

# Natural organic matter as precursor to disinfection byproducts and its removal using conventional and advanced processes: state of the art review

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## ABSTRACT

Natural organic matter (NOM) is ubiquitous in the aquatic environment and if present can cause varied drinking water quality issues, the major one being disinfection byproduct (DBP) formation. Trihalomethanes (THMs) are major classes of DBP that are formed during chlorination of NOM. The best way to remove DBPs is to target the precursors (NOM) directly. The main aim of this review is to study conventional as well as advanced ways of treating NOM, with a broad focus on NOM removal using advanced oxidation processes (AOPs) and biofiltration. The first part of the paper focuses on THM formation and removal using conventional processes and the second part focuses on the studies carried out during the years 2000–2018, specifically on NOM removal using AOPs and AOP-biofiltration. Considering the proven carcinogenic nature of THMs and their diverse health effects, it becomes important for any drinking water treatment industry to ameliorate the current water treatment practices and focus on techniques like AOP or synergy of AOP-biofiltration which showed up to 50–60% NOM reduction. The use of AOP alone provides a cost barrier which can be compensated by the use of biofiltration along with AOP with low energy inputs, making it a technoeconomically feasible option for NOM removal.

**Key words** | AOP, biofiltration, disinfection byproducts, drinking water treatment, trihalomethanes

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## INTRODUCTION

Providing safe drinking water is essential for sustaining human life on earth. With the growing demand for water, it is becoming difficult for drinking water industries to meet the quality needs, both chemically and microbiologically. The chemical aspect refers to chemical contaminants in water sources that are a direct threat to human life. One such contaminant is disinfection byproducts (DBPs) which are formed as a result of disinfection of the water in the treatment process itself. Disinfection is crucial for maintaining the microbiological safety of water, i.e. it aids in inactivating microbial pathogens (bacteria, virus, protozoa etc.) that can cause various water-borne diseases (Gomez-Alvarez *et al.* 2016). One such disinfectant is chlorine and it is the most widely used across the globe. DBPs are generally formed by

the reaction of disinfectants such as chlorine with organic precursors present in source water; these organic precursors are mainly called natural organic matter (NOM) and NOM acts as a forerunner to DBPs. Some of the chlorination disinfection byproducts are shown in Table 1. Trihalomethanes (THMs) are the major class of DBPs formed. Though THMs is not a regular water quality parameter, various studies have reported their occurrence in water systems across the globe and stringent guidelines have been imposed for controlling THM levels in water supply systems (Golfopoulos 2000; Rodriguez *et al.* 2003; Ivahnenko & Zogorski 2006; Wang *et al.* 2007; Kumari *et al.* 2015). THMs constitute four main volatile organic compounds (VOCs): trichloromethane (chloroform), bromodichloromethane (BDCM),

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**Table 1** | Chlorination disinfection byproducts (Tak & Kumar 2017)

Regulated DBPS	DBP	Chemical formula
Trihalomethanes	Chloroform	CHCl <sub>3</sub>
	Bromodichloromethane	CH <sub>2</sub> BrCl
	Dibromochloromethane	CHBr <sub>2</sub> Cl
	Bromoform	CHBr <sub>3</sub>
Haloacetic acids	Bromochloroacetic acid	C <sub>2</sub> H <sub>2</sub> BrClO <sub>2</sub>
	Bromodichloroacetic acid	BrCl <sub>2</sub> CCOOH
	Chlorodibromoacetic acid	C <sub>2</sub> HBr <sub>2</sub> ClO <sub>2</sub>
	Dibromoacetic acid	C <sub>2</sub> H <sub>2</sub> Br <sub>2</sub> O <sub>2</sub>
	Dichloroacetic acid	C <sub>2</sub> H <sub>2</sub> Cl <sub>2</sub> O <sub>2</sub>
Chlorate		
Chlorite		
Bromate		

dibromochloromethane (DBCM) and tribromomethane (bromoform). Total trihalomethanes (TTHMs) are the sum of the mass concentrations of chloroform, BDCM, DBCM and bromoform in  $\mu\text{g L}^{-1}$  (Frimmel & Jahnel 2003). THMs have been classified as a probable and possible human carcinogen in group 2B and C (IARC 1999). The removal of THMs after their formation is difficult and involves resource-intensive processes such as activated carbon adsorption or air stripping. Therefore, efforts should be directed towards optimizing the operation of existing water treatment plants to minimize THM formation or developing treatment techniques to degrade natural organic matter (NOM), which are the DBP precursors (Rook 1974).

NOM is a complex mixture of heterogeneous chemical fractions with different polarity, chemical composition, charge and molecular weights (Nebbioso & Piccolo 2013). The chemical characteristics of NOM can be a useful tool to study their correlation with DBP formation. The complete removal of NOM by conventional water treatment processes is relatively inefficient, leading to the formation of DBPs, during either post- or pre-chlorination (Murray & Parsons 2004). NOMs are usually quantified in terms of dissolved organic carbon (DOC). DOC is the part of total organic carbon (TOC) which can be filtered through a 0.45  $\mu\text{m}$  membrane filter. The absence of regulatory guidelines for DOC strengthens the need for more focus on NOM removal as it can be a source of various water quality issues such as color, taste, odor and DBPs. Advanced oxidation processes (AOPs) are highly efficient water treatment processes that

can degrade natural and recalcitrant organic matter. AOPs oxidize the highly complex organic matter into simpler compounds, therefore increasing the biodegradability of the NOM. Biological activated carbon (BAC) or biofiltration is also known to remove biological organic matter from source water (Chien *et al.* 2008; Korotta-Gamage & Sathasivan 2017). AOPs can completely mineralize the NOM, but at higher energy and thus higher cost inputs. Therefore, combined with biofiltration process BAC can be an economical solution for the removal of NOM.

## NOM AND ISSUES IN WATER TREATMENT INDUSTRY

The organic matter in surface and ground water is predominantly natural organic matter (NOM) and this NOM is a complex mixture of organic compounds with different molecular size and properties (Lamsal *et al.* 2011; Sillanpää & Matilainen 2014). NOM is derived from plants, animals, microorganisms and their waste and metabolic products. Therefore NOM is omnipresent in all natural water sources and even in soil and sediments (Aiken 1985; Suffet & MacCarthy 1988). It is present in particulate, dissolved and colloidal forms. The amount and characteristics of NOM are site-specific, i.e. they are climate, topography and geology dependent (Fabris *et al.* 2008; Wei *et al.* 2008). The characteristics of NOM vary both regionally and with time (Wei *et al.* 2008). Aquatic NOM is a heterogeneous mixture consisting of both hydrophobic and hydrophilic compounds. The hydrophobic fraction, which accounts for more than half of total dissolved organic carbon (DOC), is predominated by humic substances (Sillanpää & Matilainen 2014), primarily humic acids and fulvic acids and other phenolic compounds and carbon with conjugated double bonds. Aquatic fulvic acid is considered to be the major portion of hydrophobic fraction (Aiken *et al.* 1992). Hydrophobic NOM is rich in aromatic content and is composed of primarily humic material. Humic material is formed by decaying vegetative matter, such as lignin. Lignin is found in plants and is quite resistant to biodegradation, yet is reactive to oxidants, such as chlorine. These characteristics of the aromatic hydrophobic humic material tend to form higher THM levels. The hydrophilic fraction of NOM primarily consists

of aliphatic carbon and nitrogen bearing compounds such as carbohydrates, proteins and amino-acids (Sillanpää & Matilainen 2014). The composition of NOM is presented in Table 2.

NOM is predominantly responsible for water quality issues such as color, odor and taste. Colorless water may also have NOM present in significant levels. NOM can act as a major source of microbial re-growth in the water distribution system, if present in treated water. The major issue with NOM is formation of unwanted products such as DBPs upon reaction with chemicals like chlorine. Therefore, it can be concluded that NOM can pose serious water quality issues in any drinking water treatment industry if not well treated. The majority of studies suggest that hydrophobic compounds are the major contributors of DBPs (Fabris *et al.* 2008; Wei *et al.* 2008) while few consider the hydrophilic part to be the contributor of DBPs. The source of origin of NOM also plays a very important role in deciding the nature of NOM. Autochthonous and allochthonous are two classes based on the source of origin of NOM. Allochthonous NOM is derived from sources on land that are

external to the aquatic system and autochthonous NOM is generated within the water column having mainly algae as a source (algal NOM) (Wershaw *et al.* 2004; Leenheer *et al.* 2004; Winter *et al.* 2007; Berggren *et al.* 2015). Allochthonous NOM is dominated by hydrophobic content whereas autochthonous NOM is dominated by lower molecular weight hydrophilic molecules (Wershaw *et al.* 2005). Therefore defining NOM into operationally defined chemical fractions, i.e. hydrophobic, transphilic and hydrophilic, will also help in determining the source of NOM origin.

## DBP FORMATION AND NOM CHARACTERIZATION

The presence of NOM in water is well acknowledged but it was in the late 1970s that NOM was identified as a precursor to disinfection byproducts, mainly THMs. THMs have been shown to cause severe health impacts in various epidemiological studies and health risk assessments (Dodds *et al.* 1999; Richardson 2003; Villanueva *et al.* 2006, 2015; Wang *et al.* 2013). Since then the reaction of NOM with

**Table 2** | NOM composition and chemical groups (Edzwald 1993; Świetlik *et al.* 2004; Ghernaout 2014)

Fraction	Chemical groups	Composition/organic compound class
Hydrophobic		
Acids		Soil fulvic acids, C <sub>5</sub> –C <sub>9</sub> aliphatic carboxylic acids, 1- and 2-ring aromatic carboxylic acids, 1- and 2-ring phenols
Strong	Humic and fulvic acids, high MW alkyl monocarboxylic and dicarboxylic acids, aromatic acids	
Weak	Phenols, tannins, intermediate MW alkyl monocarboxylic and dicarboxylic acids	
Bases	Proteins, aromatic amines, high MW alkyl amines	1- and 2-ring aromatics (except pyridine), proteinaceous substances
Neutrals	Hydrocarbons, aldehydes, high MW methyl ketones and alkyl alcohols, ethers, furans, pyrrole	Mixture of hydrocarbons, >C <sub>5</sub> aliphatic alcohols, amides, aldehydes, ketones, esters, >C <sub>9</sub> aliphatic carboxylic acids and amines, >3 ring aromatic carboxylic acids and amines
Hydrophilic		
Acids	Hydroxy acids, sugars, sulfonics, low MW alkyl monocarboxylic and dicarboxylic acids	Mixtures of hydroxy acids, <C <sub>5</sub> aliphatic carboxylic acids, polyfunctional carboxylic acids
Bases	Amino acids, purines, pyrimidine, low MW alkyl amines	Pyridine, amphoteric proteinaceous material (i.e. aliphatic amino acids, amino sugars, <C <sub>9</sub> aliphatic amines, peptides and proteins)
Neutrals	Polysaccharides, low MW alkyl alcohols, aldehydes, and ketones	<C <sub>5</sub> aliphatic alcohols, polyfunctional alcohols, short-chain aliphatic amines, amides, aldehydes, ketones, esters, cyclic amides, polysaccharides and carbohydrates

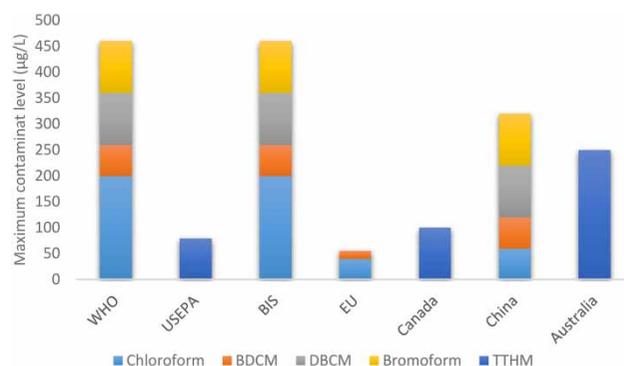
disinfectants and other chemicals used in water treatment, and the influence it exerts on virtually every aspect of water treatment, has begun to be appreciated. The idea of haloform formation in water treatment plants stated by Rook (1974) is still a problem in many developing nations like India. The history of THM recognition is shown in Table 3. The United States Environmental Protection Agency (USEPA) was the first agency to set THM standards

**Table 3** | History of THM identification and regulation development (globally) updated and adapted from Bond *et al.* (2012)

Year	Milestone	References
1974	Formation of haloforms during chlorination in drinking water	Bellar <i>et al.</i> (1974) and Rook (1974)
1976	The carcinogenicity of chloroform was suspected in animals	National Cancer Institute USA (1976)
1979	USEPA guidelines for THM (100 ppb)	USEPA (1983)
1984	WHO guidelines for chloroform	Gorchev & Ozolins (1984)
1989	UK guidelines for THM regulation (100 ppb)	
1988–89	Survey/monitoring of THM formation in drinking water started across USA by USEPA	Krasner <i>et al.</i> (1989)
1999	THM classified as a suspected human carcinogen by IARC	IARC (1999)
2000	More than 300 chlorinated DBPs identified	–
2004	Central Pollution Control Board (CPCB), India initiation of THM identification in India	–
2006	500–600 DBPs reported for chemical disinfectants including chlorine, chloramine, ozone and chlorine dioxide	Krasner <i>et al.</i> (2006)
2008	THM guideline values in countries like Canada, China, and Europe have been established	–
2012	BIS standards for trihalomethanes	–
2015	Risk assessment studies of trihalomethanes for cancer and non-cancer based affects	Villanueva <i>et al.</i> (2015)
2016	Point of use surface water disinfection led to THM formation	Werner <i>et al.</i> (2016)

in 1979. Later on, USEPA also implemented first and second disinfectants/disinfection by-products rules (D/DBP) in 2000 and 2006 respectively. Later on, the European Union (EU) and the World Health Organization (WHO) also set guidelines and standards for THMs. Since then, THMs have been regulated in different nations across the world, primarily developed nations. A few guidelines set for THMs across different parts of the world are depicted in Figure 1. The identification and monitoring of THMs and their sources in developing nations like India is non-existent. In 2012, in its new draft the Bureau of Indian Standards (BIS) included standards for THM levels in BIS code: IS 10500: 2012. Very few studies to date have reported the THM identified in some states of the country (Rajan *et al.* 1990; Thacker *et al.* 2002; Sharma & Goel 2007; Hasan *et al.* 2010a, 2010b; Basu *et al.* 2011; Mishra *et al.* 2012).

