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Natural organic matter-cations complexation and its impact on water treatment
A critical review

Adusei-Gyamfi, Junias; Ouddane, Baghdad; Rietveld, Luuk; Cornard, Jean Paul; Criquet, Justine

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Review

Natural organic matter-cations complexation and its impact on water treatment: A critical review

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ABSTRACT

The quality and quantity of natural organic matter (NOM) has been observed to evolve which poses challenges to water treatment facilities. Even though NOM may not be toxic itself, its presence in water has aesthetic effects, enhances biological growth in distribution networks, binds with pollutants and controls the bioavailability of trace metals. Even though NOM has heterogeneous functional groups, the predominant ones are the carboxyl and the phenolic groups, which have high affinities for metals depending on the pH. The properties of both the NOM and the trace elements influence the binding kinetics and preferences. Ca^{2+} prefers to bind with the carboxylic groups especially at a low pH while Zn^{2+} prefers the amine groups though practically, most cations bind to several functions groups. The nature of the chemical environment (neighboring ligands) the ligand finds itself equally influences its preference for a cation. The presence of NOM, cations or a complex of NOM-cations may have significant impact on the efficiency of water processes such as coagulation, adsorption, ion exchange resin and membrane filtration. In coagulation, the complexation between the coagulant salts and NOM helps to remove NOM from solution. This positive influence can further be enhanced by the addition of Ca^{2+}. A negative influence is however, observed in lime-softening method as NOM complexes with Ca^{2+}. A negative influence is also seen in membrane filtration where divalent cations partially neutralize the carboxyl functional groups of NOM thereby reducing the repulsion effect on NOM and increasing membrane fouling. The formation of disinfection by-products could either be increased or reduced during chlorination, the speciation of products formed is modified with generally the enhancement of haloacetic acid formation observed in presence of metal cations. This current work, presents in details the interactions of cations and NOM in the environment, the preference of cations for each functional group and the possible competition between cations for binding sites, as well as the possible impacts of the presence of cations, NOM, or their complex on water treatment processes.

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1. Introduction

The presence of natural organic matter (NOM) in water bodies has recently been observed to increase as well as vary significantly (Eikebrokk et al., 2004). High seasonal variability and elevated concentrations of NOM would pose challenges to water treatment plants in terms of operational optimization and proper process control (Sillanpää, 2015; Sillanpää et al., 2018). Even though NOM may not be toxic itself, it has the tendency of changing both the chemical and physical properties of the water. It may result in colour and odour of the water, influences the concentrations of dissolved O, N, P, and S and serve as a carrier of toxic pollutants like pesticides and radionuclides (Knauer et al., 2017; Santschi et al., 2017). In addition, NOM serves as both a source and sink for carbon, which may have an indirect climatic effect (Dore, 2005; Delpla et al., 2009; Hruška et al., 2009).

NOM refers to a complex mixture of different organic compounds that are present in fresh water which is principally formed by the weathering or decay of living material (Stevenson, 1994; Iskrenova-Tchoukova et al., 2010). The different chemical constituents of NOM do not make it practically feasible to characterize it based on individual compounds. There even exists some ambiguity on whether NOM is chemically a true macromolecular entity (Kononova, 1961; LeBoeuf and Weber, 2000) or just an assembly of relatively small molecules held together by relatively weak non-covalent interactions (primary electrostatic and hydrogen bonding) to form a supramolecule (Kalinichev and Kirkpatrick, 2007). Notwithstanding NOM being a complex mixture of organic compounds, there are fractions with distinct chemical formulae such as carbohydrates, fats, waxes, alkanes, peptides, amino acids, proteins, lipids and organic acids. The other fractions, with no distinct chemical formulae and unknown unique identity, are referred to as humic substances. The non humic fractions are easily degraded while the humic fraction, together with soil minerals, can persist for centuries (Pettit, 2004). The elemental analysis of the different components of humic substances reveals that they are primarily composed of carbon (55–57%), oxygen (34–36%), hydrogen (4–6%), nitrogen (0.9–3%), and sulfur (0.4–1.8%) in complex carbon chains (Dixon et al., 1989; Rice and MacCarthy, 1991; Pettit, 2004; Bravo et al., 2017). Very little is known about the nitrogen and sulfur containing functional groups (Filella, 2008). Humic substances can be divided further into three classes based on their solubility and molecular weight (MW). Humin (MW range of approximately 100,000 to 10,000,000) is insoluble in aqueous systems at all pH. Humic acid (mixture of weak aliphatic and aromatic organic acids with MW range of approximately 10,000 to 100,000) is soluble at pH > 2 and fulvic acid (mixture of weak aliphatic and aromatic organic acids with MW range of approximately 1,000 to 10,000) is soluble at all pH. Fulvic and humic acids are ubiquitous in water systems, and constitute about 10–30% of dissolved NOM in seawater, 70–90% dissolved NOM in wetland water, 40–90% of dissolved NOM in streams and about 50% of dissolved NOM in lake waters, depending on hardness (Xue and Sigg, 1999; Thurman, 2012; Lipczynska-Kochany, 2018a). This is because the presence of hardness cations apparently suppresses the solubility of high molecular weight fulvic acids (Aiken and Malcolm, 1987; Breault et al., 1996).

NOM could also be defined by its origin, *i.e.* allochthonous or autochthonous. Allochthonous NOM, on the one hand, refers to NOM that originates from a distant place. It may have been transported to the present matrix by agents of erosion and are susceptible to degradation and removal processes during its transport. Allochthonous NOM is typically derived from lignin-containing plants, the degradation of which yields fulvic acids relatively rich in aromatic carbon content and phenolic compounds but low in nitrogen content. Autochthonous NOM, on the other hand, refers to NOM that is indigenous to the matrix and are often algal derived (Luider et al., 2004). Aquatic algal derived NOM has a relatively high nitrogen content, low concentration of aromatic carbon and phenolic compounds (Fabris et al., 2008).

NOM can further be classified based on its polarity and hydrophobicity (Sillanpää et al., 2015). The hydrophobic (non-polar) fraction, which, generally constitutes a higher percentage of the NOM fraction, consists of aromatic rings with conjugated double bonds and phenolic structures, while the hydrophilic (polar) fraction is mainly made up of aliphatic carbons and nitrogenous compounds like proteins, sugars and amino acids (Baghoth, 2012). Some functional groups observed in NOM are the substituted alkyl carbons, unsaturated carbons, amides, carboxylic groups, aldehydes and ketones, amino groups, alcohols and phosphate esters, sulfur (Karlsson et al., 2006; Mopper et al., 2007). Fig. 1 gives a summarized scheme of the broad characteristics of NOM.

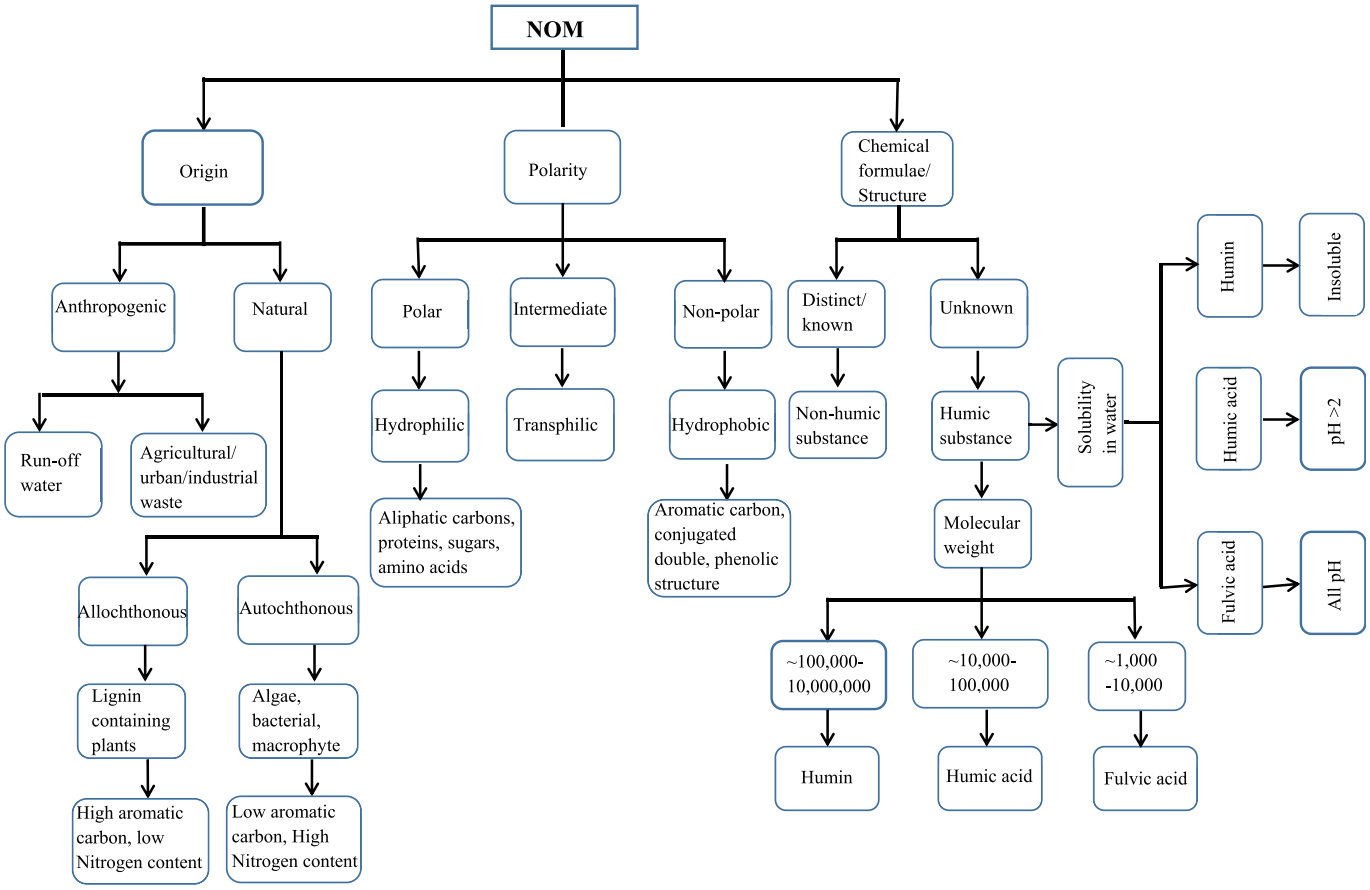

Fig. 1. A summary of the major characteristic classes of NOM.

