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A Comprehensive Review on the Progress of Coagulation for Natural Organic Matter Removal in Water Treatment

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Abstract

Natural organic matter (NOM) seriously challenges the drinking water supply. It typically exists as complex organic substances generated in the natural water ecosystem as part of hydrologic, biological, and geological cycles. The significant variation, composition, and abundance of NOM in natural water or wastewater necessitate the implementation of robust and adaptive technologies, particularly in addressing even more stringent standards of drinking water supply or treated water discharge. Coagulation is one of the most common processes for water and wastewater treatments. It is highly desirable to treat feed containing NOM because it prevents the disinfection of by-products formation. Therefore, current dynamics of NOM in terms of varying compositions and concentrations demand improvement in handling the coagulation process through optimization of operational parameters (dosing and the control of pH), application of novel and more effective coagulants, and as a combination with other processes through process intensification. This review provides a comprehensive analysis of recent literature on developments of coagulation for NOM removal. The coagulants are grouped systematically and assessed. Next, enhanced coagulation via process intensification with other processes (membrane filtration, oxidation, adsorption, and ion exchange) is discussed. Lastly, the future outlook on research direction on sustainable coagulation process is listed to support circular and bioeconomy.

Keywords: Coagulation; Drinking water treatment; Natural organic matter; Process intensification; Sustainable process

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INTRODUCTION

The complex organic material matrix in aquatic bodies is known as natural organic matter (NOM). Many hydrological, ecological, and geological processes combine to make it. It is generated naturally in the water bodies as part of microbial, algal, and other biological activities (classified as autochthonous NOM). It can also be delivered through water drainage within watersheds, including chemicals released from terrestrial organisms' breakdown (classified as allochthonous NOM) (Sillanpää et al., 2018).

This distinction between autochthonous and allochthonous NOM is crucial. The specific characteristics of each type demand a unique strategy for effective NOM removal in drinking water or wastewater treatments. The autochthonous NOM is typically (dark-brown colored) and is mainly composed of humic chemicals. Their composition is dictated by variations of geological and hydrological conditions where they exist (Hudson et al., 2007). On the other hand, the biological activities of the "insider" autochthonous NOM (light-colored) are dictated by the metabolism processes of the biological species implicated. These processes produce soluble extracellular and intracellular macromolecules like carbohydrates, amino acids, peptides, enzymes, and toxins, to name a few (Amy, 2008; Her et al., 2004).

Other physical and chemical aspects (such as pH, water chemistry, temperature, and anthropologic pollution), and biological activities occurring in the water source tend to affect the dynamics of NOM and its biochemical makeup. As a result, the volume and composition of NOM may differ significantly from one site to the next and within the same water body due to seasonal variations impacting natural events such as floods, droughts, and rainfalls (Hirabayashi et al., 2008). Those phenomena, as mentioned earlier, increase the abundance of NOM and its spatial and temporal variations in water bodies worldwide (Matilainen & Sillanpää, 2010).

Pure NOM is generally not hazardous in and of itself, but its presence in bodies of water is exceedingly dangerous. The presence of NOM in a water body reduces its potential as potable water by altering the color, taste, and odor, also known as the organoleptic attributes. Nevertheless, the abundance of NOM in the water body must be cautioned because of its potential as hazardous inorganic and organic carrier contaminants, like insecticides and radionuclides (Knauer et al., 2017; Santschi et al., 2017). It also increased the solubility of anthropogenic hydrophobic compounds in natural water bodies (Reid et al., 2001). Furthermore, several NOM components, particularly humic acids (HA) and fulvic acids (FA) shown in Figure 1, can act as bio-carrier of heavy metals. They form stable complexes with heavy metals via coordination chemistry, developing organometallic complexes with enhanced transport, toxicity, and bioavailability (Tang et al., 2014).

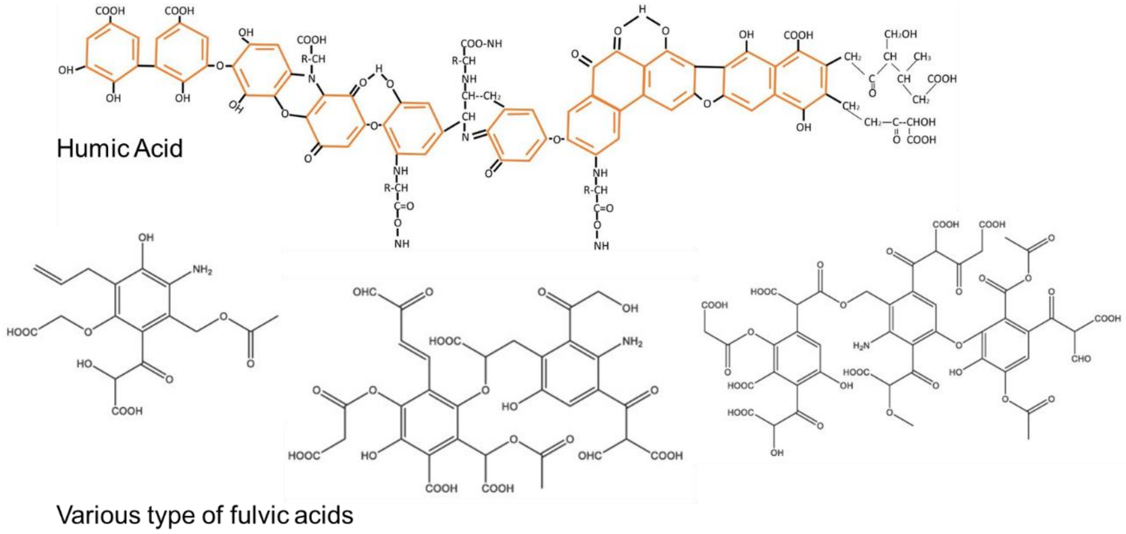

Figure 1 Chemical structure of humic and fulvic acids, main components of natural organic matter (Gong et al., 2020; Mirza et al., 2011).

NOM can play roles in forming disinfection by-products (DBPs) in the treated water involving the chlorination process for biological disinfection (Golea et al., 2017; Goslan et al., 2017). Some DBPs may be carcinogenic compounds, such as haloacetonitriles, haloacetic acids, or aliphatic halogenated trihalomethanes (Y. Jiang et al., 2016; J. Li et al., 2016). Research has revealed that aromatic halo-DBPs have much higher developmental growth inhibitory effects and toxicity than aliphatic (Liu & Zhang, 2014; Yang & Zhang, 2013). As a result, NOM removal from drinking water sources is becoming mandatory and a problematic undertaking requiring dependable, highly effective, and robust technologies capable of dealing with NOM's high spatiotemporal variability and rising concentration in aquatic life habitats.