The reaction of NOM with chlorine is dependent on the chemical characteristics of NOM itself, i.e. hydrophobicity, polarity, nature of functional groups present, aromaticity etc. Chlorinated DBPs such as THMs are generally formed by the reaction of naturally derived organic matter with chlorine (Farkas *et al.* 1949; Gallard & von Guntem 2002; Westerhoff *et al.* 2004), but THMs or DBPs can be formed from anthropogenic sources like wastewater treatment plants (Yang *et al.* 2014). The properties of wastewater effluent derived organic matter (EfOM) are completely different from NOM; EfOM from biological wastewater treatment plants consists of biodegradation and soluble microbial products. The characteristics of NOM and EfOM converge but aromatic moieties in both are of completely different origin (Yang *et al.* 2014). THMs are mainly studied in drinking



**Figure 1** | Trihalomethanes guideline value (worldwide).

water treatment plants where the main source of influent is surface water (lesser anthropogenic influence), but sometimes there can be incidental introduction of treated wastewater into the drinking water treatment plant (in developing nations). NOMs have complex chemical composition; different chemical fractions contribute differently to THM formation. Humic and fulvic acids (hydrophobic fractions) are the most important precursors to DBPs. NOMs can be fractionated on the basis of polarity into hydrophobic, transphilic and hydrophilic using XAD resin fractionation. The different NOM fractions react differently according to coagulant, amount of coagulant, chlorine, ozone and in terms of DBP formation potential (DBPFP) (Fabris *et al.* 2008). Table 4 describes the role of different chemical groups on THM formation. Various studies have

**Table 4** | Impact of NOM chemical groups on THM formation (Croue *et al.* 1999)

Chemical group	Impact on THM formation	References
Humic acid and fulvic acid	Major impact on THM formation; major precursor to DBPs	Singer (1999) and Ibrahim <i>et al.</i> (2016)
Carbohydrates/ Polysaccharides	Not a major precedent to THMs; comprises mainly of hydrophilic matter; slow THM formation kinetics with pH being an important process parameter	Bond <i>et al.</i> (2012) and Ramavandi <i>et al.</i> (2015)
Amino acids & proteins	Not all free amino acids but mostly aromatic ones like tyrtophan and tyrosine contribute to THM formation; polypeptide groups are non-reactive towards chlorine as the amide group involved is unavailable for reaction with chlorine	Hong <i>et al.</i> (2009)
Carboxylic acids	Generally low for simple carboxylic acids like fatty acids, palmitic acid or stearic acid, exceptions being $\beta$ -dicarbonyl acids oxopentanedioic acid with high DBP yields upon chlorination	Bond <i>et al.</i> (2012)

researched NOM surrogates instead of the source NOM itself, with major compounds being aniline, resorcinol etc. in aromatic moieties and L-aspartic acid, 3-oxopentanedioic acid, 2,4-pentanedione etc. in aliphatic properties (Bond *et al.* 2012). NOM characterization provides a useful insight into NOM composition, reactivity towards chlorine and removal options. Among all the techniques well established in literature, this review will focus on techniques such as UV absorbance at 254 nm ( $\text{cm}^{-1}$ ), specific UV absorbance (SUVA) ( $\text{SUVA} = \text{UV}_{254}/\text{DOC} \times 100$ ), Fourier transform infrared spectroscopy (FTIR), XAD resin fractionation, and fluorescence excitation – emission matrix (FEEM). SUVA is widely used for estimating the chemical characteristics of DOC in the source water, its amenability to coagulation, and the reactivity with chlorine toward DBP formation (Kitis *et al.* 2001; Weishaar *et al.* 2003; Fearing *et al.* 2004; Van Verseveld *et al.* 2007; Hua *et al.* 2015). The significance of SUVA in characterizing NOM in terms of THM forming potential (THMFP) is shown in Table 5 and Table 6 describes the efficiency and use of different NOM characterization techniques.

**Table 5** | SUVA and THM formation (Edzwald & Tobiason 1999)

SUVA value (L/mg cm)	Characteristics of NOM	Correlation with THM formation	References
>4	Mostly aquatic humic, hydrophobic, high molar mass (HMM) organic material	Water with high SUVA value tend to form high number of DBPs	Hua <i>et al.</i> (2015)
4–2	Mixture of aquatic and other NOMs, Intermediate of hydrophobic and hydrophilic, mixture of molecular masses	Good correlation with THM formations	Edzwald & Tobiason (1999) and Lu <i>et al.</i> (2009)
<2	Non-humic, organic compounds which are hydrophilic, low molar mass (LMM) and low in charge density	No significant correlation between THM formation in water with low SUVA values	Sharp <i>et al.</i> (2006) and Ates <i>et al.</i> (2007)

**Table 6** | NOM characterization techniques

	Significance	References
DOC and UV	DOC gives a quantitative idea about the aqueous organic matter. UV <sub>254</sub> depicts aromaticity in the water, as aromatic compounds tend to absorb UV at 254 nm. Also, it can be used to estimate the aromaticity of the water which in turn is the major property of DBP precursors for, for example, resorcinol	Sillanpää & Matilainen (2014)
SUVA	SUVA is a good indicator of hydrophobicity and has good correlation with THM formation yields	Hua <i>et al.</i> (2015)
XAD resin fractionation	Fractionation procedure is used to characterize aqueous organic matter into hydrophobic, hydrophilic and transphilic which can be used to predict the fraction with the highest THMFP	Thurman & Malcolm (1981) and Aiken (1985)
Absorbance spectra	UV absorbance spectra (220–280 nm) is considered as most appropriate for NOM measurements. NOM contains different chromophores with different molar absorptivities at various wavelengths, each wavelength being associated with different kinds of chromophore	Sillanpää & Matilainen (2014)
Fourier Transform Infrared (FTIR) spectroscopy	FTIR is the less widely used technique for NOM characterization. It aids in identifying specific functional group composition in aqueous organic matter	Davis <i>et al.</i> (1999)
Fluorescence excitation emission matrix (FEEM)	A technique that has emerged only in the last decade for identifying the structural composition of fluorophore NOM. FEEM aids in providing information regarding fluorescence characteristics of NOM by changing excitation and emission wavelengths. Raw surface water mainly gives two major fluorescence peaks, one of humic acid, tryptophan, fulvic acid like compounds and the other minor peaks of a few low molecular weight compounds	Her <i>et al.</i> (2003), Świetlik <i>et al.</i> (2004) and Wang <i>et al.</i> (2017)

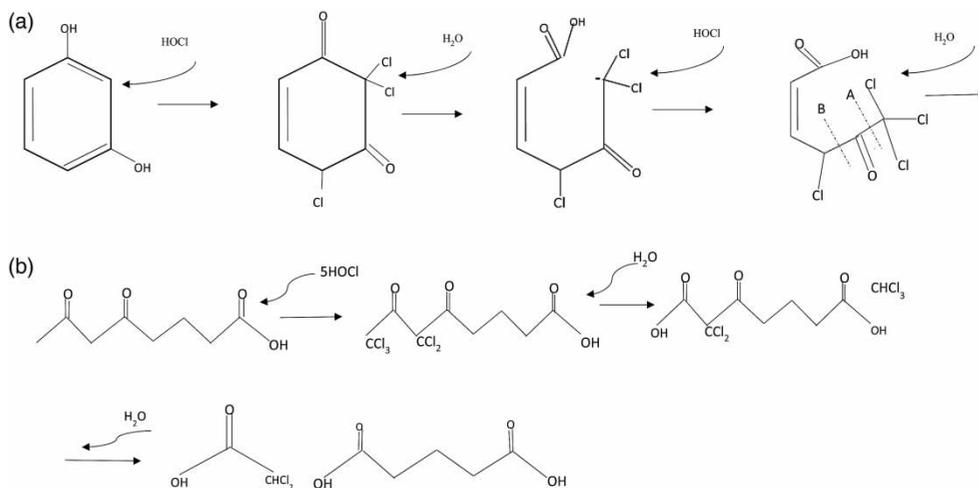
## THM FORMATION: REACTION CHEMISTRY

The detailed mechanism of THM formation and the effect of different process parameters on THM formation is well explained by Rook (1974). Chlorine is usually applied in the form of sodium hypochlorite or in gaseous form. Chlorine readily reacts with water and forms hypochlorous acid (HOCl) which in turn dissociates into hypochlorite ion (OCl<sup>-</sup>). The structure of NOM, especially humic acid, is very complex. The compounds such as resorcinol bear a close resemblance to aromatic NOM with chlorine, with most of the research focused on surrogates such as resorcinol (Frimmel & Jahnel 2003; Bond 2009). Aromatic or phenolic compounds such as resorcinol are considered as the main precursors of THMs. One such reaction mechanism is shown in Figure 2. The formation of THM is affected by various process parameters like chlorine dose, residual chlorine, reaction time, temperature, pH, NOM

source, concentration and inorganic sources like bromide ion etc.

## EFFECT OF DRINKING WATER PROCESSES ON NOM REDUCTION

The most common technique employed for the removal of NOM from water treatment systems is coagulation-flocculation followed by clarification (sedimentation or flotation), filtration and disinfection. Coagulation is mainly employed for the removal of turbidity and with that NOM and some of the hydrophobic compounds are also removed. This is the most conventional method employed by drinking water treatment systems across the globe. There is no specific technique employed for the removal of TOC or DOC, but various treatment techniques employed remove TOC/DOC along the way. Non-conventional or advanced methods include adsorption, membrane filtration, ion



**Figure 2** | (a) Chlorination of resorcinol (Rook 1977). Cleavage at A will result in the production of CHCl<sub>3</sub> and cleavage at B will form TCAA. (b) Chlorination of 5, 7-dioxooctanoic acid (Dickenson *et al.* 2008; Bond *et al.* 2012).

exchange, biofiltration, AOPs or integrated methods such as AOP followed by biologically activated carbon (BAC).

### Coagulation/flocculation – sedimentation

Coagulation is the destabilizing of solid colloidal matter which will result in the formation of micro flocs. The micro flocs thus formed start to agglomerate, leading to the formation of larger flocs due to Brownian motion and this process is called flocculation. Chemical coagulation is generally achieved by the addition of iron or aluminum salts. Coagulating aids such as PACl (poly aluminum chloride) can also be used to enhance coagulation. The possible mechanism of NOM removal by coagulation is shown in Figure 3(a). Most of the NOM is believed to be removed by coagulation. However there is still ambiguity regarding reduction in the hydrophobic or hydrophilic part by coagulation. Most of the studies suggest the removal of the hydrophobic higher molecular weight (HMW) part is more efficient as compared to the hydrophilic lower molecular weight (LMW) part. Such a phenomenon may be due to higher aromaticity of the HMW fraction which carries high charge density and a higher level of negative charge due to the presence of ionic groups such as carboxylic and phenolic groups. Therefore, the HMW fraction tends to dominate the colloidal charge nature of water and is more amenable to removal by coagulation. Enhanced coagulation was introduced as a new regulatory requirement in the USA, primarily aimed at removing DOC and thereby DBP

precursor. The main aim is also comparable with optimized coagulation, i.e. maximum removal efficiencies in terms of turbidity, particulate TOC, DBP precursor, least residual coagulant, sludge production and operating cost (Edzwald & Tobiason 1999). All this is mainly achieved by increasing coagulant dose and adjusting pH (Yan *et al.* 2006).

