dose, mixing, pH, temperature, particle and NOM properties. During coagulation, the most effective range of pH is suggested to be about 5–6.5.	Stable, easily handled, readily soluble. Better turbidity removal than with ferric salts in many cases. Can be more effective than ferric in low doses. Higher colour removal efficiency.	Relative high coagulant residuals in the finished water in some cases. Possibility towards Alzheimer's disease. Ferric salts have been noted to be better in removing NOM than aluminium salts in many investigations. High alkalinity consumption. Sulphate and/or chloride in finished water increases corrosivity.	[4,11,24,28,37–39,42,46,51,55–57,65,86,90]
<i>Ferric chloride, Ferric sulphate</i>	Ferric salts hydrolyse similarly as aluminium salts when added to water and form different hydrolysis products. Effectiveness of coagulation depends on the same factors than during alum salt coagulation. The most effective range of pH is suggested to be pH 4.5–6	Ferric salts have been noted to be better in removing NOM than aluminium salts in many investigations. Especially the removal of middle size NOM fractions is noted to be more efficient. Not so sensitive to temperature changes compared to alum.	Ferric-based coagulant acid strength and associated optimized flocculation pH ranges can produce purified water with less buffering capacity and require greater chemical addition for stabilization and corrosion control. High alkalinity consumption. Sulphate and/or chloride in finished water increases corrosivity.	[3,23,24,26,28,42,50,51,86]
Polymeric coagulants <i>PACl</i>	Made by partially neutralized (prehydrolyzed) aluminium chloride. Enhanced amounts of high-charged, moderate-molar-mass hydrolysis species e.g. Al_{13} .	Less temperature and pH dependent than alum salts. Smaller alkalinity consumption. Better NOM removal capacity than alum in many cases. Lower dose requirement and less sludge produced. Lower residual aluminium in treated water.	The effectiveness of coagulant is significantly affected by coagulant hydrolysis species speciation. Preformed Al species are stable and cannot be further hydrolysed during coagulation. Might not be so efficient in removing HMM and highly hydrophobic NOM.	[30,54,63–65,90]
<i>PICl, PFC</i>	Made by partially neutralized (prehydrolyzed) ferric chloride. Enhanced amounts of high-charged, moderate-molar-mass hydrolysis species.	Wider pH range, lower sensitivity to temperature, reduced amounts of coagulants, lower residual iron concentration. Less corrosive than ferric chloride.	More at development stage. Not so widely used.	[76,77]
<i>PFS</i>	Made by partially neutralized (prehydrolyzed) ferric sulphate. Enhanced amounts of high-charged, moderate-molar-mass hydrolysis species.	Wider pH range, lower sensitivity to temperature, reduced amounts of coagulants, lower residual iron concentration. Less corrosive than ferric chloride.	Hydrolysis conditions have major impact on speciation of hydrolysis/polymeric species. More at development stage. Not so widely used.	[49,75]
<i>PASiC, PAF-SiC, PFSiS, PSF</i>	Combination of aluminium and/or ferric-based polymeric flocculants with polysilicate.	Enhancement of bridging ability of coagulant. Flocs formed are relatively large. More resistant to pH variations. Wider pH range.	Although flocs are large, they are non-settleable thus creating high turbidity values with too low dosages. More at development stage (especially ferric-based coagulants).	[25,29,54,61,70,78–81]
Organic polyelectrolytes <i>Cationic (e.g. PDADMAC, CPAMs, and chitosan)</i>	Cationic polyelectrolytes are the most commonly used polyelectrolytes because of their charge density. Charge neutralization is most probably the predominant removal mechanism of NOM molecules.	High charge density polyelectrolytes are effective in removal of hydrophobic NOM. Produce smaller amounts of sludge, which are easier to dewater.	The higher the polymer dose required, the higher the cost. Toxic effects. Formation of smaller flocs because of charge neutralization.	[25,51,77,82,83,86]
<i>Anionic (e.g. APAMs)</i>	High MM carboxylic acid polymers. Remove NOM mainly by bridging mechanism.	Improve LMM matter removal in some cases.	Not as effective as cationic polymers in every case.	[51,82]
<i>Inorganic salt + polyelectrolyte</i>	Coagulation of NOM with inorganic salts using polyelectrolytes as coagulant and/or flocculant aid. Intension to maximize the benefits of both coagulants.	Larger and stronger flocs are formed than with either of them alone. Lower coagulant dose requirements. Smaller volume of sludge. Cost saving.	The higher the polymer dose required, the higher the cost. Toxic effects.	[51,82]
Composite inorganic–organic coagulants <i>HPAC</i>	Composition of organic polymer (PDADMAC) and inorganic polymeric coagulant (PACl) with additives such as active silicates.	Effective in waters with high alkalinity or pH. Wider working pH range.	Flocs formed can be small or incompact thus not favorable to sedimentation, although flotation is much more efficient.	[25,69,90,91]
<i>PFC–PDADMAC</i>	Composition of organic polymer (PDADMAC) and inorganic polymeric coagulant (PFC). High content of Fe_b hydrolysis species.	Stronger charge neutralization, and hence efficient DOC, SUVA and turbidity removal capacity.	More at development stage. Not so widely used.	[77,83,87–89]
Electrocoagulation	High NOM removal efficiencies achieved. Stabilize the charged NOM particles via additional electrical charge, by which the surface charge of the particles are neutralized and several particles are combined into larger and separable agglomerates.	Effective in all temperatures. Remove also the smallest charged particles. Produce small amounts of sludge.	Energy consumption raises as initial NOM concentration increases.	[94–97]

