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Natural organic matter and cationic interaction effecting water treatment process- A review

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Abstract

One of the significant challenges faced by water treatment plants is the transformation of natural organic matter with reference to their quality and quantity owing to the changing climatic conditions. The natural organic matter consists of heterogeneous functionalized groups among which phenolic and carboxyl groups are the dominant groups that are pH-dependent and shows a stronger affinity towards the metals. Properties of natural organic matter and trace elements govern the binding kinetics influencing binding of cations to functionalized groups at lower pH; precisely, Ca^{2+} ions form strong bonds with carboxylic groups and Zn^{2+} ions bond with the amine groups. The water treatment process mechanisms like adsorption, coagulation, membrane filtration, and ion exchange efficiencies are strongly affected by the presence of natural organic matter with cations complex/cations and /or by the natural organic matter alone. The complexation among the natural organic matter and coagulants enhances the natural organic matter removal from the coagulation processes'; further, Ca^{2+} ions addition enhances the process positively. The current review illustrates detailed interactions between natural organic matter and cationic interactions in the environment, cations' preference and competition for the functionalized groups, and the potential impacts of cations on natural organic matter in the treatment facilities.

Key words: Cations, Natural Organic Matter, Water Treatment, Effects, Pollutant Removal

1. INTRODUCTION

All spheres of the environment have been facing deviations in their physical and chemical properties, leading to disturbances and destruction of the ecosystem. One such change in the aquatic environment is NOM (natural organic matter), which has been detected to increase during the recent decades, differing considerably [1]. Among several other effects, one of the significant effects of seasonal changes is enhanced NOM concentrations, which affects the process control and optimization of the treatment plant, exerting more challenging conditions [2]. Even though NOM is non-toxic by nature, it tends to change water's physicochemical properties, including odor and color of water, directly and indirectly influence dissolved oxygen, nitrogen, sulfur, and phosphorus concentrations, acting as a carrier of the toxic pollutants. NOM also serves as a carbon sink and source, affecting climate change [3-5]. NOM is understood as a complex combination of various organic compounds existing in freshwater, majorly formed by environmental factors, like weathering or decaying biotic materials [6, 7]. Owing to the complexity of NOM's wide variety of chemical constituents, it is challenging to characterize them individually and precisely. Further, an ambiguity exists with regard to NOM, which consists of a macromolecular entity or micro molecules [8, 9], bound together by weak interaction noncovalent bonds, forming supramolecules [10]. NOM is an intricate substance consisting of carbon- based compounds, small segments of different chemical forms, like alkanes, proteins, fats, carbohydrates, amino acids, organic acids, and lipids. The other parts of NOM, which possess no specific chemical formula or compounds and which are not known, are understood to be humic materials [11]. Being not readily degradable in soil, humic fractions remain persistent for several years in comparison to non-humic substances. Elemental analysis of humic substances showed that they mainly consist of 57% of carbon, 36% of oxygen, 6% of hydrogen, 3% of nitrogen, and about 0.4 to 1.8% of sulfur [12, 13], and also smaller quantities of functionalized groups (sulfur and nitrogen) [14, 15]. The humic substances can be classified into three classes: humins, fluvic acids, and humic acids, based on molar mass and solubility. The humin's molar mass is 105 and it is unsolvable at all pH ranges in an aqueous medium. The humic acids consist of weak aromatic/aliphatic organic acids with molar mass ranging from 104 to 105, and are soluble at pH≥2. In contrast, the fluvic acid is soluble at all ranges of pH [16]. Humic and fulvic acids are pervasive and found in all water systems; depending on the hardness, the seawater consists of 10-30 % of dissolved natural organic matter (DNOM), 70-90% of DNOM is reported in wetland waters, while 40-90% and 50% of DNOM are observed in waters of streams and lakes [16-18]. These variations are due to the cationic hardness, as these substances suppress the solubility of fulvic acids that contain high molecular weights [19]. By origin, the NOM can be defined as "allochthonous" or "autochthonous." Allochthonous NOM refers to NOM that originates from different niche; these NOMs are transported into the water matrix with the help of erosion agents and are sensitive to the removal and degradation process. Allochthonous NOM is obtained from the plants consisting of lignins, producing fulvic acids consisting of high aromatic/phenolic compounds with low nitrogen contents upon degradation. In contrast, Autochthonous NOM is the term that refers to the indigenous complex usually derived from algae [20]. The NOM derived from aquatic algae consists of a high amount of nitrogen compared to allochthons and has lower phenolic/aromatic compounds [21]. The non-polar fractions (hydrophobic) consist of more significant NOM fractions with conjugated aromatic/phenolic bonds. In contrast, polar particles (hydrophilic) consist of aliphatic and nitrogenous compounds [22]. The functionalized groups present in the NOM might be replaced by the unsaturated/alkyl carbons, aldehydes, amino/ alcohol groups, ketones, esters, and carboxylic groups [23, 24]. Xia *et al.* reported that the NOM could control bioavailability and biogeochemical cycles of the environment's trace elements due to higher reactivity. Upon finding an uncomplexed metal, it is to be noted that complexation of NOMmetal occurs due to binding of the metals to the prevailing sites of ions or replacing protons' positions [25]. This could be attribtued to enhanced electrostatic interactions among cations and functional groups deprotonated with an increase in pH. Owing to the complexity and heterogeneity of NOM, several reviews and research papers have focused on classifying and characterizing NOM [26-28]. The present review aims to examine the interaction between the NOM and cations comprehensively. Furthermore, attention has been paid to the functionalized groups, cations, and their interactions. Moreover, after reviewing the propensity of positively charged ions for functionalized groups and feasible competition among cations towards attachment sites, the impacts of NOM, cations, and their complexation in the potable water treatment systems have also been assessed.