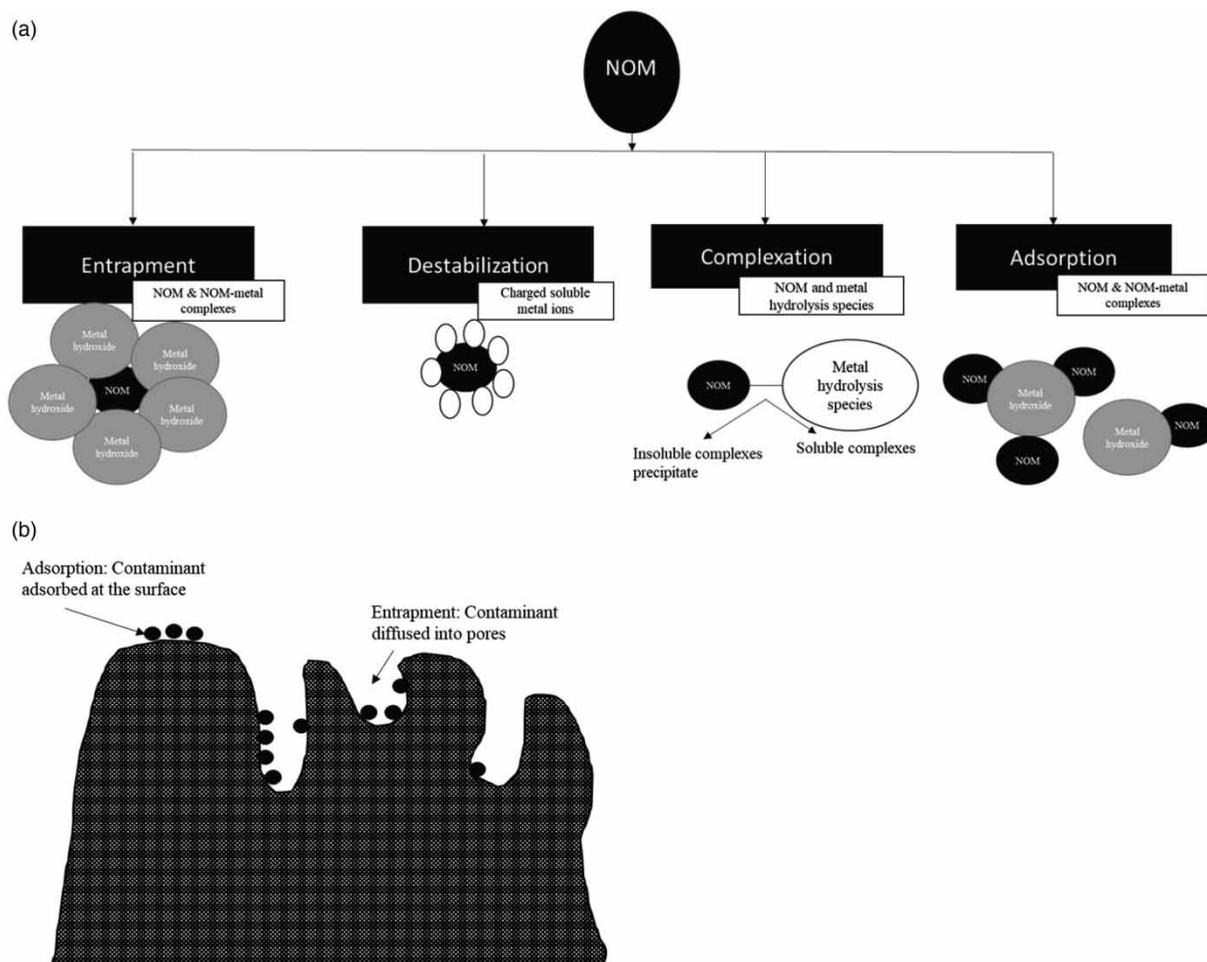
### Filtration

#### Slow sand filtration (SSF)

Collins *et al.* (1992) studied the effect of slow sand filtration for NOM and subsequently THM precursor removal. The possible mechanism of removal was physical straining, adsorption and biodegradation. The organic matter degradation was found to be dependent on filter biomass which in turn was found to be dependent on the cleaning and maintenance procedures adopted (the filter harrowing technique is more effective than surface scraping cleaning) (Collins *et al.* 1992). Although slow sand filtration is inexpensive and is the most widely employed water treatment process, it is unable to decrease the DOC to those levels that will prevent DBP formation below the set standard limit (Moncayo-Lasso *et al.* 2008).

#### Rapid sand filtration (RSF)

Rapid sand filtration can also contribute to DOC reduction and the main mechanism involved here is adsorption on the



**Figure 3** | (a) The possible mechanism of NOM removal by coagulation (Matilainen *et al.* 2010). (b) AC surface adsorption and entrapment of organic matter (Simpson 2008; Korotk-Gamage & Sathasivan 2017).

flocs and biodegradation. The net DOC removal is dependent on the operating conditions or bioprocesses occurring inside the filtration system. Biological processes occurring inside the filtration system may lead to biodegradable DOC (BDOC) elimination whereas assimilable organic carbon (AOC) removal is dependent on the oxygen concentration in the filter bed (Korth *et al.* 2001). In both RSF and SSF, biodegradation is among the major pathways for NOM reduction.

### Microfiltration (MF)/ultrafiltration (UF)/membrane filtration

Membrane filtration alone is not effective in DBP precursor removal. It is able to achieve only less than 10% DOC

removal. However, with pre-treatment or in combination with conventional techniques such as coagulation, comparatively better NOM removal can be achieved.

### Coagulation followed by microfiltration

The DBP removal through microfiltration along with coagulant is a site specific system and should be optimized for a particular site because of spatial variation of NOM. One more advantage of using membrane filtration along with coagulation is that the membrane filtration uses a physical barrier for achieving microbial and particle removal, therefore coagulation is not required to achieve the filtration objective and the process chemistry is specifically optimized for the removal of NOM (Vickers *et al.* 1995).

### Granular activated carbon (GAC)

GAC is a highly porous, effective adsorbent widely used for drinking water treatment for color, odor, taste and organic contaminants including NOM removal. GAC has macroporous, rough surfaces with widely distributed fissures and ridges in contrast with the non-porous smooth surfaces of sand filters. The mechanism of DOC removal by GAC is represented in Figure 3(b). The total organic carbon (TOC) concentration was found to be lower in GAC-filtered water than in sand-filtered water (Hyde *et al.* 1987). The adsorption process of the GAC mainly depends on the surface area, pore structure and surface chemistry (Moreno-Castilla 2004). The rough surfaces of GAC also provide an excellent site for microbial attachment and provide shelter to newly attached bacteria, protecting them from shear forces that are a major hindrance during biofilm development. The type of GAC also plays a very important role in DOC removal and biodegradation occurring in the biofilters or biologically activated carbon filters (BAC) (Karanfil *et al.* 1999). GACs are either chemically or steam activated and are prepared from different sources such as coconut husk, wood or coal. Various studies reported steam activated coal based carbon to be the best adsorbent for DOC removal (Yapsakli & Çeçen 2010). The major advantage of GAC in terms of adsorption is that it can adsorb both readily and slowly biodegradable organics although higher molecular weight compounds are not easily removed by GAC due to their larger size (sieving effect), whereas intermediate and lower molecular weight compounds are easy to remove (Yan *et al.* 2006; Xing *et al.* 2008). GAC filtration is suggested to be most effective in the removal of intermediate molecular weight compounds (IMWs). The GAC, which has bioactivity on its surface and removes a significant amount of DOC by biodegradation, is called biological activated carbon (BAC) (Nishijima & Speitel 2004). Pre-treatment of water supplied to GAC may lead to increased BAC performance. Therefore, in the case of pre-treatment before GAC, such as oxidation where all the non-biodegradable DOC is converted to biodegradable DOC (BDOC), it becomes easier to remove the BDOC fraction by BAC (Yapsakli & Çeçen 2010).

The effect of each unit process on organic matter removal needs to be assessed to obtain a better

perspective while choosing the appropriate water treatment process for enhanced NOM removal. One such study has been conducted by Chen *et al.* (2007), who reported the effect of conventional processes (along with different modifications) on organic matter removal. The effect of different process parameters in terms of TOC, UV<sub>254</sub>, TTHMFP (total trihalomethane formation potential), THAAFP (total haloacetic acid formation potential) reduction was reported. Maximum removal was 30, 36, 41 and 55% for TOC, UV<sub>254</sub>, TTHMFP and THAAFP respectively (Chen *et al.* 2007). The effect of different treatment processes in drinking water treatment plants on DOC and THMFP reduction is described in Table 7.

### AOPS

NOMs act as a forerunner to DBPs and conventional removal processes such as coagulation, filtration etc. do not guarantee the total NOM removal or reduction in DBP formation potential (DBPFP) (Moncayo-Lasso *et al.* 2008). A well-explained review on removal of NOM from drinking water by AOPs is given by Matilainen & Sillanpää (2010). The next section will cover the advancements in AOP for NOM removal in the last 10 years.

AOPs involve the generation of highly reactive radical intermediates, especially the OH<sup>•</sup> radical (Glaze *et al.* 1987). The advantage of AOPs is the conversion of high molecular weight (hydrophobic) organic compounds (HMWs) into low molecular weight (hydrophilic) organic compounds (LMWs) with a system operating at ambient pressure and temperature and sometimes complete mineralization. Most studies suggest HMWs to be the root precursor of DBPs (Zhang & Jian 2006; Liu *et al.* 2010). The factors that make OH<sup>•</sup> radical advantageous over other oxidants are its higher oxidizing capacity (Table 8), non-selective nature and the fact that the reaction rate constant of OH<sup>•</sup> radical with organic species is usually several orders of magnitude higher than oxidation processes, as shown in Table 9. Westerhoff *et al.* (2007) studied the reaction of several dissolved organic matter surrogates and have established their reaction rate constants, as demonstrated in Table 10.

**Table 7** | DOC reduction by different water treatment processes

Process	% DOC reduction	Possible mechanism	Impact on THM formation/reduction	References
Coagulation-flocculation/sedimentation				
	40–60%	Adsorption Entrapment Complexation Destabilization Enmeshment	Effective in TOC reduction, correlation with THMFP is not well established, although considerable removal of HMW fraction is observed in many studies	Musikavong <i>et al.</i> (2005), Uyak & Toroz (2007) and Zhao <i>et al.</i> (2014)
Filtration				
Rapid sand filtration	21–23%	Adsorption Biodegradation	Effective to some extent	Korth <i>et al.</i> (2001)
Slow sand filtration	15%	Physical straining Adsorption Biodegradation	Relatively less effective in DBPFP reduction	Collins <i>et al.</i> (1992)
Membrane filtration	10%	Physical barrier	Requires additional inputs like pre-coagulation for targeting DBP precursors	Vickers <i>et al.</i> (1995) and Yan <i>et al.</i> (2006)
Membrane filtration with coagulation	5–70%	Pretreatment before filtration	Maintenance issue will hamper the quality of the water	
GAC				
	33.7%	Adsorption Entrapment	Effective in first six months of operation, after that efficiency decreased. Also, requires continuous maintenance for, for example, GAC regeneration or replacement	Kim & Kang (2008)
AOP				
	O <sub>3</sub> /H <sub>2</sub> O <sub>2</sub> – 10–70% UV/H <sub>2</sub> O <sub>2</sub> – 11–60% O <sub>3</sub> /UV – 30–70% UV – 1–2% O <sub>3</sub> – 6–41% UV/TiO <sub>2</sub> – 65–70% Fenton Reagent – 80–85% Photo Fenton Reagent – 70–80%	OH <sup>•</sup> radical generated NOM mineralization	Effective but costly. The extent of NOM mineralization depends on various factors, i.e. ozone dose, UV dose, H <sub>2</sub> O <sub>2</sub> dose and reaction time	Bekbolet <i>et al.</i> (2005), Chin & Bérubé (2005), Wang <i>et al.</i> (2006) and Lamsal <i>et al.</i> (2011)
BAC				
	20–40%	Bioadsorption	Effective in DOC and THM removal; more practical than GAC alone	Gibert <i>et al.</i> (2013a, 2013b)
AOP-BAC				
	60–70%	Oxidation (partial mineralization) followed by biodegradation	Very effective	Toor & Mohseni (2007) and Sarathy <i>et al.</i> (2011)

The most commonly used combination for AOPs is O<sub>3</sub>/H<sub>2</sub>O<sub>2</sub>, UV/H<sub>2</sub>O<sub>2</sub>, UV/O<sub>3</sub>, Fe<sup>2+</sup>/H<sub>2</sub>O<sub>2</sub>, Fe<sup>2+</sup>/H<sub>2</sub>O<sub>2</sub> + hv, vacuum UV (VUV), and UV/TiO<sub>2</sub>. The first free radicals

are generated followed by a chain of reactions as shown in Table 11. The reaction of NOM with OH<sup>•</sup> radical occurs in three ways (Matilainen & Sillanpää 2010):

**Table 8** | Oxidation potential of some common species (Parsons 2004)

Species	Oxidation potential (V)
Fluorine	3.03
Hydroxyl radical	2.80
Atomic oxygen	2.42
Ozone	2.07
Hydrogen peroxide	1.78
Perhydroxyl radical	1.70
permanganate	1.68
Hypobromous acid	1.59
Chlorine dioxide	1.57
Hypochlorous acid	1.49
Chlorine	1.36

**Table 9** | Reaction rate constant; comparison of ozone and hydroxyl radical (Parsons 2004)

Species	Reaction rate constant between oxidant and organic species	
	O <sub>3</sub>	HO <sup>•</sup>
Benzene	2	7.8 × 10 <sup>9</sup>
Toulene	14	7.8 × 10 <sup>9</sup>
Chlorobenzene	0.75	4 × 10 <sup>9</sup>
Trichloroethylene	17	4 × 10 <sup>9</sup>
Tetrachloroethylene	<0.1	1.7 × 10 <sup>9</sup>
m-butanol	0.6	4.6 × 10 <sup>9</sup>
t-butanol	0.03	0.4 × 10 <sup>9</sup>

**Table 10** | Hydroxyl radical reaction rate constants at near neutral pH levels (pH 7–9) for model NOM compounds (Westerhoff *et al.* 2007)

Representative compound	k <sub>•OH</sub> (×10 <sup>8</sup> M <sup>-1</sup> s <sup>-1</sup> )
Salicylic acid	120
Citric acid	3
Tartaric acid	14
Catechol	110
Phthalic acid	59
Hydroquinone	52
Camphor	41
Oxalic acid	1
Benzaldehyde	44
Cysteine	190

1. addition of OH<sup>•</sup> radical to double bond;
2. H-atom abstraction yielding a carbon centered double bond which can react rapidly with oxygen to form organic peroxy radicals which can subsequently lead to the production of aldehyde, ketone or CO<sub>2</sub>;
3. OH<sup>•</sup> radical gaining electron from organic species.

