

Natural organic matter in aquatic systems – a South African perspective

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ABSTRACT

Natural organic matter (NOM) is a complex heterogeneous mixture of humic (HS) and non-humic substances which are widespread in the aquatic environment. Other constituents are amino acids, aliphatic and aromatic hydrocarbons containing oxygen, nitrogen and hydroxyl groups. It is the combination and proportions of these motifs which give NOM its overall polarity and reactivity. Its main origins include soils, residues of fauna and flora, microbial excrements and anthropogenic faecal loads, agriculture activities and urban landscapes. Due to the different origins of the precursor material and the extent of transformation it undergoes, the composition of NOM in different water bodies varies. Characterization methods for NOM can be divided into three broad categories namely: (i) direct measuring methods, which measure the amount of organic matter in the sample; (ii) spectrometric methods, which measure the amount of radiation absorbed and/or released by chromophores; and (iii) fractionation methods, which separate NOM according to size and polarity. South Africa has 6 distinct water quality regions, and each region has a unique NOM character and quantity. Existing water treatment plants do not remove NOM to levels low enough to inhibit the formation of disinfection by-products (DBPs). Currently, research is focusing more on the use of alternative techniques for NOM removal; these include advanced oxidation processes (AOPs), nanomaterials, and ceramic membranes. While NOM is well studied in other parts of the world, to the best of our knowledge, there is no state-of-the-art investigation of the occurrence and removal of NOM in South African source waters. This review aims at (i) synthesizing literature on the nature, occurrence and ecological impact of NOM, (ii) evaluating the removal of NOM in the six different water quality regions of South Africa, and (iii) suggesting novel approaches that can be used to remove NOM in South Africa.

Keywords: advanced oxidation, ceramic membranes, disinfection byproducts, treatability, water treatment

INTRODUCTION

The rapid growth of the human population and the emergence of rapid industrialization and agricultural activities have brought about an increase in organic and other pollutants in drinking water systems. Organic pollutants are broadly classified as man-made organics and natural organics. While man-made organic contaminants are further grouped into subcategories as industrial/pharmaceuticals, hydrocarbons, pesticides, and herbicides (Hunter et al., 2010), natural organic pollutants are collectively known as natural organic matter (NOM) (Fig. 1). These are the product of the degradation of animal, plant and microorganism remains, including microbial excretions (Lavonen, 2015).

According to Swietlik and Sikorska (2006), NOM is composed of aquatic refractory organic matter (5–20%), pedogenic and aquatic polysaccharides (10–20%), pedogenic refractory organic matter (50–80%) and pedogenic and aquatic proteinaceous compounds (5–10%). Pedogenic refractory organic matter refers to fulvic acid components found in soil. NOM can be derived from both the sources within the aquatic environment (autochthonous) and from external sources (allochthonous) (Wershaw et al., 2005; Nkambule et al., 2012). Basically, the allochthonous NOM

is dependent on the type of plant and animal remains that finds its way to the water sources. In plants, for instance, the soluble compounds that can easily leach from the plant tissue are the main components of NOM (Wershaw et al. 2005). Previous studies have shown that allochthonous NOM is typically enriched in fulvic acids and is highly aromatic and coloured, while autochthonous NOM is characterised by a lower fulvic acid content and C:N ratio (Lee, 2005; Rostad et al., 2000).

Thus NOM is composed of different organic compounds, from highly aliphatic to highly coloured aromatic compounds (Matilainen et al., 2010; Wei-Bin et al., 2013). It consists of lignin, cutin, proteins, polyphenols and other polymers as its main building blocks (Wu et al., 2003; Kim and Yu, 2005; Grinhut et al., 2007; Fabris et al., 2008) whereas haloacetic acids formation potential (HAAFP). Because of the negatively charged carboxylic groups found on its surface, NOM carries an overall negative charge with a range of molecular sizes and chemical compositions (Anderson, 2013). For this reason, NOM has hydrophilic, hydrophobic, and transphilic components (Matilainen et al., 2010). The hydrophobic component consists of fulvic and humic acids, is made up of phenolic structures, aromatic carbon and conjugated double bonds, and is responsible for the brownish colour observed in most surface water sources (Goslan et al., 2004; Rostad et al., 2000). Almost 50–75% of the total organic carbon (TOC) is humic in nature (Bagtho, 2012; Rostad et al., 2000; Wu et al., 2003; Sobantu, 2015) oxidation, adsorption, and membrane filtration. In addition to aesthetic problems such as colour, taste and odour,

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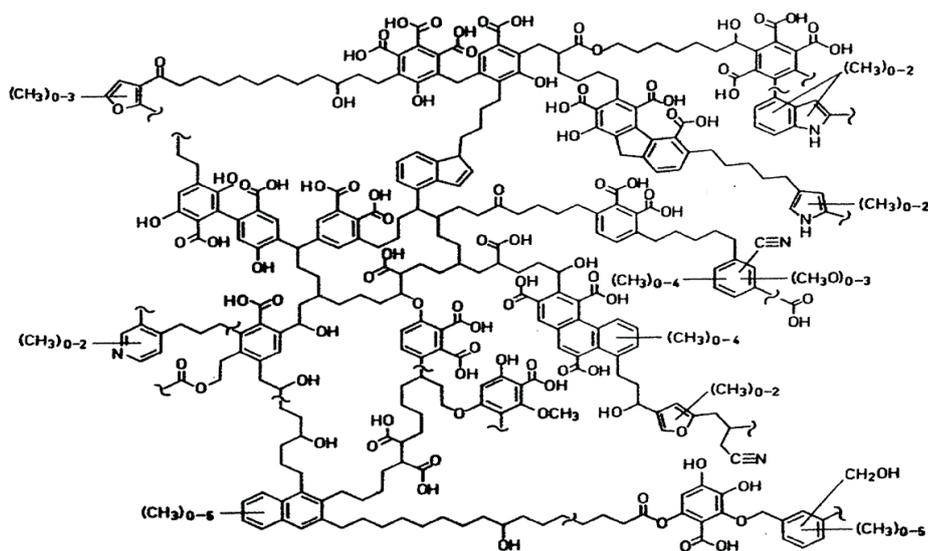