Because of its high reactivity, NOM also controls the bioavailability and biogeochemical cycling of trace elements in the environment (Xia et al., 1997). Considering the fact that it is rare to find a metal un-complexed, 'naked', in the environment, metal-NOM complexation occurs by metal binding to already existing ionized sites or by displacing a proton from its position. This can be due to an increase in the electrostatic interaction between the deprotonated functional groups and the cations as they are deprotonated at higher pH.

NOM and climate change affect each other; whereas NOM contributes to climate change through the release of greenhouse gases, climate change influences the quantity, structure and reactivity (biotic and abiotic interactions with aquatic pollutants such as trace elements) of NOM affecting surface and groundwater quality. Climatic conditions that are known to have a positive correlation with DOC concentration in waters include high precipitation, high temperature, storm, floods and runoff (Ågren et al., 2010; Bhurtun et al., 2019). An increase in temperature for instance can increase biological activities and the decomposition of organic matter, which can subsequently be eroded into water bodies during floods or rainfalls. Hurricane Irene alone which occurred in 2011 is estimated to have contributed to 19% of the 2011 annual dissolved organic matter (DOM) exports from a forested catchment in Cecil County, Maryland (Dhillon and Inamdar, 2013). Areas of mean temperatures of about 5 °C and 30 °C would have 10% and 3% carbon loss respectively with a temperature increase of 1 °C. The change in temperature would also influence the bioavailability and toxicity of pollutants since adsorption processes are temperature dependent (Ripszam et al., 2015). The activity of microbial organism is further enhanced as humic substances act as electron donors acceptors during anaerobic respiration (Lau et al., 2015; Lipczynska-Kochany, 2018b).

Available database shows that the increase in DOC quantities started from the early 1980s (Evans et al., 2005). Data on 315 records from across Britain shows that about 69% of the sites studied showed a significant increase in DOC concentration (up to 16% annual percentage change) between 1975 and 2002. A lower proportion (38%) has been found across Europe and northern American countries (189 sites – 11 years) (Skjelkvåle, 2003).

Even though underground waters are less sensitive to climate change than surface waters, its quality is also expected to deteriorate due to its exchanges (recharge and discharge) with surface waters (Kjøller et al., 2004) which would have grave consequences on drinking water production and may increase treatment cost. The browning of surface waters by NOM reduces the disinfection capacity as it shield pathogens by absorbing of UV rays (Williamson et al., 2017; Lipczynska-Kochany, 2018a). The formation of disinfection by products (DBPs) in drinking water is expected to rise as well as the release of trace metals into the environment (Lipczynska-Kochany, 2018a). Acidification of groundwater due to acid rains would results in less than 10% NOM-metal complexes making about 90% of trace metals bioavailable (Kjøller et al., 2004).

Due to its highly complex structure and heterogeneity, numerous papers and reviews are focused on NOM classification and/or characterization. (Edzwald et al., 1985; Aiken et al., 1992; Bryan et al., 2000; Luider et al., 2004; Sutton et al., 2005; Karlsson et al., 2006; Kalinichev and Kirkpatrick, 2007; Mopper et al., 2007; Fabris et al., 2008; Sillanpää, 2015). The aim of this review is to (1)

extensively examine the interactions of cations and NOM in the environment. Much attention is given to the major functional groups as well as cations and the different types of interactions that can exist between them, (2) examine the preference of cations for each functional group and the possible competition between cations for binding sites, (3) assess the impact of the presence of cation, NOM, or their complex on drinking water treatment processes.

2. Theoretical aspects of complexation of metals to NOM

2.1. Central atom and ligands

Bonding that occurs through the donation of electron pairs from an orbital of an atom (electron pair donor or ligand) to a partner atom (electron pair acceptor) is referred to as coordinate bonding or coordinate covalent bonding. The ligand can be an ion (possibly an ionic form of the central metal atom) or a molecule. Broadly speaking, the electron pair acceptors are generally referred to as Lewis acids while the electron pair donors, Lewis bases (Lawrance, 2010). Once coordination happens, structural properties like the number of bonds, bond angles and bond distances of the new substance formed causes it to have an altered physical property compared to their individual components. Thus, the new physical properties are dependent on the nature of central atom (either same or different atom type) and the ligands involved. The electron pair acceptor, which serves as the central atom, is usually a metal or a metalloid. When there is only one central atom involved, the newly formed structure is called a monomer. When the number of linked units are low, the structure is considered to be an oligomer (Naka, 2014). If several central atoms are involved, they would either be held together by an atom-atom bond or be bridged by a ligand making them a polymer. This linkage can be done through a common donor atom, simultaneously binding to the central metal atoms, or through different donor atoms. The metal atoms can also be encapsulated in a polydentate ligand with each metal coordinating with several donors (Lawrance, 2010).

Ligands can be grouped into two main classes; simple and heterogeneous ligands according to their structural properties and the ability to chemically define their structures and metal complexation chemistry. In the case of a simple ligand like EDTA, its molecular structure (composition and geometry), concentration (activity) of itself and its complexes, stoichiometry of its complexation with metals, metal-ligand formation free energy or thermodynamic equilibrium constant are known or can be known. However, heterogeneous ligands like humic substances may exhibit characteristics that are opposite to that of the simple ligands; polyfunctionality which results in high electrical charge density, structural modification as a function of *e.g.* pH, ionic strength, metal binding, and variation in molecular weights (Buffle et al., 1990; Filella, 2008). Thus, the ligand can present either a single or multiple donor atoms; if only one donor atom is coordinated, it is referred to as a monodentate ligand. If multiple donor atoms are involved, it is referred to as polydentate ligands. The 'denticity' therefore defines the number of donor atoms or groups that are available or used in bonding. For polydentate ligands, the subsequent lone pair after the first coordination is oriented in a way that prevents them from coordinating with the same central atom. In an instance where the existing covalent bond is deformed, two lone pairs from a ligand can be attached to the same metal forming a cyclic compound referred to as a chelate. Even though the shape of the ligand influences the strength of the complex formed and the coordination, there are no rules to really predict a particular shape to be formed by a ligand in complex structure. In general, chelate rings exhibit an enhanced stability compared to monodentate ligand since the size of the stability constant is almost invariably proportional to the number of coordinated donor atoms in a ligand (Lawrance, 2010). Fig. 2 shows various possible coordination of a central metal atom to a ligand.

Carbon can act as a ligand (*e.g.* carbanion (H_3C^-)) and effectively donate electrons to coordinate a metal. This type of coordination can occur either by σ covalent bonds or π covalent bonds when side of carbons equidistance from the central metal are involved. The d_z^2 and d_{x-y}^{22} orbitals of the transition metals are also often involved in σ bonding while the other three more stable orbitals d_{xy}, d_{xz}, d_{yz} are mostly involved in π bonding. They have incomplete d-orbital and an electronic configuration of ns, (n-1)d, np with varied oxidation numbers (Lawrance, 2010). The oxidation number indicates the number of available spaces that have been created because of loss or gain of electrons, which influences the tendency to coordinate with ligands to make up for this loss. For metals with different oxidations states, the chemistry of each state distinctively differs from the others. The effect of ionic interactions on the valence electrons (p orbitals for main group, d orbitals for transition group and f orbitals for lanthanides) influences its bonding and coordination. The valence shell of a d-block element can be considered as having a total of 9 orbitals (18 electrons) which comprises, 5 nd orbitals, (n+1)s and (n+1)p orbitals respectively. To achieve stable oxidation state, elements in the d-block (transition metals) of the periodic table ought to have a partially filled nd subshell. The 5 d (d_{xy}, d_{xz}, d_{yz}, d_z^2 and d_{x-y}^{22}) orbitals occupy different spatial orientations and presents two different shapes. Two of the five orbitals lie along the axes while the other three lie between the axes of the coordinate system. This is however different for elements in the main block which require either a fully occupied or empty subshell to attain oxidation stability.

When there is a direct linkage between the metal atom and the ligand, it is referred to as a direct or inner sphere complexation. If however the metal atom is bridged to the ligand by water molecule, it is referred to as indirect or outer sphere complexation. For carboxylic group, the metal atom can be directly linked to one of the oxygen atoms of the carboxylate (monodentate) or both oxygen atoms (bidentate) as shown in Fig. 3. However, this behavior depends on the metal ion involved as *e.g.* in the case of Ca^{2+} as the central atom, there can be a proton transfer from water to the carboxylic group at lower water content (Aquino et al., 2011). Small ions preferentially form monodentate outer sphere complexes to avoid steric hindrance (Falck, 1989; Allen, 1993; Dudev and Lim, 2004; Kunhi Mouvenchery et al., 2012). An increase in the number of water molecules in the coordination shell of the cations favours more monodentate coordination than bidentate coordination.

2.2. Preferential binding sites

Two major types of functional groups, usually indicated as being

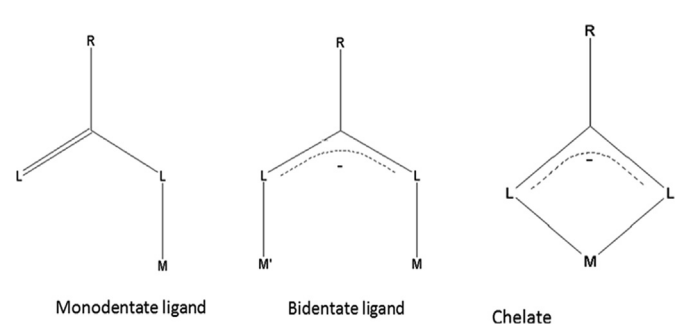

Fig. 2. Possible coordination of metals (M) to ligands (L) (Lawrance, 2010).