with hydrophilic NOM [22]. Thus, optimization of water treatment should be done in order to remove both hydrophobic and hydrophilic organic compounds, that can mitigate the formation of DBPs. Due to water quality problems and stricter regulations for drinking water treatment, there is a need for more efficient and still economical methods for the removal of NOM. Generally, the most common and economically feasible processes for the removal of NOM are considered to be coagulation and flocculation followed by sedimentation/flotation and sand filtration [19]. Hence, the enhanced and/or optimized coagulation has been suggested to be the main treatment options for better control of NOM and hence DBP formation.

A summary of recently published investigations regarding NOM removal in drinking water treatment with various coagulants and treatment techniques in relation to coagulation has been presented in this article. An overview of different coagulant types and their features are given in Table 1.

2. Principles of coagulation

In general, coagulation is a process where the repulsive potential of electrical double layers of colloids is reduced in such a way that micro-particles can be produced. These micro-particles collide with each other and form larger structures (flocs) in the flocculation process. Historically, coagulation has been employed in water treatment to decrease turbidity and colour and to remove pathogens. However, optimum conditions for turbidity or colour removal are not always the same as those for NOM removal [23–25]. In the baseline coagulation, the coagulation conditions are optimized for turbidity removal, whereas optimized coagulation refers to dose and pH conditions optimized especially for organic matter reduction. Enhanced coagulation refers to conditions where more (excess) coagulant

is used than would be needed for baseline coagulation, with also changes in pH, order of chemical addition or use of alternative coagulant chemicals, thus gaining more efficient TOC and thus NOM removal [23,26].

Chemical coagulation is achieved by addition of inorganic coagulants, such as aluminium and iron salts [16]. When added to water, aqueous Al(III) and Fe(III) salts are dissociated to their respective trivalent ions, i.e. Al^{3+} and Fe^{3+} . After that they are hydrolyzed and form several soluble complexes possessing high positive charges, thus adsorbing onto the surface of the negative colloids [17,27,28]. According to the literature, at pH higher than the minimum solubility of the coagulants (e.g. 5.8 and 6.3 for ferric chloride and aluminium chloride, respectively) the hydrolysis products are HMM polymers or colloidal/precipitated species while at a pH slightly lower than the minimum solubility the hydrolysis products are mainly medium polymers or monomers [25]. The degree of polymerization can be determined by means of ferron-timed spectroscopy method. The different species can be classified into three categories: the mononuclear (Al_a and Fe_a), medium polynuclear (Al_b and Fe_b) and precipitated/colloidal (Al_c and Fe_c) species, in which the Al_b and Fe_b species are considered to be the most efficient species for DOC removal [16,29,30].

The aggregation mechanisms through which NOM is removed include a combination of charge neutralization, entrapment, adsorption and complexation with coagulant metal ions into insoluble particulate aggregates (Fig. 2) [31]. Because of the variable composition of NOM, the removal mechanism will be different for specific types of NOM molecules in water [13,31], however the charge driven mechanisms have been concluded to be the most evident when pH is optimized [13,32,33]. Moreover, the HMM polymer species (e.g. Al_c) have been concluded to efficiently remove particles through bridging or sweep flocculation, while medium polymer or monomer species