Figure 1

Chemical representation of NOM. Reproduced from Bhatnagar and Sillanpaa, (2017) with permission of the copyright holder, Elsevier

NOM also contributes to the fouling of filtration membranes, serves as a precursor for disinfection by-products (DBPs). The major difference between the humic and fulvic acids is based on their solubility, with humic acids soluble only at higher pH levels and fulvics soluble at all pH levels (Chen et al., 2002; Sobantu, 2015) an aquatic NOM was fractionated into the polyphenolic-rich (NOM-PP. Research has shown that humic acids and humin are recalcitrant to microbial degradation (Grinhut et al., 2007). The charge density of both humic and non-humic substances is not uniform, with the humics having higher charge density compared to the non-humics. Because of this, humic substances can be easily removed in water using techniques such as coagulation (Rostad et al., 2000). The other differences between humic acid and fulvic acid are based on the molecular weight, numbers of functional groups (carboxyl, phenolic OH) and extent of polymerisation (Lee, 2005). The molecular weight distributions for aquatic fulvic acid and humic acid are reported to be from 500 to 2 000 Da and 2 000 to 5 000 Da, respectively (Lee, 2005). Overall, NOM is mainly composed of carbon, oxygen, hydrogen and nitrogen elements (Lee, 2005), with humic acids having the lower content of oxygen but being higher in carbon (Lee, 2005). Conversely, the hydrophilic component has a high content of aliphatic carbons and nitrogenous compounds, such as amino acids, carbohydrates and sugars (Matilainen et al., 2011; Metsamuuronen et al., 2014). The transphilic component is made up of a mixture of hydrocarbon and carboxyl compounds, aliphatic amides, alcohols, aldehydes, esters, polysaccharides, and ketones with less than 5 carbons.

The characteristics and amount of NOM depend on the climate, topography and geology, and the type of agricultural and industrial activities practised at a certain location (Nkambule et al., 2012) Raman, XRD, DRUV-vis, SEM, TEM, EDS, XPS and TGA. FT-IR confirmed the presence of OH groups on thermally stable, nearly spherical anatase nanoparticles with an average diameter of 20 nm. PdO species appeared on the surface of the TiO₂. While upland and agricultural locations with dense vegetation have very turbid runoff with a high content of humic substances, lowland areas are generally high in non-humic substances

(Rostad et al., 2000). Equally important, seasonal variations have a great impact on NOM character, and most researchers have concluded that there is a high NOM quantity during the summer season due to high temperature and heavy storms, which deposit about 50% NOM into water sources. Moreover, due to climate change, changes in soil acidity and land use variations over the years, the quantity of NOM has increased in water sources (Rostad et al. 2000). It is therefore essential to understand the composition of NOM in water sources, taking into consideration the local conditions, and then NOM removal technologies/methods can be developed (Nkambule et al., 2012) Raman, XRD, DRUV-vis, SEM, TEM, EDS, XPS and TGA. FT-IR confirmed the presence of OH groups on thermally stable, nearly spherical anatase nanoparticles with an average diameter of 20 nm. PdO species appeared on the surface of the TiO₂.

While NOM is fairly well researched in other parts of the world (e.g. Taiwan – Lee et al., 2013; Scotland – Sutherland et al., 2015; USA – Fu et al., 2017; and Republic of Korea – So et al., 2017), to the best of our knowledge, there is no state-of-the-art investigation of the occurrence and removal of NOM in South African water systems. This review therefore aims at (i) synthesizing literature on the nature, occurrence and ecological impact of natural organic matter, (ii) evaluating the removal of natural organic matter in the 6 different water quality regions of South Africa, and (iii) suggesting novel approaches that can be used to remove natural organic matter in South Africa.

Ecological impacts of natural organic matter

Although NOM in natural waters poses no known harm, its occurrence in raw water poses a challenge to water treatment plants (WTPs) (Haarhoff et al., 2013). Such challenges include: (i) the presence of NOM imparts repulsive organoleptic properties to water; (ii) NOM combines with pollutants and also provides a shielding surface for microorganisms, this leads to increased coagulant dosage, oxidants and disinfectants required for drinking water treatment; (iii) NOM reacts with disinfectants (e.g. chlorine or ozone) to produce disinfection by-products (DBPs), many of which

are carcinogenic (Vasyukova et al., 2013); (iv) because of its macromolecular size, NOM fouls membranes by forming a cake layer, thereby reducing the flux, resulting in increased energy demand and frequency of downtime for backwashing and cleaning of membranes (Ghadimkhani et al., 2016); (v) by acting as substrate for bacteria, residual NOM, known as biodegradable dissolved organic carbon (BDOC), promotes bacterial re-growth in the distribution systems – the re-growth is compounded when insufficient disinfectant residual is maintained in the distribution system (Metsamuuronen et al., 2014), and some of the bacteria are responsible for the microbial-induced corrosion of pipes in the water distribution system (Burleigh et al., 2014).