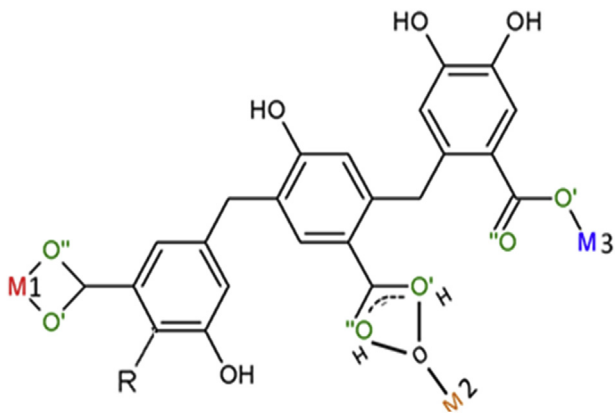

Fig. 3. An image of bidentate inner sphere (M1), outer sphere coordinated (M2) and monodentate inner sphere complexation (M3) contact ion pairs for two carboxilic groups respectively.

of greatest importance with respect to NOM-cation binding, are carboxyl and phenolic groups (Kalinichev and Kirkpatrick, 2007; Chappaz and Curtis, 2013), phenolic groups are much less abundant than carboxylic groups. In accessing the composition of these two main functional groups in 14 IHSS standards (Ritchie and Perdue, 2003), concluded that carboxyl groups constitute 78%–90% of the total acidity for fulvic acids and 69%–82% for humic acids. Thus, the average of phenolic-to-carboxyl groups for the IHSS samples studies is about 21: 79. The high affinity of these two groups to cations compared to other minor groups (ester, amine, alcohols, aldehydes and ketones) is highly dependent on the pH (Nederlof et al., 1993; Mota et al., 1996). At high pH, there is an increase in deprotonation, which increases the available binding sites of ligands. A lower pH, however, increases protonation reducing the available binding sites.

Fig. 4, gives a summary of preference for the two main functional groups of NOM and their characteristic paths in complexation.

2.2.1. Carboxylic group

The carboxylic group which is more acidic than the phenolic group starts to dissociate at pH > 4.4; *e.g.* the dissociation of the carboxylic group of Suwanee river humic substance occurs at pH of 4.42 (Baalousha et al., 2006) making it responsible for the formation of negative sites on DOM (Aquino et al., 2011). During dissociation, a net negative charge is created which causes the production of large potentials at the surface of humic substance, and the formation of a double layer in their surrounding (Bryan et al., 2000). For humic substance to achieve steric stability there has to be a repulsion of like charges. This repulsion of the negative charges causes an electrical double layer to be formed at each interface, which in effect increases the surface area for smaller sized particles as well as their binding affinities with cations. Fig. 5 shows some of the different carboxylic structures likely to be found in humic substances. As counter ions approach the locality of macro ions such as humic substances, they electrostatically interact with any available site (non-specific) or a targeted site (specific). The choice of which site can be quite challenging to determine. Some surface complexation models that have sought to improve the prediction of metal behavior and their speciation in the environment are the NICA and Donnan Models. While the NICA model describes specific association, the Donnan model rather describes non-specific association (Kinniburgh et al., 1996). However for all models, one of the basic requirements is that both the functional groups and the humic substance should be simplified (Zhao, 2008).

Aside the affinities of the individual ligands, the nature of the environment in which they find themselves cannot be ignored. Thus carboxylate binding, depends on both the availability and type of interactions between the central metal atom and the carboxylate O atom, as well as between the carboxylate O atoms and its neighboring ligands (Dudev and Lim, 2004). The presence of functional groups containing heteroatoms in the close vicinity of COOH groups affects their ionization efficiency due to inductive effects. Electron withdrawing substituents on C atoms in α position to the COOH groups, decreases the electron density leading to an increase in the asymmetric vibrational modes, enhance their acidity, and may also participate in chelation reactions (Hay and Myneni, 2007). Additionally, in macro ions such as humic molecules, where multiple ionizable groups are in close proximity, electrostatic effects result in transmission of polarization through the solvent medium. This may affect the carboxylic group pKa values, which are a measure of their reactivity (Deshmukh et al., 2007).

2.2.2. Phenolic group

Phenols are considered as one of the most important groups for complexation with metal atoms (Chappaz and Curtis, 2013). Phenolic compounds are naturally leached from plant materials into the soil and water matrix and constitute about 60% of the plant dry mass (Cates and Rhoades, 1977). Fig. 6 shows some phenolic structures that can be found in humic substances. If two hydroxyl

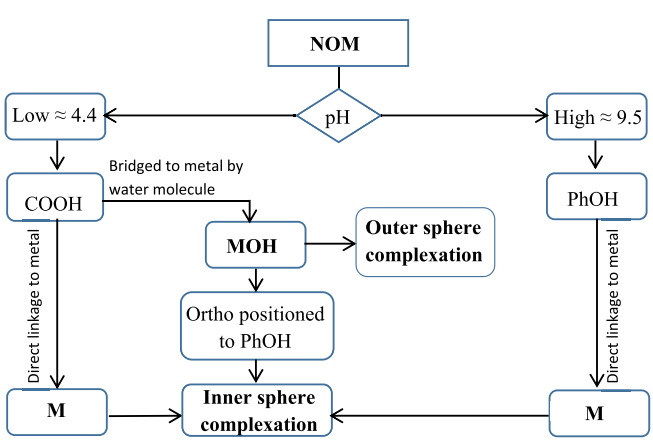

Fig. 4. A scheme of the Characteristic of carboxyl and phenolic (PhOH) group in complexation with metals (M) and hydro-metal (MOH).

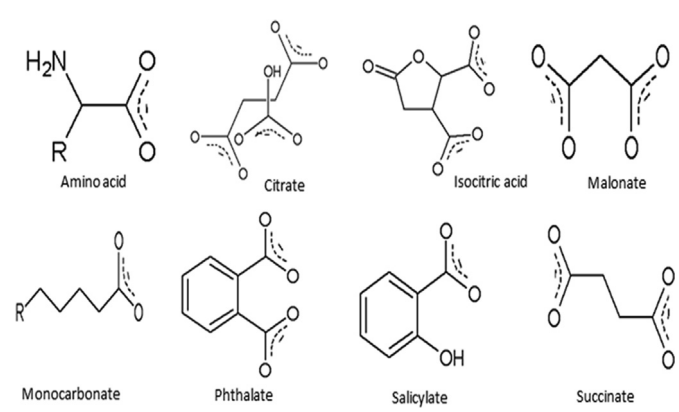

Fig. 5. Carboxilic group moieties likely to be found in humic substances (Deshmukh et al., 2007).

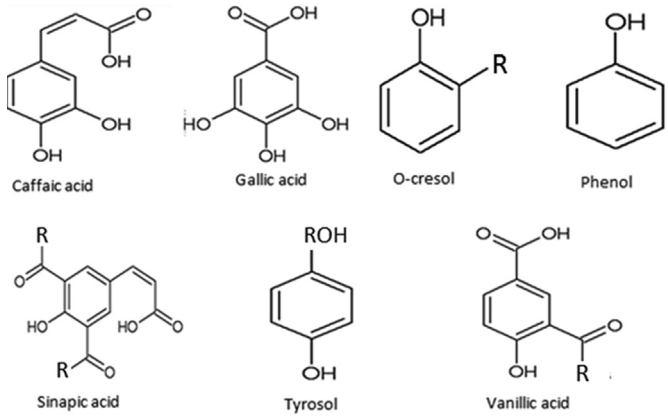

Fig. 6. Phenolic moieties that can be found in humic substances (Rappoport, 2003).

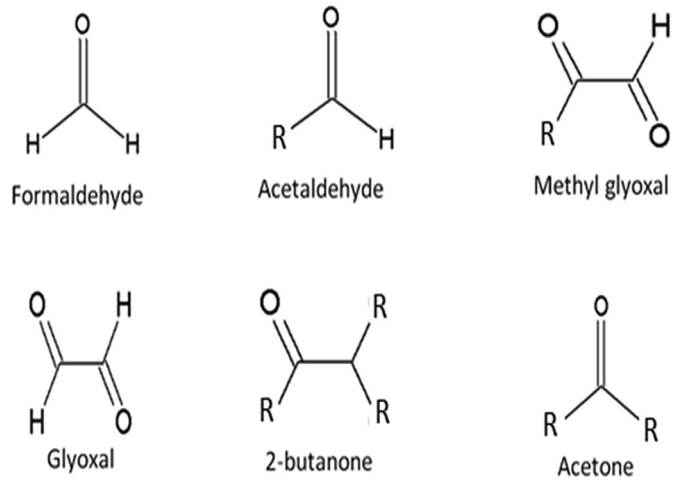

Fig. 7. Ketone and aldehyde moieties that can be found in humic substances (Shilov and Shul'pin, 1997).

groups are positioned ortho to each other, they can bidentatively complex with a metal atom (Guan et al., 2006). At higher pH (>9.5), the phenolic group involves more in complexation as it is easily deprotonated at this pH. The dissociation of phenolic groups of Suwanee river humic substance occurs at pH of 9.68 (Benedetti et al., 1995; Baalousha et al., 2006). When molecules get larger in size, they tend to become less soluble and so its tendency to be coordinated to a metal ion is limited even though the rules of coordination do not change (Lawrance, 2010). The presence of phenolic groups enhances the complexation capacity of carboxylic groups especially when it is located at the ortho position and at lower pH. This is because the ortho-phenolic-oxygen increases the electron density of the carboxylic group, which subsequently favors inner sphere complexation between the carboxylic group and the metal hydroxide even though aromatic carboxylic acids usually form outer sphere complexes with metal hydroxides (Nordin et al., 1998; Guan et al., 2006).

2.2.3. Other functional groups

Amines, a derivative of ammonia that has one or more of its hydrogen atoms substituted by an alkyl or aryl group constitutes a nitrogen atom with a lone pair of electrons. While Ammine, is a complex compound that contains ammonia molecule. This difference is important because the substitution of the hydrogen atom alters the electronic effect and polarity as well as the size of the molecule, which subsequently redefines the preferences of the ligands. At higher pH, a monodentate ammonia ligand already coordinated to a metal atom can deprotonate (NH_2^-) to increase its lone pairs of electrons to two and forms a bridge with a second metal atom. Thus, ligands can coordinate to two metals either by using a lone pair from each of the two donor atoms or using two lone pairs from the same donor atom. Amines are less 'sterically efficient' than carboxylate because the size of amine causes it to bump into other ligands when occupying coordination sites around a metal which often leads to lower stability (Lawrance, 2010).

Aldehydes and ketones although not abundant, are known to serve as ligands in transition metal complexes (Huang and Gladysz, 1988). They consist of a carbonyl functional group (C=O) where the tetravalent carbon atom has two available sites for bonding. Aldehydes and ketones species are produced as by-products during ozonation in drinking water treatment (Shilov and Shul'pin, 1997; Choi et al., 1998; Świetlik et al., 2004). Fig. 7 gives some of ketones and aldehydes found in humic substances or in drinking waters as by-products. Ketonyl metal complexes can be formed either through *trans*-metalation (transfer of ligands from one metals to another), oxidative addition or by the interaction of electrophilic metal centers with ketones in their enol or enolate form. When the central metal atom is softly electrophilic during keto-enol equilibrium, a complex with a π-bonded enol can be formed which can evolve into a ketonyl complex (Barone et al., 2012). The absorbance and emission properties (especially at visible wavelengths) of humic substances, can be greatly influenced by the presence of ketones and aldehydes, because they act as the primary acceptors in charge-transfer transitions within these samples (Del Vecchio et al., 2017).