Ozonation can also be considered as an AOP in the case of higher pH values and in combination with peroxide. Ozone is unstable in water and tends to decompose rapidly and another major oxidant that is formed from ozone decomposition in water is OH<sup>•</sup> radical. Table 11 shows the reaction mechanism of ozone with NOM.

The extent of NOM mineralization depends on various factors, i.e. radiation dose, oxidant dose and reaction time. Factors that affect radical formation are mainly pH, temperature, presence of ions, pollutant type as well as presence of scavenging agents such as bicarbonate ion. The rate of oxidation is dependent on radical, NOM and oxygen concentration. This section also combines the literature from 2000–2018 on various studies of AOP for NOM removal, as explained in Table 12.

## BAC

The GAC which has bioactivity on its surface and removes a significant amount of DOC by biodegradation is called biological activated carbon (BAC) (Nishijima & Speitel 2004). BAC is one of the most promising, eco-friendly and economically feasible processes for enhancing water treatment performance. BAC is advantageous compared to GAC as eventually adsorption sites become saturated with organics leading to GAC exhaustion. The biofilm formation starts over the rough porous surface of GAC and bacterial colonization starts utilizing organics on the surface as the food source. The biofilm developed has the potential to degrade organic pollutants, including biodegradable organic matter by biodegradation, therefore prolonging the life of the carbon bed and without requiring regeneration like GAC (Dong *et al.* 2015; Korotta-Gamage & Sathasivan 2017). Since microbes are attached to the surface, the supply of organics or substrate to microbes in biofilm is mainly controlled by a bulk and surface transport phenomenon. The

**Table 11** | Reaction mechanism of few AOPs

UV/H <sub>2</sub> O <sub>2</sub>	O <sub>3</sub> /H <sub>2</sub> O <sub>2</sub>	O <sub>3</sub> /UV	O <sub>3</sub> (Von Gunten (2003))
H <sub>2</sub> O <sub>2</sub> + <i>hν</i> → 2OH·	O <sub>3</sub> + H <sub>2</sub> O + <i>hν</i> → (2OH·) → H <sub>2</sub> O <sub>2</sub>	O <sub>3</sub> + <i>hν</i> + H <sub>2</sub> O → 2OH· + O <sub>2</sub>	Initiation
·OH + H <sub>2</sub> O <sub>2</sub> → H <sub>2</sub> O + HO <sub>2</sub> · + H <sub>2</sub> O	H <sub>2</sub> O <sub>2</sub> + <i>hν</i> → 2OH·	O <sub>3</sub> + OH· → HO <sub>2</sub> · + O <sub>2</sub>	O <sub>3</sub> + OH· → HO <sub>2</sub> · + O <sub>2</sub>
HO <sub>2</sub> · + H <sub>2</sub> O <sub>2</sub> → ·OH + H <sub>2</sub> O + O <sub>2</sub>	O <sub>3</sub> + OH· → HO <sub>2</sub> · + O <sub>2</sub>	O <sub>3</sub> + HO <sub>2</sub> · → OH· + 2O <sub>2</sub>	O <sub>3</sub> + HO <sub>2</sub> · → OH· + O <sub>2</sub>
·OH + HO <sub>2</sub> · → HO <sub>2</sub> + OH <sup>-</sup>	H <sub>2</sub> O <sub>2</sub> ⇌ HO <sub>2</sub> · + H <sup>+</sup> pK = 11.7	OH· + HO <sub>2</sub> · → H <sub>2</sub> O + O <sub>2</sub>	O <sub>3</sub> + O <sub>2</sub> · → O <sub>3</sub> · + O <sub>2</sub>
2OH <sub>2</sub> → H <sub>2</sub> O <sub>2</sub> + O <sub>2</sub>	HO <sub>2</sub> · + O <sub>3</sub> → HO <sub>2</sub> + O <sub>3</sub>	2OH· → H <sub>2</sub> O <sub>2</sub>	pH < 8
·OH + HO <sub>2</sub> → H <sub>2</sub> O + O <sub>2</sub>	HO <sub>2</sub> · ⇌ H + + O <sub>2</sub> ·		O <sub>3</sub> · + H <sup>+</sup> ⇌ HO <sub>3</sub>
2·OH → H <sub>2</sub> O <sub>2</sub>	O <sub>2</sub> · + O <sub>3</sub> → O <sub>2</sub> + O <sub>3</sub> ·		HO <sub>3</sub> → OH· + O <sub>2</sub>
	O <sub>3</sub> · + H → HO <sub>3</sub> · → HO· + O <sub>2</sub>		pH > 8
			O <sub>3</sub> · ⇌ O· + O <sub>2</sub>
			O· → OH· + OH <sup>-</sup>
			OH· + O <sub>3</sub> → HO <sub>2</sub> + O <sub>2</sub>
			Propogation
			OH· + NOM1 → NOM1· + H <sub>2</sub> O or
			NOM1· + OH <sup>-</sup>
			NOM1· + O <sub>2</sub> → NOM-O <sub>2</sub> · → NOM1 + O <sub>2</sub> ·
			Termination
			OH· + NOM2 → NOM2· + H <sub>2</sub> O
			NOM2· + O <sub>2</sub> → NOM2-O <sub>2</sub> · → no O <sub>2</sub> · formation
			OH· + CO <sub>3</sub> <sup>2-</sup> → CO <sub>3</sub> · + OH <sup>-</sup>
			OH· + HCO <sub>3</sub> <sup>-</sup> → CO <sub>3</sub> · + H <sub>2</sub> O

substrate must be transported from the liquid phase to the biofilm outer surface and then to microbes inside the biofilm by diffusion. The factors that affect the rate of substrate utilization within a biofilm are: (a) substrate transfer to biofilm; (b) diffusion of substrate into the biofilm; (c) substrate utilization within the biofilm; (d) substrate growth yield; and (e) biofilm detachment.

Other factors affecting BAC performance are as follows:

- (a) **Filter media and characteristics:** Media characteristics play a huge role in pollutant removal and the choice of media depends on type of pollutant to be removed. In the case of drinking water pollutants, GAC is the best media type, though GAC particle size has been shown to have little to no effect on NOM removal (Velten *et al.* 2011).
- (b) **EBCT:** This is a key design and operational parameter of any biofilter. The removal of organics usually increase with increase in EBCT up to optimum value (Laurent *et al.* 1999). Han *et al.* (2013) compared up-flow (UBACF) and down-flow (DBACF) BACs and showed that the retention time for UBACF (10 min) was slightly higher than DBACF (8 min) due to 25% bed expansion

in the case of UBACF. The NOM removal by BAC took place in two phases, the first phase being the start-up phase in which non-ozonated feed water was directly supplied to initiate bacterial colonization; and the second phase is steady state of biodegradation in which bacterial respiration and biomass assimilation accounted for most of the NOM removal. Most of the studies suggest that it takes around 60–90 days to achieve the steady state (Velten *et al.* 2011; Han *et al.* 2013). In the start-up phase, NOM removal efficiency of DBACF was slightly higher than UBACF whereas in the steady phase removal efficiency of UBACF was 10% higher than DBACF.

- (c) **Backwashing:** It is important to use an appropriate backwashing technique for filter backwashing to maintain the microbial attachment on the BAC surface and to restore head losses (Miltner *et al.* 1995; Ahmad & Amirtharajah 1998; Putz *et al.* 2005). Though backwashing is an important aspect to be considered while running a BAC system, a few studies neglected backwashing for the sake of an in-depth depth study of the overall distribution of biomass over the BAC bed (Gibert *et al.* 2013a, 2013b).

**Table 12** | Studies on AOP for NOM reduction

Target compound	AOP type and dose	Sample matrix	Objective	Parameter monitored	Result summary	Screened AOP	Reference
TOC, THM and HAA	UV, O <sub>3</sub> , O <sub>3</sub> /UV, H <sub>2</sub> O <sub>2</sub> /UV H <sub>2</sub> O <sub>2</sub> /O <sub>3</sub> O <sub>3</sub> = 4.04 ± 0.110 mg/L UV = 1,140 mJ/cm <sup>2</sup>	French River water, Nova Scotia, Canada	AOP screening for TOC, THM, HAA and UV <sub>254</sub> reduction	UV <sub>254</sub> , TOC, THMFP, HAAFP	1. UV or O <sub>3</sub> alone were not sufficient enough for TOC and UV <sub>254</sub> reduction 2. O <sub>3</sub> /UV was able to achieve highest NOM reduction with 31% TOC and 88% UV <sub>254</sub> reduction 3. THM and HAA formed were most effectively removed by H <sub>2</sub> O <sub>2</sub> /UV system under uniform operating conditions which may be due to higher doses of UV and H <sub>2</sub> O <sub>2</sub> leading to generation of higher levels of HO radicals that consequently oxidize THM and HAA precursor, particularly HMW compounds	UV/H <sub>2</sub> O <sub>2</sub>	Lamsal <i>et al.</i> (2011)
DBPs, Fractionated NOM	UV/H <sub>2</sub> O <sub>2</sub> (450 W high pressure mercury lamp)	WTP water (high DOC), Taiwan	To find the effectiveness of UV/H <sub>2</sub> O <sub>2</sub> system for NOM removal and removal of fractionated NOMs	DOC, THMFP	UV/H <sub>2</sub> O <sub>2</sub> and conventional systems targeted mainly hydrophobic acid part, which was also shown to be the main precursor of THM formation after chlorination	UV/H <sub>2</sub> O <sub>2</sub>	Lin & Wang (2011)
NOM	UV/H <sub>2</sub> O <sub>2</sub> (UV fluence: 2000 mJ/cm <sup>2</sup> ) Low pressure mercury amalgam lamp; H <sub>2</sub> O <sub>2</sub> = 10 ppm	Reservoir water, British Columbia, Canada	To determine molecular distribution of NOM and bio stability of different source water after AOP treatment	AOC, BDOC	UV/H <sub>2</sub> O <sub>2</sub> increased the smaller organics by breaking down the complex organic molecules into simpler ones, subsequently increasing the AOC and BDOC of the sample water	UV/H <sub>2</sub> O <sub>2</sub>	Bazri <i>et al.</i> (2012)
NOM	UV/H <sub>2</sub> O <sub>2</sub> UV dose = 0–1,500 mJ/cm <sup>2</sup> Low pressure mercury lamp (27.7 W); H <sub>2</sub> O <sub>2</sub> = 20 ppm	Raw and unfiltered surface water. British Columbia, Canada	To study the effect of UV/H <sub>2</sub> O <sub>2</sub> AOP on spectral characteristics, hydrophobicity, and biodegradability of NOM	TOC, BDOC	UV/H <sub>2</sub> O <sub>2</sub> was capable of mineralizing NOM (15–27%) at higher UV fluence AOP was capable of converting recalcitrant NOM into more biodegradable compounds like formaldehyde Thus indicating the need for any downstream process for improving biological stability of the water	UV/H <sub>2</sub> O <sub>2</sub> (high fluence)	Sarathy & Mohseni (2008)
Humic substances	Heterogeneous catalytic ozonation with bone charcoal as catalyst H <sub>2</sub> O <sub>2</sub> = 0.015 M; O <sub>3</sub> = 0.5 mg/L	Synthetic humic acid	To study degradation kinetics of humic acids	TOC, UV <sub>254</sub>	Heterogeneous catalytic ozonation was able to achieve 97.5% humic acid and 38% TOC reduction	Catalytic ozonation with bone charcoal	Mortazavi <i>et al.</i> (2010)

