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Review

Removal of natural organic matter from drinking water by advanced oxidation processes

Anu Matilainen[a], Mika Sillanpää[a,b,*]

[a] Laboratory of Applied Environmental Chemistry, Department of Environmental Sciences, University of Eastern Finland, Patteristonkatu 1, FI-50100 Mikkeli, Finland
[b] Faculty of Technology, Lappeenranta University of Technology, Patteristonkatu 1, FI-50100 Mikkeli, Finland

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ABSTRACT

Over the past 10–20 years the amount of the natural organic matter (NOM) has been increased in raw water supplies on several areas. The presence of NOM causes many problems in drinking water treatment processes, including: (i) negative effect on water quality by colour, taste and odor problems, (ii) increased coagulant and disinfectant dose requirements (which in turn results increased sludge and potential harmful disinfection by-product formation), (iii) promoted biological growth in distribution system, and (iv) increased levels of complexed heavy metals and adsorbed organic pollutants. Thus, more efficient methods for the removal of NOM have emerged. Among these are advanced oxidation processes (AOPs). These include O_3/H_2O_2, O_3/UV, UV/H_2O_2, TiO_2/UV, H_2O_2/catalyst, Fenton and photo-Fenton prosesses as well as ultrasound. In the present work, an overview of the recent research studies dealing with AOP methods for the removal of NOM and related compounds from drinking water is presented.

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1. Introduction

Natural organic matter (NOM) is present in all surface, ground and soil waters. NOM consists of a range of compounds, from largely aliphatic to highly coloured and aromatic, as well as highly charged to uncharged, having also a wide variety of chemical compositions and molecular sizes. The amount of NOM in water differs with climate and the hydrological regime as well as a number of other environmental factors. Thus the character of NOM can vary with source and time (season) (Sharp et al., 2006a,b; Fabris et al., 2008). A considerable increase in the content of NOM in surface waters has been observed to occur during the past 20 years in several areas (Eikebrokk et al., 2004; Korth et al., 2004; Worrall and Burt, 2007, 2009). Many potential factors, including air and surface

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[*] Corresponding author at: Laboratory of Applied Environmental Chemistry, Department of Environmental Sciences, University of Eastern Finland, Patteristonkatu 1, FI-50100 Mikkeli, Finland. Tel.: +358 40 020 5215; fax: +358 15 336 013.
E-mail address: mika.sillanpaa@uef.fi (M. Sillanpää).

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water temperature raising, increase in rainfall intensity, atmospheric CO_2 increase or/and decline in acid deposition, have been proposed to explain this trend, although there are no scientific consensus about the matter (Delpla et al., 2009). Noteworthy is also that change in NOM quality besides of quantity has been observed to happen. Colour and UV absorption has been noticed to increase in some cases more than total organic carbon (TOC) content (Eikebrokk et al., 2004), which implies also elevated values of specific UV-absorbance (SUVA). Thus these altered SUVA values means a change in NOM characteristics, and thereby its treatability.

NOM found in natural waters consists of both hydrophobic and hydrophilic components, where the largest fraction is generally hydrophobic acids, which makes up approximately 50% of the TOC in water (Thurman, 1985). These hydrophobic acids can be described as humic substances comprising of humic acids (HA), fulvic acids (FA) and humin. Hydrophobic NOM is rich in aromatic carbon, phenolic structures and conjugated double bonds, while hydrophilic NOM contains more aliphatic carbon and nitrogenous compounds, such as carbohydrates, sugars and amino acids. Physical and chemical fractionation of aquatic NOM at specific pH can be used to classify organic solutes into these broadly defined hydrophobic and hydrophilic fractions (Chow et al., 2004; Leenher, 2004; Sharp et al., 2006a,b). Whilst these fractions are more operationally than structurally defined, organic compounds can be judiciously assigned to a particular fraction according to their chain length and functional groups (Swietlik et al., 2004; Buchanan et al., 2005) as shown in Table 1.

Another approach to define hydrophobicity is determination of SUVA value (which is UV_{254} absorbance divided by the TOC concentration). High SUVA value indicates that the organic matter is composed largely of hydrophobic, high molar mass (HMM) organic material, in comparison of low SUVA value which means that water includes mainly organic compounds which are hydrophilic, low molar mass (LMM) and low in charge density (Edzwald and Tobiason, 1999; Sharp et al., 2006a,b). The different NOM fractions exhibit different properties in terms of treatability by coagulation, coagulant demand, chlorine and ozone reactivity and disinfection by-product formation potential (DBPFP) (Sharp et al., 2006a,b; Fabris et al., 2008).

Table 1

Proposed composition of NOM fractions separated using fractionation techniques (adapted from Swietlik et al. (2004)).