Water disinfection is one of the fundamental developments in the past century for improving human health (Latifoglu, 2003; Bond et al., 2014). Disinfecting water is important because it kills micro-organisms that can cause waterborne diseases such as cholera, with chlorine being the preferred disinfectant because of its high oxidising potential (Latifoglu, 2003; Gopal et al., 2007; Bond et al., 2014). The presence of NOM in water results in the formation of disinfection by-products (DBPs) during the disinfection step (chlorination) of the water treatment plant (Nkambule et al., 2012; Sobantu, 2014; Jaouadi et al., 2012). More than 600 DBP compounds have been identified and their formation in drinking water is based on various factors such as pH, temperature, contact time, dose, inorganic compounds, the type of NOM present in water, and the treatment processes being used (Gopal et al., 2007; Kim and Yu, 2007). Previous studies have shown that the highest contributor of DBP precursors is the hydrophilic fraction of NOM; however, even the hydrophobic fraction contributes to the disinfection by-product formation (DBPF) if it is not effectively removed after coagulation (Matilainen and Sillanpaa, 2010; Li et al., 2014). In contrast, other studies shows that humic substances are the main contributor of DBPF (Kim et al., 2006). Thus, understanding the composition of both the hydrophilic and hydrophobic fractions of NOM will have a positive impact towards the choice of remediation approach to remove DBPs from water. The main DBPs found in highest concentration in drinking water throughout the world involve trihalomethanes (THMs) and haloacetic acids (HAAs) (Matilainen and Sillanpaa, 2010; Fabris et al., 2008). THMs are volatile and can be categorised into chloroform, bromoform dichlorobromomethane and dibromochloromethane (Cedergren et al., 2002; Latifoglu, 2003). According to the United States Environmental Protection Agency (USEPA), the allowable THMs and HAAs limits in water are 80 µg/L and 60 µg/L, respectively (Anderson, 2013; USEPA, 2012). Various alternative approaches have been suggested and tested to be effective in one way or the other compared to the use of chlorine as a disinfectant (Gopal et al., 2007). One such way of reducing DBPs is to reduce the chlorine dosages and/or to remove as much NOM as possible before the disinfection step (Bond et al., 2014; Do et al., 2015). Other researchers prefer the use of chloramine as a disinfectant instead of chlorine (Pifer and Fairey, 2012). However, switching to chloramine disinfectant has some disadvantages such as corrosion in the distribution system and also increased occurrence of nitrification (Pifer and Fairey, 2012). Moreover, it is less effective compared to chlorine due to the fact that it requires longer contact time and produces volatile by-products that are responsible for bad taste and malodour in water (Gopal et al., 2007). In addition, the use of iodine and bromine can result in the formation of more hazardous DBPs compared to the

chlorinated precursors because they are highly reactive to the hydrophilic fraction of NOM (Matilainen and Sillanpaa, 2010; Li et al., 2014).

Characterisation of natural organic matter

Characterization methods for NOM can be divided into 3 broad categories namely: (i) direct measuring methods, which measure the amount of carbon released as carbon dioxide after combustion (TOC, DOC); (ii) spectrometric methods, which measure the amount of radiation absorbed and or released by chromophores (UV/vis; FEEM; SUVA); and (iii) fractionation methods, which separate NOM according to size and polarity (SEC; membrane filtration, ion exchange resins, liquid chromatography coupled with organic carbon detection (LC-OCD), PRAM).

Direct measuring methods

These methods include TOC and DOC. While DOC is the organic carbon present in water after it has been filtered through a 0.45 µm filter, TOC represents all non-purgeable organic carbon (Matilainen et al., 2011). Both methods used for TOC and DOC measurement involve oxidation (either with UV persulfate or high thermal combustion) of the organic carbon in the water to form CO₂. The evolved CO₂ is then subsequently measured using infra-red spectroscopy (Matilainen et al., 2011).

Spectrometric methods

Spectroscopic methods used for NOM characterisation are mainly UV-vis and fluorescence excitation-emission matrix (FEEM) spectroscopy.

Ultraviolet-visible spectroscopy

Research has shown that any wavelength within the range 220–280 nm is suitable for NOM measurement (Matilainen et al., 2011). However, due to the range of chromophores present in NOM, the molar absorptivity values vary. In particular, λ = 220 nm is associated with both aromatic and carboxylic chromophores, while λ = 254 nm corresponds to the aromatic character of the molecule (Matilainen et al., 2011). In addition, λ = 272 nm is useful as a predictor for trihalomethane (THM) formation, while λ = 300 nm is used as a measure of DOC by treatment plants in South Africa (Nkambule et al., 2012). Raman, XRD, DRUV-vis, SEM, TEM, EDS, XPS and TGA. FT-IR confirmed the presence of OH groups on thermally stable, nearly spherical anatase nanoparticles with an average diameter of 20 nm. PdO species appeared on the surface of the TiO₂. UV-vis data can be used to compute the specific UV-absorbance (SUVA) parameter (Eq. 1) (Matilainen et al. 2011):

$$SUVA = \frac{UV_{254}}{DOC} \quad (1)$$

SUVA > 4 indicates that there are mostly hydrophobic and aromatic organic material present, and SUVA < 2 indicates the presence of mainly hydrophilic material (Matilainen et al., 2011). Matilainen et al. (2011) reported a correlation between high SUVA and the treatability of NOM by coagulation.

Up to the mid-2000s, synchronous fluorescence spectroscopy was commonly used for monitoring NOM in drinking water plants. The disadvantage, however, is this technique does not measure the entire EEM, but only one or two characteristic peaks. Generally, fluorescence is used to determine the presence of biodegradable NOM in water (Matilainen et al., 2011; Bagtho, 2012). The development of FEEM spectroscopy enabled more rapid qualitative determination of NOM components, and, when coupled to modelling techniques, can quantify these components. FEEM spectroscopy is used to determine various forms of humic substances by collecting all the emission spectra at different excitation wavelengths (Bagtho, 2012). The location and size of the resulting peaks depend on the composition of NOM present in water. This method is particularly important because of its ability to detect changes in properties of the species of interest. In order to identify specific components of the sample that can fluoresce, FEEM data can be manipulated by models such as parallel factor analysis (PARAFAC). It models FEEM data into individual components of fluorophores, and can segregate components into protein-like and humic-like forms (Nkambule et al., 2012; Pifer and Fairey, 2012). While rudimentary peak-picking methods were previously used to identify the fluorescence components of a sample, PARAFAC is more robust because it permits individual components of NOM to be extracted for further analysis (Pifer and Fairey, 2012).