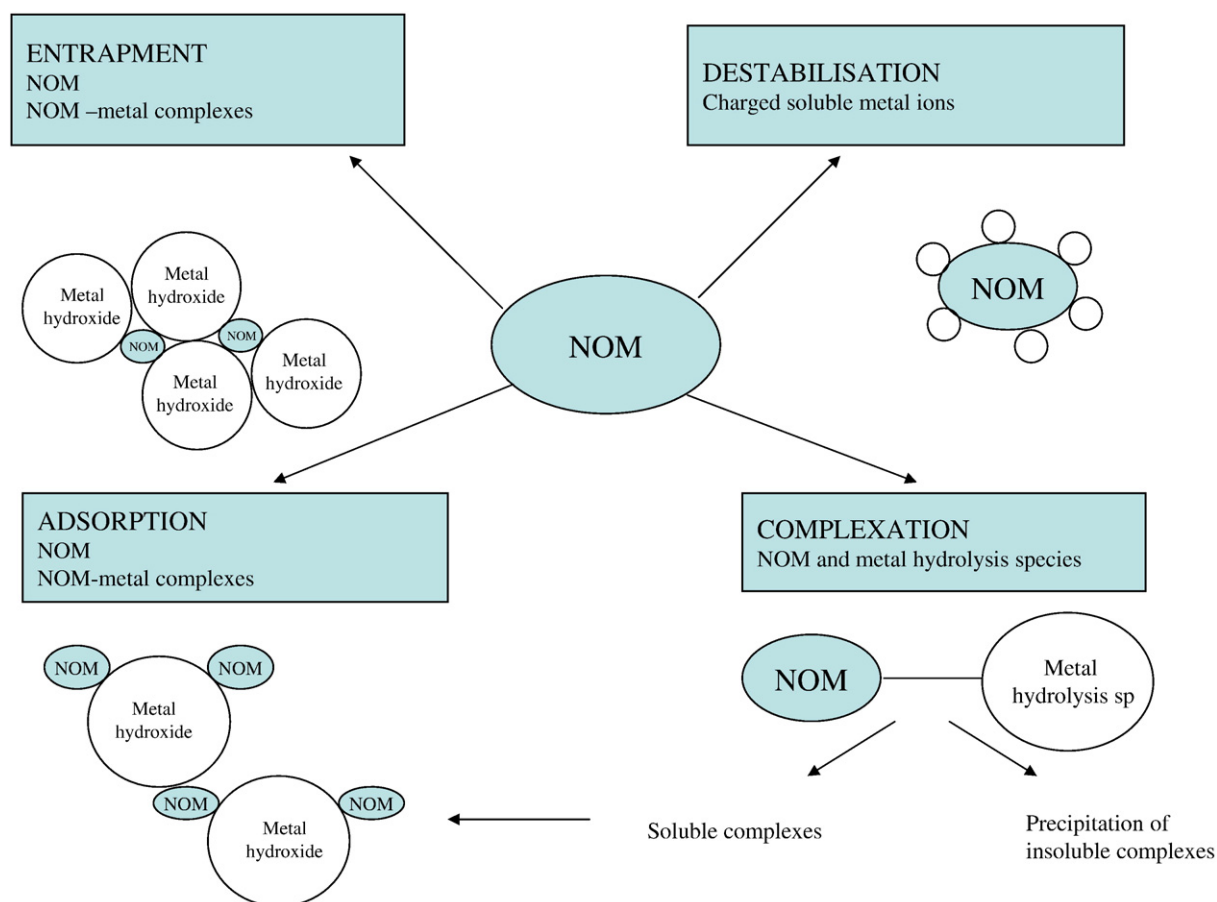


Fig. 2. The possible removal mechanisms of NOM during coagulation (adapted from Jarvis et al. [31]).

have been suggested to have a high ability to remove DOC by complexation, adsorption, charge neutralization or co-precipitation [25]. The flocs formed during various coagulation mechanisms have been detected to have different properties (as size, structure and strength) [34].

The effectiveness of coagulation to remove NOM and particles depends on several factors, including coagulant type and dosage, mixing conditions, pH, temperature, particle and NOM properties (such as size, functionality, charge and hydrophobicity), as well as the presence of divalent cations and concentrations of destabilizing anions (bicarbonate, chloride, and sulfate) [13,16,19,35–37]. Ferric chloride and ferric sulphate as well as alum are acidic, thus lowering the pH after application. Hence, low alkalinity waters may need addition of base, while high alkalinity may sometimes need to be lowered by acid addition to reach efficient pH range [19]. However, high alkalinity waters have higher buffer capacity over low alkalinity waters against pH decrease [23].

The nature of NOM has a significant effect on the coagulant dose. At water with HMM NOM the optimal coagulant dose is expected to be low because the removal mechanism is mostly charge neutralization, however, if NOM consists of LMM or non-humic substances, the removal mechanism is expected to be adsorption onto metal hydroxide surfaces and optimal coagulant dose is thus much larger. The hydrophobic fraction of NOM is generally removed in coagulation more efficiently than the hydrophilic fraction. Furthermore, HMM compounds are more readily removed than LMM compounds [12,13,33,38–40] most likely because HMM matter is quite hydrophobic in nature, consisting more of aromatic compounds [14]. The ability of high SUVA value to reflect the better reactivity of organic compounds in water towards removal by coagulation is discussed by many researchers [17,18,41]. The suggested relationship between SUVA and TOC is illustrated in Table 2 [17]. Compared to DOC, UV₂₅₄ has been noted to reduce more, suggesting that aromatic materials are removed more effectively than other NOM fractions [28,42,43]. Hydrophobic NOM has been noted to carry high levels of negative charge due to the presence of ionized groups such as carboxylic and phenolic groups. Thus, the hydrophobic fraction is noted to dominate the specific colloidal charge character of water, and fractions with higher charge are observed to be more amenable to removal [3,33,41]. NOM removal can be monitored by the removal of negative charge from the suspension. Maximum NOM removal has been achieved in a zeta potential window between −10 and +5 mV [3,33,44,45].