(continued)

Table 12 | continued

Target compound	AOP type and dose	Sample matrix	Objective	Parameter monitored	Result summary	Screened AOP	Reference
NOM	UV/H <sub>2</sub> O <sub>2</sub> , UV/per carbonate, and UV/perborate (UV fluence: 2.6–26.1 J cm <sup>-2</sup> ; Low-pressure UV lamp (8 W); H <sub>2</sub> O <sub>2</sub> dose = 100 mg L <sup>-1</sup> )	Storm water treatment area, Florida	Screening of three AOPs for NOM reduction	DOC, UV <sub>254</sub>	1. All of the three AOPs were able to reduce aromatic carbon (UV <sub>254</sub> ) by 46–66% and DOC by 11–19% 2. Reduction was better in terms of UV <sub>254</sub> for all three oxidants whereas for DOC, H <sub>2</sub> O <sub>2</sub> performed statistically better followed by perborate and per carbonate respectively	UV/H <sub>2</sub> O <sub>2</sub>	Sindelar <i>et al.</i> (2014)
NOM	1. Ozonation (2.2 g O <sub>3</sub> /m <sup>3</sup> ) 2. O <sub>3</sub> /H <sub>2</sub> O <sub>2</sub> process (2.2 g O <sub>3</sub> /m <sup>3</sup> ; H <sub>2</sub> O <sub>2</sub> : O <sub>3</sub> = 1:2) 3. O <sub>3</sub> /H <sub>2</sub> O <sub>2</sub> process (2.2 g O <sub>3</sub> /m <sup>3</sup> ; H <sub>2</sub> O <sub>2</sub> :O <sub>3</sub> = 2:1)	Ground water, Central Banat, Republic of Serbia	To study NOM removal at water treatment plant (by modifying conventional treatment schematics)	DOC, UV <sub>254</sub> , SUVA	The pre-oxidation step increased the overall DOC and UV <sub>254</sub> removal	O <sub>3</sub> /H <sub>2</sub> O <sub>2</sub> with higher ozone in higher ratio than H <sub>2</sub> O <sub>2</sub> (2:1)	Tubić <i>et al.</i> (2011)
NOM	UV/H <sub>2</sub> O <sub>2</sub> UV fluence = up to 1,500 mJ/cm <sup>2</sup> ; low pressure mercury lamp; collimated beam set-up; H <sub>2</sub> O <sub>2</sub> = 15 mg/L	Reservoir water, British Columbia, Canada and DAX-8 fractionated water	To study the impact of UV/H <sub>2</sub> O <sub>2</sub> on NOM's aromaticity, hydrophobicity, and potential to form THM and HAAs	TOC, UV <sub>254</sub> , THMFP, HAAFP	1. There was a decrease in UV <sub>254</sub> value but not a significant reduction in TOC, indicating partial oxidation of NOM 2. Removing the hydrophobic fraction before oxidation led to complete mineralization of NOM and subsequently DBPFP	UV/H <sub>2</sub> O <sub>2</sub> with pre-treatment	Sarathy & Mohseni (2010)
NOM	Fenton process	Ground water, Serbia	Impact of Fenton process on TOC and THMFP reduction	TOC, THMFP, HAAFP, HANFP, HKFP	1. THMFP and HAAFP was reduced by 90% (at higher doses) 2. TOC removal was higher during coagulation 3. Aldehyde, ketone, halo nitriles increased during the oxidation process	Fenton reagent (higher doses)	Molnar <i>et al.</i> (2011)
NOM, turbidity, particular matter	O <sub>3</sub> /H <sub>2</sub> O <sub>2</sub> O <sub>3</sub> = 2–2.3 mg/L; H <sub>2</sub> O <sub>2</sub> = 0.2 mg/L	Lake Huron Water, Canada	Impact on turbidity, particles and organic matter removal	DOC, UV <sub>254</sub>	1. Better particle and turbidity removal than conventional treatment process. 2. AOP decreased UV <sub>254</sub> but no change in DOC values	1. Higher particle removal efficiency than conventional process 2. Not effective in DOC reduction but UV <sub>254</sub> was reduced substantially	Rahman <i>et al.</i> (2010)
THMFP, PPCP, EDC	Ozone and UV/H <sub>2</sub> O <sub>2</sub>	Surface water and ground water, Ontario, Canada	To study conventional process, ozone and UV/H <sub>2</sub> O <sub>2</sub> for removal of emerging contaminants and THM-FPs	THMFP	1. Ozone + conventional treatment provided excellent THM-FP removal 2. Conventional + UV/H <sub>2</sub> O <sub>2</sub> treatment demonstrated an increase in THM-FP	Conventional followed by ozonation was most effective	Borikar <i>et al.</i> (2015)

- (d) **Temperature:** Bacterial activity tends to increase with temperature increase within a range of 10–30 °C because this temperature range is favorable to bioactivity of many bacterial communities (Billen *et al.* 1992; Chaudhary *et al.* 2003).
- (e) **Pre-oxidation:** BACs mainly target the lesser complex or LMW organic compounds and have been shown to reduce the chemical dose, i.e. chlorine, coagulant etc. (Seredyńska-Sobecka *et al.* 2006), thereby increasing the performance of the BAC filter.
- (f) **Depth of the filter:** The apparent BET surface area of GAC particles tends to decrease faster in the top portion of the DBACF over time, indicating a higher level of adsorption and thus NOM removal in the upper portion of the filter (Moore *et al.* 2001). Also, bacterial growth varies along the depth of the filter; in UBACF, the highest attached biomass concentration is mainly found in the middle because of the presence of oxidant at the entry preventing microbial growth at the bottom of the filter (Urfer & Huck 2001; Han *et al.* 2013; Fu *et al.* 2017) whereas in DBACF the highest biomass concentration is found at the top and decreases along the depth due to nutrient limitation (Servais *et al.* 1994).
- (g) **Biomass concentration:** The performance of BAC is dependent on the attached biomass concentration, which varies separately in UBACF and DBACF filters. UBACF tend to show better NOM removal performance because of the more diverse microbial environment and more even distribution of species in UBACF than DBACF. This higher NOM removal efficiency may be attributed to the easy wash out of deposited extracellular metabolites in UBACF leading to enhanced biological activity and thus biodegradation of NOM. The characterization of biofilm, i.e. predicting their occurrence and behavior especially in a full-scale drinking water treatment plant, is still not a much studied topic and requires an in-depth study from a research point of view (Gibert *et al.* 2013a, 2013b).

## AOP-BAC

NOM removal by AOP can lead to mineralization of organic matter but with higher energy requirements and

thus cost inputs. Oxidation is generally achieved at higher doses, as lower doses are proven to be insufficient for DOC reduction (Toor & Mohseni 2007; Sarathy *et al.* 2011). Therefore, for achieving economic viability of the system, integration of AOP with a biological system like BAC is the best possible alternative. The AOP in conjunction with BAC takes advantage of the partial oxidation products formed by AOP that are further utilized by microbes in BAC as substrate, thereby minimizing the DOC to the best possible concentration. NOM is partially oxidized and HMW compounds are transformed into smaller and more biodegradable compounds such as carboxylic acids and aldehydes (which are byproducts in the case of ozonation). Hydrogen peroxide is the most commonly used oxidant in AOPs, which remains unchanged in treated water and needs to be removed; BAC aids in that also. Sarathy *et al.* (2011) showed that raw water spiked with 10–12 mg/L of H<sub>2</sub>O<sub>2</sub> after passing through the BAC column for 10 days (EBCT = 4.2 min) showed a 93% reduction in H<sub>2</sub>O<sub>2</sub> and a 100% reduction with EBCT of 20 min. This H<sub>2</sub>O<sub>2</sub> degradation in BAC can be attributed to the presence of catalase produced by bacterial species to protect themselves from external H<sub>2</sub>O<sub>2</sub>. A few studies that utilized AOP in conjunction with BAC for DOC removal are shown in Table 13.

## ECONOMIC FEASIBILITY IN TERMS OF ELECTRICAL ENERGY PER ORDER (E<sub>EO</sub>)

E<sub>EO</sub> is a figure of merit measure for electrical efficiency of the system. E<sub>EO</sub> is the amount of electrical energy (kW h) required to reduce contaminant by one order of magnitude in 1 m<sup>3</sup> of water (Bolton *et al.* 1995; Sindelar *et al.* 2014):

$$E_{EO} = \frac{Pt}{V \log C_i/C_f} \text{ Batch system} \quad (1)$$

$$E_{EO} = \frac{P}{F \log C_i/C_f} \text{ Flow through systems} \quad (2)$$

where  $P$  is lamp power (kW);  $t$  is time (hours);  $V$  is volume irradiated (L);  $C_i$  is initial concentration of the contaminant;  $C_f$  is final concentration of the contaminant;  $E_{EO}$  is units

**Table 13** | Studies on AOP-BAC for NOM reduction

Target compound	AOP type	BAC features	Study scale	Sample matrix	Parameter monitored	Result summary	Biodegradability	Economic importance	Reference
THM/HAA	UV/H <sub>2</sub> O <sub>2</sub> Low-pressure mercury UV lamp: UV fluence = 0–3,500 mJ/cm <sup>2</sup> H <sub>2</sub> O <sub>2</sub> = 0–25 mg/L AOP-BAC cut-offs for doses: UV fluence = 500 mJ/cm <sup>2</sup> H <sub>2</sub> O <sub>2</sub>	Up-flow	Lab-scale	Raw water, Canada	NPOC, UV <sub>254</sub> , THM-FP, DCAA-FP, TCAA-FP	1. Higher UV fluence (>1,000 mJ cm <sup>-2</sup> ) and H <sub>2</sub> O <sub>2</sub> concentration (25 mg L <sup>-1</sup> ) were effective in reducing DBP. 2. Combined AOP-BAC showed reductions of 43, 52, and 59% for DBPs, TOC, and UV <sub>254</sub> , respectively whilst using lower UV doses	BDOC concentration increases	Combined AOP-BAC increases the overall efficiency of DBP reduction while maintaining the cost of AOP involved	Toor & Mohseni (2007)
DOC, THM	Ozone, UV/H <sub>2</sub> O <sub>2</sub> Ozone dose = 1–2 mg O <sub>3</sub> /mg DOC; H <sub>2</sub> O <sub>2</sub> = 10 ppm; Low pressure mercury UV lamp (5.7 kW), UV fluence = 2,000–4,000 mJ/cm <sup>2</sup>	Up-flow	Lab-scale, Vancouver, British Columbia	Pond water, Vancouver, British Columbia	DOC, UV <sub>254</sub> , DBP	Oxidant does not react preferentially with biodegradable or non-biodegradable part of DOC	Oxidation before biofiltration increased the BDOC concentration and overall DOC removal but not rate of biodegradation	Oxidation followed by biofiltration increased the overall DOC removal efficiency with lower energy inputs	Black & Bérubé (2014)
DBP	UV/H <sub>2</sub> O <sub>2</sub> , low-pressure (2 kW) and medium pressure (11.7 kW) UV amalgam lamp, H <sub>2</sub> O <sub>2</sub> = 10 mg/L; EBCT = 20 min	Up-flow	Pilot scale	Raw surface water, Fanshawe Lake, London, Ontario, Canada	THMFP, HAAFP, BDOC	Formation of DBP reduced up to 60% for THMs and 75% for HAAs	Partial oxidation by UV/H <sub>2</sub> O <sub>2</sub> AOP led to decrease in aromaticity, subsequently increasing the biodegradability. BAC also removed the biodegradable products and residual H <sub>2</sub> O <sub>2</sub> effectively	UV/H <sub>2</sub> O <sub>2</sub> -BAC proved to be efficient in terms of THM-HAA reduction both in terms of cost and performance	Sarathy <i>et al.</i> (2011)
NOM surrogates	UV-C, UV/H <sub>2</sub> O <sub>2</sub> and VUV UV fluence = 0–200 J/cm <sup>2</sup> , H <sub>2</sub> O <sub>2</sub> = 68 mg/L	Sand filter plus BAC	Lab-scale	Synthetic water	BDOC, HAAFP	AOP for the sample water with high amino acid concentration (especially glutamic acid and leucine) led to an increase in HAA levels	Downstream BAC was able to remove amino acid but HAAFP of hydrophilic acids increased		Bond <i>et al.</i> (2009)
THM, HAA	O <sub>3</sub> , O <sub>3</sub> /TiO <sub>2</sub> O <sub>3</sub> dose = 0–10 mg/L	FBR (carbon based)	Lab-scale	River water	DOC, BDOC, SUVA, UV	Ozonation/catalytic ozonation tend to decrease UV <sub>254</sub> , SUVA, THM and HAA precursor values but increased the formation of ozonated byproducts like formaldehyde and acetaldehyde	Biofiltration was able to remove these ozonated byproducts		Chen & Wang (2012)

(continued)