Fractionation methods

One of the transformations NOM undergoes along the treatment train is changes in polarity (Rosario-Ortiz et al. 2007). This transformation can be simulated at laboratory scale using the polarity rapid assessment (PRAM) method allowing an accurate representation of its polarity as it exists in the environment. Additionally, analysis only requires 200 mL of sample and can be performed in 2 h. In this paper, the underlying theory of the method is presented, followed by its optimization, with emphasis on the development of conditions for the analysis of NOM in natural waters. A series of organic probe compounds showed that the most important physicochemical property describing the interaction between the NOM and the SPE sorbents was the hydrophobic surface area, allowing for the estimation of the hydrophobic character under ambient conditions. Evaluation of the effects of chemical concentration, pH, and ionic strength show that (1, which relies on the preferential adsorption of NOM fractions on solid phase extraction (SPE) sorbents (Table 1). This method produces 9 fractions of NOM, namely: hydrophobic acid, base and neutral; hydrophilic acid, base and neutral, and transphilic acid, base and neutral. Using PRAM, the transphilic fraction passes through the C18 and CN columns. In the XAD fractionation method, the transphilic fraction is not sorbed onto XAD-8 but sorbed on the XAD-4 (Nkambule et al., 2012).

This method was further modified to produce 3 fractions, namely, hydrophobic, hydrophilic and transphilic (Nkambule et al., 2012). These fractions give the same information as the original PRAM method. Once the fractions making up the bulk NOM are isolated, they can then be individually characterized in order to gain more insight, in order to remove the prevalent NOM. Each of these techniques yields specific information, and each method employed individually does not give conclusive data on the character of NOM. Thus, a series of characterization

SPE cartridge	Type of sorbent
C18, C8, C2	Hydrophobic
CN, silica, diol	Hydrophilic
NH ₂	Weak anion exchange
SAX	Strong ion exchange

techniques is employed to give detailed information. It is important to firstly identify NOM character, as the type of organics present will affect both the choice of treatment process and its performance (Jefferson and Goslan, 2016).

Most of these techniques are expensive, time consuming, and involve a lot of chemical procedures to produce clean resins and for regeneration, and hence cannot be used for routine water quality monitoring. It therefore is imperative to either (i) periodically send samples to a central laboratory to check the levels of NOM, or (ii) use a surrogate parameter, such as DOC or TOC in order to control NOM concentrations.

Natural organic matter removal approaches

Research has shown that water availability problems are expected to increase in the coming years even in those regions that are currently recognized as water rich (Nkambule et al., 2009). This challenge requires intensive research to identify effective and robust new methods for water treatment at low cost using less energy, while minimizing the use of chemicals which could have negative impacts on the environment. To remove organic pollutants, most WTPs include some of the following processes: (i) coagulation; (ii) adsorption using granular activated carbon (GAC) and ion exchangers; (iii) filtration using micro-filtration membranes (MF), ultra-filtration (UF), nano-filtration (NF), reverse osmosis (RO), and ceramic membranes; and (iv) bioremediation.

Coagulation

Coagulation has been used to reduce colour, turbidity and to eliminate pathogens during the water treatment process (Anderson, 2013). However, the conditions used for colour removal and turbidity are not exactly the same for those for NOM removal, thus, enhanced coagulation is used. In the enhanced coagulation process, more coagulant is used compared to the baseline coagulation process and this allows the removal of about 80% of NOM from the water source (Matilainen et al. 2010; Murray and Parsons, 2004). Nevertheless, increasing the coagulant dosage will increase production of sludge, the disposal of which is problematic due to the high content of metal ions (Murray and Parsons, 2004). Equally important, the residual hydrophobic fraction can result in disinfectant by-product formation. Moreover, because the hydrophilic fraction consists of the highest content of acidic functional groups which are difficult to destabilize by the coagulation process, the hydrophilic fraction is not effectively removed by coagulation compared to the hydrophobic fraction (Matilainen, 2007; Matilainen et al. 2010).

Adsorption

Activated carbon (AC) is an adsorbent that effectively reduces the proportion of biodegradable and assimilated elements in water. During the filtration process, taste, odour, pesticides, industrial chemicals and algal toxins are efficiently removed. While NOM can also be removed during filtration processes, it decreases the efficiency of the removal of other pollutants by competing for the active sites with other target molecules. In order to overcome this problem powdered or granular AC is used (Matilainen et al., 2010). The lower the size of the molecule, the easier it is for it to enter nanopores, excluding the macromolecules (Matilainen, 2007). For this reason, lower molecular weight species are more adsorbable on activated carbon than higher molecular weight molecules.

Filtration

Filtration is a key separation process for the removal of particulate and colloidal matter in water treatment facilities. Reverse osmosis, ultrafiltration, microfiltration and nanofiltration are pressure-driven membrane filtration methods with various NOM removal potentials (Matilainen et al., 2010). Reverse osmosis and ultrafiltration membranes have been widely used to separate NOM based on its molecular sizes (Rostad et al., 2000). Due to its attractive properties, such as easier maintenance, small size and very high water quality produced by this technology, it has the potential to replace conventional water treatment processes such as coagulation, flocculation, gravel filtration, chlorination and ozonation (Zularisam et al., 2006) this effort is hampered by the fouling issue, which restricts its widespread application due to increases in hydraulic resistances, operational and maintenance costs, deterioration of productivity and frequency of membrane regeneration problems. This paper discusses natural organic matter (NOM). Furthermore, membrane filtration is environmentally friendly, and capable of handling a wide range of fluctuations in feed quality, with low energy consumption (Zularisam et al., 2006) this effort is hampered by the fouling issue, which restricts its widespread application due to increases in hydraulic resistances, operational and maintenance costs, deterioration of productivity and frequency of membrane regeneration problems. This paper discusses natural organic matter (NOM). Although some research has shown that ultrafiltration and microfiltration can be employed for the removal of microparticles and macromolecules, which include dissolved organic matter, it does not directly eliminate the problem of DBPs (Zularisam et al., 2006) this effort is hampered by the fouling issue, which restricts its widespread application due to increases in hydraulic resistances, operational and maintenance costs, deterioration of productivity and frequency of membrane regeneration problems. This paper discusses natural organic matter (NOM). Some of the disadvantages of

membranes include membrane fouling resulting in a decline of flux (Matilainen et al., 2010). In order to minimise this adverse effect, pre-treatment with coagulation is usually used.