Fraction	Organic compound class	Reference
Humic acid	Portion of humic substances precipitated at pH 1	Peuravuori et al. (1997)
Hydrophobic acid	Soil fulvic acids, C_5–C_9 aliphatic carboxylic acids, 1- and 2-ring aromatic carboxylic acids, 1- and 2-ring phenols	Leenher (1981), Aiken et al. (1992), Marhaba et al. (2000), Barber et al. (2001)
Hydrophobic base	1- and 2-ring aromatics (except pyridine), proteinaceous substances	Leenher (1981), Marhaba et al. (2000), Barber et al. (2001)
Hydrophobic neutral	Mixture of hydrocarbons, $>C_5$ aliphatic alcohols, amides, aldehydes, ketones, esters, $>C_9$ aliphatic carboxylic acids and amines, >3 ring aromatic carboxylic acids and amines	Leenher (1981), Marhaba et al. (2000), Barber et al. (2001)
Hydrophilic acid	Mixtures of hydroxy acids, $<C_5$ aliphatic carboxylic acids, polyfunctional carboxylic acids	Leenher (1981), Aiken et al. (1992), Marhaba et al. (2000); Barber et al. (2001)
Hydrophilic base	Pyridine, amphoteric proteinaceous material (i.e. aliphatic amino acids, amino sugars, $<C_9$ aliphatic amines, peptides and proteins)	Leenher (1981), Marhaba et al. (2000), Barber et al. (2001)
Hydrophilic neutral	$<C_5$ aliphatic alcohols, polyfunctional alcohols, short-chain aliphatic amines, amides, aldehydes, ketones, esters, cyclic amides, polysaccharides and carbohydrates	Leenher (1981), Marhaba et al. (2000), Barber et al. (2001)

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Dissolved organic carbon (DOC), UV_{254}, pH, turbidity and colour are common water quality parameters assessed by water treatment facilities in their quality control. These parameters do not require sophisticated equipments, they are simple and fast to perform and hence can also be automated. However, these methods illustrate more of the quantity of organic matter and offer only limited information on the character of NOM. The characterization of the NOM can be made, e.g. by high performance size-exclusion chromatography (HPSEC) analysis or fractionation techniques (Goslan et al., 2006; Sharp et al., 2006a,b; Tercero Espinoza et al., 2009a). Although these parameters provide useful information regarding the change in the organic characteristics during treatment and impact to the disinfection by-products (DBP) formation, it has been suggested that they may not alone be efficient techniques in predicting of DBP formation (Sanly et al., 2007).

DBPs have raised a lot of attention in water treatment during the past decades. More than 700 compounds of DBPs have been confirmed, among which trihalomethanes (THMs) and haloacetic acids (HAAs) are the two groups found in highest concentrations and most commonly in drinking waters worldwide (Krasner et al., 2006). Chlorine, ozone, chlorine dioxide and chloramine are the most common disinfectants in use today, and each produces its own suite of chemical DBPs in drinking water (Krasner et al., 2006). Although major concern has been focused in chlorinated DBPs, brominated DBPs have been considered to be even more hazardous than their chlorinated counterparts (Singer, 2006), and also the formation of the iodinated and nitrogen containing DBPs have been studied more intensively (Krasner et al., 2006; Hua and Reckhow, 2007; Zhao et al., 2008). DBPs have been associated with adverse health effects, as bladder cancer, spontaneous abortations and birth defects (Singer, 2006). Thus their occurrence in drinking water has been regulated in most countries. The main DBP precursor has been generally considered to be NOM, and especially the hydrophobic and HMM NOM, with high aromatic carbon content (Hua and Reckhow, 2007; Bond et al., 2009; Liu et al., 2010). Also hydrophilic and LMM NOM have been observed to play a significant role in DBP formation (Hua and Reckhow, 2007; Bond et al., 2009). For example bromine and iodine have been noted to be more reactive with hydrophilic and LMM fractions of NOM in the formation of THMs and HAAs. On the other hand chlorine has been observed to react more readily with HMM and hydrophobic NOM compounds (Hua and Reckhow, 2007).

NOM is a key parameter with respect to design and operation of water treatment processes. It is responsible for the majority of the demand for coagulants and disinfectants, it has tendency to interfere with removal of other contaminants (e.g. competition of adsorption sites in activated carbon), it is responsible for fouling of membranes as well as it has potential to contribute to corrosion and act as substrate for bacterial growths in distribution systems. NOM also contributes to annoying colour, taste and odor problems, forms DBPs and acts as a carrier for metals and hydrophobic organic chemicals (Jacangelo et al., 1995). The most common and economically feasible processes to remove NOM are coagulation and flocculation followed by sedimentation/flotation and sand filtration. Coagulation removes most of the NOM and especially its hydrophobic fraction (Sharp et al., 2006a,b). This fraction is generally more aromatic and larger in molecular size than the hydro-