2. CONCEPTUAL CHARACTERISTICS OF COMPLEXATION OF METAL TO NOM

2.1. Central Atoms - Organic Linkers In general, bonding between the atoms occurs by transferring electrons from one orbit to another of neighboring atoms, called coordinate covalent bonds. The organic linkers or ligands might be an ion or a molecule. Lawrance stated that acceptors of electron pairs are commonly known as Lewis acids; in contrast, donor electron pairs are called Lewis bases [28-39]. During the coordination, the atoms' morphological properties like bond angle, bonds, and distance between the bonds are altered, leading to physical characteristic changes. Thereby, the atoms' new physical features do not depend on the central atoms or organic linkers involved. If a single atom is involved in binding, newly formed structures are referred to as monomers; if the link ing units are less, then the formed structures are called oligomers [40]. The bonding between the atoms or bridging by organic linkers involve polymers consisting of many central atoms. The atoms' linkage might occur through the atoms having common donors while binding to the main metal atoms. The metal atoms might even encapsulate in polydentate ligand, coordinating many donors [39].

2.2. Binding Sites with Preferentiality The carboxylic phenolic groups are considered essential for NOM-cations binding; phenol functional groups are lower in abundance over carboxylic functional groups [40- 46]. Ritchie and Perdue studied (using 14 IHSS standards) carboxylic and phenolic groups' compositions and stated that the carboxylic groups consist of 78-90% of fulvic acid in total and 70-82% of humic acids [47]. The average of carboxyl to phenolic compounds was found to be 79:21 for the IHSS studies; the higher affinities of these groups to the cations were compared to the minority groups, like ester, amines, ketones, aldehydes, and alcohols, which are greatly dependent on pH, as reported by Nederlof *et al.* [48]. At higher pH, the deprotonation was found to be increased, enhancing the ligands' availability of binding sites. In contrast, at lower pH, the protonation was found to be increased and binding sites reduced for the ligands [49].

2.3.Carboxylic Functionalized Groups

At a pH greater than 4.4. carboxylic groups tend to dissociate faster than phenolic groups as they are more acidic. For instance, Baalousha *et al.* reported that at pH 4.42, the carboxylic functionalized groups dissociation released humic substances at Suwanee river, responsible for the negative impacts on the dissolved organic matter (DOM) sites [50, 51]. Bryan *et al.* reported the negative charge generation during the dissociations in the carboxylic groups, resulting in enormous potentialities of the humic substance surfaces to form a double layer around the surroundings [37]. Like charges, repulsions are required to attain the steric stability for humic substances. The surface areas and binding affinities with the cations are enhanced due to these repulsions as they create an electrical double layer at the interfaces. When the oppositely charged ions reach the humic acids' surroundings (macro ions), both interact within available sites electrostatically; however, selection of specific areas is quite challenging to determine. NICA and Donnan models are used for improving the prediction of metal behaviors for the few surfaces with complex models in the environment. Kinniburgh *et al.* reported that NICA models precisely describe the associations, whereas Donnan models represent non-specific associations [52].