The efficiency of different water treatment procedures is still compromised by these two major concerns and the complex nature of the NOM substances (Mao et al., 2017). Together with transparent exopolymeric particles, NOM is widely recognized as a significant fouling factor in membrane filtration, leading to pore constriction and creating a loose cake layer atop the membrane surface (X. Cheng et al., 2019; Discart et al., 2012, 2015). Increasing NOM concentrations necessitates using additional chemicals or materials (e.g., for physical adsorption or chemical oxidation) in chemical and material-based processes ending up with an increasing volume of sludge or waste (Y. Xu et al., 2016). NOM can complicate the process by occupying the active sites in the adsorption process instead of the targeted pollutants, decreasing the adsorption efficacy when simultaneously targeting a wide range of pollutants (Qi & Schideman, 2008; Zietzschmann et al., 2014).

In the last two decades, extensive research on water and wastewater treatment via coagulation has been done. The publication records in the Scopus database from 2001 to 2022, shown in Figure 2 demonstrate that this topic is still gaining some traction, particularly in the last ten years. The number of published articles grows exponentially from 64 in 2001 to 1021 in 2021 and is expected to increase further. Those publications included a total of 7,862 articles; 961 reviews, and the rest were conference papers, book chapters, and books. Such tremendous research has been driven by the recent increase in the presence of NOM in water resources, creating an operational issue for the existing water treatment plants that were designed under modest NOM content.

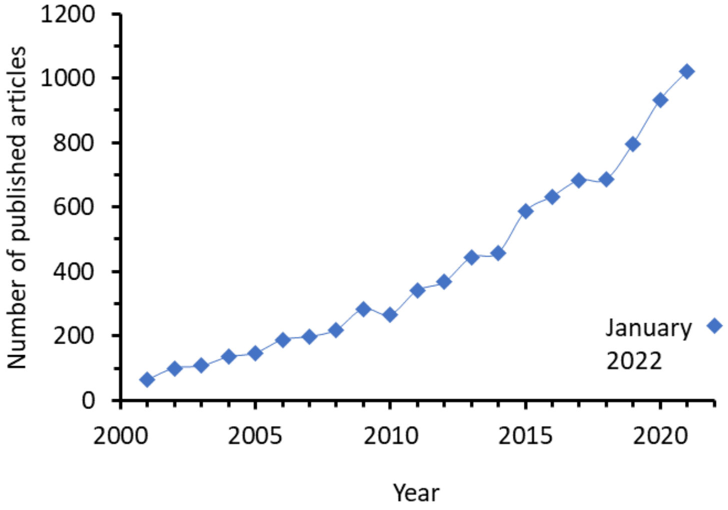

Figure 2. The number of published articles on coagulation for natural organic matter removal process obtained from the Scopus database accessed on January 29th, 2022 using the keywords: natural organic matter, coagulation, humic, water listed on all fields.

This paper reviews the literature on coagulation to remove NOM from drinking water. The mechanism of coagulation using different types of coagulants is first overviewed. The literature report on the development, application and optimization of each group of coagulants is detailed because of a broader understanding of their roles in NOM removal. Next, enhanced coagulations are discussed via integration with other processes, namely membrane filtration, ion exchange, oxidation, and adsorption. Finally, a future outlook on sustainable coagulation concerning process sustainability via circular and bio-based economy is proposed.

MECHANISM OF NOM COAGULATION

Coagulation is a physical-chemical process that uses different chemical agents (known as coagulants) to stabilize colloids by neutralizing charged particles. Introducing the coagulant promotes the clumping of colloidal microparticles forming bigger particles called flocs (see Figure 3A). The agglomeration involves charge neutralization, trapping, adsorption, and complexation of the targeted particles with the coagulating agent (Henderson et al., 2006). Because of the considerable variety of NOM's size and charge characteristics, the mechanism changes significantly according to the feed, also affected by seasonal fluctuations. As a result, coagulation removal effectiveness will vary, and flocs of various sizes and shapes will emerge (Jarvis et al., 2006; Sharp et al., 2006), posing a severe issue in water treatment.

Coagulation has long been used to remove turbidity and color, including suspension of a stable particle in drinking water treatment. Optimizing the operational condition has to consider all those purposes since the optimum condition for turbidity removal can differ from the condition for color and NOM. Coagulation is accomplished by adding a predetermined coagulant (mostly inorganic, like aluminum or iron) to the feed water. The metal is then dissociated into the multi-valent cationic forms (i.e., polyelectrolytes, $Fe^{3+,}$ and Al^{3+}), hydrolyzed, and form positively charged complexes that interact well with the negatively charged colloids (Figure3B), including NOM (Duan & Gregory, 2003).

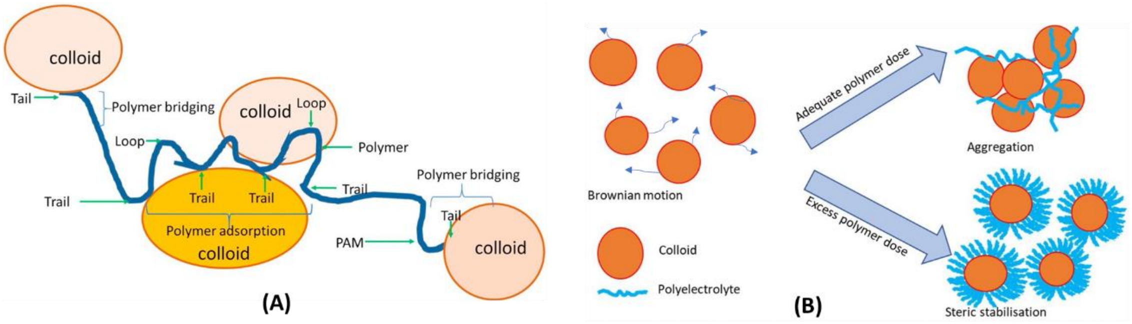

Figure 3. Illustration of the flocculation mechanism and floc size development in the coagulation process, adapted from (Jarvis et al., 2012).

The key factors influencing coagulation efficiency are the solution pH, the chemical, and the coagulant dose. pH higher than the coagulant's minimum solubility (5.8 for ferric chloride and 6.3 for aluminum chloride) results in high molar mass (HMM) polymers or colloidal/precipitated. Conversely, lower pH leads to medium and smaller polymers (Yan et al., 2008). Optimizing the coagulant dosing is essential: overdosing results in excess sludge and low pH, while underdosing leaves residue of coagulants in the product water (Ibrahim & Aziz, 2014) since the coagulant did not form a large enough complex to allow separation.

In addition, the properties of the pollutants, either chemical or molecular, are also crucial. Enhancing the removal efficiencies of NOM necessitates in-depth comprehension of its properties and spatiotemporal dynamics of the component and the amount in the feed (Chiang et al., 2002). They help to assess the reactivity of NOM components or their surrogates and predict, plan, and implement effective and sustainable coagulation. It has been widely reported that coagulation is more effective for larger, hydrophobic humic-like NOM fractions (1-4 kDa) (Yee et al., 2009).