Table 13 | continued

Target compound	AOP type	BAC features	Study scale	Sample matrix	Parameter monitored	Result summary	Biodegradability	Economic importance	Reference
TOC, COD <sub>Mn</sub> , THMFP, THAAFP	O <sub>3</sub> , O <sub>3</sub> dose = 1–2.5 mg/L	BAC	Pilot scale	River water	TOC, UV <sub>254</sub> , THMFP and HAAFP	O <sub>3</sub> -BAC COD <sub>Mn</sub> (36%) TOC (32%) UV <sub>254</sub> (54%) THMFP (24%) HAAFP (48%)	Conventional-O <sub>3</sub> -BAC has led to decrease in COD <sub>Mn</sub> (55%) TOC (42%) UV <sub>254</sub> (61%) THMFP (68%) HAAFP (23%) AOC (67%)	The efficiency of each unit process and different combinations were investigated in this study to choose the water treatment processes for the future. Combining conventional techniques with O <sub>3</sub> -BAC is the best possible solution for organic matter removal	Chen <i>et al.</i> (2007)
TOC, THM, HAA	Ozone/UV; O <sub>3</sub> dose = 2.7–3.0 mg/L, UV irradiance = 240 mW s/cm <sup>2</sup> (15 W), EBCT = 15–25 min	BAC	Pilot scale	River water	THM, HAA TOC, DOC, UV <sub>254</sub> , and SUVA	TOC, DOC, UV <sub>254</sub> , and SUVA removal 19.1, 17.6, 30.7, and 16.4%, THM: 70.6% and HAA 67.6%	BDOC increased after oxidation which made subsequent organic matter removal easy		Trang <i>et al.</i> (2014)
	Ozone vs O <sub>3</sub> /H <sub>2</sub> O <sub>2</sub> 1. ozonation (3.0 g O <sub>3</sub> /m <sup>3</sup> ); 2. H <sub>2</sub> O <sub>2</sub> /O <sub>3</sub> (3.3 g O <sub>3</sub> /m <sup>3</sup> ); H <sub>2</sub> O <sub>2</sub> :O <sub>3</sub> = 1:1	GAC	Pilot	Ground water	As, THM, HAA	Two modifications to conventional process of treating water were made as follows: 1. Using Polyaluminium chloride in combination with ferric chloride for coagulation 2. Two different pre-treatment were used, one with O <sub>3</sub> and other O <sub>3</sub> -H <sub>2</sub> O <sub>2</sub> (1:1) Both the systems were followed by sand filtration and GAC	It was concluded that pre-treatment before the conventional + GAC process is the best possible solution for the removal of chlorinated DBP and arsenic		Tubić <i>et al.</i> (2010)
Trihalomethanes	Ozonation, EBCT = 15 min, O <sub>3</sub> dose = 0.65 ± 0.05 mg O <sub>3</sub> /L	BAC	Full-scale	Reservoir water	DOC, DON, BDOC, BDON, AOC	Ozonation in conversion of complex compounds into simpler ones	Biodegradability increased after ozonation (by conversion of high molecular weight compounds into lower one)		Vasyukova <i>et al.</i> (2013)
NOM	Conventional treatment followed by ozonation	BAC		Raw water	DOC, BDOC	Preferred and more effective than conventional way of organic matter removal	BDOC increased	Cost effective	Kastl <i>et al.</i> (2016)
Hydrophilic natural organic matter (NOM)	UV/TiO <sub>2</sub> , Medium pressure lamp (630 W)	BAC	Lab-scale	Water treatment plant	NPOC, UV <sub>254</sub> and THMFP	For 1 min irradiation time and 1 g L <sup>-1</sup> dose of TiO <sub>2</sub> , DOC and UV <sub>254</sub> removals were 40 and 55%, respectively. The THMFP content reduced to 144 µg L <sup>-1</sup> from 305 µg L <sup>-1</sup> in raw water 10 min treatment	Final DOC and THMFP reduction was 60 and 70%, respectively, after photocatalytic oxidation and GAC columns	Cost barrier in case of individual AOP	Philippe <i>et al.</i> (2010)

$kWh/m^3/order$ ;  $F$  is flow rate ( $m^3/h$ ) in flow through systems;  $k$  is pseudo first-order rate constant ( $min^{-1}$ ).

Equation (1) can also be expressed in terms of rate constants (Stefan & Bolton 2005):

$$E_{EO} = \frac{38.38P}{Vk}$$

$E_{EO}$  of less than 10 is generally considered as economically feasible (Andrews *et al.* 1995).  $E_{EO}$  can be calculated in terms of either DOC or  $UV_{254}$ . Various studies suggested AOP or oxidant alone is not feasible from an economical point of view, especially for water with high DOC values, giving higher  $E_{EO}$  values ( $UV_{254}$   $E_{EO}$ : 11.9–45.6, DOC  $E_{EO}$ : 43.4–196.5) (Sindelar *et al.* 2014). AOPs like  $TiO_2$  photolysis and sonolysis are not practical in terms of energy efficiency (Bolton *et al.* 1995).

## SUMMARY

Growing water demands combating heightening emerging contaminants in the water matrices calls for new advancements in the drinking water treatment sector. One such contaminant is DBP, especially THMs, which are formed upon reaction of chlorine (the most commonly used disinfectant) with NOM. THMs came into the limelight in 1970 and within the space of a year became a significant public health parameter in the USA with its first disinfection byproduct rule. Stringent guidelines are available across the globe for THMs but mostly for developed nations. The cognizance of THMs in developing nations like India is still lacking. THMs have proven to have a carcinogenic nature and thus need major focus from a public health point of view. For targeting THMs generally instead of targeting them directly, their precursors, i.e. NOM, are targeted as they are the root cause of other water quality issues in drinking water treatment industries. NOMs occur ubiquitously in surface water regimes and are site-specific too; their complexity in terms of their chemical nature makes it more difficult to treat them, especially from a THM point of view. The conventional treatment processes like coagulation, flocculation, sedimentation, filtration etc. are not able to remove NOM, especially in terms of its THMFP, and thus

require a more advanced form of treatment. AOPs are promising a technology that can completely mineralize NOM but its high performance efficiency is compensated by its high cost (higher electrical energy per order), therefore there is a need to rely on a more techno-economically feasible option. AOP in conjunction with biofiltration or BAC is one such viable option. AOP with lower energy inputs can partially oxidize NOM into simpler or more biodegradable products which can be further removed by BAC column with no or minimum cost inputs, thereby making it overall a more techno-economically feasible way of treating NOM.

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## REFERENCES

- Ahmad, R. & Amirtharajah, A. 1998 [Detachment of particles during biofilter backwashing](#). *J. Am. Water Works Assoc.* **90**, 74.
- Aiken, G. R. (ed.) 1985 *Humic Substances in Soil, Sediment, and Water: Geochemistry, Isolation, and Characterization*, Vol. 1. Wiley-Interscience, New York.
- Aiken, G., McKnight, D. M., Thorn, K. A. & Thurman, E. M. 1992 [Isolation of hydrophilic organic acids from water using nonionic macroporous resins](#). *Org. Geochem.* **18**, 567–573.
- Andrews, S. A., Huck, P. M., Chute, A. J., Bolton, J. R. & Anderson, W. A. 1995 UV oxidation for drinking water—feasibility studies for addressing specific water quality issues. In: *Proceedings of the AWWA WQTC*, New Orleans, LA, pp. 1881–1898.
- Ates, N., Kitis, M. & Yetis, U. 2007 [Formation of chlorination by-products in waters with low SUVA – correlations with SUVA and differential UV spectroscopy](#). *Water Res.* **41**, 4139–4148.
- Basu, M., Gupta, S. K., Singh, G. & Mukhopadhyay, U. 2011 [Multi-route risk assessment from trihalomethanes in drinking water supplies](#). *Environ. Monit. Assess.* **178**, 121–134.
- Bazri, M. M., Barbeau, B. & Mohseni, M. 2012 [Impact of UV/h<sub>2</sub>O<sub>2</sub> advanced oxidation treatment on molecular weight distribution of NOM and biostability of water](#). *Water Res.* **46**, 5297–5304.
- Bekbolet, M., Uyguner, C. S., Selcuk, H., Rizzo, L., Nikolaou, A. D., Meric, S. & Belgiorno, V. 2005 [Application of oxidative removal of NOM to drinking water and formation of disinfection by-products](#). *Desalination* **176**, 155–166.

- Bellar, T. A., Lichtenberg, J. J. & Kroner, R. C. 1974 The occurrence of organohalides in chlorinated drinking waters. *J. Am. Water Works Assoc.* **66**, 703–706.
- Berggren, M., Bergström, A.-K. & Karlsson, J. 2015 Intraspecific autochthonous and allochthonous resource use by zooplankton in a humic lake during the transitions between winter, summer and fall. *PLoS ONE* **10**, e0120575.
- Billen, G., Servais, P., Bouillot, P. & Ventresque, C. 1992 Functioning of biological filters used in drinking water treatment—the Chabrol model. *Aqua* **41**, 231–241.
- Black, K. E. & Bérubé, P. R. 2014 Rate and extent NOM removal during oxidation and biofiltration. *Water Res.* **52**, 40–50.
- Bolton, J. R., Bircher, K. G., Tumas, W. & Tolman, C. A. 1995 Figures-of-merit for the technical development and application of advanced oxidation technologies for both electric-and solar-driven systems (IUPAC Technical Report). *Pure Appl. Chem.* **73**, 627–637.
- Bond, T. 2009 *Treatment of Disinfection Byproduct Precursors*. PhD Thesis, Cranfield University, UK.
- Bond, T., Goslan, E. H., Jefferson, B., Roddick, F., Fan, L. & Parsons, S. A. 2009 Chemical and biological oxidation of NOM surrogates and effect on HAA formation. *Water Res.* **43** (10), 2615–2622.
- Bond, T., Goslan, E. H., Parsons, S. A. & Jefferson, B. 2012 A critical review of trihalomethane and haloacetic acid formation from natural organic matter surrogates. *Environ. Technol. Rev.* **1**, 93–113.
- Borikar, D., Mohseni, M. & Jasim, S. 2015 Evaluations of conventional, ozone and UV/H<sub>2</sub>O<sub>2</sub> for removal of emerging contaminants and THM-FPs. *Water Qual. Res. J.* **50**, 140–151.
- Chaudhary, D. S., Vigneswaran, S., Ngo, H. H., Shim, W. G. & Moon, H. 2003 Biofilter in water and wastewater treatment. *Korean J. Chem. Eng.* **20** (6), 1054–1065.
- Chen, K. C. & Wang, Y. H. 2012 Control of disinfection by-product formation using ozone-based advanced oxidation processes. *Environ. Technol.* **33**, 487–495.
- Chen, C., Zhang, X., He, W., Lu, W. & Han, H. 2007 Comparison of seven kinds of drinking water treatment processes to enhance organic material removal: a pilot test. *Sci. Total Environ.* **382**, 93–102.
- Chien, C. C., Kao, C. M., Chen, C. W., Dong, C. D. & Wu, C. Y. 2008 Application of biofiltration system on AOC removal: column and field studies. *Chemosphere* **71**, 1786–1793.
- Chin, A. & Bérubé, P. R. 2005 Removal of disinfection by-product precursors with ozone-UV advanced oxidation process. *Water Res.* **39**, 2136–2144.
- Collins, M. R., Eighmy, T. T., Fenstermacher Jr, J. M. & Spanos, S. K. 1992 Removing natural organic matter by conventional slow sand filtration. *J. Am. Water Works Assoc.* **84** (5), 80–90.
- Croue, J. P., Debroux, J. F., Amy, G. L., Aiken, G. R. & Leenheer, J. A. 1999 Natural organic matter: structural characteristics and reactive properties. *Formation Control of Disinfection By-Products in Drinking Water*. American Water Works Association, Denver, CO, pp. 65–93.
- Davis, W. M., Erickson, C. L., Johnston, C. T., Delfino, J. J. & Porter, J. E. 1999 Quantitative Fourier Transform Infrared spectroscopic investigation humic substance functional group composition. *Chemosphere* **38**, 2913–2928.
- Dickenson, E. R., Summers, R. S., Croué, J. P. & Gallard, H. 2008 Haloacetic acid and trihalomethane formation from the chlorination and bromination of aliphatic  $\beta$ -dicarbonyl acid model compounds. *Environ. Sci. Technol.* **42**, 3226–3233.
- Dodds, L., King, W., Woolcott, C. & Pole, J. 1999 Trihalomethanes in public water supplies and adverse birth outcomes. *Epidemiology* **10** (3), 233–237.
- Dong, L., Liu, W., Jiang, R. & Wang, Z. 2015 Study on reactivation cycle of biological activated carbon (BAC) in water treatment. *Int. Biodeter. Biodegrad.* **102**, 209–213.
- Edzwald, J. 1993 Coagulation in drinking water treatment: particles, organics and coagulants. *Water Sci. Technol.* **27**, 21–35.
- Edzwald, J. K. & Tobiasson, J. E. 1999 Enhanced coagulation: US requirements and a broader view. *Water Sci. Technol.* **40**, 63–70.
- Fabris, R., Chow, C. W., Drikas, M. & Eikebrokk, B. 2008 Comparison of NOM character in selected Australian and Norwegian drinking waters. *Water Res.* **42**, 4188–4196.
- Farkas, L., Lewin, M. & Bloch, R. 1949 The reaction between hypochlorite and bromides. *J. Am. Chem. Soc.* **71** (6), 1988–1991.
- Fearing, D. A., Goslan, E. H., Banks, J., Wilson, D., Hillis, P., Campbell, A. T. & Parsons, S. A. 2004 Staged coagulation for treatment of refractory organics. *J. Environ. Eng.* **130**, 975–982.
- Frimmel, F. H. & Jahnel, J. B. 2003 Formation of haloforms in drinking water. In: *Haloforms and Related Compounds in Drinking Water. The Handbook of Environmental Chemistry (Water Pollution)*, vol 5/5G (A. D. Nikolaou, ed.). Springer, Berlin, Heidelberg.
- Fu, J., Lee, W. N., Coleman, C., Meyer, M., Carter, J., Nowack, K. & Huang, C. H. 2017 Pilot investigation of two-stage biofiltration for removal of natural organic matter in drinking water treatment. *Chemosphere* **166**, 311–322.
- Gallard, H. & von Gunten, U. 2002 Chlorination of phenols: kinetics and formation of chloroform. *Environ. Sci. Technol.* **36** (5), 884–890.
- Ghernaout, D. 2014 The hydrophilic/hydrophobic ratio vs. dissolved organics removal by coagulation – a review. *J. King Saud Uni. Sci.* **26**, 169–180.
- Gibert, O., Lefèvre, B., Fernández, M., Bernat, X., Paraira, M. & Pons, M. 2013a Fractionation and removal of dissolved organic carbon in a full-scale granular activated carbon filter used for drinking water production. *Water Res.* **47**, 2821–2829.
- Gibert, O., Lefèvre, B., Fernández, M., Bernat, X., Paraira, M., Calderer, M. & Martínez-Lladó, X. 2013b Characterising biofilm development on granular activated carbon used for drinking water production. *Water Res.* **47**, 1101–1110.