Polymeric membranes

The advent of pressure gradient membranes has come as a welcome development in the water treatment industry. They are compatible with the conventional treatment processes in that they can be placed at a pre-treatment step or at the end of the treatment train. Membrane processes differ in some aspects, despite being overlapping in other aspects, in their removal potential for various compounds. The functionality of porous membranes is governed by the pore sizes and the method of separation takes place by molecular sieving (Table 2). For example, while MF and UF can remove suspended particles and macromolecular colloids, proteins, viruses, oil emulsions and some sugars to the molecular ranges (500 000 to 1 000 g/mol), NF can remove multivalent ions and small solutes like proteins, soluble salts, endotoxins and some sugars in the ionic to molecular ranges (10 000 to 100 g/mol). RO works in the ionic range removing metals and salts.

The limiting factor in the use of membranes in water treatment is fouling. The factors that influence membrane fouling include membrane properties, solution chemistry (pH, ionic strength, and temperature), solute concentration and character (e.g. NOM hydrophobicity/ hydrophilicity) and the hydrodynamic conditions of the system (Wang et al., 2010). Wang et al. (2010) evaluated a range of NF, UF and MF membrane modules in order to determine the influence of NOM on the fouling of the membranes (Wang and Hsieh, 2001). The results showed that solution chemistry of the feed water and hydrodynamic conditions influence the propensity to fouling when humic acid was used as the model foulant. Divalent cations like Ca^{2+} and Mg^{2+} were more readily adsorbed on NF membrane surfaces than divalent and monovalent anions. This was expected, because these ions have the ability to chelate with humic acid, promoting intra- and inter-molecular binding forming layering between the membrane surface and the negatively charged humic acid molecules, as well as between the negatively charged carboxyl groups of the humic acid that are not in contact with the membrane. Another study reported that increasing the cross-flow velocity reduced the rate and extent of fouling by reducing the residence time of Ca^{2+} at the membrane surface (Nguyen et al., 2012). The character of NOM plays a role in the rate of fouling. On the basis of comparable DOC concentration, the order of the fouling potential of the fractionated NOM was consistently hydrophilic neutral > hydrophobic acids > transphilic acids > hydrophilic charged (Barrouk et al., 2015). Although most membranes are polymeric, research is also exploring the potential of ceramic membranes.

TABLE 2
Membrane pore sizes and applications (Nakashima et al. 2000)

	Pressure (bar)	Pore size	Pollutants retained
MF	0.1–3	0.1–5 μm	Suspended particles (bacteria, blood cells, fine dust)
UF	2–10	20–0.1 μm	Selected macromolecules (silica, viruses, endotoxins, proteins)
NF	5–30	> 1 nm	Multivalent salts and small solutes (salts, synthetic dyes and sugars)
RO	10–100	0.1–1 nm	Salts

Ceramic membranes

Ceramic membranes are made from inorganic materials such as silicon carbide, zirconia oxides, alumina, titania or some glassy materials (Bouwmeester, 2003). Ceramic membranes are generally composed of 3 layers: (i) the outer layer or the macro layer is the most porous and mechanically robust, its function is to offer support for the inner membrane framework; (ii) the second layer or the meso layer, which has smaller pore sizes compared to the macro layer, is coated over the support layer, it acts as a bridge between the support layer and the inner layer; (iii) the last layer is the active layer or micro layer at which the processes of separation occur. There are two types of ceramic membranes, namely, dense and porous membranes. On the one hand, dense ceramic membranes are used for gas separation, for example, oxygen transportation in zirconium oxide at high temperature. In this type of ceramic membrane, the gas permeates into the non-porous membrane then diffuses through the membrane and finally desorbs from the membrane (Jeong et al., 2017). On the other hand, porous membranes are generally identified by pore size, surface porosity and thickness (Table 3). This class of membranes is attracting interest in the water treatment industry due to their ability to effectively remove particulate matter (Dilaver et al., 2018). The advantages of their intrinsic properties of chemical, mechanical and thermal stability make them attractive in diverse applications such as environmental, pharmaceutical and gas separation (Hofs et al., 2011). Additional properties of porosity and hydrophilicity make them even more attractive in drinking water laden with NOM. Hofs et al. (2011) reported that substituting conventional steps (coagulation, sedimentation, and filtration) in water treatment by ceramic membranes is equally effective in removing particulate matter. Compared to polymeric membranes, the production costs of ceramic membranes are 3 to 5 times higher, but this can be compensated by their longer operational lifetime of up to 10 years instead of 1 year for polymeric membranes (Wang and Hsieh, 2001; Nelke, 2001). In order to decrease the membrane cost, locally available raw materials such as natural ball clay, bentonite, feldspar, quartz, alumina, and chemical additives can be used to prepare ceramic membranes (Ciora and Liu, 2003).

Oxidation

An alternative approach for NOM abatement is pre-oxidation. This approach removes NOM more efficiently than the coagulation process (Matilainen et al. 2010). Ozonation, which also removes odour, colour and taste in water, is the preferred pre-oxidation method (Matilainen et al., 2010). This has the potential of decreasing the SUVA values by increasing fractions with low molecular weights. Pre-ozonation increases the biodegradability of NOM, thus enhancing its removal by increasing the biological activity in the filter of biologically activated carbon (BAC) (Matilainen et al., 2010).