NOM REMOVAL BY COAGULATION

Conventionally, coagulation is generally adequate for removing high molecular weight organics (Nissinen et al., 2001). Variable NOM composition thus poses challenges to coagulation. The higher charge density of the hydrophobic NOM is more preferably coagulated than the hydrophilic fraction (Jarvis et al., 2006; Volk et al., 2000), which necessitates the coagulation optimization for more comprehensive removals of both hydrophobic and hydrophilic fractions. Therefore, feeding water with high NOM required an advanced process (Vepsäläinen et al., 2009), involving coagulation.

Metallic-based coagulants

Metal salt coagulants are the most widely used in industry. They are ferric salts (ferric chloride, ferric and ferrous sulfates) and aluminum salts (sulfate, sodium aluminate, and chloride)(Bahadori et al., 2013). They are mainly chosen due to their low cost and effectiveness for turbidity and color removals (Bratby, 2006). When dissolving inorganic salts into liquid water, metal hydrolysis species are formed from vigorous hydrolysis of the metallic ions (J.-Q. Jiang & Graham, 1998).

Ferric-based coagulants have recently gained more ground over aluminum-based due to better NOM removal capacity and in response to the potential risk associated with the residual aluminum (Flaten, 2001). Ferric salts perform better in NOM removal (Budd et al., 2004; Umar et al., 2016; Uyak & Toroz, 2007).

Ferric and aluminum-based coagulants work under different mechanisms. In some cases, when water contains large NOM (MW> 3kDa), coagulation using ferric chloride ($FeCl_3$) is more effective in removing NOM than aluminum sulfate ($Al_2(SO_4)_3$) (Matilainen et al., 2005). They were also more effective for intermediate NOM MWs of 1-4kDa. Such advantages are attributed to the higher charge density of ferric than the aluminum-based coagulants (Song et al., 2002). Ferric salts result in larger floc during the coagulation (Fitzpatrick et al., 2004). The median size of floc formed by Fe- and Al-based coagulants were 710 and 450 µm, respectively (Jarvis et al., 2012).

Aluminum-based

Aluminum sulfate (Alum [$Al_2(SO_4)_3$] and aluminum chloride [AlCl3]) are the most commonly usedaluminum-based coagulants(Crittenden et al., 2012). Solution pH is critical during coagulation using an aluminum-based coagulant. When introduced to water, monomeric aluminum species are formed through hydrolysis with aluminum hydroxide [$Al(OH)_3$] as precipitates. The dosing rate and the solution pH affect the distributions of monomeric aluminum and aluminum hydroxide. For instance, for dosing 90 mg alum/L, $Al(OH)_3$ precipitates were the predominant species at pH 4.6 (Gregory & Duan, 2001).

The typical pH range for alum hydrolysis is 5.5-7.7. Optimum pH maximizes solid floc particle formation and minimizes solubilization. Below optimum pH, more [Al species]- are formed, while $[Alspecies]^+$ are generated(Pernitsky & Edzwald, 2006). For pH far from the optimum value (>11 or <3), small particles do not aggregate and remain in the water due to their low destabilization potential (J. Wang et al., 2016). The destabilization occurs through charge neutralization. It happened by the adsorption of the OH on the surface of the negatively charged particles.

Since NOM composes mainly negatively charged functional groups, their removal is thus more efficient in an abundance of $[Al\ species]^+$. As reported earlier, humic acid is highly negatively-charged at pH >4.7; as such, the positively-charged hydroxide precipitates could destabilize it (Gregory & Duan, 2001) to lower its solubility and induce precipitation (Pourrezaei et al., 2011). Phenolic and carboxylic groups could be neutralized by forming $Al(OH)^{2+}$ as a minor component in alum hydrolysis (Duan & Gregory, 2003).

Under low pH, NOM removal could sometimes occur using metallic-based coagulants, suggesting that the characteristics of the NOM constituents (an MW, charge, isoelectric point, etc.) are also significant in affecting NOM removal. Table 1 summarizes the NOM removals using aluminum-based coagulants.

Iron-based

Iron-based coagulants are mainly ferric salts of solid or liquid $FeCl_3$ and $Fe_2(SO_4)_3$. They have been used under various dosing rates of 5-150 ppm and 20-250ppm for $FeCl_3$ and $Fe_2(SO_4)_3$, respectively (Crittenden et al., 2012). The significant variations originated from the spatiotemporal variations of the NOM component and the raw water characteristics. Like other coagulants, pH is also crucial in affecting iron-based coagulation performance.

The optimum pH ranges from 4.5 to 7 (Jarvis et al., 2012; Park & Yoon, 2009b; Umar et al., 2016), slightly lower than the Al-based pH of 5.5 to 7.7 (alum). Due to variations of NOM both in types and concentrations, periodical optimization of pH and ferric coagulant dosing is required in practice. The NOM content varies largely over time and must be accommodated by adjusting operational conditions. The optimum conditions lead to efficient NOM removal, minimizing chemical consumption, minimizing sludge volume, and enhanced overall performance (Y. Jiang et al., 2016; Sadri Moghaddam et al., 2010; Yan et al., 2009).

Various chemical species are generated during ferric-based coagulation, suggesting the complexity of its chemistry. The chemistry is highly affected by the solution pH and temperature (Ntwampe et al., 2016). In practice, a solubility diagram shows the distribution of monomeric ferric species under various pH, temperature, and metal salt concentrations(Calza & Vione, 2015). The diagram guides the determination of dosage under variable feed conditions.

Table 2 summarizes the recent reports employing ferric-based coagulants for NOM removals from natural or synthetic water. Many reports showed that ferric-based was better than the Al-based coagulants in removing NOM (Gonzalez-Torres et al., 2014; Jarvis et al., 2012; Volk et al., 2000). Nonetheless, ferric-based coagulants were less effective in removing color and turbidity than aluminum-based coagulants (Matilainen et al., 2010).