- Glaze, W. H., Kang, J. W. & Chapin, D. H. 1987 The chemistry of water treatment processes involving ozone, hydrogen peroxide and ultraviolet radiation. *Ozone Sci. Eng.* **9** (4), 335–352.
- Golfinopoulos, S. K. 2000 The occurrence of trihalomethanes in the drinking water in Greece. *Chemosphere* **41**, 1761–1767.
- Gomez-Alvarez, V., Pfaller, S., Pressman, J. G., Wahman, D. G. & Revetta, R. P. 2016 Resilience of microbial communities in a simulated drinking water distribution system subjected to disturbances: role of conditionally rare taxa and potential implications for antibiotic-resistant bacteria. *Environ. Sci. Water Res. Technol.* **2**, 645–657.
- Gorchev, H. G. & Ozolins, G. 1984 WHO guidelines for drinking-water quality. *WHO Chron.* **38** (3), 104–108.
- Han, L., Liu, W., Chen, M., Zhang, M., Liu, S., Sun, R. & Fei, X. 2013 Comparison of NOM removal and microbial properties in up-flow/down-flow BAC filter. *Water Res.* **47**, 4861–4868.
- Hasan, A., Thacker, N. & Bassin, J. 2010a Seasonal variation of trihalomethane formation potential in treated water supplies of Delhi City (India). *J. Environ. Sci. Eng.* **52**, 235–240.
- Hasan, A., Thacker, N. P. & Bassin, J. 2010b Trihalomethane formation potential in treated water supplies in urban metro city. *Environ. Monit. Assess.* **168**, 489–497.
- Her, N., Amy, G., McKnight, D., Sohn, J. & Yoon, Y. 2003 Characterization of DOM as a function of MW by fluorescence EEM and HPLC-SEC using UVA, DOC, and fluorescence detection. *Water Res.* **37**, 4295–4303.
- Hong, H. C., Wong, M. H. & Liang, Y. 2009 Amino acids as precursors of trihalomethane and haloacetic acid formation during chlorination. *Arch. Environ. Contam. Toxicol.* **56** (4), 638–645.
- Hua, G., Reckhow, D. A. & Abusallout, I. 2015 Correlation between SUVA and DBP formation during chlorination and chloramination of NOM fractions from different sources. *Chemosphere* **130**, 82–89.
- Hyde, R. A., Hill, D. G., Zabel, T. F. & Burke, T. 1987 Replacing sand with GAC in rapid gravity filters. *J. Am. Water Works Assoc.* **79** (12), 33–38.
- Ibrahim, M. B., Radwan, E. K., Moursy, A. S. & Bedair, A. H. 2016 Humic substances as precursors for trihalomethanes yields upon chlorination. *Desal. Water Treat.* **57** (55), 26494–26500.
- International Agency for Research on Cancer (IARC) 1999 *IARC monogr. Eval. Carcinog. Risks Hum.* **7**, 73.
- Ivahnenco, T. & Zogorski, J. S. 2006 *Sources and Occurrence of Chloroform and Other Trihalomethanes in Drinking-Water Supply Wells in the United States, 1986–2001 (No. 2006–5015)*. US Geological Survey, USA.
- Karanfil, T., Kitis, M., Kilduff, J. E. & Wigton, A. 1999 Role of granular activated carbon surface chemistry on the adsorption of organic compounds. 2. Natural organic matter. *Environ. Sci. Technol.* **33** (18), 3225–3233.
- Kastl, G., Sathasivan, A. & Fisher, I. 2016 A selection framework for NOM removal process for drinking water treatment. *Desal. Water Treat.* **57**, 7679–7689.
- Kim, J. & Kang, B. 2008 DBPs removal in GAC filter-adsorber. *Water Res.* **42**, 145–152.
- Kitis, M., Karanfil, T., Kilduff, J. E. & Wigton, A. 2001 The reactivity of natural organic matter to disinfection by-products formation and its relation to specific ultraviolet absorbance. *Water Sci. Technol.* **43**, 9–16.
- Korotta-Gamage, S. M. & Sathasivan, A. 2017 A review: potential and challenges of biologically activated carbon to remove natural organic matter in drinking water purification process. *Chemosphere* **167**, 120–138.
- Korth, A., Bendinger, B., Czekalla, C. & Wichmann, K. 2001 Biodegradation of NOM in rapid sand filters for removing iron and manganese. *Clean. Soil Air Water* **29**, 289–295.
- Krasner, S. W., McGuire, M. J., Jacangelo, J. G., Patania, N. L., Reagan, K. M. & Aietta, E. M. 1989 The occurrence of disinfection by-products in US drinking water. *J. Am. Water Works Assoc.* **81** (8), 41–53.
- Krasner, S. W., Weinberg, H. S., Richardson, S. D., Pastor, S. J., Chinn, R., Scilimenti, M. J. & Thruston, A. D. 2006 Occurrence of a new generation of disinfection byproducts. *Environ. Sci. Technol.* **40**, 7175–7185.
- Kumari, M., Gupta, S. K. & Mishra, B. K. 2015 Multi-exposure cancer and non-cancer risk assessment of trihalomethanes in drinking water supplies – a case study of Eastern region of India. *Ecotoxicol. Environ. Saf.* **113**, 433–438.
- Lamsal, R., Walsh, M. E. & Gagnon, G. A. 2011 Comparison of advanced oxidation processes for the removal of natural organic matter. *Water Res.* **45**, 3263–3269.
- Laurent, P., Prévost, M., Cigana, J., Niquette, P. & Servais, P. 1999 Biodegradable organic matter removal in biological filters: evaluation of the CHABROL model. *Water Res.* **33**, 1387–1398.
- Leenheer, J. A., Noyes, T. I., Rostad, C. E. & Davisson, M. L. 2004 Characterization and origin of polar dissolved organic matter from the Great Salt Lake. *Biogeochemistry* **69**, 125–141.
- Lin, H. C. & Wang, G. S. 2011 Effects of UV/H<sub>2</sub>O<sub>2</sub> on NOM fractionation and corresponding DBPs formation. *Desalination* **270**, 221–226.
- Liu, S., Lim, M., Fabris, R., Chow, C., Drikas, M. & Amal, R. 2010 Comparison of photocatalytic degradation of natural organic matter in two Australian surface waters using multiple analytical techniques. *Org. Geochem.* **41**, 124–129.
- Lu, J., Zhang, T., Ma, J. & Chen, Z. 2009 Evaluation of disinfection by-products formation during chlorination and chloramination of dissolved natural organic matter fractions isolated from a filtered river water. *J. Hazard. Mater.* **162** (1), 140–145.
- Matilainen, A. & Sillanpää, M. 2010 Removal of natural organic matter from drinking water by advanced oxidation processes. *Chemosphere* **80**, 351–365.
- Matilainen, A., Vepsäläinen, M. & Sillanpää, M. 2010 Natural organic matter removal by coagulation during drinking water treatment: a review. *Adv. Colloid Interface Sci.* **159**, 189–197.

- Miltner, R. J., Summers, R. S. & Wang, J. Z. 1995 Biofiltration performance: part 2, effect of backwashing. *J. Am. Water Works Assoc.* **87**, 64–70.
- Mishra, N. D., Dixit, S. C. & Srivastava, H. C. 2012 Evaluation of trihalomethane formation potential due to anthropogenic sources in the ground water of Kanpur. *J. Chem.* **9**, 693–699.
- Molnar, J. J., Agbaba, J. R., Dalmacija, B. D., Rončević, S. D., Maletić, S. P. & Kragulj, M. M. 2011 A study on the removal of natural organic matter and disinfection byproducts formation potential from groundwater using Fenton's process. *J. Adv. Oxi. Technol.* **14**, 54–62.
- Moncayo-Lasso, A., Pulgarin, C. & Benítez, N. 2008 Degradation of DBPs' precursors in river water before and after slow sand filtration by photo-Fenton process at pH 5 in a solar CPC reactor. *Water Res.* **42**, 4125–4132.
- Moore, B. C., Cannon, F. S., Westrick, J. A., Metz, D. H., Shrive, C. A., DeMarco, J. & Hartman, D. J. 2001 Changes in GAC pore structure during full-scale water treatment at Cincinnati: a comparison between virgin and thermally reactivated GAC. *Carbon* **39**, 789–807.
- Moreno-Castilla, C. 2004 Adsorption of organic molecules from aqueous solutions on carbon materials. *Carbon* **42**, 83–94.
- Mortazavi, S. B., Asgari, G., Hashemian, S. J. & Moussavi, G. 2010 Degradation of humic acids through heterogeneous catalytic ozonation with bone charcoal. *React. Kinet. Mech. Catalysis* **100**, 471–485.
- Murray, C. A. & Parsons, S. A. 2004 Removal of NOM from drinking water: Fenton's and photo-Fenton's processes. *Chemosphere* **54**, 1017–1023.
- Musikavong, C., Wattanachira, S., Marhaba, T. F. & Pavasant, P. 2005 Reduction of organic matter and trihalomethane formation potential in reclaimed water from treated industrial estate wastewater by coagulation. *J. Hazard. Mater* **127**, 48–57.
- National Cancer Institute, USA 1976 US Environmental Protection Agency, Washington, DC. Available from: [https://cfpub.epa.gov/ncea/iris/iris\\_documents/documents/toxreviews/0025tr.pdf](https://cfpub.epa.gov/ncea/iris/iris_documents/documents/toxreviews/0025tr.pdf).
- Nebbioso, A. & Piccolo, A. 2013 Molecular characterization of dissolved organic matter (DOM): a critical review. *Anal. Bioanal. Chem.* **405**, 109–124.
- Nishijima, W. & Speitel, G. E. 2004 Fate of biodegradable dissolved organic carbon produced by ozonation on biological activated carbon. *Chemosphere* **56**, 113–119.
- Parsons, S. (ed.) 2004 *Advanced Oxidation Processes for Water and Wastewater Treatment*. IWA Publishing, London.
- Philippe, K. K., Hans, C., MacAdam, J., Jefferson, B., Hart, J. & Parsons, S. A. 2010 Photocatalytic oxidation, GAC and biotreatment combinations: an alternative to the coagulation of hydrophilic rich waters? *Environmental Technology* **31** (13), 1423–1434. <https://doi.org/10.1080/09593330.2010.484074>.
- Putz, A. R., Losh, D. E. & Speitel Jr, G. E. 2005 Removal of nonbiodegradable chemicals from mixtures during granular activated carbon bioregeneration. *J. Environ. Eng.* **131** (2), 196–205.
- Rahman, M. F., Jasim, S. Y., Yanful, E. K., Ndongue, S. & Borikar, D. 2010 Advanced oxidation treatment of drinking water: Part II. Turbidity, particles and organics removal from Lake Huron water. *Ozone Sci. Eng.* **32** (5), 295–304.
- Rajan, S., Azariah, J. & Bauer, U. 1990 Trihalomethane levels in Madras public drinking water supply system and its impact on public health. *Int. J. Hyg. Environ. Med.* **189** (4), 312–332.
- Ramavandi, B., Farjadfar, S., Ardjmand, M. & Dobaradaran, S. 2015 Effect of water quality and operational parameters on trihalomethanes formation potential in Dez River water, Iran. *Water Resour. Ind.* **11**, 1–12.
- Richardson, S. D. 2003 Disinfection by-products and other emerging contaminants in drinking water. *TrAC Trends Anal. Chem.* **22**, 666–684.
- Rodriguez, M. J., Vinette, Y., Sérodes, J. B. & Bouchard, C. 2003 Trihalomethanes in drinking water of greater Québec region (Canada): occurrence, variations and modelling. *Environ. Monit. Assess.* **89**, 69–93.
- Rook, J. J. 1974 Formation of haloforms during chlorination of natural waters. *Water Treat. Exam.* **23**, 234–243.
- Rook, J. J. 1977 Chlorination reactions of fulvic acids in natural waters. *Environ. Sci. Technol.* **11**, 478–482.
- Sarathy, S. & Mohseni, M. 2008 The fate of natural organic matter during UV/H<sub>2</sub>O<sub>2</sub> advanced oxidation of drinking water A paper submitted to the Journal of Environmental Engineering and Science. *Can. J. Civil Eng.* **36** (1), 160–169.
- Sarathy, S. & Mohseni, M. 2010 Effects of UV/H<sub>2</sub>O<sub>2</sub> advanced oxidation on chemical characteristics and chlorine reactivity of surface water natural organic matter. *Water Res.* **44**, 4087–4096.
- Sarathy, S. R., Stefan, M. I., Royce, A. & Mohseni, M. 2011 Pilot-scale UV/H<sub>2</sub>O<sub>2</sub> advanced oxidation process for surface water treatment and downstream biological treatment: effects on natural organic matter characteristics and DBP formation potential. *Environ. Technol.* **32**, 1709–1718.
- Seredyńska-Sobecka, B., Tomaszewska, M., Janus, M. & Morawski, A. W. 2006 Biological activation of carbon filters. *Water Res.* **40**, 355–363.
- Servais, P., Billen, G. & Bouillot, P. 1994 Biological colonization of granular activated carbon filters in drinking-water treatment. *J. Environ. Eng.* **120**, 888–899.
- Sharma, R. N. & Goel, S. 2007 Chlorinated drinking water, cancers and adverse health outcomes in Gangtok, Sikkim, India. *J. Environ. Sci. Eng.* **49**, 247.
- Sharp, E. L., Jarvis, P., Parsons, S. A. & Jefferson, B. 2006 Impact of fractional character on the coagulation of NOM. *Colloids Surf. A Physicochem. Eng. Asp.* **286**, 104–111.
- Sillanpää, M. & Matilainen, A. 2014 NOM removal by coagulation. *Natural organic matter in water: characterization and treatment methods*. Butterworth-Heinemann, pp. 55–80. <https://doi.org/10.1016/B978-0-12-801503-2.00003-3>.
- Simpson, D. R. 2008 Biofilm processes in biologically active carbon water purification. *Water Res.* **42**, 2839–2848.