Bioremediation

Most conventional methods used for NOM removal in water treatment plants involve the use of chemicals, resulting in the generation of large quantities of sludge with high concentrations of NOM, which constitutes disposal problems (Solarska et al., 2009; Lee, 2005). Consequently, research into the development of alternative methods that will degrade

TABLE 3
Types of ceramic membranes
(Jeong et al. 2017; Dilaver et al. 2018)

Type	Pore size (nm)	Application
Macro-porous	> 50	UF, MF
Meso-porous	2–50	UF, NF, GS
Micro-porous	< 2	GS
Dense	–	GS, reaction

NOM to harmless products is a priority. Such methods include bioremediation using fungi, enzymatic, UV-based advanced oxidation processes, and the use of nanomaterials and nanocomposites.

Bioremediation which involves the use of microorganisms such as fungi and bacteria, or isolated enzymes, to degrade organic pollutants into harmless products is attractive because it is environmentally friendly, cost-effective, and limits by-product formation (Lee, 2005). This method removes biodegradable organic matter, and reduces chlorine demand during the disinfection step as there will be very little NOM available to react with free chlorine (Barrett et al., 2000). Furthermore, this technology is not only applicable to drinking water treatment, but also in the treatment of concentrated NOM wastes from water treatment processes. Enzymes are generally substrate-specific, so that each enzyme normally catalyses only a single type of reaction (Solarska et al., 2009). By binding to the specific substrate in the NOM molecule, the enzyme can start degrading that part of the molecule into smaller pieces which will be easier to remove from the water source using specific treatment processes (Solarska et al., 2009). They break certain bonds in the NOM structure, which other methods fail to do. The amino acids, carbohydrates, proteins and carboxylic acids found in source water vary in their susceptibility to microbial biodegradability (Solarska et al., 2009). The use of enzymes and bacteria to degrade NOM results in the formation of NOM fractions with lower molecular weight (Wershaw et al., 2005). Examples of fungi used to degrade humic substances include saprotrophic fungi and white rot fungi (WRF) (Gramss et al., 1999; Grinhut et al., 2007). Their activity is due to their non-specific extracellular oxidative enzyme system, which may include lignin peroxidase (LiP), laccase (Lac) and manganese-dependent peroxidase (MnP), which completely mineralize lignin to CO₂ and H₂O. Because they are non-specific, they can oxidize a variety of xenobiotic compounds which are structurally similar to lignin substructures. These enzymes degraded the humic substances to form carboxyl and phenoxy radicals and low molecular weight compounds, which are organic acids, fulvic acids and low molecular weight humics (Solarska et al., 2009). The most extensively studied of the ligninolytic WRF that mineralize NOM is *Phanerochaete chrysosporium* ATCC 34541, which removed 40–50% NOM from solution. However, this was due to adsorption and a partially metabolically linked activity (Rojek et al., 2004). The capacity of this fungus to remove colour was affected by environmental conditions such as pH, carbon and nitrogen content, and NOM concentration. In a separate study, Rojek (2003) reported that a combination of yeast contaminants isolated from a MIEX concentrate with *P. chrysosporium* gave NOM removals of 70–80%.

However, these methods do not effectively remove NOM or its fractions. For example, although coagulation is more than 50% effective in removing hydrophobic fractions, smaller molecular fractions are not effectively removed (Jefferson and Goslan, 2016). Membrane filtration is energy and operationally intensive yet only capable of removing low molecular weight NOM and is thus not economical at a commercial scale (Metsamuuronen et al., 2014). While adsorption techniques such as GAC are effective in removing NOM, their effectiveness is limited by presence of other pollutants like atrazine and heavy metals, which compete for adsorption sites (Wang et al., 2010).

Natural organic matter in South African waters

Thus far, we have demonstrated that (i) NOM is undesirable in drinking water for various reasons, (ii) NOM is not routinely monitored in WTPs due to high cost of equipment, and (iii) the commonly used NOM removal techniques are not effective. This section explores the occurrence of NOM, and treatment methods commonly used in South Africa and their strengths and limitations. Apart from the Water Research Commission (WRC) funded survey performed by the NOM research group, in the Nanotechnology and Water Sustainability (NanoWS) Research Unit, at the University of South Africa (Marais et al., 2017), very little research has been carried out in South Africa on NOM occurrence and treatability. South Africa has 6 different types of water depending on the geographical location (Fig. 2). These are: (A) the north-eastern part of the country, where source waters are clear to turbid, with fairly high NOM, and dissolved salts are low, this is mainly Montaigne water flowing eastwards from the Drakensburg and Amatola escarpments, and is used by Amatola and Umgeni Water, for example; (B) the north-western part, with mostly turbid rivers and variable salt levels, this is mainly eutrophic water found in most of the dams on the Highveld, with the eutrophication being influenced by large return flows and agricultural runoff; (C) the central part, with high levels of suspended salts and clay; (D) Western Cape, with clear acidic waters; (E) the Southern Cape waters are dark brown due to the presence of humic and fulvic compounds – both regions D and E have highly coloured water; for instance water found on the south-western coast that is very high in colour, usually from humic and fulvic substances; (F) the Free State where waters are from the highlands of Lesotho, transparent with low dissolved salt levels, mostly oligotrophic water, such as that from the Vaal Dam, serves Rand Water – this is by far the largest water supplier in South Africa. In all regions, treated sewage effluent, which dominates NOM character of many streams and rivers in South Africa especially during periods of low flow, is introduced into drinking WTPs in de facto recycling. The nature and type of NOM is influenced by a number of factors including: (i) geological formation (ii) climatic and hydrological conditions, and (iii) anthropogenic activities (Lobanga, 2012).

Geological formation

Rocks and soils are composed of various chemical determinants. Through hydrological processes, the dissolved solutes penetrate the upper layers of the rocks either through irrigation, flood water, upward groundwater flow in seepage zones, rising groundwater levels or capillary rise (Briggs et al., 2017). Depending on the type and concentration, certain metals, e.g., calcium, chelate with NOM, transforming it into a form that is recalcitrant to certain water treatment processes.