Table 1. Aluminum-based [$Al_2(SO_4)_3$] coagulants for NOM removals

Target	Feed source and characteristics					Coagulation conditions			Removal performances				Ref.
	Source	Turbidity (NTU)	pH	DOC (mg/L)	UV_{254} (cm^{-1})	$Al_2(SO_4)_3$ (mg/L), stirring time and speed	pH	Optimum coagulant (mg/L) and pH	DOC (%)	UV_{254} (cm^{-1})	Turbidity	Floc size (µm) and growth rate (µm/min)	
NOM	River	6.2	8-8.5	3.9-4.6	0.067-0.073	5-50	4-9	30 and 7	43.2	41.2		130-110 and 65.1	(Y. X. Zhao et al., 2014)
NOM	Reservoir	3.5	-	12.9	4.8 (SUVA (L/mg-m)	5-15 (30 min, 30-200 rpm)	4-8	5-15 and 5-6	77	-	86	430-490 and 520	(Jarvis et al., 2012)
AOM and HA	Synthetic	Bovine serum albumin, Peptides/proteins				0.2-10 (15 min, shear rates 50-200/s)	-	1.6 and 5.6-6.2	-	-	-	-	(Pivokonsky et al., 2015)
HA	Synthetic	15	8.23-8.47	3.9	0.45	2 (30 min, 40-200 rpm)	ZP 14.3 mV	2	57.3	91.3	93	142-646 and 36.8	(Y. X. Zhao, Gao, Shon, Kim, et al., 2011)
NOM (8-15 C/L)	River	-	-	-	-	2-8 (45 min, 20-400 rpm)		4 and 6	-	-	-	-	(Y. X. Zhao, Gao, Shon, Kim, et al., 2011)
HA	Synthetic	15	8.2	4.38	0.43	1-6 (40 min, 40-200 rpm)	4-Sep	2	75.9	93.4	96	405 and -	(Y. X. Zhao, Gao, Shon, Cao, et al., 2011)

AOM: algogenic organic matter, NOM: Natural organic matter, HA: humic acid, ZP: zeta potential

Table 2. NOM removals using iron-based coagulants ($FeCl_3$, Ferripol XL, $Fe_2(SO_4)_3$)

Target	Feed source and characteristics					Coagulation conditions			Removal performances				Ref.
	Source	Turbidity (NTU)	pH	DOC (mg/L)	UV_{254} (cm^{-1})	$Al_2(SO_4)_3$ (mg/L), stirring time and speed	pH	Optimum coagulant (mg/L) and pH	DOC (%)	UV_{254} (cm^{-1})	Turbidity	Floc size (µm) and growth rate (µm/min)	
NOM	River	6.2	8-8.5	3.9-4.6	0.067-0.073	5-50	4-9	30 and 7	43.2	41.2		130-110 and 65.1	(Y. X. Zhao et al., 2014)
NOM	Reservoir	3.5	-	12.9	4.8 (SUVA (L/mg-m)	5-15 (30 min, 30-200 rpm)	4-8	5-15 and 5-6	77	-	86	430-490 and 520	(Jarvis et al., 2012)
AOM and HA	Synthetic	Bovine serum albumin, Peptides/proteins				0.2-10 (15 min, shear rates 50-200/s)	-	1.6 and 5.6-6.2	-	-	-	-	(Pivokonsky et al., 2015)
HA	Synthetic	15	8.23-8.47	3.9	0.45	2 (30 min, 40-200 rpm)	ZP 14.3 mV	2	57.3	91.3	93	142-646 and 36.8	(Y. X. Zhao, Gao, Shon, Kim, et al., 2011)
NOM (8-15 C/L)	River	-	-	-	-	2-8 (45 min, 20-400 rpm)		4 and 6	-	-	-	-	(Y. X. Zhao, Gao, Shon, Kim, et al., 2011)
HA	Synthetic	15	8.2	4.38	0.43	1-6 (40 min, 40-200 rpm)	4-Sep	2	75.9	93.4	96	405 and -	(Y. X. Zhao, Gao, Shon, Cao, et al., 2011)

AOM: algogenic organic matter, NOM: Natural organic matter, HA: humic acid, ZP: zeta potential. Unit and coagulants are provided with the value when they differ from the heading of the columns

Titanium and zirconium-based

Titanium (Ti) and zirconium (Zr) have also been applied effectively as coagulants in the form of zirconium chloride/sulfate[$ZrCl_4$/$Zr(SO_4)_2$] or titanium chloride/sulfate [$TiCl_4$/$Ti(SO_4)_2$](Hussain et al., 2014; J.-Q. Jiang, 2015; Okour et al., 2009). They have been explored since the late 1930s (Upton & Buswell, 1937) but have only been recently implemented on a large scale. Their NOM removals performance was reported to exceed the Al- or Fe-based coagulants.

The performance of $TiCl_4$ and $ZrCl_4$ in removing NOM from a drinking water source was compared with the aluminum sulfate through jar test experiments (Hussain et al., 2014). $ZrCl_4$ performed better with minimum HA, FA, and soluble microbial residual. It was highly efficient to remove medium to low MW fractions of NOM (0.1-2 kDa). The dissolved organic compound (DOC) and color removals (at pH 4.5) were 61.4% and 92.1% for $ZrCl_4$; 44.1% and 84.2% for $TiCl_4$, and 40.8% and 89.9% for $Al_2(SO_4)_3$, respectively.

The NOM removals from HA-kaolin synthetic water using various coagulants of $TiCl_4$, $FeCl_3$, and $Al_2(SO_4)_3$ were compared (Y. X. Zhao et al., 2014). $TiCl_4$ was best with UV_{254} removal of up to 55%, higher than $FeCl_3$ and $Al_2(SO_4)_3$ with 48% and 41% removals, respectively. However, its DOC removal (of 55%) was slightly lower than the ferric coagulant (58%). TiCl4 showed a fast rate of floc aggregation, forming the largest size but weakest and the worst re-growth after breakage.

The performance of NOM removal in a coagulation/ultrafiltration process from synthetic HA-kaolin solution using $Ti(SO_4)_2$ was compared with alum and ferric sulfate (X. Huang et al., 2016). Their dosing was aimed as a pre-treatment of the subsequent ultrafiltration process. It showed that $Ti(SO_4)_2$ resulted in a more compact, stronger, and larger floc under pH 7–9 than the others generated, resulting in the lost membrane fouling potential.

Polymeric coagulants

Polymeric coagulants can be natural or synthetic compounds made of monomers that destabilize solutes to form quickly settled floc. This Section discusses various polymeric coagulants used for NOM removals.

Synthetic

Fe, Al, Ti, and Zr chlorides or sulfate are used as a coagulant in their salts and in the forms of inorganic polymeric coagulants. They are formed by partially neutralizing supersaturated metal salts in a solution using a base before the intended coagulation.

For example, adding a base (i.e., NaOH) to a solution supersaturated with aluminum salt rapidly forms amorphous $Al(OH)_3$ that quickly precipitates. Increasing the bases lowers the hydroxides' positive surface charge forming large polymeric species (Duan & Gregory, 2003). A similar mechanism occurred from the pre-hydrolysis of ferric sulfate and chloride reported by others (X. Huang et al., 2015; Zin et al., 2015).

The studied metal-ion pre-hydrolysis included polyaluminum chloride (PAC) (Hu et al., 2015; Z. Wang et al., 2017), polyferric chloride (PFC) (Cao et al., 2011), polyferric sulfate (PFS) (Zouboulis et al., 2008), as well as polymers of phosphate aluminum chloride (PPAC), ferric zinc sulfate (PFZS) and aluminum ferric sulfate (PAFS)(Y. Wei et al., 2016; Zheng et al., 2011; Zhu et al., 2011). Polymers of titanium salts have also been explored for NOM removal (Chekli et al., 2017; X. Huang et al., 2016; Y. X. Zhao et al., 2015).