Esters, which are mostly formed by the replacement of a hydrogen of an acid with an alkyl or any organic group are known to form partial bonds with transition metals (Verkade et al., 1965). The presence of metals ions can increase the hydrolysis of amino esters. Hence, in the absence of a suitable metal ion, the hydrolysis of amino esters is very slow, but upon addition of metal ion, a rapid reaction is observed due to the cleavage of the metallic complex and pH. Upon further increase in the metal concentration, a 1:1 ester-metal complex formation is observed (Kroll, 1952). Phosphate di-esters, on the one hand, do not exhibit a chelating mode of coordination but rather prefers bridging to two adjacent metal ions. Phosphate monoesters, on the other hand, are likely to attract more metal ions around them and form larger aggregates due to the presence of two acidic protons and one phosphoryl oxygen (Murugavel et al., 2008).

Sulfur functional groups, although present in humic substances in various oxidation states as thiol, thiophene or disulfide, sulfoxide, sulfone, sulfonate and sulfate esters are considered as minor functional groups (Filella, 2008). Fig. 8 shows some Sulfur moieties that could be present in NOM.

According to Bloom et al. (2001), a humic acid (HA) containing 0.2% of reduced sulfur has 63 $\mu mol g^{-1}$ of thiol sites. In peatland, sulfate reduction leads to the formation of sulfur which then reacts with metal (oid)s like antimony (Sb) or arsenic to form complexed precipitate at low or neutral pH values (Rittle et al., 1995; Dijkstra et al., 2004). The high affinity of Sb(III) for thiol can result in up to 44% of total Sb forming a 3-fold coordination to sulfur at a distance of 2.46 Å (Xia et al., 1999). (Besold et al., 2019), however recently found that sulfur-reacted peat increases sorption of antimonite to as high as 98%. Carboxylic and phenolic groups are likely to make available additional sorption sites for antimonite in this particular matrix only when the amount of reduced sulfur is low no metal (oxyhydr)oxides are available. In the case of low Hg concentration, thiols groups are seen to be the most preferred binding

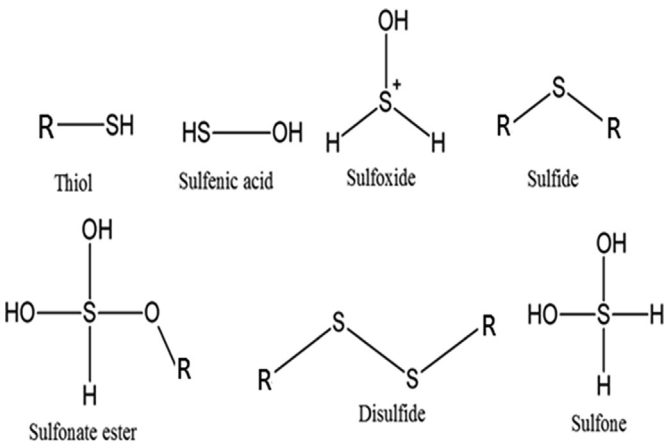

Fig. 8. Sulfur in organic compounds (Filella, 2008).

sites and likewise responsible for the binding of methylmercury (CH_3Hg^+) (Skyllberg et al., 2003).

2.3. Preferences of central atoms (cations) for ligands

Protons are present in aqueous systems and originally occupy most of the binding sites of NOM. Thus, metal ions must compete with the protons for binding sites. When a metal (M) reacts with equimolar amounts of ligands L_A and L_B, the amounts of ML_A and ML_B, will depend on the cation preference and are rarely equivalent. This section looks at some S, D and P block cations that are present in the environment at significant concentrations and their preference for ligands.

2.3.1. s-block (calcium, magnesium, sodium)

Even though calcium (Ca^{2+}) exhibits a relatively weak bonding with humic acids, compared to trivalent cations, they cannot be ignored considering their high concentration in most fresh waters. Ca^{2+} predominantly binds with carboxylic sites at low pH but would equally bind with phenolic sites at high pH (Kinniburgh et al., 1999). Amine moieties show the same binding preference as carboxylic acid towards calcium. However calcium has a preference for binding to larger and more negatively charged molecules because they generally have large ligand groups (Cabaniss, 2011). In calculating the potential mean force for the interaction of cations and carboxylic groups of NOM in aqueous solutions, Iskrenova-Tchoukova et al. (2010), found that, Ca^{2+} binding depended on the distance between the Ca^{2+} and the carbon atom of the carboxylic moieties. The presence of Ca^{2+} also results in competition with other cations for available binding sites (Cao et al., 2006) and the modification of redox transformation of some competing cations like Fe (Jiang et al., 2017). Iglesias et al. (2003), concludes that at concentration above 2.5 mM, calcium can significantly compete with copper of concentration 1 μM for adsorption sites on NOM. The presence of Ca^{2+} further causes relatively small NOM to aggregate and form larger colloidal particles of supramolecular structure (Kalinichev and Kirkpatrick, 2007). This role (probably specific to Ca^{2+}, as the same observations were not made for other cations studied, Na^+ and Mg^{2+}), can be explained in two main geometrical paths (Iskrenova-Tchoukova et al., 2010);

1. Directly, by cationic bridging between carboxylic groups from different NOM molecules. Generally metal bridging can occur at a monodentate or bidentate configuration through inner and outer sphere coordination depending on the ion charge and the local ligand environment (Tipping and Hurley, 1992; Kalinichev and Kirkpatrick, 2007). Bidentate complexes can occur only if the two functional groups involved are close enough to undergo interaction with the same cation otherwise monodentate complexes may be formed (Kunhi Mouvenchery et al., 2012).
2. Indirectly, by Ca^{2+} simultaneously complexing with two or more carboxylic groups of the same NOM molecules. This coordination reduces the net charge and repulsion of the complex, thus allowing the complexes to approach each other more readily.

Magnesium (Mg^{2+}) is with calcium, the primary cation responsible for the hardness of water. When dissolved in water, magnesium interacts with NOM present and results in the formation of soluble and sorbed complexes, and a variety of solid phases. Mg^{2+} equally competes with other cations for binding sites. (Kalinichev and Kirkpatrick, 2007), suggest that, the strongly held hydration shell makes Mg^{2+} interact little with NOM. This is however, contradicted by Yan et al. (2015), who in studying Mg^{2+}-NOM interaction using differential absorbance spectroscopy confirms the existence of strong interactions between Mg^{2+} and NOM. This is however dependent on pH and the ability of Mg^{2+} to deprotonate phenolic and carboxylic groups of NOM. While there was an increase in differential absorbance with increase in Mg^{2+} concentration, an increase in pH (5–11), increases the concentration of Mg bound onto SRHA and SRFA although the effect of pH was more pronounce for SRHA. This noticeable effect in humic acid is probably because it has about 2 third less of carboxyl group content compared to fulvic acids. The phenolic content in fulvic and humic acids are statistically similar (Ritchie and Perdue, 2003). An explanation to the supposed minimal interaction could be due to the bond between Mg^{2+} and NOM which is mainly by nonspecific Donnan electrostatic interaction and so the quantity of Mg^{2+} that is bonded to NOM is minimal (Li and Elimelech, 2004). The carboxylic group, forms strong association with Mg^{2+} compared to the phenolic group (Ahn et al., 2008). Even at higher pH, Mg^{2+} shares similar properties to Ca^{2+} and can still bond to the carboxylic groups and to a lesser extent to the phenolic groups of the NOM (Lu and Allen, 2002; Iglesias et al., 2003; Yan et al., 2015). This binding was accompanied by the replacement of protons in the protonation-active phenolic and carboxylic groups (Korshin et al., 2009).

Regarding sodium (Na^+), on the one hand, it is considered that this cation forms only very weak outer-sphere complexes with NOM and the ions remain almost entirely in the solution to be hydrated by the water molecules. Therefore, Na^+ does not bind to NOM and even its outer-sphere coordination to the carboxylate groups is statistically weak (Kalinichev and Kirkpatrick, 2007). On the other hand, it is considered that Na^+ could act as relatively effective cross-linker for NOM (Aquino et al., 2011). An increase in the cation charge density increases equally the tendency to form a contact ion pair (Kalinichev and Kirkpatrick, 2007). Iskrenova-Tchoukova et al. (2010), however, has disagreed with the conclusion of (Kalinichev and Kirkpatrick, 2007) that Na^+ does not bind to NOM, and states that Na^+, like Ca^{2+}, rather shows a strong preference for bidentate carboxylate groups even though the bond for the latter may be weak.

2.3.2. d-block (cadmium, copper, iron, zinc)

Cadmium (Cd^{2+}) complexes with NOM under natural water conditions (Hertkorn et al., 2004). Cd^{2+} shows, a relatively weak binding, even though they prefer amine-containing sites to pure carboxylates and bind to smaller, less aromatic molecules (Cabaniss, 2009, 2011). Li et al. (1998), however, have stated that Cd^{2+} is rather primarily coordinated to O donor atoms (carboxyl groups) and would be coordinated to N donor atoms only at high

pH with no observed coordination with S. In disagreement, Hertkorn et al. (2004), have stated that the coordination with S is possible. This has been evidenced in the case of soil organic matter where Cd^{2+} at a concentration of below 1000 μg/g is exclusively bonded to the reduced organic sulfur ligands (thiols). Cd^{2+} forms inner-sphere complexes with two S groups in an octahedral geometry (Xia et al., 1997; Karlsson et al., 2005). At higher concentration, however, there is contribution from the organic O and N containing ligands (Karlsson et al., 2005, 2007). According to the bond distances and coordination numbers, in soil organic matter, Cd^{2+} is complexed to a mixture of a 4-coordination with S (thiols) and 4- and 6-coordinations with O and N containing ligands respectively (Karlsson et al., 2005).