The most widely used coagulant in drinking water production has been aluminium sulphate (alum), but recently the use of ferric salts has become more common [16]. This may be due to a suggestion that aluminium in drinking water may pose a risk towards Alzheimer's disease [46]. Many investigations have been made to compare the effectiveness of one coagulant with another. According to these studies ferric-based coagulants have been generally noted to remove NOM, measured as DOC and UV₂₅₄, more effectively than aluminium-based [3,23,26,28,42] and found to be less sensitive to low temperatures than

alum in regard to turbidity removal [24], although contradictory results have also been gained in some cases [47]. The removal mechanism of ferric and alum coagulants has been proposed to be different [3,48,49]. Ferric-based coagulants have been noted to be more effective especially in removing NOM with intermediate MM (1000–4000 g mol^{−1}). This fraction is suggested to be composed mostly of fulvic acids, and possibly be removed more efficiently by ferric because of higher charge density of ferric coagulants [50,51]. Moreover, the flocs formed during ferric coagulation are noted to be both larger and more numerous than those formed during aluminium coagulation, therefore increasing the likelihood of collisions and subsequent removal [50–52]. However, the choice of proper coagulant depends largely from the characteristics of the water to be treated.

New inorganic polymer flocculants (IPFs) have been developed during the past few years based on inorganic salts. Prehydrolyzed coagulants are formed by a forced hydrolysis of a simple coagulant, such as alum. Concerning their coagulation–flocculation properties, IPFs are considered to lie in a position between the traditional inorganic salts and organic flocculants [53]. Along with aluminium and ferric-based polymeric flocculants, also a combination of the two, i.e. poly-aluminium-ferric-silicate-chloride (PAF-SiC) coagulant has been studied [54]. It was observed that flocs formed during coagulation were relatively large but non-settleable, causing high turbidity, when dosage was insufficient. However at high coagulant dosages the removal of turbidity was effective.

3. Aluminium based coagulants

The most commonly used aluminium-based coagulant has been alum (Al₂(SO₄)₃), with other coagulants including aluminium chloride (AlCl₃). However, the use of alum can leave, especially during periods of cold temperatures or at low pH levels, relatively high aluminium residuals in the finished water, which can cause possible health hazard or other problems in distribution system, e.g. spontaneous flocculation [39,46,55,56]. This can be avoided by pH control, but turbidity and NOM removal are thus also affected [55,56].

Increasing the alum dose has been noticed to increase NOM removal to a certain point. At very high doses (>100 mg L^{−1}), NOM removal is not significantly improved, suggesting the presence of components of NOM recalcitrant to removal by coagulation. Larger MM components have been found to be removed efficiently, whereas LMM compounds are observed to be resistant to removal [11,38,39]. Hydrophilic neutral NOM fraction has been detected to be hard to remove with the addition of alum at any concentration. Furthermore, this fraction has been observed to have the highest BDOC contribution to the treated water, having thus the potential to support biofilm formation in the distribution system, and also contribute to THM formation [38]. The recalcitrant fraction of NOM is indicated to be polysaccharides and their derivatives [39]. Coagulation pH has a significant effect on coagulation efficiency, and optimal pH for the alum coagulation has been observed to be in the range of 5.0–6.5 (with alum doses between 5 and 100 mg Al L^{−1}), resulting on average 25–67, 44–77, 25–66 and 97 % of DOC, UV₂₅₄, THMFP and turbidity removal, respectively [4,24,28,37–39,42,57].

In recent years, prehydrolyzed aluminium coagulants, e.g. poly-aluminium chloride (PACl) and polyaluminium sulphate (PAS), have been developed and researched [30,58–63]. PACl has been made by partially neutralizing AlCl₃ to different basicity ratios, and its use has been continuously spreading. Prehydrolyzing the AlCl₃ can enhance the amount of Al₁₃ (AlO₄Al₁₂(OH)₂₄)⁷⁺ in the coagulation process, which, in turn, has been noted to be the most efficient Al-species for contaminant removal [58,64,65]. These coagulant species (Al₁₃ or Al_b) are considered to be the most efficient Al-species due to their larger size and higher positive charges. In several studies the flocs formed under various aluminium coagulant species are observed to have different properties [58,61,62,64,66], and also the destabilization

Table 2
Relationship between SUVA and DOC removal during coagulation (adapted from Edzwald and Tobiasson [17]).