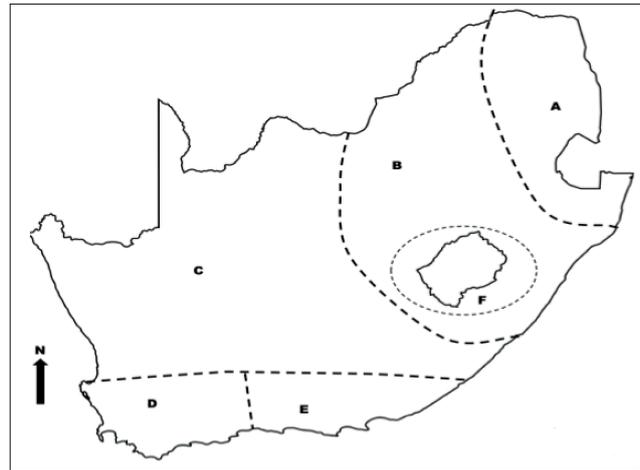


Figure 2

Water quality regions of South Africa, showing A – North East; B – North West; C – Central; D – Western Cape; E – Southern Cape; F – Free State

This reduces the efficiency of WTPs, for example causing membrane fouling and clogging filters. The water quality regions follow the geological map of South Africa, suggesting that the underlying rock has a bearing on the surface water quality. For example, regions D and E are underlain by a strongly leaching rock type, thus giving the water a characteristic brownish colour, probably due to the presence of manganese and iron in these waters.

Climatic and hydrological conditions

The most significant and direct reaction to a change in climate is observed in temperature of a water body (EEA, 2007). Surface water temperature and air temperature are closely correlated, thus a rise in air temperature results in a rise in surface water temperature. This influences the occurrence, transport and fate of NOM. Since NOM is a result of the decomposition of fauna and flora, temperate regions like Region A will experience high organic matter content in their surface waters. This is due to accelerated biogeochemical processes brought about by elevated temperatures. Coupled to that, elevated temperatures favour the growth and proliferation of biota such as phytoplankton, macrophytes and epiphytes, which leads to hypoxic conditions thus suffocating aquatic organisms in turn increasing the autochthonous NOM (Durance and Ormerod, 2007).

Anthropogenic activities

Anthropogenic activities which affect the nature and quantity of NOM include agriculture, mining, industry, human settlements and waste disposal methods (Rashid and Ramshoo, 2013). Agriculture and urban activities are non-point sources of pollutants such as phosphorus and nitrogen, while settlements and an increase in population in urban areas have caused sewage from industry and households to increase (Wang, 2009). Premised on the concept of infinite dilution of pollutants into water bodies, it is common practice in South Africa to dispose treated sewage water into water bodies. However, South Africa, being a developing country, is overwhelmed by economic challenges, and consequently budgetary allocation for

environmental management is limited. This has seen partially treated or inadequately treated sewage being disposed of into water bodies, which introduces anthropogenically derived NOM loads, exerting pressure on WTPs.

It should thus be expected to have high variability in the concentration and composition of NOM in South African water sources in the different regions. This infers that no single treatment process can be prescribed for all regions. Further, NOM undergoes compositional transformation during the water treatment process, hence its treatability varies along the water treatment train. This implies that there are dissimilar levels of efficacy in the removal of NOM by the different water treatment processes around the country. Most water treatment plants rely on the following methods to remove NOM and other organics: coagulation (enhanced), ozonation in combination

with bio-filtration, adsorption and membrane filtration (Nkambule et al., 2012). This is, unfortunately, not the case in most treatment plants in South Africa, because such processes require high capital and maintenance costs coupled with skilled operators. In addition, research on NOM is in its infancy, such that water treatment companies and water practitioners do not see the need and urgency of additional steps to abate NOM. Overall, NOM removal efficiencies differ across different plants in the country because (i) the NOM expected at each treatment plant is diverse due to the variability of the raw water, and (ii) the configuration and treatment processes of each WTP are different (Table 4).

The processes used for drinking water treatment around South Africa vary. Overall, it appears the majority of WTPs are not adequately designed to remove NOM (Table 4). It is,

Region	Plant Name	NOM removal efficiency*				Remarks	Reference
		Autumn	Winter	Spring	Summer		
A	Lepelle Plants::					Conventional treatment processes** are used in these plants, except for Ebenezer, which has an aeration stage after raw water abstraction. The drought of 2016 resulted in low water levels and concentrated NOM in summer.	Marais et al., 2017
	Ebenezer	100	100	–	51		
	Olifantspoort	23	26	–	15		
	Flag Boshielo	13	14	–	23		
B	Rietvlei		26	18	28	Rietvlei uses an additional GAC and DAFF*** stage.	Nkambule et al., 2012; Marais et al., 2017
	Vereening	61	61	56	49		
	Stilfontein		50	31	35		
	Lourie		16	21	48		
	Magalies:		30	51	46	Magalies Plants use pre-chlorination with chlorine dioxide and a post-ozonation step.	
	Plant 1	38	38	25			
	Plant 2	31	34				
Plant 3	36	29	33				
C	-	-	-	-	-	Research in this region is underway.	
D	Preekstoel		65	93		These plants treat highly coloured borehole water using biologically active sand with microorganisms attached to the grain surfaces for Fe and Mn removal.	Marais et al., 2017
	Hermanus						
E	Plettenberg Bay		85	63	58	These plants follow a conventional method	Nkambule et al., 2012; Marais et al., 2017
	Plettenberg Bay		83	92			
	Umzoniana		825	26	37		
F	Umgeni plants::					Umgeni plants use conventional treatment methods to treat water impacted by agricultural activities especially sugarcane plantations.	Nkambule et al., 2012; Marais et al., 2017
	Wiggins		29	22	64		
	Amanzimtoti		–	22	–		
	Umzinto		85	27	–		
	Hazelmere		–	33	–		
	Mtwalume		12	34	–		