In the environment, Copper (Cu^{2+}) can exist in four different oxidation states (0, +1, +2 and +3), with the most abundant speciation found in pure water being Cu^{2+}. The speciation of copper is influenced by pH and available oxygen (WHO, 2003). The type of coordination it undergoes is determined by several factors, the most important being the ligand-to-metal ratio (Carrera et al., 2004). Cu^{2+} is very strongly bounded to humic acids even though this interaction is pH dependent, especially at trace concentrations. At a pH between 4 and 8, most of the binding can be attributed to the phenolic sites (Kinniburgh et al., 1999). However, Cabaniss (2011) has suggested that at pH below 7, the largest reactive sites in NOM are the carboxylate fractions and can form a vast number of coordination complexes with Cu^{2+}. In terms of strength, the strongest bonds are expected to be formed with carboxyl ligands. Cu^{2+} also shows high affinity for amine containing sites which are often located on small (MW < 1000 Da) lower aromaticity molecules (Cabaniss, 2011). Cu^{2+} is complexed by O and N functional groups in NOM, forming a structure involving one or two five-membered chelate rings (Karlsson et al., 2006).

The remarkable affinity of Cu^{2+} towards NOM, compared to other cations, may probably be due to the excellent match in size between the cupric ion and one or several ligands (*e.g.* oxygen and sulfur) (Kinniburgh et al., 1999; Manceau and Matynia, 2010). Thus NOM has a high sorption capacity and selectivity for Cu^{2+} over a large concentration range (Gao et al., 1997). The size-match fit (strain energy), is a function of the bond-length and bond-angle deformation, the torsional strain of the chelate, and van der Waals interactions among non-bonded atoms (Manceau and Matynia, 2010). Considering the poly-functional nature of NOM, Cu^{2+} is likely bonded to more than one functional group in proportions that may vary with the metal concentration, the pH and the chemical composition of the organic matter. In the presence of other cations however, Cu^{2+} would have to compete for binding sites. Chappaz and Curtis (2013), in studying the simultaneous interaction of Cu–Al-DOM, observed that Cu is strongly complexed with the high molecular weight fraction of NOM than the low molecular weight fractions. Due to the availability of relative sensitive and inexpensive electrochemical methods for the measurement of Cu^{2+} in Cu-NOM complexation, copper complexation has been the model choice of many studies (Filella, 2008).

Iron (Fe) mainly forms complexes with NOM as Fe^{2+} or Fe^{3+} with the speciation being highly influenced by pH. The presence of humic substances, however, slows down the oxidation of Fe^{2+} as well as the aggregation of the Fe particles (Pédrot et al., 2011). Even though hydroxide and oxide forms of Fe have low solubility in water, it is still possible to find high concentrations of such Fe speciation associated with organic colloids in water rich in organic matter (Pokrovsky et al., 2005; Pédrot et al., 2011). Humic substances equally inhibit the crystallization of iron hydroxide and iron oxides, by forming Fe nano-(hydr)oxides coated with DOM and Fe(III)-DOM complexes (Pédrot et al., 2011). At pH lower than 3 and higher than 6, Fe species bind to humic acids thereby indicating that it has the same relative affinity for carboxylic and phenolic humic acid sites (Dudev and Lim, 2004; Marsac et al., 2013).

In the presence of EDTA in wastewater, transition metals especially Fe^{3+} because of its increased valence electrons interacts strongly with the nitrogen groups of EDTA (Muñoz and von Sonntag, 2000).

Zinc (Zn) in the aquatic environment can either be linked to the organic or inorganic phases. At low concentrations, the sorption of Zn^{2+} occurs mostly on pH-dependent binding sites of oxyhydroxides competing with its binding to organic matter. Zn could sorb to clay minerals by ion exchange processes (Mertens and Smolders, 2013). Zn^{2+} generally show a weaker binding compared to other transition metals like Cu^{2+} and Ni^{2+}, and prefers to bind rather to amine groups and smaller less aromatic molecules instead of carboxylates (Cabaniss, 2011, 2009). Zinc is most likely to be involved in inner sphere complexation and can be coordinated to four or six O atoms and also form 4 coordination with N and S ligands (Karlsson et al., 2007).

2.3.3. p-block (aluminium, lead)

In the aquatic environment, aluminium (Al^{3+}) complexes with NOM, which subsequently modifies its speciation and influences its toxicity. The exchange reaction between Al^{3+} and H^{+} and the hydrolysis of Al^{3+} on organic matter exchange sites are important factors to buffer pH and control the activity of Al^{3+}. In the presence of other competing cations like Cd^{2+} and Pb^{2+}, Al^{3+} can reduce the amount of Pb^{2+} ions bound to the carboxylic functional group by a factor of 2–3 especially at lower pH of 3–5.5 (Pinheiro et al., 2000). This competition effect is solely dependent on its affinity for carboxylic, phenolic or chelate ligands, which is pH dependent. Al^{3+} like Fe^{3+} strongly influences the speciation of rare earth element in organic rich waters. At pH $\geq$ 3, Al^{3+} competes with rare earth elements/lanthanides suggesting that Al^{3+} is bound to carboxylic sites rather than phenolic sites. At neutral pH such as in natural waters, Al^{3+} is expected to bond to weak carboxylic groups (Dudev and Lim, 2004; Marsac et al., 2012). Other studies observed that Al^{3+} has a unique preference for phenol-containing sites and larger, more aromatic molecules (Cabaniss, 2011).

In the natural aquatic environment, Lead (Pb) may exist in two oxidation forms (+2 and +4) with the +2 being dominate. Pb^{2+} exhibits a binding strength which is similar to that of Cu^{2+} and form strong binding with amines dominated NOM. It equally binds with other groups such as phenols, alcohols, ether groups and larger molecules but forms slightly weaker bonds with carboxylate (Cabaniss, 2009, 2011). The large ionic radius of Pb^{2+} (1.19 Å) makes it possible for it to form complexes with varied coordination numbers (2–15) of central atom. The complexation of Pb^{2+}, with oxygen donor atoms, forms products with two different bond lengths. While the primary bond exhibit a predominate covalent property, the secondary bonds are to a larger extent ionic and in most cases serving as a bridge for molecules (Davidovich et al., 2009).

Table 1 gives a summary of the cation preference for each of the main functional groups. When there are contradictory results from different researchers, both results are presented.

2.4. Complexation equilibrium of NOM

Metals (s, p and d) as well as ligands have their preferences that are largely determined by their electronegativity, a factor of both the size of the atom and number of valence electrons. Generally, p-block and d-block elements have higher affinities compared to s-block elements. Hence, very electronegative ligands prefer less electronegative metals (and vice versa). Further, there is a stronger

Table 1
Cations preference for the main functional groups of NOM.

Functional groups	Carboxylic group	Phenolic	Amine	Sulfur	References
Cations					
Al	++	+	n.a	n.a	(Pinheiro et al., 2000; Cabaniss, 2011; Marsac et al., 2012)
Ca	+ (low pH)	+ (high pH)	+	n.a	(Kinniburgh et al., 1999; Iskrenova-Tchoukova et al., 2010; Cabaniss, 2011).
Cd	+	n.a	+	+	(Perdue et al., 1984; Hertkorn et al., 2004; Cabaniss, 2009, 2011).
Cu	+ (pH < 7)	++	++	n.a	(Kinniburgh et al., 1999; Karlsson et al., 2006; Cabaniss, 2011)
Fe	+	+	++	n.a	(Muñoz and von Sonntag, 2000; Pédrot et al., 2011; Marsac et al., 2013).
Mg	++	+	n.a	n.a	(Lu and Allen, 2002; Iglesias et al., 2003; Ahn et al., 2008; Korshin et al., 2009; Yan et al., 2015).
Na	+	n.a	n.a	n.a	Iskrenova-Tchoukova et al. (2010)
Pb	+	++	++	n.a	(Cabaniss, 2009, 2011).
Zn	+	n.a	++	+	(Karlsson and Skyllberg, 2007; Cabaniss, 2009, 2011).

adsorption between metal cations and acidic functional groups when the acid is weaker and cation valence is higher. The complexation strength for lighter metals increases with charge to size ratio of the binding ion (Skyllberg and Magnusson, 1995; Kalinichev and Kirkpatrick, 2007). Metal ions can be bound either as counterions (due to electrostatic forces), or bound specifically to reactive groups. The competition between metal ions may be largely due to the chemical nature of the bound ions. Depending on the deprotonation state and type of cation, the cation-NOM interaction can be specific or unspecific which may be indirectly influenced by the non-polar moieties (Tipping and Hurley, 1992). Unlike cation exchange mechanism where there is a fixed and permanent negative charge, the ion exchange behavior shown by humic substances is not in general charge equivalent (Kinniburgh et al., 1999). The cation-proton exchange depends on the polyelectrolyte structural charge density, the degree of ionization, the type of cation and the total cation concentration in solution. The release of protons during dissociation can either be due to competition from cations for the same binding sites or a decrease in the intrinsic deprotonation constant of non-dissociated groups due to the binding of cations at neighboring polymeric sites (Mota et al., 1996).

The low ionic charge and relatively large size makes alkali metal ions form complexes faster than other ions on the periodic table, though formed complexes are generally weak. When they react with multidentate ligands, the rate of reaction depends to some extent on the nature of the chelating agent and the differences in the stabilities of the complexes are seen in its dissociation rate. Alkaline earth ions however demonstrate considerable variation in reaction rate depending on the element involved. For example, the greater charge density on Mg^{2+} makes its bonding considerably faster and stronger compared to Ca^{2+}. The rate of reaction is therefore dependent largely on ionic size. The rate of Ni^{2+} is however, about a power of 10 slower than that of Mg^{2+} although they have similar ionic radii. Likewise is the rate of Cu^{2+} adhesion much higher than that of Ni^{2+}. The rate of reactions for trivalent metal ion reaction is slower compared to divalent ions but they form stronger bonds (McAuley and Hill, 1969).

From sections 2.3, it can be established that the complex and ill-defined nature of NOM place a huge limitation on our ability to measure and interpret the complexation equilibria of NOM (Filella, 2008). In particular, Town and Filella (2000), in a review of trace metal complexation parameters for natural waters highlighted the variation in results of each work, which was probably, due to the different experimental conditions and techniques used for each study. The use of varied methods for the determination of cation complex with functional groups makes it challenging to quantify and assign a unique definition to 'strong' or 'weak' affinity. For instance, while on the one hand, Cabaniss (2011), used *a priori* model to define binding strength/affinity ("weak" log $K_{ML} < 5$, "moderate" $5 < \log K_{ML} < 10$, and 'strong' log $K_{ML} > 10$), based on the conditional formation constant (K_{ML}) for complex 'ML' from 'M' and 'L', Iskrenova-Tchoukov et al. (2010), on the other hand, used bond angles and lengths (radial distribution functions and potential mean force), to define the strength of affinity.