SUVA	Composition	Coagulation	DOC removals
>4	Mostly aquatic humics, high hydrophobicity, high MM compounds.	NOM controls, good DOC removals.	>50% for alum, little greater for ferric.
2–4	Mixture of aquatic humics and other NOMs, mixture of hydrophobic and hydrophilic NOM, mixture of MMs.	NOM influences, DOC removals should be fair to good.	25–50% for alum, little greater for ferric.
<2	Mostly non-humics, low hydrophobicity, low MM compounds.	NOM has little influence, poor DOC removals.	<25% for alum, little greater for ferric.

mechanisms of different aluminium species have been investigated [32,65,67,68]. The prehydrolyzed polymer coagulants have been reported to have advantages over conventional coagulants, including less temperature or pH dependence, as well as smaller alkalinity consumption [59,62,64,66,69], but the characteristics of the water to be treated (e.g. alkalinity, pH, and NOM content) play a major role in the choice of a proper coagulant [58,63]. Consequently, prehydrolyzed coagulants have not been noticed to enhance the removal efficiency of NOM in all cases [58,66].

Activated silica has been detected to be efficient coagulant aid, and has noticed to enhance the bridging ability of PACl [25]. Hence, another new type of coagulant has been studied, namely polymeric aluminium coagulant with supplemented activated SiO_2 . It has a larger molecular weight and smaller surface charge than PACl [25,54,70]. Poly-aluminium-silicate-chloride (PASiC) has been investigated in order to enhance the efficiency of NOM and turbidity removal, and has been proved to be more efficient than PACl in the treatment of low-turbidity waters [54]. Improvement of coagulation properties has been noticed to depend on basicity and silica content of a polymer as well as the preparation technique. PASiC has been observed to be more resistant to pH variations (effective pH range is 6.5–9) than PACl and flocs formed under optimum conditions have been noticed to be bigger, thus contributing to greater removal efficiency [70].

4. Ferric-based coagulants

Ferric salts commonly used in coagulation processes include ferric chloride (FeCl_3) and ferric sulphate ($\text{Fe}_2(\text{SO}_4)_3$) [23]. The optimum pH level in ferric-based coagulation has been observed to be between 4.5 and 6, with indicated removal of NOM about 29–70% as DOC [23,24,26,33,42,71–73]. DOC removal, as well as THMFP mitigation, has been noticed to increase with increasing coagulant dose (up to 100 mg L^{-1}) [43]. At low coagulant doses, the anionic humic network has been concluded to reorganize upon association with cationic coagulant species to yield more compact structures, while upon increasing the coagulant dose, the aggregation of humic acid with hydrolyzed-Fe species has been ascribed to as competition between humic network reformation rate and collision rate of destabilized colloids [74].

Recently, increasing attention has been subjected on polymeric iron coagulants, including polyferric sulphate (PFS), polymeric iron chloride (PICl) or polyferric chloride (PFC) [49,75,76]. These coagulants may have some advantages over monomeric forms of ferric salts, such as wider working pH range, lower sensitivity to water temperature, reduced amounts of coagulant and lower residual iron concentrations [73,76], although they are still more in a development stage and the applications are limited. Prehydrolyzed coagulants are prepared by partial neutralization of metal salts, e.g. PFS from ferric sulphate. The prime advantage of these coagulants is that only the most favorable hydrolysis and polymeric species for coagulation can be produced. The performance of the prehydrolyzed coagulants depends on the nature of the polymeric species formed in the process of preparation [49,53]. The possible dominant removal mechanisms during PFC coagulation have been suggested to be adsorption, entrapment and complexation rather than charge neutralization [77].

Polymeric coagulants' efficiency can be improved by adding other components to the polymer, such as polysilic acid, to produce new composite coagulants such as polysilicate-ferric (PSF) and polyferric silicate sulphate (PFSiS) [29,61,78–81]. These coagulants have been suggested to work in the wide pH range, and exhibit a markedly better coagulation performance than e.g. ferric sulphate.

5. Organic polyelectrolytes as coagulants or coagulant aids

A polymer is termed as a polyelectrolyte, when its monomeric unit contains ionizable groups (e.g. carboxyl, amino or sulfonic). Polyelec-

trolytes are characterized, hence, by their charge, and also by charge density and MW. Consequently, polyelectrolytes can be cationic, anionic or ampholytic, while polymers without ionizable groups are termed non-ionic. Cationic polyelectrolytes include polydiallyldimethyl ammonium chloride (PDADMAC), cationic polyacrylamides (CPAMs) and natural cationic polymers (e.g. chitosan, starch), whereas anionic polyelectrolytes include anionic PAMs or natural biopolymers. Non-ionic polyelectrolytes include e.g. polyacrylamide (PAA) [82].