NOM is removed using inorganic polymer coagulants through complexation, entrapment, adsorption, and charge neutralization (W. P. Cheng & Chi, 2002; J. C. Wei et al., 2009). They showed higher NOM and organics removal capacity than the traditional coagulants such as ferric and aluminum sulfate (J. Q. Jiang & Graham, 1996; J.-Q. Jiang, 2015). They also performed better for turbidity removal under cold climates or low alkalinity (W. P. Cheng et al., 2008). However, such an advantage was demonstrated by metal salt coagulants (i.e., $TiCl_4$ and $FeCl_3$) when compared with the polymeric PAC (Gkotsis et al., 2017; Park & Yoon, 2009a). Hybrid coagulants composed of aluminum-based and doped with ion-exchange groups showed enhanced NOM removal than alum, ferric chloride, and polymeric PAC, specifically charged and low MW organics (H. Zhao et al., 2016).

A polymer is composed of covalently bonded repetitive monomers. It can become an anionic polymer, commonly called polyelectrolyte, containing ionizable sites. A cationic polymer has a positive charge (cationic), while an anionic polymer poses a negative charge (anionic), and a neutral polymer has no charge (non-ionic). When hydrolyzed, an organic polymer can destabilize soluble, colloidal, or suspended species through charge neutralization or bridging, thanks to its large size and charges (B. Bolto et al., 2002).

NOM removal is primarily achieved through charge neutralization via organic polymer coagulation (B. A. Bolto et al., 1998; B. Bolto & Gregory, 2007; Matilainen et al., 2010). For NOM removal, only cationic polyelectrolytes are applied. Common synthetic cationic polyelectrolytes include polyacrylamide and polydiallyldimethyl ammonium chloride (pDADMAC). pDADMAC is made of polymers from epichlorohydrin and dimethylamine. In comparison, natural-based polymers include starch and chitosan. A predominant humic fraction in NOM is negatively charged at the pH of natural water, hence could be neutralized by a cationic polymer through electrostatic interactions. It was reported that under certain circumstances, the polyelectrolyte size was insignificant in affecting the Coagulation of HA predominantly NOM (Kvinnesland & Ødegaard, 2004).

Cationic polyelectrolyte coagulants generally require lesser dosage, produce a reduced volume of sludge, are less sensitive to pH, and do not produce residue of unbound metal (Chang et al., 2005; Gao et al., 2008). Therefore, they are highly desirable for water treatment systems. Cationic polyelectrolyte coagulants can offer 25–30% cost savings compared to conventional metallic counterparts (Nozaic et al., 2001). Table 3 summarizes synthetic polymeric coagulants' performance in removing NOM or its derivatives.

Despite the widespread use of metallic-based and polymeric coagulants for NOM removals, they still have various drawbacks. The metallic-based coagulants include high volumes of sludge production, costs ineffective, the requirement of acid or base for pH adjustments, and the presence of residual coagulant in the treated water (Ncibi et al., 2017). In contrast, synthetic polymers could be contaminated during production and contain harmful residual monomers and by-products of reactions. The formation of polyelectrolytes during the initial stage could form other auxiliary by-products that are undesirable (Oladoja, 2016). Therefore, extensive research has been done to produce biomass-based coagulants as greener alternatives.

Table 3. NOM and its derivatives removals using synthetic polymeric coagulants

Target	Feed					Coagulation conditions					Removal performances (%)				Ref
	Source	Turbidity (NTU)	pH	DOC (mg/L)	UV_{254} (cm^{-1}) or *Con (mS/cm)	Type	Dose (mg/l)	pH	Optimum dose (mg/L) and pH	Stirring duration (min), Speed (rpm)	DOC (mg/L)	UV_{254} (cm^{-1})	Turbidity (NTU)	Floc size (μm), growth rate (μm/min)	
HA	Synthetic	15	8.2	4.38	0.43	PAC, PFS	1-6, 4-12	4-9	3 and 10	40, 40-200	77, 94	91, 81	-		(Y. X. Zhao, Gao, Shon, Cao, et al., 2011)
HA	Synthetic	4.7-5.3	8-9	5.1-5.6	0.33	PTC	8-14	5-10	8	30, 40-200	61.1	88	62-66	227-839 and 93.2	(Y. X. Zhao et al., 2013)
DOM	River	91.3	7.3	14.1	0.325	PAC	5-16	5.5-8.5	11, pH 6	30, 20-200	Complete removal 2-10kDa NOM, ineffective for 0.1-0.6 kDa			-	(Hussain et al., 2013)
HA	Synthetic	19	7.7	8.04	0.257	PTC	0.05-0.5	3-9	0.15	-	36.1	89.6	97.4	326-820 and 279	(Chekli et al., 2015)
DOM	River	1.3-3.2	7.5-8	7.7-9.3	0.18	PTS	6-16	5-10	30, pH9	30, 40-200	76	70	-	-	(Y. Zhao et al., 2017)
Organic polymeric coagulants															
HA	Synthetic	-	7.2	[a]8.2	*1.5	pDADMAC	0-60	7	60, Ph7.2	20, 200/s	80	-	-	-	(Kim, 2015b)
NOM	River	9	8.14	10.8	0.32	pDADMAC, PACA, PAC	[c]5	-	25 PAC	22, 30-100	48.7, [b]64.8	77.6	-	-	(S. Wang et al., 2013)
HA	Synthetic	8.1	7.2	8.1 TOC	0.67, *1.5	Epi/DMA	0-18	7	18	30, 400/s	78	87	-	-	(Kim, 2015a)
HA	Synthetic	13.2	7.9	4.6	0.12, *0.9	Alum and PAM			0.2-0.5 PAM	15, 50-200	52	83	99.5	-	(Yu et al., 2013)

[a]TOC: total organic carbon, HA: humic acid, DOM: dissolved organic matter, NOM: natural organic matter, DOC: dissolved organic carbon, PAC: phosphate aluminum chloride, [b]when added with 5ppm pDADMAC, [c]variation of ratios to PAC., PFS: polyferric sulfate,PTC: polytitanium chloride, PTS: polytitanium sulfate, pDADMAC: polydiallyldimethyl ammonium chloride, PAM: polyacrylamide, Epi/DMA: Epichlorohydrin/dimethylamine.

Bio-based

Many bio-based coagulants (mainly proteins and polysaccharides) and bioresources derivatives (from terrestrial plants, marine species, or microorganisms) have been explored. They can be used either as the main coagulants or as an aid in coagulation. The two most common and commercially available are tannin-based and chitosan (Graham et al., 2008; Heiderscheidt et al., 2016; Oladoja, 2016; Renault et al., 2009). Bio-based coagulants are preferred because of their renewable nature, non-toxic, and possibly cost-effective.