2.4. ***Phenolic Functionalized Groups***

Phenolic functionalized groups are among the other groups primarily useful for the complexation with metals. These compounds originate from the plants and leach into the soil/water matrix. For instance, Cates and Rhoades reported that the dry plant masses nearly constitute 60% of the phenolic groups, contributing the NOM to the matrix [55]. Fig. (**2**) depicts the commonly found phenolic functionalized groups in the humic substances. Bidentate complexation of metals is formed when the hydroxyl groups are ortho positioned [56]. Phenolic groups deprotonate fastly at greater pH (>9.5) and enhance the complexations with metal atoms. Baalousha *et al.* described that at a pH of 9.68, the Suwanee river consisting of humic substances enhanced the dissociation of phenolic functionalized groups [57]. The solubility and tendency to coordinate metal ions are limited due to the increase in molecular sizes, even though the coordination principles are not altered [39]. The groups of phenols enhance carboxylic functionalized group complexations as they are present at less pH at ortho positions. This might be credited to the ortho positions of oxygen atoms in the phenolic groups. They increase the density of electrons in the carboxylic functionalized groups, eventually enhancing the inner-sphere complexations among the metal hydroxides and functionalized carboxylic groups; however, these groups form complexations at outer spheres [58].

3. Cation Central Atom Preferences for Organic Linkers (Ligands) The protons occupy the NOM's binding sites in the aqueous mediums, and these ions ought to compete for binding sites. Metal ions (M) reaction with ligands (L) having equal molar concentrations, *i.e.*, LA and LB, M-LA and M-LB quantities, depends on the central cations' preferences for ligands. The current section focuses on selected cations of S, D, and P blocks in the periodic table, presenting their significant concentrations in the environment and their affinity for organic linkers

3.1. Cations of s-block (Ca, Mg, Na)

The calcium (Ca2+) ions, in comparison to trivalent cations, do not exhibit a strong affinity for bondings with humic acids; however, these cations cannot be ignored as these ions exist at elevated concentrations in freshwaters. Kinniburgh *et al.* stated that the calcium ions bind with the carboxylic binding sites at lower pH. At higher pH, these ions bind to the phenolic binding sites [59-74]. The moieties of the amine-functionalized groups showed the same affinity as carboxylic functionalized groups towards calcium ions. Nevertheless, the calcium cations have more bonding associations towards the negatively charged, larger molecules, as they have larger ligands [75]. Iskrenova- Tchoukova *et al.* calculated the PMF (potential mean forces) for the carboxyl functionalized groups and calcium cations and found that affinity of binding mainly depends on the distances between the moieties of carboxyl and calcium ions [6]. The Ca2+ ions in the matrix compete for binding sites with the other available cations [76] and result in the alteration of a few cations (Fe) through redox reactions [77]. Other research groups reported that at 2.5 millimolar concentrations, cations of the calcium (Ca2+) compete with the Cu2+ (Copper) ions with one millimolar for adsorption sites (NOM) [78]. The presence of calcium ions causes NOM to form supramolecular structures by aggregating smaller NOM [10]; however, the same observations were not found for Na2+or Mg2+ cations.

3.2. ***Cations of p-block (Al, Pb)*** Aluminum ions (Al3+) complex with the NOM in the water matrix, modifying the metal ions' speciations and toxicity. The hydrolysis of Al3+ and exchange responses between the H+ and Al3+ ions on the NOM sites are essential to control the Al3+ activity and pH. In the presence of other cations, these ions decrease the amount of Pb2+ ions that are bonded to the carboxyl functionalized groups at lower pH (3-5). The ion competition for binding sites mainly depends on the ions for phenolic or carboxylic, or ligands, as they rely on the pH. Iron and aluminum ions affect rare earth metals' speciations present in the water consisting of high organic matter. At pH≥3, the aluminum ions compete with the lanthanides/rare earth metals, suggesting that aluminum ions bind to carboxylic functionalized groups' sites than phenolic groups; whereas at neutral pH, aluminum ions bond with the carboxyl functionalized groups with weak bonds [94]. However, the studies conducted by Cabaniss revealed that aluminum ions tend to bind more extensive phenol groups' moieties than aromatic molecules [75-97]. Lead ions in the natural water matrixes are found in two speciations (Pb2+ and Pb4+) in which Pb2+ ions are dominant. Lead ions show similar properties as copper ions in terms of briding strength and stronger bonds with the aminefunctionalized groups. The ions bind to phenols, alcohols or ether functionalized groups, with larger molecules forming a weak bond with the carboxylate functionalize groups [96]. The lead ions have an ionic radius (1.1 Angstroms), making it possible to form complexes with a central atom with a coordination number between 2 and 15. The lead ion complexation with donor atoms of the oxygen develops products with diverse bond lengths. Davidovich *et al.* stated that primary bonds display predominant properties, and secondary bonds are more considerable and serve as bridging molecules [98].