- Sindelar, H. R., Brown, M. T. & Boyer, T. H. 2014 Evaluating UV/H<sub>2</sub>O<sub>2</sub>, UV/percarbonate, and UV/perborate for natural organic matter reduction from alternative water sources. *Chemosphere* **105**, 112–118.
- Singer, P. C. 1999 Humic substances as precursors for potentially harmful disinfection by-products. *Water Sci. Technol.* **40**, 25–30.
- Stefan, M. I. & Bolton, J. R. 2005 Fundamental approach to the fluence-based kinetic and electrical energy efficiency parameters in photochemical degradation reactions: polychromatic light. *J. Environ. Eng. Sci.* **4** (S1), S13–S18.
- Suffet, I. H. & MacCarthy, P. (eds) 1988 *Aquatic Humic Substances: Influence on Fate and Treatment of Pollutants*. American Chemical Society, Washington, DC.
- Świetlik, J., Dąbrowska, A., Raczyk-Stanisławiak, U. & Nawrocki, J. 2004 Reactivity of natural organic matter fractions with chlorine dioxide and ozone. *Water Res.* **38**, 547–558.
- Tak, S. & Kumar, A. 2017 Chlorination disinfection by-products and comparative cost analysis of chlorination and UV disinfection in sewage treatment plants: Indian scenario. *Environ. Sci. Pollut. Res.* **24**, 26269–26278.
- Thacker, N. P., Kaur, P. & Rudra, A. 2002 Trihalomethane formation potential and concentration changes during water treatment at Mumbai (India). *Environ. Monit. Assess.* **73**, 253–262.
- Thurman, E. M. & Malcolm, R. L. 1981 Preparative isolation of aquatic humic substances. *Environ. Sci. Technol.* **15** (4), 463–466.
- Toor, R. & Mohseni, M. 2007 UV-H<sub>2</sub>O<sub>2</sub> based AOP and its integration with biological activated carbon treatment for DBP reduction in drinking water. *Chemosphere* **66**, 2087–2095.
- Trang, V. N., Dan, N. P., Phuong, L. D. & Thanh, B. X. 2014 Pilot study on the removal of TOC, THMs, and HAAs in drinking water using ozone/UV-BAC. *Desal. Water Treat.* **52**, 990–998.
- Tubić, A., Dalmacija, B., Agbaba, J., Ivančev-Tumbas, I., Klačnja, M. & Dalmacija, M. 2010 Tracking disinfection by-products and arsenic removal during various drinking water treatment trains. *Water Sci. Technol.* **61**, 3169–3177.
- Tubić, A., Agbaba, J., Dalmacija, B., Perović, S. U., Klačnja, M., Rončević, S. & Ivančev-Tumbas, I. 2011 Removal of natural organic matter from groundwater using advanced oxidation processes at a pilot scale drinking water treatment plant in the Central Banat Region (Serbia). *Ozone Sci. Eng.* **33**, 267–278.
- USEPA 1983 Trihalomethanes in Drinking Water: Sampling, Analysis, Monitoring, and Compliance. Office of Drinking Water, Washington, DC. <https://nepis.epa.gov>.
- Urfer, D. & Huck, P. M. 2001 Measurement of biomass activity in drinking water biofilters using a respirometric method. *Water Res.* **35**, 1469–1477.
- Uyak, V. & Toroz, I. 2007 Disinfection by-product precursors reduction by various coagulation techniques in Istanbul water supplies. *J. Hazard. Mater.* **141**, 320–328.
- Van Verseveld, W. J., Lajtha, K. & McDonnell, J. J. 2007 Fingerprinting dissolved organic carbon (DOC) sources with specific UV absorbance (SUVA) and fluorescence. In: *American Geophysical Union, Fall Meeting*, abstract id. H53G-1510.
- Vasyukova, E., Proft, R., Jousten, J., Slavik, I. & Uhl, W. 2013 Removal of natural organic matter and trihalomethane formation potential in a full-scale drinking water treatment plant. *Water Sci. Technol. Water Suppl.* **13**, 1099–1108.
- Velten, S., Boller, M., Köster, O., Helbing, J., Weilenmann, H. U. & Hammes, F. 2011 Development of biomass in a drinking water granular active carbon (GAC) filter. *Water Res.* **45**, 6347–6354.
- Vickers, J. C., Thompson, M. A. & Kelkar, U. G. 1995 The use of membrane filtration in conjunction with coagulation processes for improved NOM removal. *Desalination* **102**, 57–61.
- Villanueva, C. M., Cantor, K. P., Grimalt, J. O., Malats, N., Silverman, D., Tardon, A. & Marcos, R. 2006 Bladder cancer and exposure to water disinfection by-products through ingestion, bathing, showering, and swimming in pools. *Am. J. Epidemiol.* **165** (2), 148–156.
- Villanueva, C. M., Cordier, S., Font-Ribera, L., Salas, L. A. & Levallois, P. 2015 Overview of disinfection by-products and associated health effects. *Curr. Environ. Health Rep.* **2**, 107–115.
- Von Gunten, U. 2003 Ozonation of drinking water: Part I. Oxidation kinetics and product formation. *Water Res.* **37**, 1443–1467.
- Wang, G. S., Liao, C. H., Chen, H. W. & Yang, H. C. 2006 Characteristics of natural organic matter degradation in water by UV/H<sub>2</sub>O<sub>2</sub> treatment. *Environ. Technol.* **27**, 277–287.
- Wang, G. S., Deng, Y. C. & Lin, T. F. 2007 Cancer risk assessment from trihalomethanes in drinking water. *Sci. Total Environ.* **387**, 86–95.
- Wang, C. C., Niu, Z. G. & Zhang, Y. 2013 Health risk assessment of inhalation exposure of irrigation workers and the public to trihalomethanes from reclaimed water in landscape irrigation in Tianjin, North China. *J. Hazard. Mater.* **262**, 179–188.
- Wang, H. W., Li, X. Y., Hao, Z. P., Sun, Y. J., Wang, Y. N., Li, W. H. & Tsang, Y. F. 2017 Transformation of dissolved organic matter in concentrated leachate from nanofiltration during ozone-based oxidation processes (O<sub>3</sub>, O<sub>3</sub>/H<sub>2</sub>O<sub>2</sub> and O<sub>3</sub>/UV). *J. Environ. Manage.* **191**, 244–251.
- Wei, Q. S., Feng, C. H., Wang, D. S., Shi, B. Y., Zhang, L. T., Wei, Q. & Tang, H. X. 2008 Seasonal variations of chemical and physical characteristics of dissolved organic matter and trihalomethane precursors in a reservoir: a case study. *J. Hazard. Mater.* **150**, 257–264.
- Weishaar, J. L., Aiken, G. R., Bergamaschi, B. A., Fram, M. S., Fujii, R. & Mopper, K. 2003 Evaluation of specific ultraviolet absorbance as an indicator of the chemical composition and reactivity of dissolved organic carbon. *Environ. Sci. Technol.* **37**, 4702–4708.

- Werner, D., Valdivia-Garcia, M., Weir, P. & Haffey, M. 2016 Trihalomethanes formation in point of use surface water disinfection with chlorine or chlorine dioxide tablets. *Water Environ. J.* **30** (3–4), 271–277.
- Wershaw, R. L. 2004 *Evaluation of Conceptual Models of Natural Organic Matter (Humus) From A Consideration of the Chemical and Biochemical Processes of Humification. Scientific Investigations Report*. Retrieved from <http://pubs.er.usgs.gov/publication/sir20045121>.
- Wershaw, R. L., Leenheer, J. A. & Cox, L. G. 2005 *Characterization of Dissolved and Particulate Natural Organic Matter (NOM) in Neversink Reservoir, New York*. US Geological Survey Scientific Investigations Report 2005-5108, New York, 19 p.
- Westerhoff, P., Chao, P. & Mash, H. 2004 Reactivity of natural organic matter with aqueous chlorine and bromine. *Water Res.* **38**, 1502–1513.
- Westerhoff, P., Mezyk, S. P., Cooper, W. J. & Minakata, D. 2007 Electron pulse radiolysis determination of hydroxyl radical rate constants with Suwannee River fulvic acid and other dissolved organic matter isolates. *Environ. Sci. Technol.* **41**, 4640–4646.
- Winter, A. R., Fish, T. A. E., Playle, R. C., Smith, D. S. & Curtis, P. J. 2007 Photodegradation of natural organic matter from diverse freshwater sources. *Aquat. Toxicol.* **84**, 215–222.
- Xing, W., Ngo, H. H., Kim, S. H., Guo, W. S. & Hagare, P. 2008 Adsorption and bioadsorption of granular activated carbon (GAC) for dissolved organic carbon (DOC) removal in wastewater. *Bioresour. Technol.* **99**, 8674–8678.
- Yan, M., Wang, D., You, S., Qu, J. & Tang, H. 2006 Enhanced coagulation in a typical North-China water treatment plant. *Water Res.* **40**, 3621–3627.
- Yang, X., Meng, F., Huang, G., Sun, L. & Lin, Z. 2014 Sunlight-induced changes in chromophores and fluorophores of wastewater-derived organic matter in receiving waters – the role of salinity. *Water Res.* **62**, 281–292.
- Yapsakli, K. & Çeçen, F. 2010 Effect of type of granular activated carbon on DOC biodegradation in biological activated carbon filters. *Proc. Biochem.* **45**, 355–362.
- Zhang, P. & Jian, L. 2006 Ozone-enhanced photocatalytic degradation of natural organic matter in water. *Water Sci. Technol. Water Suppl.* **6**, 53–61.
- Zhao, Y. X., Gao, B. Y., Zhang, G. Z., Qi, Q. B., Wang, Y., Phuntsho, S. & Li, Q. 2014 Coagulation and sludge recovery using titanium tetrachloride as coagulant for real water treatment: a comparison against traditional aluminum and iron salts. *Separ. Purif. Technol.* **130**, 19–27.

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