Many studies have been reported on applying bio-based coagulants for NOM removals, as summarized in Table 4. It details the performance and operational condition of applying biocoagulants NOM and its derivative removal from synthetic or natural fresh feed water. As shown in Table 4, only limited research is available, despite vast bio-based polymer developments, which showed their potential as a coagulant aid. Using bio-based material will promote a more sustainable circular and bio-based economy concept.

Metallic–organic polymeric coagulants

Combining coagulant types like metallic and polymeric can offer mutual advantages. It can get benefits from both while mutually overcoming its shortcomings. Polyferric aluminum chloride and p-DADMAC were explored for NOM removal. The behavior of the floc formation was closely monitored, namely the growth, breakage, re-growth, and fractal nature under various shear forces and pH (C. Sun et al., 2011). Their potential in the aggregating ability for the HA removal from synthetic HA-kaolin solutions was assessed. It showed that the formed flocs were more compact and recoverable (i.e., a recovery of 43.3% at pH 5) under acidic conditions than those in the alkaline HA solutions (with a recovery of 21.3% at pH 8). They undergo charge neutralization under acidic conditions and physical precipitate adsorption under alkali conditions.

The hybrid of PAC with chitosan (PAC–chitosan) has been explored for NOM removals (Ng et al., 2013). It showed better efficacy of PAC-chitosan than the standalone PAC for NOM removal from the synthetic feed. Still, it showed an insignificant difference for NOM removal from actual natural surface water. The SUVA value decreased from 5.8 L/m-mg in the synthetic water sample to 2.7 and 4.4 L/m-mg treated with PAC–chitosan and standalone PAC, respectively. Both set of coagulants reduced the SUVA value of water to ~2.1 L/m-mg. Nonetheless, dosing the composite PAC–chitosan lowered the total THMFPs from 506 to 199 µg/L in the natural feed water, much lower than the standalone PAC of 294 µg/L.

Apart from the aforementioned combinations, several others have also been reported, as listed in Table 4: polyferric aluminum–pDADMAC, polyferric sulfate–pDADMAC, polyferric chloride–lignin–acrylamide polymer, lignin–pDADMAC–acrylamide, and zirconium–glycine complex. The findings on the outcome of the composite coagulants suggest the need to optimize combined coagulants, particularly on the organometallic combination in the preparation phase, possibly with optimization software (such as RSM). The assessment can be more focused on the effect of operational conditions concerning the characteristics of flocs generation, breakage, re-growth, and fractal structure.

Table 4. Performance of biocoagulant for removal of NOM from water

Target	Feed					Coagulation conditions					Removal performances (%)		Ref
	Source	Turbidity (NTU)	pH	DOC (mg/L)	UV254 (cm^{-1})	Type	Dose (mg/l)	pH	Optimum dose (mg/L), pH	Stirring duration (min), Speed (rpm)	[a]DOC	[a]UV254	
HA	Peat runoff	6.9	4.5	76.2	3.8 SUVA (L/mg-m)	Chitosan, Tannin-based	0-80 and 0-200		40 ph4.5 and 110 pH6.5	45, 50-300	43 and 52	-	(Heiderscheidt et al., 2016)
HA	Synthetic	14.5-15.5	8.2-8.4	5.1-5.3	0.30-0.34	Biocoagulant	0.1-0.6	4-9	0.1	45, 50-300	66->56	97->90	(S. Zhao et al., 2013)
NOM	River	9	-	4 BOD	-	Biocoagulant	0.2-1	-		25, 45-120	31.7->65	32,5-75	(Al-Wasify et al., 2015)

[a]The coagulant was used as an aid. The arrow sign indicates the performance before and after adding biocoagulant. NOM: natural organic matter, HA: humic acid, BOD: biological oxygen demand, DOC: dissolved organic carbon.

Electrocoagulation

Electrocoagulation (EC) has been established recently as an alternative to traditional metallic salt-based coagulation, particularly for the decontamination step in drinking water production (Malakootian et al., 2010; Wan et al., 2011) and wastewater treatments (Al-Shannag et al., 2013; Demirci et al., 2015; Hanafi et al., 2010). It was s applied on an industrial scale for the decontamination of organic, heavy metals, inorganics, dyes, pathogens, pesticides, etc.

In EC, solid metal, i.e., containing aluminum or iron, is used as anode and, through electrolysis, dissolved to form the charged ion in the water medium. The dissolved ions near the anode are hydrolyzed immediately to form coagulating polymeric iron or Aluminum hydroxides through three primary stages: (i) oxidation of the anode to form coagulants in-situ, (ii) the destabilization of targeted species, (iii) the aggregation of the destabilized species forming flocs (Dermouchi et al., 2015). The fundamental difference with traditional flocculation is that the formation of ions in EC is done with an electric current from a sacrificing metal anode. The destabilization phase in stage 2 is crucial. It undergoes a few possible mechanisms (Comninellis & Chen, 2010): (1) The interaction of electrolyzed ions facilitates compression of the diffuse double-layer around the charged species. (2) Charge neutralization by the coagulants. (3) The entrapment of the remaining suspended species by a sludge blanket formed by bridged flocs.

Unlike traditional (chemical) coagulation, EC delivers coagulant in-situ without dosing other chemicals. This method made the treatment unit more compact, along with other side reactions (pH change and hydrogen bubble formation), helping in destabilizing pollutants (Särkkä et al., 2015; Vepsäläinen et al., 2009). Such features could enhance pollutant removal and lower the excess sludge [115,116] at the expense of higher energy consumption. The previous report stated that EC efficiency for water treatment is affected by the overall chemistry of the feed water, including pH, conductivity, and the abundance of the targeted pollutants (Yildiz et al., 2007). Table 5 summarizes electrocoagulation development for NOM and its derivatives removals from water. It includes the primary operational condition and the most important findings.

Coagulation in process integration

The metallic and polymers-based coagulants have long been applied in full-scale water and wastewater treatments. Yet, they cannot be implemented as standalone processes and still face a few challenges, mainly technological/process complications and cost-sustainability. Some residual coagulants are still present in the product water; their dosing alters the pH; they incur operational costs and leave a large sludge volume. The excess sludge production is even more significant in the enhanced system, where higher dosing of coagulants is required.

Coagulation is often accompanied by various technologies to meet the required drinking water quality, including membrane (micro, ultra, and nano) filtration (Discart et al., 2014; Guo et al., 2010; Metsämuuronen et al., 2014), advanced oxidation processes (Matilainen et al., 2010), ion exchange (B. Bolto et al., 2002), reverse osmosis (Chun et al., 2017; Malaeb & Ayoub, 2011), and activated carbon adsorption (Bhatnagar & Sillanpää, 2017) or simple sand filtration. Some process integration seems inevitable to meet the more stringent drinking water standard. Process integration involves more than one technology (Wibisono & Bilad, 2019). They are proven approaches in NOM removals. Subsequently, an overview of the integration of coagulation with other processes is provided.