3. Impact of complexation on physico-chemical characterization of NOM

Complexation reactions modify the basic fractioning constituents of the NOM; concentration, polarity, size, solubility, absorbance properties and acid, base, and neutral characteristics (Yan and Korshin, 2014). This session highlights some of the possible modifications due to NOM-metal complexation and their impact on NOM characterization.

3.1. Morphology (size, hydrophobicity, charges)

Factors that are influenced by the cation-NOM binding include molecular size, composition and configuration of the organic matter, pH and ionic strength of the solution and chemical properties of cation and cation/NOM composition (Ritchie and Perdue, 2003; Kalinichev and Kirkpatrick, 2007). In analyzing the effective MW distribution of the different fractions of NOM in the presence and absence of ions using light scattering techniques and high performance size exclusion chromatography (HPSEC), it can be observed that the size of NOM is significantly reduced when the ionic strength (for Na^{+}) of the solution is increased. This is probably due to coil-to-globule conversion and polyelectrolyte interaction that caused the NOM conformation to change from linear to spherical. However, the effect on the size would also be dependent on the cation involved, since the size of NOM is rather increased when the cation under consideration is Ca^{2+} instead of Na^{+}. This is possibly due to the aggregation or chelating between humic acids and Ca^{2+} (Xi et al., 2004).

Bowers et al. (2015), in using ^{43}Ca NMR, X-ray diffraction and helium ion microscopy to study cation binding and dynamics in flocculated NOM, however observed no changes in the floc morphologies with the type of NOM fraction, solution pH, or solution ionic strength, though admittedly certain pH and ionic strength were needed to induce flocculation.

In varying the pH at which NOM complexes with cations, Ritchie and Perdue (2003), observed a downwards drift in pH above 6.5 even when aliquots of NaOH was added. This suggests that the slow reactions of some ligands generate additional acidity. Proton association and dissociation from a ligand is influenced by its molecular structure through polar substituents and resonance effects. In comparing formic acid (HCOOH) to acetic acid (CH_3COOH), though they both have an −OH group, the former is seen as a stronger acid because the ability of the hydrogen atoms to attract electrons more strongly by displacing electrons from the −OH

group in the direction of the O atom. An increase in the distance from the acid group decreases the influence of polar constituents present. Likewise, saturated hydrocarbons groups are electron-repelling while unsaturated ones are electron-withdrawing (Tipping, 2002).

3.2. Electronic spectral changes

The optical properties (absorbance and fluorescence) of DOM have been greatly explored in studying its characteristics. This is because of the presence of chromophores and/or fluorophores in the ligands of NOM. Optical properties of DOM are highly variable and controlled by different physico-chemical parameters (pH, photoreactivity, redox conditions) and biological processes (Jaffé et al., 2008). When chromophores or fluorophores absorb light in the UV–vis region, electrons in the ground state are excited to higher energy states. The nature of the transition is mainly $\pi\pi^*$ and $n\pi^*$. The molecular structure therefore determines the absorption maximum and intensity. As conjugation increases in a structure, the maximum wavelength moves to longer wavelength. Classical optical spectroscopy techniques are widely used to study DOM and its interaction with metal cations. Indeed, absorbance or fluorescence measurements are inexpensive, easy, relatively rapid and do not require sophisticate pretreatment.

UV–vis spectroscopy can provide some structural information about the organic matter in water. Spectral features obtained for a complex mixture of molecules can be generally considered as the average of individual compounds that form the solution. Specific UV absorbance (SUVA), ascertained as the UV absorbance of a solution at a given wavelength normalized for DOC concentration, is strongly correlated with the degree of aromaticity of DOM (Weishaar et al., 2003). This indicator of DOM aromaticity is often calculated at 254 nm ($SUVA_{254}$) (Kim et al., 2018; Lee et al., 2018). Numerous studies have shown that the variation of the $SUVA_{254}$ descriptor is directly bound to metal complexation. Studies on copper, zinc, cadmium and nickel complexation with DOM on surface waters, isolated using reverse osmosis, have highlighted important positive correlation between the absorbance indices and the metal binding affinity pointing out that in those waters, aromatic humic substances are the predominant metal chelators (Baken et al., 2011). This result was also confirmed for iron in naturel fresh water (Fujii et al., 2014; Kikuchi et al., 2017). In anthropogenically influenced waters however, nickel is mainly complexed to EDTA and can account for about 87% of all EDTA sites bonded (Baken et al., 2011). The complexation of Na^+ and Mg^{2+} with tocopheroxyl radicals results in an increase in UV-absorbance (Mukai et al., 2012). Trivalent cations (Al, Fe, Cr) complexes with anthocyanins and its derivatives resulted in a stronger decrease in absorbance than Mg^{2+} (Sigurdson et al., 2016). While an increase in absorbance intensity could be due to band broadening resulting from the superposition of un-associated and chelate form of the NOM, a decrease in absorbance intensity could also be due to a decrease in the energy needed to cause light-induced electron transition in a chromophore, shifting the absorption maximum to a longer wavelength (Fedenko et al., 2017). The spectral modification observed in the absorption spectra upon metal complexation is very difficult to explain in term of binding sites. This is why it is possible to have more detailed structural information by using absorption spectroscopy coupled with quantum chemistry methods to determine the preferential binding site on a multisite ligand that constitutes a model molecule of humic substances (Cornard and Lapouge, 2004). The difference in the metals' effect on spectral properties of NOM is due to the individual preference of metals for certain binding sites and pH (Langford and Khan, 1975; Cabaniss, 1992).

However, the spectral changes observed in the UV–visible absorption spectra remain limited and difficult to interpret. Those observed in fluorescence emission are much more important and especially allows to highlight finer phenomena and further analysis of the data. The presence of metals can serve as quenchers or enhancers of fluorescence intensities due to the high affinity between metals and aromatic moieties though metals can sometimes be associated with oxygenated aliphatic carbons (Cabaniss, 2011). During complexation with metals, the properties of the fluorophores are modified making it possible to compare the free and the complexed ligands.

Fluorescence quenching, on the one hand, occurs by the fluorophore donating electrons to the quencher. Generally, quenching can occur without any permanent alteration of the molecule or photochemical reaction (Lakowicz, 2006). The complexation of Cu^{2+} and Ni^{2+} for instance, result in fluorescence quenching while that of Al^{3+} enhances the fluorescence of phenolic compounds at pH 5.0 and quenches at pH 7.5 (Cabaniss, 2011). A change in pH affects both the shape and magnitude of the quenching spectrum of Cu^{2+}; at pH < 6, Cu^{2+} is more bonded to the carboxylic functional groups while at pH > 8, it is more bonded to the phenolic groups of fulvic acid. Likewise, Fe^{3+} quenches fluorescence very weakly when complexed with poly-acid ligands at pH 7.5 due to the formation of iron oxyhydroxides which sequester much of the Fe^{3+} though a much stronger quenching is observed at pH 5.0 (Cabaniss, 1992). On the other hand, fluorescence enhancement, occurs by a modification in the NOM complex through; (a) the movement of fluorophores into solvent regions (b) an increase in the rigidity of the molecular structure which consequently increases the fluorescence quantum yield (Lakowicz and Masters, 2008). Due to the indirect nature of optical measurements, quenching or increase of fluorescence may not necessarily be due metal binding but also the presence of marginal aromatic ligands surrounded by abundant aliphatic ligands in the environment (Cabaniss, 2011).

Fluorescence excitation-emission matrix (EEM) coupled with parallel factor analysis (PARAFAC) allows categorizing NOM samples into combination of several groups of fluorophores with similar optical properties. This method is widely used to characterize the metal binding with DOM (Stedmon and Bro, 2008; Xu et al., 2013). The fit of fluorescence quenching by models, (for example, the Ryan-Weber model) enables the characterization of the fluorophore affinity for a given metal cation and the estimation of a complexation constant (McIntyre and Guéguen, 2013; Yuan et al., 2015). Recently, two dimensional fluorescence/Fourier transform infrared correlation spectroscopy allowed the localization of functional groups in different fractions of humic substances and thus to observe the ability of these groups to complex metal cations (Tang et al., 2019). Because molecular spectroscopy methods alone can be limiting in information about the coordination, and the structure of the metal ion binding site as well as conformational changes that occurs on the ligand sites, they may require other supporting techniques (Cornard and Merlin, 2002). One of such techniques that can accompany spectroscopic techniques to provide additional information on the different fractions of NOM with respect to their molecular weight is the high performance size exclusion chromatography (HP-SEC) (Her et al., 2002). The advent of ultrahigh resolution Fourier transform ion cyclotron resonance mass spectrometry (FT-ICR-MS) has equally helped to advance knowledge on NOM characterization. FT-ICR-MS is capable of resolving simultaneously thousands of individual molecules from complex organic mixtures like NOM and subsequently provides the molecular formulas for most of the resolved ions (Koch et al., 2008). One major challenge however with this technique is the difficulty in separating noise from analyte peaks (Riedel and Dittmar, 2014).

4. Impact of cations–NOM interaction on water treatment efficiencies

The main goal of the drinking water industry in characterizing NOM is to predict its behavior in the different treatment processes. This section looks at the impact of the presence of NOM-cation complexes on treatment efficiencies of most common techniques used in drinking water treatment plants.