Synthetic or natural polymers have been used as both primary coagulants and coagulant or flocculant aids. Cationic polyelectrolytes have most commonly been used for NOM removal because NOM in the water is likely to be negatively charged, thus emphasizing NOM removal by charge neutralization rather than bridging. Cationic polymer, PDADMAC, has been used as primary coagulant for NOM removal, since it is highly charged and has HMM, although the high cost has been the limiting factor in the use of PDADMAC [82,83]. When polymer is used in combination with a conventional coagulant the aim is to lower the process costs by lowering the coagulant demand, and resulting larger aggregates from already formed microflocs [82,84]. Polyelectrolytes have achieved better floc characteristics in terms of size, strength, settleability and filterability thus producing smaller volume of sludge, and they have been noticed to be more resistant to pH changes than conventional coagulants [17,31,34,82,85]. Moreover, cationic polymers have been detected to be efficient coagulation aids in improving PACl coagulation performance by enhancing the neutralization ability of PACl [25] and improving PFS ability to remove DOC and turbidity [77]. However, results with no improvement in floc characteristics or NOM removal efficiency have also been reported [84,86]. The NOM removal capacity of different polyelectrolytes has varied case by case [24,25], and hence polyelectrolytes are not always considered to be suitable coagulants for e.g. turbidity removal [24]. Moreover, especially cationic organic polyelectrolytes are considered to be quite toxic to aquatic organisms and several countries have thus restricted their use in water purification [82,86].

6. Composite inorganic–organic coagulants

New innovation has been introduced to coagulation process, namely combining organic polymers to IPFs, thus creating a composite inorganic–organic coagulant. The aim is to combine the advantages of both components. Several researchers have studied the composition of PFC–PDADMAC [77,83,87–89], as well as PFS–PAA [50]. PFC–PDADMAC has efficiently removed NOM and created high content of Fe_b species, which are the most active coagulating components in ferric salt coagulants [83,87,88]. The composite coagulant has been suggested to be more suitable for surface water treatment than conventional metal coagulants or organic polymers, and moreover it has been observed to perform more efficient DOC, SUVA and turbidity removal through stronger charge neutralization [77]. PFS–PAA has exhibited a superior coagulation performance, thus producing flocs which are larger and wider on size distribution range, when compared to PSF + PAA mixture or either of them alone [53].

In addition, a highly efficient composite polyaluminium chloride (HPAC) has been developed, which is prepared from PACl and other organic and inorganic additives such as active silicates and PDADMAC. It has exhibited about 30% more efficiency on NOM removal than conventional coagulants or PACl [25,69,90,91]. HPAC has been more efficient than conventional coagulants in basic conditions, thus being effective in waters with high pH or alkalinity [25,69].

7. Electrocoagulation

Electrocoagulation (EC) technique has been studied widely in wastewater treatment [92,93], but has been recently applied also in water treatment for NOM reduction [94–97], as well as disinfection

[98]. EC is an electrochemical treatment process which uses soluble anodes made of coagulating metals such as iron and aluminium with electrolytic dissolution to Al^{3+} and Fe^{2+} ions, which are further hydrolyzed to polymeric hydroxides. Coagulation occurs when these metal cations combine with the negative particles carried toward the anode by electrophoretic motion, with various destabilization mechanisms [92] and simultaneously occurring beneficial side-reactions, such as pH change and hydrogen bubble formation [97]. Advantages over the conventional coagulation include e.g. reduction of different chemicals needed and sludge formed, alkalinity consumption mitigation, and ease of adaptation to existing treatment unit [94]. The EC has removed hydrophobic, but also hydrophilic colloids [97], which are not easily removed in conventional coagulation process. Thus, EC has been observed to be an effective method to remove NOM but the conditions of the process (e.g. pH, electric charge and supporting electrolyte) have to be determined carefully. Moreover, the EC mechanism is highly dependent on the chemistry of the aqueous medium, especially the conductivity [95–97]. Hence, the method might have some beneficial effects over conventional methods, but it has to be evaluated if it enough for feasible application [94].

8. Coagulation in combination with other treatment processes

8.1. MIEX

Magnetic ion exchange resin (MIEX®) technique is based on traditional ion exchange process, however in comparison it uses micro-sized resin particles dispersed as a slurry on a stirred contactor, thus allowing maximum surface area for adsorption. It removes both organic and inorganic contaminants like sulphate, nitrate or phosphate. The negatively charged NOM compounds are removed efficiently by this strong-base anion resin. The high density and magnetic properties of the resin provide rapid clarification following the contact stage [99]. MIEX® resin can be easily regenerated and even after several regenerations it gives almost the same organic matter removal efficiency. Moreover, it is suitable for both small and large plants and complements other water treatment technologies like coagulation or membrane filtration. MIEX® resin has been used as pretreatment method prior to coagulation to enhance the efficiency of coagulation and reduce the coagulant dose (up to 60%), with reduced sludge formation and turbidity load [100–103]. In the MIEX® process, the NOM compounds with increasing charge density are removed the most and the presence of functional groups has been noted to be more important than aromatic structures [104]. Moreover, MIEX® resin also removes hydrophilic, LMM NOM, thus being able to remove a fraction of NOM recalcitrant to coagulation [104,105]. The flocs formed after pretreatment with MIEX® have been larger and more resistant to shearing effects than those formed by conventional process [102,103]. Hence, MIEX® in combination with coagulation has increased the DOC and DBP precursor reduction [102–104], although this has not been evident in all cases [33]. According to the literature, an addition of 8–63% and about 10–30% of DOC removal has been observed in jar [105] and pilot tests [100], respectively.