*Measured as % DOC removal

**Conventional water treatment processes involve coagulation, flocculation, filtration, and disinfection

***DAFF is dissolved air floatation filtration.

therefore, imperative to conduct research into new materials and processes that can ameliorate the health risks associated with NOM. Such materials and processes are mainly based on advanced oxidation and the use of nanomaterials. While in developed countries research in this area is quite advanced (e.g. Jefferson et al. 2016), in South Africa such research is only just beginning. Significant progress, though, has been recorded in national and international collaborative research efforts. Funding is generally provided by a number of governmental and non-governmental organisations such as the National Research Foundation (NRF), the Water Research Commission (WRC), and a few others. Therefore, compared to other parts of the developing world, research in South Africa is significantly advanced. Research on water treatment technologies involving AOPs and nanomaterials, or a combination thereof, is rapidly gathering pace throughout South African research facilities. To identify the research on advanced oxidation, and nanomaterials used for water treatment, literature indexed on scholarly databases (Scopus, Web of Science, Science Direct and Google Scholar) was retrieved using the following search terms: 'advanced oxidation OR nanomaterials AND water treatment, South Africa'. Over 3 000 and 700 research articles were returned for the period 1999 to 2017 for selected findings grouped under the 'advanced oxidation' and 'nanomaterials' strands, respectively (Fig. 3). A literature search showed that a number of publications exist on the synthesis and laboratory evaluation of AOPs and nanomaterials in water treatment and future research priorities. Thus, research is dominated by laboratory-scale studies, while those on a pilot and industrial scale are still limited. Future research directions should therefore focus on up-scaling the technologies to pilot scale, in order to determine reactor and process design parameters, and ultimately to industrial scale.

CONCLUSION AND OUTLOOK

Although occurring in varying proportions, natural organic matter is ubiquitous in source waters. The environmental and

health risks associated with NOM include DBP formation, reducing WTP efficiency, facilitating bacterial re-growth in the water distribution system, and objectionable organoleptic properties. Owing to the expensive equipment used in NOM characterisation, it is not possible to routinely monitor the levels and character of NOM in source waters. This applies as much to South Africa as to the rest of the world. In light of this, central analytical facilities accessible to a number of WTPs can be established for NOM control. Alternatively, surrogate parameters such as DOC and TOC can be monitored instead. The six water quality regions of South Africa imply different strategies for NOM abatement. Water utility companies are only just beginning to appreciate the need to monitor NOM.

Conventional WTPs are not designed to effectively remove NOM. Research on alternative approaches such as nanotechnology is still in its infancy in South Africa. Nanomaterials exhibit improved biological, chemical, physical and improved functionality due to their nanoscale sizes (Joshi et al. 2008). These materials have stimulated significant research interest and elucidate a lot of environmental pollution issues. Their fate in the environment, however, is an issue of concern. Another potential method is photodegradation. Most photocatalysts are limited by large band gap, very high electron-hole recombination, and being unstable in water, which can cause the decomposition of such catalysts (Samsudin and Hamid, 2017). Nevertheless, these materials can be doped to reduce the band gap and increase quantum yield. Another area of research that is rapidly gaining prominence in NOM removal is the use of ceramic membranes. Ceramic membranes have potential for being a better alternative because of their intrinsic features. These membranes do not need chemical additives, thermal inputs and spent media regeneration, making them more popular than other water treatment technologies (Jaouadi et al., 2012). In addition, compared to polymeric membranes, ceramic membranes are superior in that they can be coupled with photocatalytic and catalytic ozonation

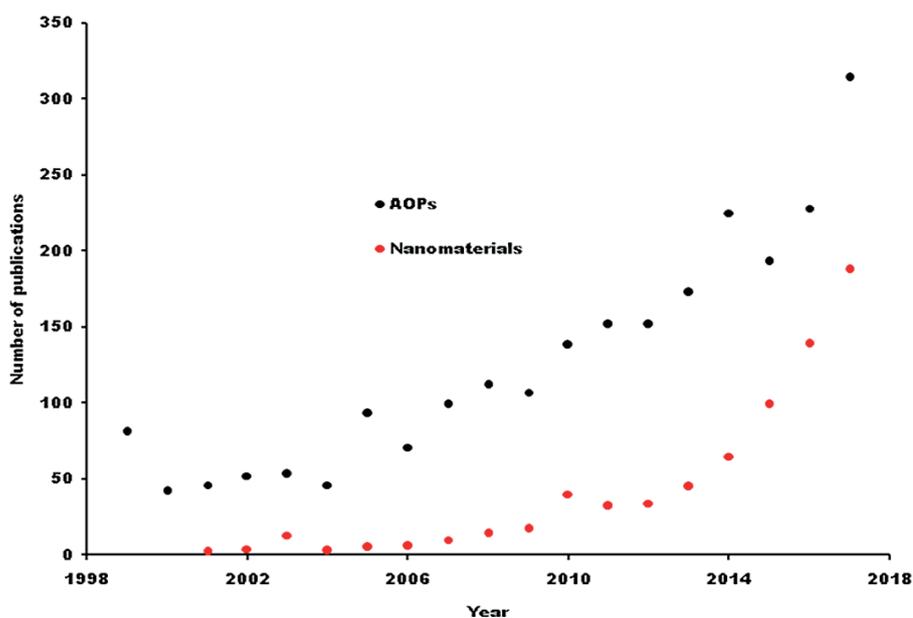


Figure 3
Research on the use of advanced oxidation processes, and nanomaterials in water treatment in South Africa

processes to reduce membrane fouling whereas the former degenerate in the presence of oxidants (Lehman et al. 2010). Water characteristics fluctuate due to climatic and seasonal variations and load, and such changes can be accommodated by ceramic membranes, unlike polymeric membranes which would collapse. Ceramic membranes, however, suffer a cost constraint. Research on the synthesis of ceramic membranes using readily available material such as zeolites and coal fly ash would be useful in this regard.

Despite being in the formative stages of research, these approaches have great potential in that they can be co-opted into existing water treatment processes and increase the NOM removal efficiency.

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