4.1. Coagulation and flocculation

Coagulants can be either inorganic salts, organic polyelectrolytes or inorganic-organic composites. Although baseline coagulation targets to remove turbidity, advanced coagulation also targets the removal of NOM as the dose and pH conditions are optimized. Several other factors such as coagulant type, mixing conditions, temperature, properties of NOM, as well as the presence of cations, influences the efficiency of coagulants to remove NOM (Matilainen et al., 2010). When the dominant fraction of NOM has a high molecular weight, the removal mechanism is mainly by charge neutralization and the required coagulant dose is low, while when the dominant fraction has a low molecular weight, the required dose is higher as the removal mechanism is mainly by adsorption onto metal hydroxide surfaces (Matilainen et al., 2010). The most common salts used in coagulation are aluminium sulfate (alum), ferric chloride and ferric sulfate. These coagulants are added to water with the aim of forming coagulant-NOM complexes to remove mainly NOM by two main mechanisms; adsorption and charge neutralization (Davis and Edwards, 2017). The main NOM removal mechanism for ferric salt is by the adsorption of NOM onto ferric hydroxide flocs (Davis and Edwards, 2014). At a low Ferric/NOM ratio however, NOM has the capacity to interfere with the hydrolysis of a low dose of Fe-based coagulant by forming Fe-NOM complexes, which subsequently influences the size, reduce zeta potential, morphology and identity of the Fe precipitates, thereby limiting the coagulation efficiency of the iron salt. The presence of other cations such as Ca^{2+} can neutralize NOM and restore the coagulation efficiency of the low dose of iron-based coagulant, thereby making enough Fe ions to be available for effective coagulation. When the Ferric/NOM ratio is high, irrespective of the presence or absence of Ca^{2+}, the coagulation efficiency is not reduced as there is sufficient Fe for coagulation (Davis and Edwards, 2017). Generally, ferric-based coagulants are seen to be more efficient in removing NOM than aluminium-based coagulants (Budd et al., 2004; Golob et al., 2005; Chow et al., 2009; Matilainen et al., 2010). Though the overall removal efficiency of both salts are very close (70 and 67% respectively for ferric and aluminium based coagulants), ferric salts have an advantage of being able to remove more (25%) intermediate molar masses (1000–4000 Da) than aluminium salts. Aluminium salts however have a higher turbidity removal efficiency (Matilainen et al., 2005).

For alum, even at low concentrations of 0.5 mg and 1.0 mg Al L^{-1}, there is the formation of small $Al(OH)_3$-humic substance colloids, and the size of the precipitate colloid formed grows with an increase in the alum concentration (Wang et al., 2014). The presence of Ca^{2+} improves the coagulation of alum and equally increases the pH range for effective removal of even the low molecular weight acids especially at pH 7 and 8 (Duan et al., 2012; Davis and Edwards, 2017). The zeta potential of DOM in the presence of Al^{3+} was observed to increase with increasing addition of Mg^{2+} indicating that unlike Ca^{2+}, the presence of Mg^{2+} may suppress the binding between coagulant Al^{3+} and DOM (Zhou et al., 2017). In using the aluminium coagulant at low dosages, residual aluminium concentrations after treatment can be relatively high because less humic substances are removed (and vice versa). High aluminium residual has been attributed to the presence of dissolved Al-NOM complexes formed when a high proportion of aluminium monomers is present in the aluminium-based coagulant (Yan et al., 2008; Kimura et al., 2013). Dissolved residual aluminium is complexed with almost all MW ranges (500 Da - 100 kDa) (Kimura et al., 2013). The use of aluminium-based coagulants is currently of concern because aside the presence of residual aluminium in treated waters affecting the aesthetic properties, it may also cause health risk as it is linked to adverse neurological effects such as Alzheimer's disease (Flaten, 2001). Although an adjustment of the pH can minimize the aluminium residue from aluminium coagulants, this is often not done as another post pH correction is needed to prevent corrosion in distribution channels.

4.2. Precipitation

4.2.1. Lime softening

The main targets of softening are calcium ions, even though this method may also remove a limited portion of the hydrophobic NOM fraction (Semmens and Staples, 1986). Caustic soda (NaOH) and calcium hydroxide (lime) are added to increase the pH of the solution (> 9.5) and cause the formation of insoluble $CaCO_3$ and $Mg(OH)_2$ which would precipitate out of solution (USEPA, 2011). Unlike $CaCO_3$ which has an overall negative charge on its surface (Stumm, 1992), $Mg(OH)_2$ precipitates as positively charged particles with high surface area and amorphous structure which aids the sorption by NOM onto its surface (Thompson et al., 1997). Russell et al. (2009), however observed that at very high pH above 11.5, both $CaCO_3$ and $Mg(OH)_2$ have positive charges with a great affinity for NOM adsorption. In addition, a limited NOM fraction is removed through precipitation, co-precipitation or both (Thompson et al., 1997). At high concentrations, (no specific values given in literature) NOM can complex with the Ca^{2+} cations and cause them to precipitate in a different phase (organo-calcium salt) from the $CaCO_3$ if the aqueous solubility of the complex is exceeded, thus inhibiting the formation of $CaCO_3$ and making the lime softening method inefficient (Liao and Randtke, 1986; Russell et al., 2009). In a jar test experiment of a modified lime-soda softening process to enhance NOM removal by the addition of $MgCl_2$, lime-soda ash removed about 43% of DOC in the presence of the magnesium salt (7.5 mg/l) compared to 13% when no magnesium was added (Bob and Walker, 2006). Polyaluminium chloride is also proposed to increase the formation of $Mg(OH)_2$ precipitates thereby increasing the removal efficiency of NOM at relatively low pH < 10 (Yan et al., 2008).

4.2.2. Chemical precipitation

Chemical precipitation is one of the principal technologies used to remove dissolved metal pollutants from wastewater streams. This process, which is dependent on the metal concentration and solution pH, is achieved by modifying the solution chemistry through the addition of precipitating agents like $Ca(OH)_2$, $Mg(OH)_2$, NaOH and Na_2CO_3. The agents are added to raise the solution pH and form insoluble complexes with target metals (Wang et al., 2005). Unlike the lime-soda softening technology that mainly focuses on the major cations, chemical precipitation can target a wide range of trace metals. The presence of simple but strong complexing ligands like EDTA in wastewater, however, reduces the efficiency of this process. The formed metal-EDTA complexes are highly soluble, poorly biodegradable and extremely stable over a broad pH range (Wu et al., 2013). In quantifying the speciation of EDTA in influents and effluents of sewage treatment plants, it is estimated that Fe(III)EDTA represents the dominant EDTA species comprising 20–90% of the total EDTA in the effluents. While no significant EDTA is removed by biological or chemical processes

during sewage treatment, nitrilotriacetic acid is degraded to a large extent (> 90%) (Kari and Giger, 1996). At higher pH (> 7), Fe(III) EDTA is not stable and so other metals present like Zn can compete for binding sites (Nowack, 2002).

4.3. Membrane separation

During membrane filtration (tight ultrafiltration, nanofiltration, reverse osmosis), NOM is removed principally through size exclusion, charge repulsion and hydrophobic interactions (Metsämuuronen et al., 2014). NOM is also known to be one of the main factors responsible for the fouling of low-pressure membrane in natural waters with the biopolymers' and hydrophobic fractions being the largest contributors. This fouling is primary caused by the adsorption of NOM onto membrane pore walls, which blocks the pore spaces. The adsorbed NOM further interacts with other substances in the solution, making the solution chemistry an important factor for fouling (Tian et al., 2013). The presence of cations in solution would therefore influence fouling. Divalent cations in particular partially neutralize the carboxyl functional groups of NOM and consequently reduce the repulsion effect on NOM. The partially neutralized NOM complex may be easily adsorbed onto the membrane surface forming a densely packed fouling layer. The presence of Ca^{2+} increases the humic acid (HA) fouling of ultrafiltration (UF). Ca^{2+} probably forms Ca-HA complexes which are larger in sizes and consequently reduces the membrane pore sizes, sometimes reaching the cut off values for acids and humics (Amy, 2001; Galjaard et al., 2004; Comerton et al., 2009). Li and Elimelech (2004), likewise, observed a decrease in the nano-filter membrane permeate flux of 49% and 16% when 1 mM of Ca^{2+} and Mg^{2+} were present, respectively. On the contrary, monovalent Na^{+} has the ability to mitigate HA fouling. The mechanism is probably due to Na^{+} ability to form neutralized Na-HA complexes with a size below the pore cut off size (Hong and Elimelech, 1997; Tian et al., 2013). Hence, both the nature of the ions as well as the NOM constituent have a considerable effect on the treatment process (Xi et al., 2004). The effect on fouling has also been attributed to high ionic strength, which reduces the electrostatic double layer thicknesses of both membrane surface and NOM resulting in fouling (Ahn et al., 2008). But even at the same ionic strength, Ahn et al. (2008), observed that Na^{+} and Mg^{2+} cause less fouling of UF polyethersulfone membrane compared to Ca^{2+}due to the strong interaction of Ca^{2+} with negatively charged carboxyl groups of NOM (Ahn et al., 2008; Iskrenova-Tchoukova et al., 2010). However, this statement has been controverted, or cannot be applied to all types of membranes as Tang et al. (2014) observed that monovalent cations caused more fouling of polyvinyl chloride UF membrane by forming a gel layer, which blocked pores compared to divalent cations, which formed a porous caked layer structure on the membrane surface.

Aside cations complexing with NOM to increase fouling, they can equally form ionic bridges (stronger for Ca^{2+}) between negatively charged sulfonate functional groups of the membranes and the carboxylic groups of NOM which increases the adhesion between the NOM ligands and the fouled membrane surface forming a very compact fouling layer (Iskrenova-Tchoukova et al., 2010). Ahn et al. (2008), however, suggested that divalent cations (Ca^{2+} and Mg^{2+}), which are strongly associated with the carboxylate groups of NOM, may boost the aggregation of NOM rather than forming ionic bridges between NOM functional groups and a polyethersulfone membrane surface as they are weakly attracted to the membrane sulfonyl groups. This suggests that the aggregation of NOM in the presence of divalent cations could be a higher contributor to membrane fouling as partially neutralized NOM molecules are easily adsorbed on membrane surface. Moreover, large size of the organic colloids complexed with trivalent cations like aluminium ($Al(OH)_3$) could also easily block membranes pores (Leenheer and Croué, 2003; Wang et al., 2014). Whereas divalent cations result in irreversible fouling, monovalent cations are only responsible for reversible fouling. The irreversibility of Ca-HA fouling was however, observed to decrease in the presence of Na^{+}, as added Na^{+} is able to reduce bond strength of Ca-HA and between HA and the membrane, due to electrostatic shielding. A similar trend was observed when bovine serum albumin (BSA) was used as a surrogate for the protein fraction of NOM, though a mixture of both organic molecules (BSA and HA) resulted in more severe fouling suggesting a synergistic fouling effect (Tian et al., 2013).

Backwashing with demineralized water instead of normal permeate can effectively control fouling of UF membrane caused by NOM-Ca complex. This is because UF permeate contains same multivalent cation concentration as feed water, while the absence of cations and NOM in demineralized water reduces the ionic strength and the Ca-bridging effect between NOM and membrane surface. Backwashing with demineralized water, then, substantially reduces the rate of increase in the transmembrane pressure. Another approach may be to raise the pH of the feed water in order to keep the carboxyl functional groups deprotonated, thus preventing their deposit onto negatively charged membrane surface (Hong and Elimelech, 1997).