8.2. Oxidation

Pre-oxidation has been traditionally used to improve coagulation process. Pre-chlorination was a widely used technique, until the discovery of DBP formation during chlorination. Some other oxidants have since been taken in use and, e.g. chloramine pre-oxidation has been noticed to enhance the coagulation of surface water [106]. Ozonation has become a preferential pre-oxidation method prior to coagulation, and is used for elimination of taste, odour, colour and inactivation of micro-organisms [91,107,108]. The influence of pre-ozonation in coagulation has been closely related to the NOM

characteristics and basic properties of water to be treated [109,110]. Moreover, the ozone dosage in pre-ozonation has been observed to be highly important. At lower ozone dosage, ozone has produced some hydrophobic neutral and intermedial MM NOM compounds, which are removed efficiently in the following coagulation process, but at higher ozone doses the NOM has been oxidized further into more hydrophilic and LMM compounds, thus being more difficult to coagulate [41,91,109–111]. Accordingly, the ozonation process placement should be carefully determined, since post ozonation rather than pre-ozonation (in combination with BAC) might get better results in some cases [110]. The beneficial effect of ozonation towards better coagulation of non-humic fraction has also been observed. Hence, to maximize DOC and SUVA removals, two-staged coagulation with intermediate ozonation, has been proposed for waters containing both humic and non-humic NOM [41]. The composite HPAC coagulant efficiency has not reduced even after high ozone doses [91], and PACI has been found to be suitable in coagulation with pre-ozonation [109].

Advanced oxidation processes (AOPs) are powerful techniques in disinfection and organic compounds (e.g. contaminants) degradation [112–121]. Photo-Fenton process where iron species can play a role as enhanced catalyst as well as coagulant has been investigated for NOM removal with rather good results [122,123]. NOM removal has been noted to be better than with conventional coagulation with iron salts and especially LMM compounds of NOM have been removed more efficiently [122]. Photocatalytic oxidation prior to coagulation is noted to decrease coagulation efficiency by 15%, most likely because the oxidation changes the characteristics of NOM and degrades NOM molecules towards LMM compounds [47]. However, when oxidation was performed after coagulation, about 5–32 and 8–33% enhancement on the removal of DOC and UV_{254} , respectively, occur [28]. Photocatalytic coagulation with nanoparticles of copper-doped titania has been noted to provide both better NOM removal and reduction of membrane fouling [124].

8.3. Activated carbon filtration

Activated carbon (AC) is an effective adsorbent used widely in drinking water treatment. Micropollutants such as pesticides, industrial chemicals, tastes, odours and algal toxins are removed efficiently in the filtration process. Also NOM has been noted to be removed in the filtration, although NOM often competes for adsorption sites decreasing the removal of other pollutants. However, if enhanced coagulation is insufficient in the reduction of NOM, the additional treatment with granular or powdered AC (GAC/PAC) has been efficient in order to maintain required water quality in terms of e.g. DBP formation [40,43,125]. AC can also be colonized by a heterotrophic biomass, creating biological AC (BAC), thus reducing the proportion of easily assimilated and biodegradable elements. In addition, efficient removal of LMM and uncharged fractions of NOM are gained [43]. However, in most of the cases a part of LMM NOM is not removed even after AC filtration [40]. The water can be filtered also only when it is necessary, e.g. during elevated NOM or alkalinity periods [4]. PAC enhanced coagulation has also been noted to reduce the required coagulant dose, while increasing the process efficiency [40].

8.4. Membrane filtration

Membranes have become more common in water treatment processes. Pressure driven membrane processes include reverse osmosis (RO), nanofiltration (NF), ultrafiltration (UF) and microfiltration (MF), which all have different NOM and particle removal potentials [19,126]. The fouling of membranes and decline of flux are the major problems associated to membrane techniques [126]. Several studies have indicated that NOM, and especially the hydrophobic fraction of NOM and HMM compounds, have great impact on the fouling and

decline of flux [126–130]. Thus the pretreatment with coagulation is an effective method to prevent these adverse effects [127–131], and combination of coagulation and membrane filtration is also reducing the amount of coagulant needed while improving turbidity and DOC reductions [132]. Moreover, coagulation has been observed to provide an effective hygienic barrier in combination with membranes [133]. However, also contradictory results have been obtained [85], and the removal of NOM has been significantly affected by the type of coagulant, coagulation conditions, the type of membrane, filtration conditions, and the characteristics of the water to be treated [33,72,73,85,129,134–139].