Coagulation–membrane filtration

Membrane filtration for NOM removal is typically implemented by incorporating pre-treatment—the latter aims to reduce the membrane fouling propensity (Dewi et al., 2021). Membrane fouling is the main limitation of membrane filtration that must be managed to allow a more sustained filtration (Rahmawati et al., 2021). The ability to manage membrane fouling helps reduce operational costs and enhance overall NOMs removal. The presence of HA -a component of NOM- is highly detrimental in promoting membrane fouling in ultrafiltration (UF) (Sutzkover-Gutman & Hasson, 2010; Yu et al., 2013). In membrane filtration, NOM is retained in the retentate stream. As such, it may accumulate on the surface of the membrane blocking the passage of water and causing the membrane fouling. Membrane fouling must be constantly monitored to ensure sustainability by maintaining the water flux during the operation (Bilad, 2017). Apart from coagulant dosing, methods for membrane fouling control have also been extensively reported, including engineered spacer, tilted panel, patterned membrane, vibrating module, wavy flow channel, and many others (Barambu et al., 2019, 2021; Bilad et al., 2012; Kharraz et al., 2015; Osman et al., 2020; Rahmawati et al., 2019, 2021).

Integration of Coagulation (chitosan and aluminum sulfate) and membrane filtration was investigated for the removal of NOM from natural water (with TOC of 6.4 mg/L and turbidity of 240 NTU) (Bergamasco et al., 2011). It showed that chitosan coagulation followed by UF resulted in the highest chemical oxygen demand removal of 91%, much higher than the standalone Coagulation and UF, with removals of 60% and 86.7%, respectively. The pre-coagulation of the feed with chitosan enhanced the membrane fouling in the subsequent UF but eventually yielded a higher stable permeate flux of twice higher than the system pre-coagulated with aluminum sulfate.

Coagulants of PAC and pDMDAAC have been explored to remove HA in a hybrid coagulation-UF process to produce drinking water (Shen et al., 2017). The optimum PAC of 1 ppm and pDMDAACof 0.1 ppm doses were used simultaneously. The results show that the combined dosing was better than the standalone PAC in lowering the membrane fouling propensity. In addition, combined dosing of pDMDAAC and PAC enhanced the removal of turbidity and NOM substantially.

A coagulation-filtration process using PAC and the ceramic membrane was explored to treat river water (M. Li et al., 2011). The removal of DOC by the integrated processes was more effective than the standalone PAC coagulation or ceramic membrane filtration, as seen from their poor removals (34-54%). Most interestingly, the hybrid process worked better under lower hydraulic retention times of 5 min with a minimum PAC dosing of 15 mg/L instead of 15 mins (for 15-25 mg/L of APC dosing).

Coagulation can also be integrated with nanofiltration, posing a much smaller pore than ultrafiltration. When evaluated for bromide removal, neither the standalone nanofiltration and alum or ferrous sulfate nor the combined process was effective. However, the hybrid process showed enhanced HA removal with higher flux under pre-coagulation with ferrous sulfate (Listiarini et al., 2010).

Table 5. NOM removal from water using electrocoagulation

Target	Feed					Coagulation conditions				Removal performances (%)			Ref
	Source	Turbidity (NTU)	pH	DOC (mg/L)	UV_{254} (cm^{-1}) or *C (mS/cm)	Electrode	Curent density (mA/cm^2)	pH	Optimum curent density (mA/cm^2)	DOC (mg/L)	UV_{254} (cm^{-1}) or *C (mS/cm)	Turbidity (NTU)	
NOM	River	0.34	ZP 15.2 mV	18.3 TOC	-	Aluminum		4-8		78 TOC	-	-	(Vepsäläinen et al., 2012)
NOM	Synthetic	-	-	13.8	*0.3	Iron steel	2.43-26.8	7	2.43-13.4	73-88	-	-	(Dubrawski & Mohseni, 2013b)
NOM	Lagoon water		6.1	13.3	0.56, *0.99	Iron foil	1-25	6.1-6.5	-	71	-	-	(Dubrawski & Mohseni, 2013a)
NOM	Lake water	-	7.3	14.8	0.41, *1.4	Aluminum, Iron and hybrid Al-Fe	3	4-8	3	71.1, 59.8, 68.6			(Ulu et al., 2015)
NOM	Synthetic	8.3	7	5	-	Aluminum	1, 5, 10	5-7	5	65	-	95	(C. Hu et al., 2016)

NOM: natural organic matter, TOC: total organic carbon, DOC: dissolved organic carbon, ZP: zetapotential.

In another report, chitosan coagulation was integrated with nanofiltration for water treatment (Ang et al., 2016). However, it was found that the chitosan was incompatible with the nano-membranes. The finding implies that chitosan effectively removed the turbidity of the HA synthetic solution by acting through the charge neutralization mechanism. However, charge neutralization caused severe membrane fouling by reducing the electrostatic repulsion from the negatively charged membrane surface. However, a positive impact of a hybrid electrocoagulation and membrane filtration for NOM removal was reported better than the standalone filtration or EC (Chellam & Sari, 2016; Han et al., 2015; W. Sun et al., 2016).

Coagulation–adsorption

Several studies reported an effective combination of coagulation with adsorption as a hybrid process for removing organic and inorganic pollutants in water treatment. The most studied adsorbent in hybrid coagulation-adsorption was activated carbon combined with various coagulants. Other adsorbents were also tested with various coagulants to remove the removals of NOM and its derivatives (FA, HA, and tannic acids). They include biochars (Jung et al., 2015), nanocrystalline Mg/Al layered double hydroxides (Wu et al., 2013), and carbon nanomaterials (Joseph et al., 2012; H. Wang et al., 2010).

Many adsorbents had been tested for NOM removal. DOC, turbidity, and UV254 reductions -parameters used to represent NOM- from river water were achieved by chemical modification of wheat straw-based adsorbent, combined with two inorganic polymers as coagulants (PFC and PAC) (Zhan et al., 2010). The hybrid coagulation–adsorption process enhanced turbidity and UV254 removal up to 95.8% for the PFC– and 94.2% for the PAC–wheat straws, respectively. The standalone coagulation removal efficiencies were 61.8% and 61.5% for the PFC– and PAC–wheat straws, respectively.

Coupling powdered activated carbon with enhanced coagulation was effective in NOM removal and controlling the release of disinfection by-products (DBPs) from river water (Kristiana et al., 2011). The activated carbon improved NOM removal by 70%, which lowered the formation of DBPs (80–95%) but somehow increased the formation of brominated DBPs. Brominated DBPs were formed because activated carbons did not remove bromide ions, allowing them to react and form more toxic DBP than their chlorinated counterpart.