4.4. Activated carbon

Activated carbon (AC) is mainly used to remove organic substances or micro-pollutants by adsorption. The carbon surface, which is predominantly hydrophobic, contains functional groups, which are formed during the activation process (Kilduff et al., 1996). When the activated surface is further oxidized, electrochemically or chemically (nitric acid and ozone), the number of oxygen containing acidic functional groups, such as carboxylic and phenolic groups, on the surface increases, which, in effect, increases its sorption capacity for cations at near neutral pH. Uptake for cations equally increases with increasing pH due to the dissociation of the weakly acidic oxygen-containing groups (Rangel-Mendez and Streat, 2002). The presence of humic substances can compete with target synthetic organic compounds and reduce the efficiency of the AC (Kilduff and Karanfil, 2002). There can likewise, be competition between cations for adsorption sites confirming that the solution chemistry can also alter the surface charges of the carbon (Sengupta, 2001). For instance, the lower ionic radius of Cu^{2+} (0.70 Å) makes it a better adsorbate than Pb^{2+} with a higher ionic radius of (1.12 Å) as higher ionic radius would result in rapid sites' saturation and steric overcrowding (Faur-Brasquet et al., 2002). Moreno-Castilla et al. (2004), observed an increase in the uptake of Cd^{2+} ions on AC pre-adsorbed with organic compounds (tannic acid). The capacity of AC to adsorb gallic acid also slightly increased in the presence of Cr^{3+}. The adsorption of organic molecules on AC increases with increasing ionic strength and divalent ion content (Ca^{2+}). The increase in adsorption may be either due to an adsorption of larger molecules or an effective adsorption of the smaller molecules, as new adsorption sites are created through cationic bridging. Partial neutralization of the surface functional groups reduces intramolecular charge repulsion and molecular expansion. The ionic strength further influences the electrostatic interactions between the adsorbate and adsorbent and/or the solvent (Kilduff et al., 1996). This has been attributed to the neutralization of its functional groups when complexed with the metal ion, making the adsorbate more hydrophobic and increasing the adsorption capacity (Ferro-Garcia et al., 1998). The effect of NOM-metal complex on AC efficiency is thus due to both the properties

of the AC (specific surface area, micropore volume, functional groups) and that of the metal ion (ionic radius and electronegativity) (Faur-Brasquet et al., 2002).

On the other hand, the presence of a chelating agent alters the adsorption properties of a metal ion as the chelates themselves are adsorbed onto surfaces (Nowack, 2002). This may affect the efficiency of adsorption depending on the targeted compound. Although tri-ammonium functionalized mesoporous silica has proven to remove about 96% of Cu(II)-EDTA chelates from aqueous solution with initial concentration of 0.1 mM, the maximum (> 97%) copper adsorption was achieved in acidic condition and low ionic strength (0.01 M) (Wu et al., 2013).

4.5. Oxidation processes

The presence of metal cations in water can influence (positively or negatively) the formation of disinfection by-products by changing the oxidation mechanism of the NOM by chlorination, depending on the cations involved and the NOM composition. For instance the presence of copper oxide reduces the formation of trihalomethanes (THMs) because the metal oxides consume chlorine while the reverse is observed for Cu^{2+} ions (Li et al., 2007; Navalon et al., 2009). The formation of trihalomethanes has been mostly seen to be reduced by the presence of metals from chlorination surrogate compounds as phenol, 2,6-dihydroxybenzoic acid or tannic acid in presence of diverse metals (Ca^{2+}, Mg^{2+}, Mn^{2+}, Fe^{2+}, Cu^{2+} and Al^{3+}) (Blatchley et al., 2003; Navalon et al., 2009; Liu et al., 2012). However, considering the chlorination of humic substances, the reverse is usually found. For instance, the increase of THM formation from humic substances in presence of Mg^{2+} and Ca^{2+}. This has been attributed to the affinity of the metals for carboxylate functional groups of the substrate which consequently increases their reactivity towards chlorination (Navalon et al., 2009; Liu et al., 2012). Also, Cu^{2+} apparently activates certain components of humic substance that are otherwise inefficient precursors and so consequently enhances the formation of chloroform from humic acids during chlorination (Blatchley et al., 2003).

On the opposite, the presence of metal ions has been shown to enhance the formation of haloacetic acids (HAAs) from tannic acid through the production of strong oxidative radicals during the chlorination (Liu et al., 2012). Furthermore, complexation of metals to the active sites of organic substrates resulting in a difference in electron densities depending on the type of cation, the change in electron density, affects the reaction activity of electrophilic substitution by chlorine with the corresponding carbon (Liu et al., 2012). The respective inhibitory or enhancement efficiency of the metals is directly proportional to their concentrations (Liu et al., 2012).

When the oxidation is by ozonation however, the presence of NOM can affect the stability of ozone by either directly reacting with the ozone or indirectly by scavenging OH radicals. In natural waters, the presence of NOM can act as inhibitors to stop ozone chain reactions by entrapping superoxides after reaction with OH radicals (Buxton et al., 1988). The protonation and complexation of amine functional groups of EDTA, nitrilotriacetic acid, decrease their reactivity towards ozone in water treatment. During complexation especially with transition metals, the rate constants are lower because the metals are able to interact with the nitrogen groups. For instance, the complexation of Fe^{3+} reduces the reactivity of EDTA to ozone by a factor of 500 since EDTA are monoprotonated at nitrogen (Muñoz and von Sonntag, 2000). This explains why EDTA is not removed from natural waters by ozonation. This interaction can however be weakened by a substitution of the ligand with OH^- (Muñoz and von Sonntag, 2000; von Gunten, 2003). To limit the negative effects of NOM complex on treatment process, advance oxidation processes such as UV/H_2O_2 or chlorine, Fenton oxidation, ozonation, TiO_2 photocatalysis and photo-electrocatalytic oxidation, discharge plasma oxidation followed by alkaline precipitation have been proposed as a pre-treatment step to degrade NOM-metal complexes (Wang et al., 2018). These techniques however either do not work for all metal complexes such as Cr(III) complexes or performs averagely. Photo-Fenton process and Fenton derived process combined with precipitation has been shown to exhibit an efficient removal of Cr(III) complexes (Ye et al., 2017, 2018) and Ca-phosphonate complexes (Sun et al., 2019).

4.6. Ion exchange

Ion exchange is used in water treatment to remove dissolved ions from waters and more recently to target NOM removal (anionic resins) (Li et al., 2014). The resin surface loaded with loosely bound ions exchanges the ions with similar charged ions in the solution (Bauman and Eichhorn, 1947). The presence of NOM or chelating agents can affect the efficiency of this method, as the formed NOM-metal complex is not in the ionic state to be exchanged. For anionic exchange resins, the presence of higher affinity chelating agents like EDTA can compete with target weakly acidic functional groups for exchange sites. Aside neutralizing cations, organic compounds and other solids present in water can foul exchange resins with anion-exchange resins being more susceptible than cation exchange resins. Fouling which occurs when very strong ions are held onto resins' surface or when the inner surface of resins are occupied by hydrophobic substance can be reversible or irreversible depending on the affinity of the ions involved (Dorfner, 2011). Fouling increases the frequency and volume of backwash requirement, increases the sensitivity to flow rate and temperature, increase conductivity of solution and reduces the overall efficiency by increasing volume of desorption concentrate (Abrams, 1982). Liu et al. (2017) recently improved the capacity of polymeric anion exchanger towards the removal of Cu(II)EDTA with nanoscale zero-valent iron deposition.

4.7. Research challenges for water treatment

The variation in the quantity and quality of NOM in the environment is likely to continue due to the effects of climate change. The variations in DOC trends and its complexation with trace elements may not only significantly impact water treatment process selection, design and operation but may also increase the risk of many treatment facilities violating water quality regulations on NOM, trace metals or DBPs. The description of the phenomena in real matrices remains challenging. The coupling of size exclusion chromatography with elemental detector, ICP-MS, looks promising but lacks at the moment a quantitative measurement validation (Piatina and Hering, 2000; Rathgeb et al., 2016). Other methods based on for example electrochemistry (Moutcine and Chtaini, 2018) are useful in elucidating complexation in real matrices but applications in the field of water treatment are missing. Progress in many different areas, from high-resolution mass spectrometry to quantum chemistry modelling, could each bring their own valuable information to the field. Also, fluorescence detector are more and more used on-line to also study the diel variability of NOM (Trubetskoj et al., 2018; Ignatev and Tuhkanen, 2019). This fast measurement will give valuable data on NOM sources, origins and dynamic in the environment and are useful for characterizing water sources. As the trace metals and major elements could modify the response of probes, researchers should attend to take into account those aspects. NOM-metal complexes impact on ozonation is an

important aspect to cover in the next years especially considering the increasing use of ozonation for the treatment of wastewaters. The high trace metal concentrations coupled with high level of organic matter make those effluents particularly exposed to such interaction.

5. Conclusion

The complex NOM structure, which contains several functional groups, controls the bioavailability and biogeochemical cycling of trace elements in water. The two main functional groups, *i.e.* carboxylic and phenolic groups show their contribution varying with their deprotonation with pH, inducing a higher contribution of carboxylic acids at lower pH due to their lower pKa values compared to phenolic moieties. The type of bonding that occurs between NOM and cations is mainly coordinate covalent bonding as electrons are donated only by the ligand(s) involved. This coordination modifies the physico-chemical properties like morphology and spectral characteristics of the newly formed product.

The NOM-metal formed complex impacts water treatment efficiencies. In coagulation, the complexation between the coagulant salts and NOM helps to remove NOM from solution. This process is further enhanced when Ca^{2+} is added. The impacts however are not always positive as for example the presence of high NOM concentration complexing with free calcium causes it to precipitate in a different form thereby reducing the efficiency of lime softening method. NOM-metal complexes are equally responsible for membrane fouling as cations partially neutralize NOM making the complexes easily adsorbed onto membrane surface. In addition, the presence of metals influences the formation of disinfection by products by modifying the mechanism in which chlorine reacts with NOM either by increasing or decreasing DBP formation or changing the species formed. The modification of rate constants during ozonation process has also been observed, although limited to model compounds, (*e.g.* EDTA and Tannic acid) which are not representative of NOM behavior.

Declaration of interests

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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