4. Equilibrium and Complexations for NOM

The preferences of metals and ligands for complexation and binding are determined primarily by the electronegativity, size of the atoms, and electron vacancies. In general, s-block elements have lesser affinities than d-block and p-block. Thus, the electronegative ligands prefer metals with high electronegative charges. Also, stronger adsorption between the cations and metals to functionalized groups (acidic) was observed when the acidity was low and metal valances were higher. This complexation strengthens the metals with low molecular weights (lighter) as the bond's size to charge ratio is low [99]. Metal ions are found as counterions or explicitly bound to the reactive functionalized groups due to electrostatic effects. The competition for binding sites among the metal ions is primarily due to the ions' chemical nature. Based on the cation type and deprotonation, interactions among NOM and cations are specific or unspecific

4.1. COMPLEXATION IMPACTS ON NOM PHYSICOCHEMICAL PROPERTIES

The complexation reactions affect NOM constituents, including polarity, size, concentrations, solubility, absorbance properties, *etc*. [103]. The current section emphasizes that modifications can be made possible by the complexation of NOM with the metals and their impacts on NOM's physicochemical properties.

4.2. NOM Morphology

The size, configurations, pH, ionic strength, chemical constituents, and molecular size affect binding between NOM cations [47]. Employing techniques like chromatography and light scattering, molar masses of different moieties in the NOM were analyzed in the presence and absence of ions, and it has been observed that the natural organic matter's molecular sizes altered the solutions' strengths. This may be attributed to coilglobule and polyelectrolyte interactions due to changing the shapes from linear to spherical. Nevertheless, the change in size mainly depends on the type of cation involved in complexation. The NOM size increases when Ca2+ ions are considered instead of Na+, possibly the Ca2+ and humic acids. The cation-NOM for the binding and dynamics was evaluated using Ca43 NMR, helion ion microscopy, and x-ray diffraction, and it has been observed that the NOM types do not alter pH, floc morphologies, and ionic strengths, even though they require specific ionic strengths and pH to stimulate the flocculation [104]. Ritchie and Perdue conducted studies at different pH ranges for the complexation of NOM with cations [47]. They identified that the complexation drifts are changed even though the aliquots are added at pH above 6.5. This phenomenon suggests that ligands enable slower reaction rates and enhance acidity. Molecular structures influence the dissociation and association of the protons in ligands through the resonance and polar substituents' effects. Compared to the acetic acids, formic acids are strong acids, even though both acids have hydroxyl groups; formic acids have a more remarkable ability to attract the electrons using hydrogen atoms replacing the hydroxyl groups and altering the direction of an oxygen atom. Polar substances present in the complex are altered (decreased) by increasing the acid groups' distance. Similarly, hydrocarbon groups with saturated compounds have electron repelling molecules, whereas unsaturated compounds have molecules capable of withdrawing electrons [100- 105].

4.3. NOM Spectral/Electronic Changes

Many researchers have explored NOM fluorescence and absorbance properties (optical properties) to study their characteristics; this might be due to the presence of chromophores/fluorophores of ligands complexing with them. Jaffe *et al.* stated that the physicochemical and biological properties control the NOM's optical properties [106]. Ligands consisting of fluorophores/chromophores in UV-vis regions adsorb the light as the electrons excite from the ground level to higher energy states. The metal transitions are due to ππ* and nπ*, thus molecular structures help determine maximum adsorption and density. The increase in design conjugations enhances the wavelengths. For identifying the cations-NOM interactions, classical optical microscopy techniques are used by many researchers. Indeed, measuring NOM's optical properties is not expensive, relatively easy, and rapid. The biogeochemical cycles and bioavailability of the trace elements in the aqueous water matrix are controlled by the natural organic matter complexes consisting of functionalized groups. The major functionalized groups, like carboxylate and phenolic groups, are responsible for these variations. As these groups deprotonate with pH, carboxylates are compared with the phenolic groups; due to the lower pKa value of these groups at lower pH, the complexations' contributions are induced.

5. Conclusions

The bondings between the NOM and cations are due to the coordinated covalent bonds between the donated electrons and ligands involved in the complexations. These coordinations modify the newly formed structure's spectral characteristics and morphology. The metal to NOM complexes significantly affect the treatment efficiencies in water industries. For water treatment using coagulation techniques, coagulants' complexations with NOM contribute to removing NOM from the solutions; these processes are further enhanced by adding the calcium ions. However, the formation of complexes by calcium ions with higher concentrations of the NOM causes precipitation, resulting in the production of by-products and reducing the lime softening methods' efficiencies. These complexes even cause fouling of membranes. The partial neutralization of NOM by the cations in slime layer formation onto the membrane's surface causes pore blockage. Furthermore, by-products are formed during the disinfection process due to the presence of metal ions in the aqueous solutions as the chlorine reacts with NOM, thus forming enhanced species. The modifications in rate constants in the ozonation process are observed, even though these modifications are only limited to EDTA/Tannic acids, thus not representing the behaviors of NOM.

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