The way of combining coagulation with ultrafiltration [85,132,139,140] or microfiltration [72,135,141] has been the “in-line” hybrid process. The coagulant dose and the duration of water treatment are reduced by batching the coagulant to the feed immediately before the membrane [140]. Moreover, a novel submerged UF membrane coagulation bioreactor (MCBR) process has been studied for treating slightly contaminated surface water to drinking water [142]. New way of reducing membrane fouling has been suggested for the immobilization of TiO_2 photocatalyst on the membrane surface thus creating a composite membrane [143]. The use of nanoparticles, like nano-alumina, silica, silver, iron oxide, etc., in membrane structures has gained a lot of interest, but their use in water treatment has to be further studied, because of for example, possible releases of nanoparticles into the water [144].

9. Summary

In this study the recent research on the field of coagulation in NOM removal during drinking water treatment has been reviewed. The character and concentration of NOM in raw water sources have been demonstrated to change regionally as well as seasonally [1,2]. In addition, a trend on the overall increase in NOM content has been observed in various regions worldwide [7]. Coagulation and especially enhanced or optimized coagulation are considered to be the major treatment options to deal with increased NOM levels. Enhanced coagulation is also considered the main treatment option for high alkalinity waters [25].

Enhanced coagulation removed more NOM than baseline coagulation in the majority of the studies presented in the literature. However, part of the LMM compounds of NOM as well as non-humic material remains in the treated water. Applying increased dosages of coagulants and controlling the raw water pH by addition of acid or base are two common options to enhance the removal of NOM by coagulation. However, an increased amount of coagulant and increased pH results in an increase in the proportion of rapidly precipitated material in the sludge or flocs, which forms looser aggregates and hence exhibits inferior dewatering properties [145,146]. Sludge can be dewatered by thickening, centrifugation or filtration. Also Fenton's reagent has been suggested for improvement of sludge dewaterability and is considered to be a good option for conditioning an alum-based sludge [147]. Moreover, the possible ways of handling the formed sludge include for example atomization and use as in addition for the cement industry [148]. Enhanced coagulation also increases the iron corrosivity of finished water due to the consumption of alkalinity and introduction of sulphate, thus gaining possible formation of discolored water [149]. It has been suggested that instead of increasing coagulant doses, the removal of NOM can be enhanced by recycling backwash streams that contain destabilized particles, especially for low-turbidity waters [150]. Moreover, since enhanced coagulation is aiming mainly for further NOM removals, it has to be remembered that also the aesthetic quality of water has to be maintained, with efficient microbial and virus deterioration [71].

Conventionally, coagulation has been performed with inorganic salts, including alum, ferric chloride and ferric sulphate. However recently prehydrolyzed ferric and alum coagulants called IPFs have

been developed (e.g. PFC and PACI). They have been noticed to have some advantages over conventional coagulants such as wider working pH range, lower sensitivity to water temperature and lower residual coagulant concentrations [64,76]. Synthetic and natural organic polyelectrolytes have long been used in combination with metal coagulants, in order to achieve better coagulation efficiency and floc characteristics [82]. A new application combines IPFs and organic polymers (e.g. PFC-PDADMAC and PFS-PAA) [53,89]. These coagulants have been observed to efficiently remove NOM. Moreover, Mg/Al hydrotalcite has been used for coagulation [151] as well as a novel coagulant Zr^{4+} , which has resulted in significantly larger flocs compared to Fe^{3+} coagulation thus having also higher DOC and recalcitrant NOM removal efficiency, however its use is under study [152]. A very promising new way to remove organics from water is nanotechnology, which has introduced new types of materials, such as dendrimers, hyperbranched polymers, carbon nanotubes and cyclodextrins [153]. These nanomaterials have exceptional adsorption properties and they are able to entrap diversity of organic molecules into them. Especially DBPs and other organic pollutants have been noted to be removed efficiently, however, also NOM removal has been observed to happen [154]. Besides these methods, emerging interest is towards electrocoagulation, which is proved to be efficient also in drinking water applications, and is considered to be one possible option for enhanced NOM removal [93].

Different treatment combinations have been studied along with coagulation process. Pre-oxidation has been used to enhance coagulation efficiency, with rather contradictory results [110]. Also pretreatment with MIEX® process has been studied widely with promising results regarding enhanced NOM removal [102]. After coagulation the adsorption process with AC filtration has been rather an efficient method to increase NOM reduction, and especially the better removal of LMM and recalcitrant NOM to coagulation has been observed [43]. Membrane filtrations have also become more common, and hybrid coagulation/membrane systems have been investigated by several researchers. Post filtration (NF) has reduced recalcitrant NOM as well as the corrosion aggressive constituents significantly [33,149]. Accordingly, for the high DOC waters the combination of MIEX®, coagulation and membrane filtration (UF) is found as highly efficient in regard to NOM reduction [101].

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