Advanced Oxidation and Coagulation

Oxidations degrade the pollutants through chemical reactions and are generally applied before the coagulation [143], which is dominant in affecting NOM removal. The oxidant (UV, Fenton, and O3-based processes) used and the final and intermediate oxidation products would then be handled in the subsequent coagulation. In this context, the properties of those chemicals would affect the coagulation process, i.e., coagulant type, dosing, pH, and others.

Photocatalytic oxidation catalyzed by titanium dioxide P25 was combined with alum coagulation for HA removal in drinking water treatment (Ayekoe et al., 2017). The photooxidation was done using a solar simulator as a UV source for a retention time of 220 mins. The alum coagulation was first optimized with the optimum pH of 5 and dose of 110 mg/L, resulting in a removal of HA substances of 70%. The hybrid process increased the HA removal up to 90%.

Hybrid ozone oxidation and alum-based coagulation were assessed for NOM and THMFP removal from feed water (Rodríguez et al., 2012). A low hydrophobic fraction of humic substance and calcium in the natural water led to an interesting finding. Higher ozone doses lowered the removal of TOC in the coagulation stage, with maximum removal of 33% achieved by the standalone coagulation. On the contrary, different findings were reported in the synthetic water containing a higher concentration of calcium and HA substances. Dosing ozone at 0.25–2.5 mg O_3/L decreased the THMFP by 5–25%. This report highlighted the limitation of employing synthetic feed as the base to assess coagulation performance, considering the large variety of actual feed water characteristics.

Despite some discouraging results of combining coagulation with other processes, process integration remains a compelling option when employed under optimum conditions.

Coagulation–ion exchange

Ion exchange removes charged organic and inorganic pollutants (B. Bolto et al., 2002; Humbert et al., 2008). It has also been opted to remove NOM in drinking water treatment (Kitis et al., 2007; Mergen et al., 2008; Nguyen et al., 2011). Several resins have been explored: DOWEX 11, DOWEX MSA, IRA938, and IRA958 (Cornelissen et al., 2008; Sillanpää, 2014). The most applied resin is the magnetic anion exchange resin (MIEX). MIEX is the chloride of a macroporous polyacrylic matrix. Its typical sizes are 150–180 µm, 20-50% smaller than conventional resins). It is incorporated with magnetic iron oxide particles to facilitate agglomeration and improve the settling (Boyer & Singer, 2006; Ding et al., 2012).

Ion exchange can be placed before or after the coagulation. Both placements have been explored to enhance the overall NOM removal with minimum coagulants input, DBPs formation, and excess sludge (Humbert et al., 2007; Singer & Bilyk, 2002).

A combination of MIEX and alum was assessed for drinking water treatment with particular attention to NOM removal over two years (Drikas et al., 2011). As a comparison, another combination between microfiltration and MIEX was also evaluated. The results showed that the MIEX pre-treatment facilitated the removal of a wide NOM range. NOM removals using MIEX–Coagulation were better than MIEX-microfiltration thanks to the efficacy of coagulation in removing NOM with sizes of > 1000 Da.

Enhanced coagulation was explored by combiningMIEX or powdered activated carbon (both placed after the coagulation) aimed for DBPs precursors from NOM removals (Watson et al., 2015). Results showed that Coagulation-MIEX was desirable for treating water with high bromide content; as such, the combination limited the brominated DBPs formation. Nevertheless, high iodide content may result in iodinated DBPs due to poor removal of the ion by MIEX.

Other reports confirmed the benefit of enhancing NOM removal via a combination of MIEX with Coagulation (J. Xu et al., 2016; Z. Xu et al., 2013). Other types of resins had also been explored in combination with coagulation (i.e., PWA9 and AMBERLITE PW16)(W. Huang et al., 2015) and a novel suspended ion exchange process (Metcalfe et al., 2015) for NOM and other organic pollutants removals.

CONCLUSION

Removing NOM from water is challenging, considering its spatiotemporal variations in quantity and composition. Therefore, detailed characterization of NOM (i.e., various fractions, reactivity) is critical to design its removals, primarily to avoid toxic by-product formation.

Coagulation is widely used for the removal of NOM from drinking water supplies. The most common coagulants include metal salts, polymers (inorganic and organic, synthetic or natural), and combinations. The NOM composition and the natural water properties highly dictate the coagulant selection. Those characteristics aid in unraveling interaction mechanisms: charge neutralization/precipitation, adsorption, co-precipitation, and hetero-coagulation (Davis & Edwards, 2014), thus selecting the most appropriate coagulant. Nonetheless, based on the literature survey, the report with the highest removal efficiencies was obtained using different coagulant types of alum, ferric, polymers, bio-coagulants, and electrocoagulation.

Data in Tables 1-5 revealed that Ferripol XL, an iron-based coagulant, was the most efficient NOM removal, demonstrating up to 80.5% DOC removal. EC demonstrated high potential by showing DOC and UV254 removals of 73% and 88%, respectively. It is mainly due to its application on-site (in-situ). The highest HA removal was achieved by PFS polymeric coagulant with UV254 and DOC removals of 91% and 84%, respectively. From the bio-based coagulant category, the extract of algal or bacteria showed promising potential to aid alum-based Coagulation in removing NOM and HA.

Process integration involving coagulation has recently been widely investigated for enhanced NOM removal, particularly to anticipate more stringent drinking water regulations. Integration of chitosan-based coagulation and UF offered substantially high chemical oxygen demand reduction (91%), much higher than the standalone coagulation (60%), and the standalone UF (86.7%) is highly prone to membrane fouling. Moreover, a hybrid of photocatalytic/coagulation showed enhanced removal of HA of up to 90%. Nevertheless, full-scale implementation of photocatalytic will be hard to achieve considering the light source required in the oxidation process.

RECOMMENDATION

Many reports showed inconsistent findings when using synthetic and read feed waters to evaluate the coagulation performance. It makes extrapolation of results in a controlled experiment using synthetic feed inadequate to represent the actual feed. The situation is worsened considering the highly dynamic nature of NOM in actual water. Judging from those findings, assessing the coagulation (type and optimum condition) is best done using the actual feed before implementation.

Future coagulation process developments must account for both the sustainability concept of both and bioeconomy. For the former, emphasis can be given to intensifying the impact (dosing less with enhanced efficiency) or developing a novel type of cost-effective coagulant that allows easy recovery as pioneered elsewhere (Davis & Edwards, 2014; Keeley et al., 2012, 2016). For the latter, polymeric bio-based coagulants, algae, plants or microorganisms seem attractive. They must be competitive with chemical-based coagulants but with enhanced eco-friendliness and cost-effectiveness. Some biobased coagulants have shown promising efficacy in NOM removal as demonstrated by a few earlier results.

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